

31. HYDROCARBON GASES IN TERTIARY AND QUATERNARY SEDIMENTS OFFSHORE PERU—RESULTS AND COMPARISONS¹

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ABSTRACT

Hydrocarbon gases (methane, ethane, propane, isobutane, *n*-butane, ethene, and propene) are present in Tertiary and Quaternary shelf, upper-slope, and lower-slope deposits of the Peruvian continental margin. Methane dominates the composition of the hydrocarbon gas at all 10 sites examined during Ocean Drilling Program (ODP) Leg 112. Generation of methane is regulated by the amount of sulfate in pore water. Wherever sulfate concentrations approach or equal zero, methane concentrations increase rapidly, reaching values near 100,000 $\mu\text{L/L}$ of wet sediment at eight of the 10 sites. Methane at all 10 sites results from methanogenesis, which is inhibited where sulfate is present and microbial reduction of sulfate occurs.

Hydrocarbon gases heavier than methane also are present, but at much lower concentrations than methane. These hydrocarbons are thought to result from early thermal and microbial diagenesis, based on relative gas compositions and trends of concentrations with depth.

With few exceptions, the results obtained in the shipboard and shore-based laboratories are comparable for methane and ethane in sediments of Leg 112. Reanalyses of canned sediments from ODP Leg 104 and from Deep Sea Drilling Project (DSDP) Legs 76 and 84 show that gas samples can be stored for as long as 8 yr, but the amounts of individual hydrocarbon gases retained vary. Nevertheless, the trends of the data sets with depth are similar for fresh and stored samples.

INTRODUCTION

Our study of hydrocarbon gases in Tertiary and Quaternary (Eocene to Holocene) sediment of the Peruvian continental margin represents a continuation of our research on gaseous hydrocarbons in sediment drilled by DSDP and ODP. The precedent for this work was established during DSDP Leg 18 in 1971 (McIver, 1973). In that early study, sediment samples from deep-sea drilling offshore Oregon were sealed in cans, and the composition of the gas released into the head space of the cans by shaking was determined by gas chromatography. This basic methodology has been modified and carried forward, and systematic studies of hydrocarbon gases using similar procedures have been conducted on sediment samples from DSDP Leg 76 (Blake Outer Ridge, Atlantic Ocean; Kvenvolden and Barnard, 1983) and Leg 84 (inner slope of Middle America Trench, Pacific Ocean; Kvenvolden and McDonald, 1985), during ODP Leg 104 (Vøring Plateau, Norwegian Sea; Kvenvolden et al., 1989), and now during ODP Leg 112 (shelf and slope deposits adjacent to the Peru-Chile Trench, Pacific Ocean).

Previous DSDP studies (indexed by Emeis and Kvenvolden, 1986) and ODP studies of deep ocean sediments, along with other investigations of near-surface ocean sediment (for example, Bernard et al., 1978; Kvenvolden and Redden, 1980; Whelan et al., 1980; Whelan and Hunt, 1983) have shown the ubiquity of hydrocarbon gases, particularly methane, in ocean sediments worldwide. In fact, at some drilling locations methane is so abundant that it takes the form of methane hydrates; for example, at sites drilled during Leg 76 (Kvenvolden and Barnard, 1983), Leg 84 (Kvenvolden and McDonald, 1985), and Leg 112 (Kvenvolden and Kastner, this volume). During these legs, as well as during Leg 104 (Kvenvolden et al., 1989),

hydrocarbon gases were collected in sealed cans for shipboard and later shore-based analyses. Here, we compare our shipboard results with shore-based results for Leg 112. In addition, we have reanalyzed samples from Legs 76 and 84; these samples, which had been stored frozen for 8 and 6 yr, respectively, were evaluated for long-term storage effects on hydrocarbon compositions. Reanalysis showed that the amounts of individual hydrocarbon gases retained during storage vary, but trends with depth of the data sets are similar.

GEOLOGIC SETTING FOR LEG 112

Ten sites (679 through 688) offshore Peru were investigated during Leg 112 (Fig. 1) to provide information about the paleoenvironmental history of Peruvian margin upwelling regimes and the tectonic evolution of the Peruvian continental margin. Outer-shelf and upper-slope sediment sequences of the forearc basins were sampled at six of the 10 sites (679, 680, 681, 684, 686, and 687), whereas lower-slope deposits near the Peru-Chile Trench were cored at the remaining four sites (682, 683, 685, and 688). Kvenvolden and Kastner (this volume) discuss these four sites in detail relative to their light hydrocarbon geochemistry and the presence of gas hydrates.

The six sites in the forearc basins were positioned to investigate various aspects of sedimentary deposits resulting from upwelling. Sites 679 (450 m water depth), 680 (250 m water depth), and 681 (150 m water depth) were located on an east-west transect at about 11°S latitude on the eastern flank of the Lima Basin and into the Salaverry Basin (Fig. 1). The Pleistocene to Holocene record of coastal upwelling was sampled at these sites; the distal edge of the sediment lens is beneath the modern upwelling plume at Site 679, and the modern upwelling center is near Site 681. Late Neogene sediment was also sampled at Sites 679 and 680. Various stages of diagenesis are evident at these sites, as revealed by the formation of calcite, dolomite, and phosphate.

Site 684 (426 m water depth) was located in a small sediment pond on the seaward flank of the Trujillo Basin (Fig. 1). The section recovered at this site contains portions

¹ Suess, E., von Huene, R., et al., 1990. *Proc. ODP, Sci. Results*, 112: College Station, TX (Ocean Drilling Program).

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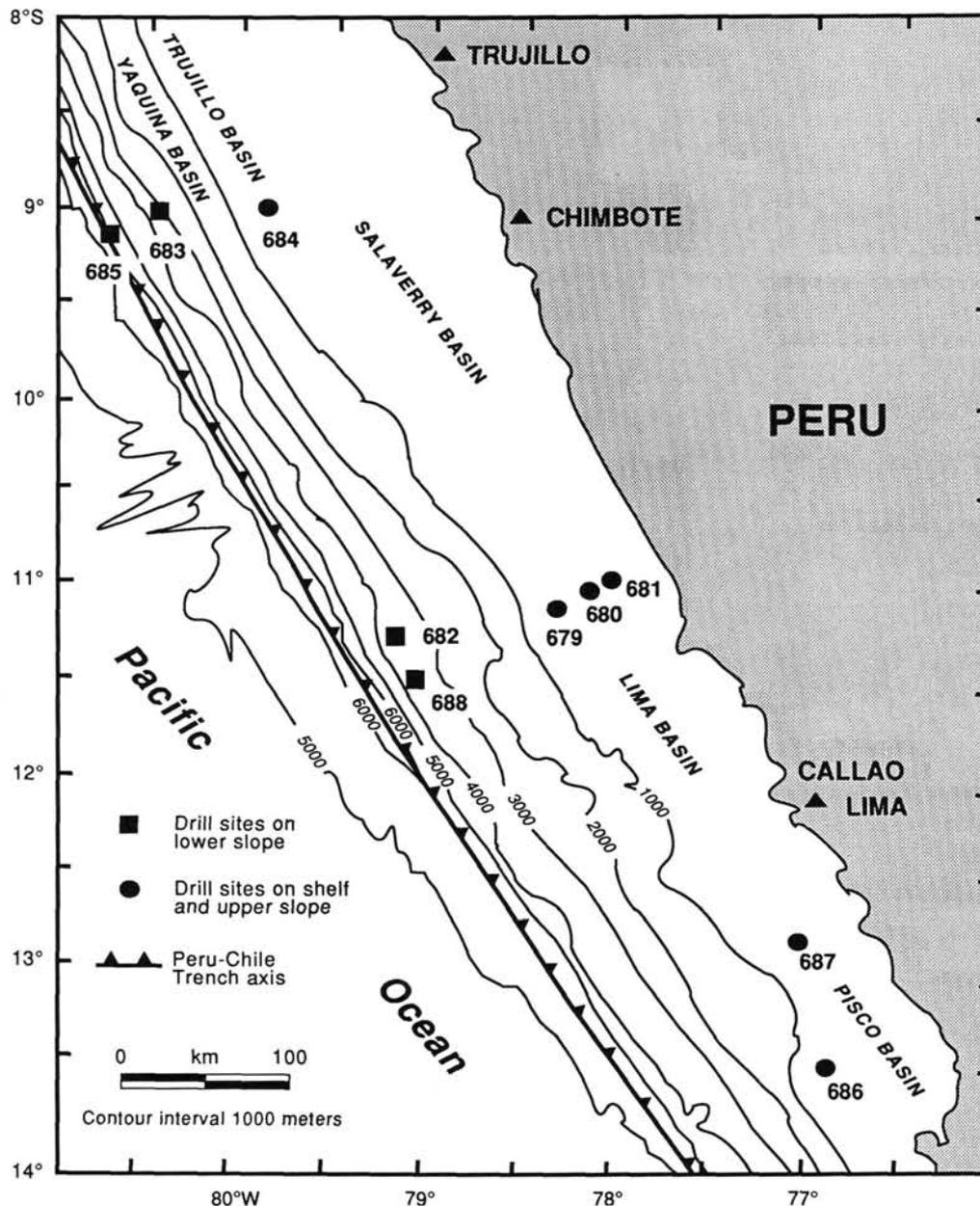


Figure 1. Location of drill sites for ODP Leg 112. Sites on the outer shelf and upper slope are indicated by filled circles, whereas lower-slope sites are indicated by filled squares.

of Miocene, Pliocene, and Quaternary records of coastal upwelling. The presence of calcite and dolomite in the section results from early diagenetic processes.

Site 686 (447 m water depth) and its companion Site 687 (306 m water depth) were located in the Pisco Basin (Fig. 1). Sediments at Site 686 contain a Quaternary record of well-developed and variable coastal upwelling, and sediments at Site 687 contain a similar upwelling record that extends into the Pliocene. Diagenetic products (calcite, dolomite, and phosphate) are present at these sites.

Diagenetic reactions leading to the formation of calcite, dolomite, and phosphate are strongly influenced by a hypersaline subsurface brine that was discovered from results of analyses of pore water obtained at Sites 680, 681, 684, 686, and 687 (Kastner et al., this volume). At these shallow-water sites, for example, chloride concentrations increase signifi-

cantly with depth from seawater values of about 559 mM to maximum concentrations that range from 718 mM at Site 686 to 1043 mM at Site 680. In contrast, chloride concentrations decrease with depth at the deep-water sites (682, 683, 685, and 688), mainly because of the presence of gas hydrates (Kvenvolden and Kastner, this volume). The subsurface hypersaline brine replenishes sulfate, which has a profound effect on the formation of methane, as discussed later.

PROCEDURES

Shipboard Methods

During Leg 112, two different procedures were used to extract hydrocarbon gases from sediment samples (see "Explanatory Notes," Shipboard Scientific Party, 1988a). Results from only one of these procedures are discussed here. This procedure, modified after

that of Kvenvolden and Redden (1980), provided samples that could be analyzed aboard ship and later reanalyzed in shore-based laboratories. For each analysis, a measured length (about 5 cm) of whole-round core (about 170 cm³) was placed in a can (about 0.5 L) that had been previously prepared with two septa-covered openings to allow for the removal of gas. Sufficient degassed water was added to the can so that a 100-cm³ headspace remained when the container was sealed. This headspace was purged with helium through the septa, after which the can was shaken for 10 min using a high-speed shaker. Gas from the sediment partitioned into the helium-filled headspace. A portion of this gas mixture was analyzed by gas chromatography, and an equivalent volume of helium was replaced in the headspace. Analytical conditions for gas chromatography are shown in Table 1. Results are reported relative to the volume of wet sediment from which the gases were extracted, i.e., microliters of gas per liter of wet sediment ($\mu\text{L/L}$). These units are unconventional, but are convenient for expressing gas concentrations that result from this procedure. After the analyses were completed, the cans were turned upside down and frozen. They remained in this condition until reanalysis in a shore-based laboratory.

Shore-Based Methods

Cans were thawed to room temperature and then were shaken for 10 min on a high-speed shaker. Portions of the headspace gas mixtures were analyzed by gas chromatography (Table 1). Not only were samples from ODP Leg 112 analyzed after a storage time of about six months, but samples from DSDP Legs 76 and 84 were also reanalyzed after storage times of 8 and 6 yr, respectively. When the analyses were completed, the cans were opened, water was decanted, and the sediment was dried and returned to the DSDP and ODP repositories.

GAS GEOCHEMISTRY

Table 2 shows the concentrations of hydrocarbon gases obtained from Leg 112 during shipboard and shore-based analyses. Shipboard results are limited to measurements of methane (C_1), ethane (C_2), and propane (C_3), whereas shore-based measurements include not only these gases, but also ethane ($C_{2,1}$), propene ($C_{3,1}$), isobutane ($i-C_4$), and n -butane ($n-C_4$). In general, the results obtained in the shipboard and shore-based laboratories are comparable for C_1 and C_2 , with some exceptions that are noted later. The higher sensitivity of the shore-based analyses is evident in the measurements of C_3 , which was often not detected in the shipboard analyses.

Table 1. Gas chromatographic conditions for shipboard analyses (ODP Leg 112) and for shore-based analyses (DSDP Legs 76 and 84; ODP Legs 104 and 112).

	Shipboard (Leg 112)	Shore-based (Legs 76, 84, 104, 112)
Gas chromatograph	Hach-Carle AGC Series 100 (Model 211).	Carle Analytical GS (Model 311).
Sample loop	1.0 cm ³	1.0 cm ³
Columns	1/8 in. \times 6 ft, 80% Poropak N + 20% Poropak Q (80/100 mesh).	1/8 in. \times 17 ft, n -octane on Poracil C (100/120 mesh). 1/8 in. \times 7 ft, 50% Poropak N + 50% Poropak Q (60/80 mesh).
Oven temperature	90°C	70°C
Detectors	Flame ionization	Flame ionization and thermal conductivity.
Pressures	Helium @ 60 psig. Air @ 10 psig. Hydrogen @ 30 psig.	Helium @ 93 psig. Air @ 14 psig. Hydrogen @ 27 psig.
Separations	$C_1, C_2, C_{2,1}, C_3$	$C_1, C_2, C_{2,1}, C_3, C_{3,1}, n-C_4, i-C_4, C_{5+}$ (backflush).

Note: Use of tradenames in this table is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Shelf and Upper-Slope Sites (679, 680, 681, 684, 686, and 687)

Results of shipboard and shore-based analyses of C_1 and C_2 in sediment samples from shelf and upper-slope sites are similar (Table 2). Two samples (112-679E-6X-2 and -679E-10X-1) could not be reanalyzed because expansion of the sediment filled the headspace and prevented removal of gas samples. Figure 2 compares the concentration of C_1 with depth, as determined in the shipboard and shore-based laboratories. It is evident from the graphs that the trends in concentrations with depth present the same overall patterns of distribution. The sudden increase in concentrations of all hydrocarbon gases in Sample 112-679E-13X, CC (Table 2) is believed to be a drilling artifact, as discussed in the "Site 679" chapter (Shipboard Scientific Party, 1988b). Excluding this sample, concentrations of C_2 are less than 10 $\mu\text{L/L}$ of wet sediment at Sites 679, 680, and 681, whereas at Sites 684, 686, and 687, C_2 concentrations generally range between 10 and 50 $\mu\text{L/L}$ of wet sediment.

The same relationship applies to the higher molecular weight hydrocarbon gases. C_{3+} saturated hydrocarbons are present in concentrations of less than 1 $\mu\text{L/L}$ at the first three sites and reach values larger than this (up to 15 $\mu\text{L/L}$) at the other three sites. At all six sites, $n-C_4$ usually dominates $i-C_4$. The unsaturated hydrocarbons ($C_{2,1}$ and $C_{3,1}$) are also present at all of these sites at low concentrations (less than 1 $\mu\text{L/L}$).

C_1 dominates the hydrocarbon gas compositions at all six sites. Generation of C_1 is apparently regulated by the amount of sulfate present in the sediment pore water. Figure 3 shows the relationships with depth of methane and sulfate concentrations. For this figure, values were taken from several site chapters (Suess, von Huene, et al., 1988). The inverse correlation between the amounts of methane and sulfate strongly suggests that methane results from methanogenesis, which is inhibited in the presence of sulfate (Claypool and Kaplan, 1974). At Site 679, sulfate reduction is complete at depths of between 145 and 170 mbsf; methane concentrations rapidly increase within the same depth interval and reach maximum values approaching 40,000 $\mu\text{L/L}$. Sulfate reduction is incomplete at Site 680, and methane concentrations remain low (less than 100 $\mu\text{L/L}$). The downhole increase in sulfate concentrations below about 50 mbsf results from diffusion of a subsurface brine (Kastner et al., this volume). At Sites 681, 684, 686, and 687, sulfate reduction is complete within 40 m of the seafloor, and methane reaches maximum concentrations, approaching 100,000 $\mu\text{L/L}$, immediately following the depletion of sulfate. Evidence for sulfate intrusion from the postulated subsurface brine at Site 680 is also present at Site 681 (Fig. 3), where a downhole increase in sulfate is accompanied by a decrease in methane concentrations to values of less than 100 $\mu\text{L/L}$. The methane and sulfate results at all six sites demonstrate the coupling between sulfate reduction, which is followed by the reduction of carbon dioxide to methane by the microbial process of methanogenesis (Claypool and Kaplan, 1974).

No dominant trends occur in the distributions of hydrocarbon gases larger than C_1 . All of the saturated hydrocarbon gases are believed to result from microbial and early thermal diagenesis, whereas the unsaturated gases are believed to result mainly from biological processes (Claypool and Kvenvolden, 1983).

Lower-Slope Sites (682, 683, 685, and 688)

Shipboard and shore-based analyses of C_1 and C_2 in sediment samples from these four lower-slope sites are generally comparable, although major exceptions occur at Site 688 (Table 2). A sample from Section 112-682A-38X-2 could not

Table 2. Comparison of hydrocarbon gas concentrations ($\mu\text{L/L}$ of wet sediment) at 10 drill sites of Leg 112, Peruvian continental margin, Pacific Ocean.

Leg-Core-Section Interval (cm)	Depth (mbsf) ¹	C ₁		C ₂		C ₃		i-C ₄	n-C ₄	C ₂ :1 USGS $\mu\text{L/L}$	C ₃ :1
		ODP $\mu\text{L/L}$	USGS	ODP $\mu\text{L/L}$	USGS	ODP $\mu\text{L/L}$	USGS				
112-679D-1H-4,140-145	6.0	16	18	0.80	0.73	nd	0.091	0.012	0.021	0.10	0.048
-679C-2H-2,138-143	11.9	27	27	1.8	1.5	nd	0.21	0.026	0.038	0.084	0.050
-679D-3H-3,135-140	21.8	50	48	2.1	1.7	nd	0.26	0.020	0.037	0.16	0.090
-679C-6H-3,145-150	51.5	81	67	2.9	2.0	nd	0.37	0.034	0.064	0.24	0.18
-679D-9H-3,135-140	78.8	85	72	3.7	1.9	nd	0.21	0.018	0.036	0.075	0.084
-679D-17X-1,135-140	143.8	210	140	4.4	2.0	nd	0.15	0.016	0.032	0.089	0.051
-679E-6X-2,135-140	292.7	32,000	na	8.8	na	na	na	na	na	na	na
-679E-10X-1,145-150	329.3	29,000	na	6.3	na	na	na	na	na	na	na
-679E-13X,CC, 7-12	359.3	37,000	52,000	11	17	nd	0.19	0.037	0.044	1.2	0.52
112-680B-1H-2,140-145	3.0	54	57	1.0	0.45	nd	0.052	0.014	0.057	0.054	0.66
-680B-3H-3,140-145	19.5	83	120	1.8	2.3	nd	0.52	0.15	0.042	0.031	nd
-680B-9H-4,135-140	77.9	66	97	2.1	2.8	nd	0.21	0.018	0.046	0.13	0.079
112-681B-1H-2,140-145	3.0	105	100	1.0	0.40	nd	nd	0.057	0.069	0.039	0.45
-681B-3H-3,135-140	19.8	446	430	2.7	1.4	0.50	0.28	0.040	0.048	0.078	0.10
-681B-7H-2,135-140	56.3	21,000	31,000	3.1	5.9	nd	0.17	0.018	0.017	nd	nd
-681C-8H-3,145-150	67.4	25,000	26,000	3.2	7.7	nd	0.34	0.021	0.020	0.043	0.048
-681B-9H-1,135-140	73.8	13,000	16,000	2.3	5.7	nd	0.16	0.013	0.019	0.084	0.036
-681B-12X-3,135-140	100.5	87	110	3.0	3.7	0.32	0.55	0.038	0.11	0.23	0.15
-681B-15X-1,145-150	126.0	75	83	2.6	3.7	0.24	0.59	0.14	0.11	0.034	0.033
112-682A-1H-3,140-145	4.4	29	39	0.7	0.69	nd	0.14	0.012	0.013	0.026	0.045
-682A-3H-3,135-140	23.7	180	450	4.7	13	nd	0.54	0.052	0.040	0.023	0.12
-682A-9X-1,101-106	77.3	95,000	51,000	45	34	16	12	1.4	2.0	0.27	0.18
-682A-15X-1,129-134	134.6	19,000	22,000	18	41	15	29	3.8	3.0	0.052	0.062
-682A-21X-1,125-130	191.6	35,000	42,000	64	84	39	50	5.7	3.2	0.088	0.068
-682A-23X-1,112-117	210.4	21,000	24,000	53	57	38	38	4.2	2.4	0.058	0.046
-682A-34X-2,135-140	307.5	29,000	19,000	123	55	45	23	0.62	1.0	0.16	0.14
-682A-38X-2,145-150	342.7	24,000	na	48	na	25	na	na	na	na	na
-682A-46X-1,135-140	409.6	41,000	92,000	160	260	140	100	11	18	50	76
112-683A-1H-1,140-145	1.5	18	20	nd	0.17	nd	0.03	nd	nd	0.050	0.030
-683A-3H-3,140-145	16.2	81,000	88,000	5.7	6.0	2.2	1.9	0.027	nd	0.031	0.060
-683A-6H-3,140-145	44.6	39,000	43,000	5.3	5.0	3.4	2.8	0.18	0.13	0.063	0.078
-683A-9H-3,145-150	73.2	34,000	44,000	11	12	11	11	1.7	0.58	0.028	0.077
-683A-12X-4,145-150	103.2	29,000	36,000	8.4	11	13	14	5.2	1.4	0.086	0.097
-683A-18X-3,140-145	158.7	20,000	17,000	111	10	14	12	4.9	1.8	0.071	0.086
-683A-24X-1,74-79	212.0	26,000	44,000	34	58	41	55	15	2.6	0.053	0.072
-683A-27X-1,128-133	241.0	7,000	12,000	33	27	40	36	5.8	1.8	0.32	0.18
-683A-30X-2,69-74	270.4	10,000	12,000	28	34	35	40	3.9	1.6	0.045	0.066
-683A-36X-3,135-140	329.6	28,000	29,000	nd	37	13	15	1.30	1.1	0.022	0.039
-683A-43X-2,135-140	393.6	30,000	28,000	17	21	3.2	2.7	0.57	0.46	0.071	0.097
-683B-6X-2,43-57	452.0	7,100	14,000	34	45	4.2	5.0	1.0	0.30	0.13	0.16
112-684B-1H-3,140-145	4.5	120	130	1.5	1.2	nd	0.034	0.006	0.020	0.027	0.044
-684B-3H-3,140-145	21.5	410	660	8.8	14	nd	0.59	0.051	0.042	0.066	nd
-684C-6X-1,140-145	40.5	18,000	16,000	36	40	4.3	3.7	0.31	0.22	0.018	0.061
-684C-9X-1,80-85	68.4	71,000	82,000	50	50	17	15	1.5	1.7	0.078	0.045
112-685A-1H-2,140-145	1.5	410	330	0.6	0.76	nd	0.16	0.0082	0.018	0.049	0.061
-685A-3H-2,140-145	18.1	83,000	77,000	2.4	2.7	nd	0.52	0.10	0.011	0.040	0.049
-685A-6X-4,140-145	48.1	25,000	29,000	1.3	1.8	nd	0.82	0.58	0.18	0.069	0.084
-685A-9X-7,140-145	79.9	14,000	34,000	0.9	1.4	0.60	0.98	1.8	0.26	0.11	0.13
-685A-15X-4,135-140	132.3	25,000	33,000	1.6	1.7	6.7	6.3	9.1	0.96	0.048	0.042
-685A-22X-1,135-140	197.0	26,000	36,000	5.8	8.5	13	18	22	2.9	0.053	0.050
-685A-28X-8,20-25	252.5	50,000	65,000	49	59	24	30	44	7.9	0.064	0.11
-685A-35X-5,135-140	315.7	36,000	48,000	26	35	47	69	61	9.4	0.069	0.064
-685A-39X-3,135-140	351.9	31,000	37,000	97	120	95	120	92	13	0.046	0.030
-685A-46X-1,145-150	413.1	41,000	62,000	130	180	70	98	76	10	0.15	0.14

Leg-Core-Section Interval (cm)	Depth (mbsf) ¹	C ₁		C ₂		C ₃		i-C ₄	n-C ₄	C _{2:1} USGS μL/L	C _{3:1}
		ODP	USGS	ODP	USGS	ODP	USGS				
		μL/L		μL/L		μL/L					
112-686B-1H-3,145-150	4.5	62	88	3.0	3.8	nd	0.088	0.018	0.020	0.024	0.096
-686B-3H-3,140-145	22.5	54,000	61,000	23	23	nd	0.74	0.14	0.042	0.029	0.036
-686B-6X-2,140-145	49.5	38,000	52,000	14	23	nd	1.5	0.40	0.26	0.43	0.071
-686B-9X-6,140-145	84.0	28,000	36,000	24	33	nd	1.7	0.10	0.22	0.026	0.067
-686B-15X-5,135-140	139.4	16,000	22,000	13	19	nd	1.4	0.045	0.12	0.082	0.11
-686B-21X-2,135-140	191.9	15,000	19,000	13	16	nd	1.5	0.034	0.10	0.029	0.091
-686B-28X-4,145-150	261.5	9,200	14,000	6.9	10	nd	0.61	0.046	0.066	0.031	0.40
-686B-32X-2,135-140	296.4	18,000	22,000	18	20	nd	0.89	0.025	0.059	0.044	0.64
112-687B-1H-3,140-145	4.5	27	36	nd	0.45	nd	0.10	0.015	0.047	0.052	0.12
-687B-3H-3,135-140	19.1	84	230	2.4	3.9	nd	0.23	0.037	0.029	0.028	0.077
-687B-6H-5,135-140	50.6	34,000	36,000	13	15	nd	0.12	0.021	0.033	0.024	0.049
-687B-10H-1,135-150	82.7	41,000	44,000	14	17	nd	0.11	0.024	0.041	0.087	0.12
-687B-16X-1,116-121	130.0	40,000	46,000	34	44	nd	1.4	0.27	0.24	0.095	0.14
112-688A-1H-4,140-145	6.0	230	350	1.4	0.89	nd	0.19	0.019	0.033	0.028	0.043
-688A-3H-4,140-145	23.8	94,000	93,000	1.7	1.9	nd	0.63	0.023	0.036	0.053	0.079
-688A-6H-3,140-145	50.8	24,000	27,000	1.4	1.2	nd	0.98	0.13	0.19	0.056	0.12
-688A-9X-5,135-140	82.2	28,000	22,000	4.1	4.1	8.9	3.7	0.40	0.067	0.54	0.86
-688A-16X-4,135-140	147.2	11,000	18,000	1.9	1.2	nd	1.2	0.22	0.67	0.14	0.16
-688A-25X-1,135-140	228.2	6,200	14,000	4.2	2.0	7.0	4.9	0.71	1.8	0.082	0.14
-688A-33X-3,135-140	307.2	5,300	21,000	3.5	4.8	7.5	8.9	1.0	1.9	0.030	0.042
-688E-3R-4,135-140	370.9	10,000	6,300	50	36	180	170	150	40	0.59	0.28
-688E-12R-1,135-140	451.9	4,700	70,000	47	350	15	80	18	2.5	0.031	nd
-688E-19R-3,135-140	521.4	23,000	20,000	170	210	16	25	4.9	1.9	0.29	0.23
-688E-30R-1,135-140	622.9	37,000	88,000	11	56	nd	0.24	0.056	0.017	0.015	0.058
-688E-38R-1,145-150	699.0	31,000	36,000	690	1,100	nd	260	8.9	18	0.016	nd

¹mbsf = meters below the seafloor to the top of the interval; ²ODP = results from shipboard laboratory;

³USGS = results from USGS shore-based laboratory.

na = not analyzed; nd = not detected.

be reanalyzed because the sediment had expanded to fill the can. A sample from Section 112-682A-46X-1 had anomalously high concentrations of all hydrocarbon gases; these results (like the results for Sample 112-679E-13X, CC) apparently represent a drilling artifact that is sometimes observed when drilling is particularly difficult (Shipboard Scientific Party, 1988c). These hydrocarbons are believed to be breakdown products of lubricants of drilling parts. The trends of the shipboard and shore-based concentrations of C₁ with depth are the same (Fig. 4). C₁ concentrations increase rapidly with depth, approaching maximum values of 100,000 μL/L. Below the depth of maximum C₁ values, the amount of extractable C₁ in the samples usually is greater than 10,000 μL/L.

The greatest discrepancy in analytical results occurs in samples from Site 688; the reason for these differences remains unexplained. For example, reanalysis of a sample from Section 112-688E-12R-1 resulted in C₁ concentrations that differ from shipboard results by more than an order of magnitude (Table 2). Samples from Sections 112-688A-25X-1, -688A-33X-3, and -688E-30R-1 gave C₁ values during shore-based analyses that are more than twice the values originally obtained onboard ship, whereas reanalysis of a sample from Section 112-688E-3R-4 resulted in a C₁ value of almost one-half that of the shipboard result.

The saturated hydrocarbon gases C₂, C₃, i-C₄, and n-C₄ generally tend to increase in concentration with depth at these four sites, with C₂, C₃, i-C₄, and n-C₄ reaching maximum amounts of 1100, 260, 150, and 40 μL/L, respectively, at Site 688 (Table 2). C_{2:1} and C_{3:1} are also present in all samples; these compounds show no obvious trends with depth.

As in sediment from the shelf and upper slope, C₁ dominates the hydrocarbon gas compositions at the lower-slope sites. Kvenvolden and Kastner (this volume) discuss in detail the geochemistry of C₁ at these sites, where intense methanogenesis led to the production of sufficient methane to form methane hydrates.

C₂, C₃, i-C₄, and n-C₄ in samples from these lower-slope sites probably result from microbial and early thermal diagenesis (Claypool and Kvenvolden, 1983). However, at the base of Hole 688E, concentrations of these compounds (Table 2) are such that thermogenic (catagenic) hydrocarbons are suspected. C_{2:1} and C_{3:1} are believed to represent the products of microbial activity, except at the base of Holes 682A, 683B, and 685A, where the high concentrations of these compounds may partly result from thermal breakdown of lubricants during difficult drilling.

COMPARISON OF RESULTS: LEGS 104, 84, AND 76

Leg 104

Our comparison study of gas compositions in Leg 112 sediments, as measured in shipboard and shore-based laboratories, was preceded by a similar study applied to sealed sediment samples from ODP Leg 104 that had been stored about 1 yr (Kvenvolden et al., 1989). Site 644 of that study is briefly considered here because sediments at this site contained high concentrations of C₁ and higher molecular-weight gases were present to C₅ (Table 3). C₁ concentrations from shore-based analyses exceed those from shipboard analyses to a depth of about 40 mbsf; below this depth, the opposite is generally true (Fig. 5). A rapid increase in the amount of C₁

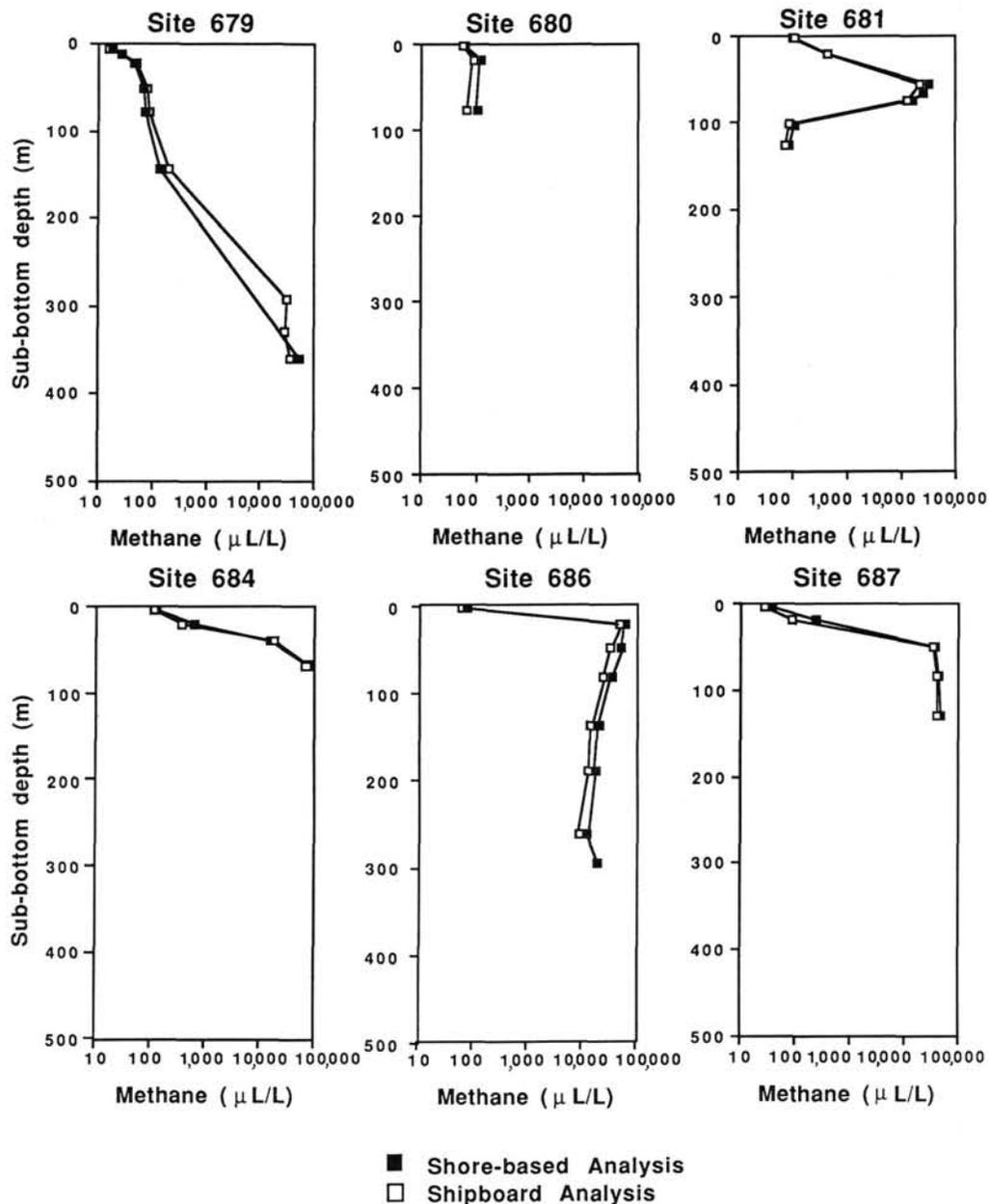


Figure 2. Comparison of C_1 concentrations with depth, as determined at shipboard and shore-based laboratories, for six shelf and upper-slope sites, ODP Leg 112, Peruvian continental margin, Pacific Ocean.

occurs with depth, reaching a maximum concentration at 77.6 mbsf.

Concentrations of C_2 , as measured at the shipboard and shore-based laboratories, are in reasonable agreement (Table 3). $C_{2,1}$ and $C_{3,1}$, which were present at low levels, were not detected on board the ship. C_3 and $n-C_4$ were observed aboard ship starting at depths of 125 and 184 mbsf, respectively; whereas these compounds were detected in all samples analyzed onshore. However, shore-based results were lower than shipboard results. Finally, $i-C_4$ was detected in all samples analyzed in the shore-based laboratory.

The large differences between shipboard and shore-based concentrations of C_1 at Site 644 are due mainly to shipboard procedural problems; the shore-based data are believed to be more accurate. Onboard the ship, high concentrations of C_1 were determined using a separate gas chromatograph having a thermal conductivity detector because the natural-gas ana-

lyzer, with its flame ionization detector, was nonlinear at high concentrations. The gas chromatograph used for C_1 did not have a calibrated sample loop; thus, the amount of gas analyzed (0.25 cm^3) was measured in an open syringe, making precise quantification difficult. In addition, calibration with standards was not reproducible.

Although a discrepancy exists between shipboard and shore-based results, particularly for C_1 , the trends with depth shown by both data sets are similar (Fig. 5). The highest concentrations of C_1 measured at the shore-based laboratory are large and correspond with amounts observed at previous gassy sites during Legs 76 and 84 (Kvenvolden, 1984) and during Leg 112 (as discussed above). Thus, because the large amounts of C_1 measured in the shipboard laboratory during Leg 104 are higher than observed elsewhere by as much as a factor of three, the Leg 104 shipboard results are considered to be in error.

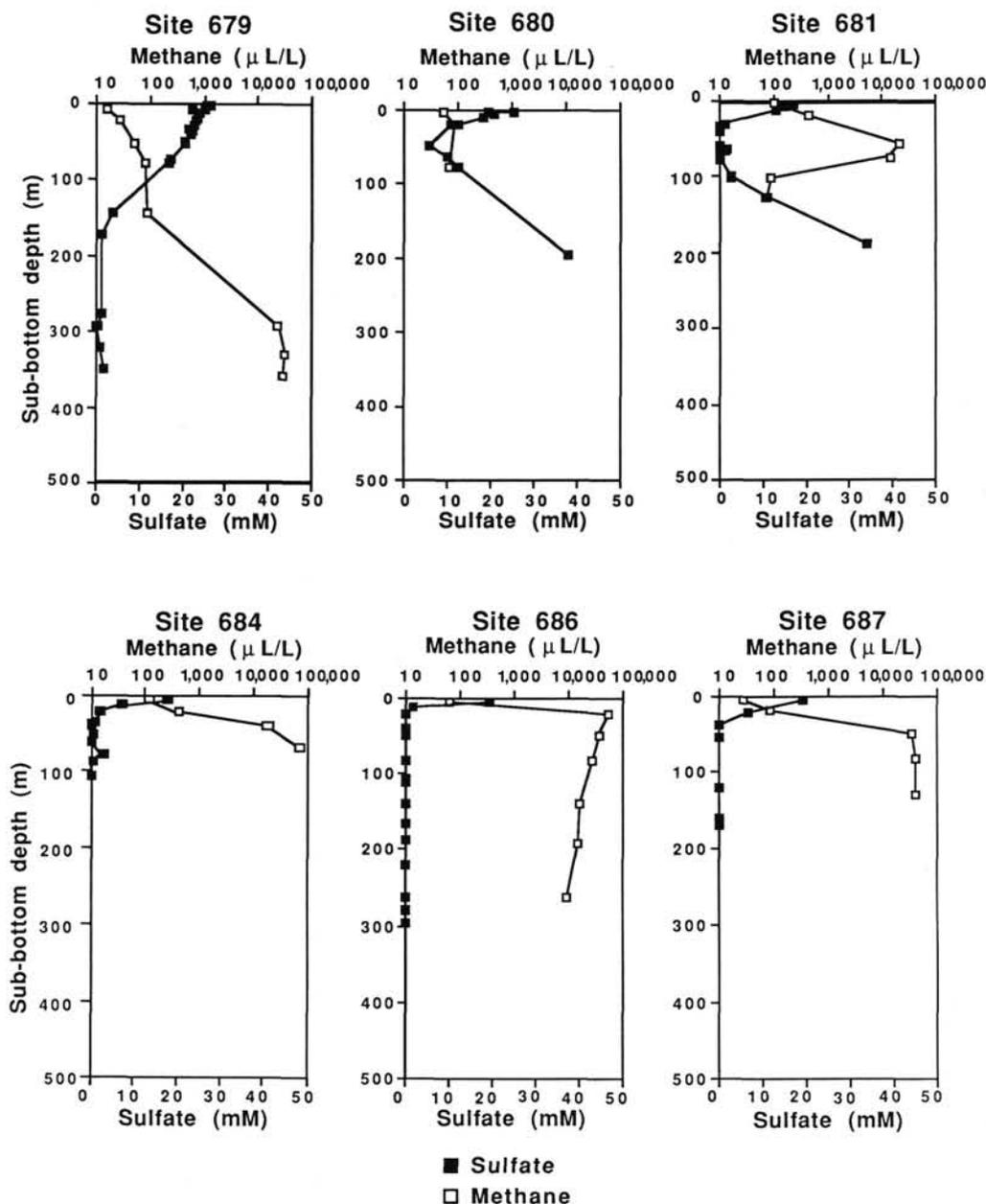


Figure 3. Profiles of C_1 and sulfate concentrations with depth at Sites 679, 680, 681, 684, 686, and 687, ODP Leg 112, Peruvian continental margin, Pacific Ocean.

Legs 76 and 84

Sediment samples, sealed in cans, were analyzed for hydrocarbon gases during DSDP Legs 76 (October through December 1980; Kvenvolden and Barnard, 1983) and 84 (January through February 1982; Kvenvolden and McDonald, 1985). After shipboard analysis, samples were stored frozen for about 8 yr (Leg 76) and 6 yr (Leg 84). These samples offered an opportunity to investigate the effects of long-term storage on sealed samples of sediment gas. Data sets for Sites 533 (Leg 76), 565, and 568 (Leg 84) are shown in Table 4. The results lack an overall consistency, but some trends are evident. C_1 concentrations are highest in sediments at less than about 100 mbsf, except at Site 568, where shore-based analyses show the highest C_1 values in the lower sediment (Fig. 5). With this exception, the C_1 values from both ship-

board and shore-based analyses of samples from the three sites show the same trends with depth. Samples having shipboard analyses that exceeded about 32,000 $\mu\text{L/L}$ always yielded lower shore-based values. This observation suggests the possibility that varying amounts of C_1 are lost from the containers during long-term storage, especially when C_1 concentrations are high. In a significant number of instances, the C_1 values from the shore-based study exceed the values obtained aboard ship. These results suggest that additional C_1 may be released from the sediments during freezing and storage.

Comparison of shipboard with shore-based analyses of C_2 and C_3 show that shore-based results for both are higher and that C_2 concentrations tend to increase with depth (Table 4). These larger values from the shore-based laboratory may also result from desorption during storage. Concentrations of $i\text{-}C_4$,

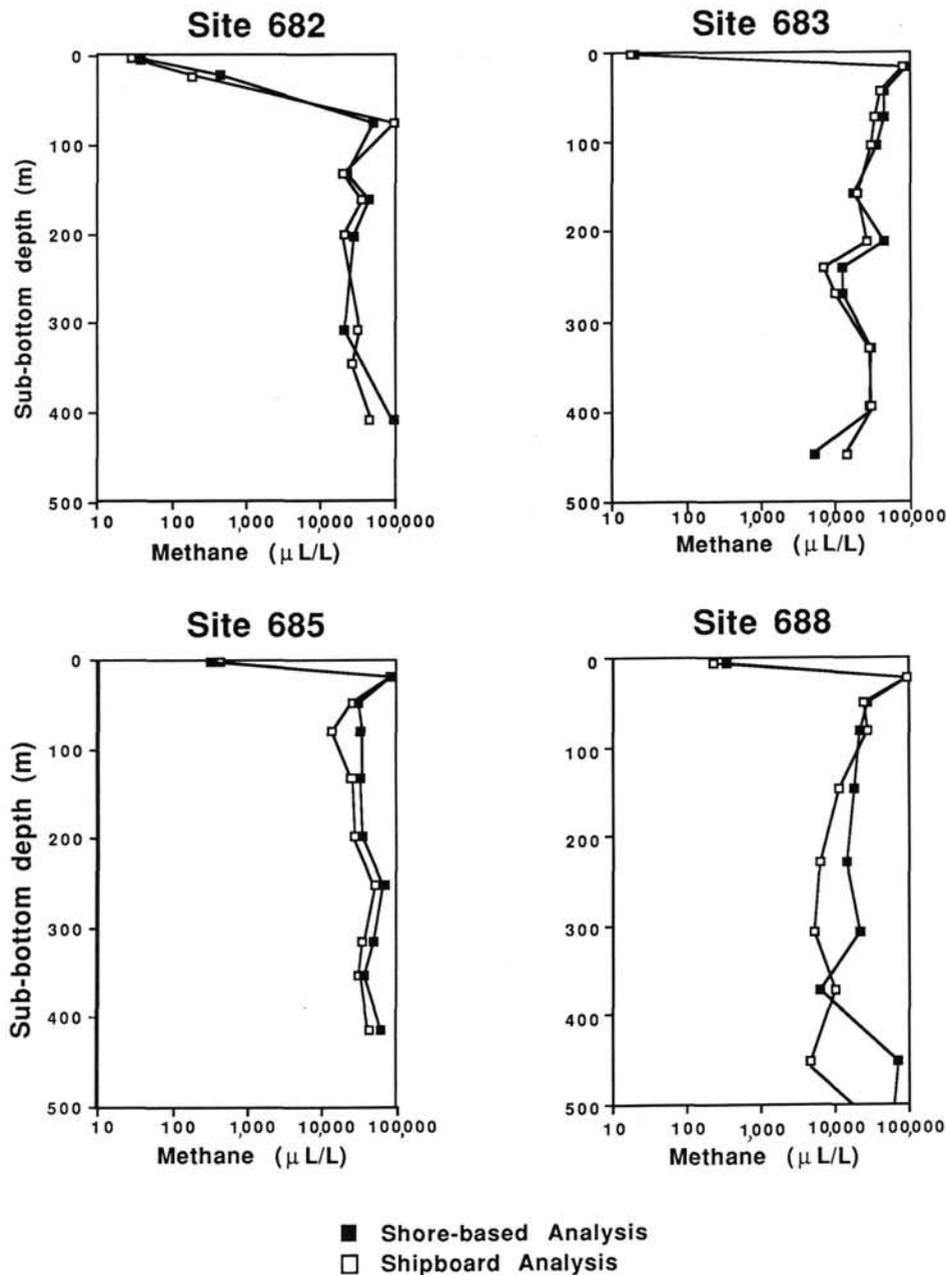


Figure 4. Comparison of C_1 concentrations with depth, as determined at shipboard and shore-based laboratories, for four lower-slope sites, ODP Leg 112, Peruvian continental margin, Pacific Ocean.

$n-C_4$, $C_{2:1}$, and $C_{3:1}$, as measured at the shore-based laboratory, are also shown in Table 4.

Although these data sets were not particularly consistent, the results do show that canned and frozen samples retain hydrocarbon gases during long-term storage but that the amounts retained vary. The trends of these data sets with depth are similar, however, so long-term storage in sealed cans does provide a means of preserving gas concentrations in a qualitative, but not quantitative, manner.

SUMMARY

The hydrocarbon-gas chemistry of Tertiary and Quaternary shelf and slope deposits of the Peruvian continental margin is dominated by C_1 , which constitutes more than 99%

of the hydrocarbon gas mixture in all samples; other hydrocarbons, such as C_2 , C_3 , $i-C_4$, $n-C_4$, $C_{2:1}$, and $C_{3:1}$ are present in small, parts-per-million concentrations. At the 10 sites drilled during Leg 112, the relationship between C_1 concentrations and amounts of sulfate in the pore water follow the classic model for microbial C_1 generation in marine sediment (Claypool and Kaplan, 1974). Methanogenesis is inhibited in the presence of sulfate, but when sulfate is depleted, methane generation becomes intense and leads to concentrations ranging from 10,000 to 100,000 $\mu\text{L/L}$ of wet sediment at eight of the 10 sites. At two of five shelf and upper-slope sites, C_1 production is apparently influenced by the presence of a subsurface, sulfate-containing brine. At four deep-water sites, C_1 generation led to the formation of methane hydrates in the sediment.

Table 3. Comparison of hydrocarbon gas concentrations ($\mu\text{L/L}$ of wet sediment) at Site 644, Leg 104 (Vøring Plateau, Norwegian Sea).

Leg-Core-Section Interval (cm)	Depth (mbsf) ¹	C ₁		C ₂		C ₃		i-C ₄	n-C ₄	C ₂ :1 USGS $\mu\text{L/L}$	C ₃ :1
		ODP	USGS	ODP	USGS	ODP	USGS				
		$\mu\text{L/L}$		$\mu\text{L/L}$		$\mu\text{L/L}$					
104-644-1-4,145-150	5.9	14	17	nd	0.65	nd	0.28	0.088	0.076	0.24	0.15
-644-3-4,145-150	22.1	480	1,000	nd	0.18	nd	0.029	0.0059	0.012	0.041	nd
-644-5-3,145-150	39.6	20,000	59,000	4.7	5.8	nd	1.5	0.023	0.022	0.023	nd
-644-7-2,145-150	57.1	230,000	61,000	5.5	6.2	nd	2.1	0.088	0.041	0.018	nd
-644-9-3,145-150	77.6	300,000	99,000	8.4	9.0	nd	2.9	0.12	0.081	0.023	0.029
-644-11-5,145-150	99.6	9,600	25,000	3.5	3.9	nd	1.0	0.058	0.071	0.029	0.018
-644-14-3,145-150	125.1	22,000	62,000	9.1	9.6	6.9	2.8	0.25	0.23	0.006	nd
-644-15-4,145-150	136.1	140,000	35,000	7.4	5.1	3.7	1.2	0.12	0.12	0.071	0.035
-644-17-2,145-150	152.1	78,000	23,000	4.8	5.2	4.5	1.6	0.24	0.22	0.081	0.053
-644-20-4,145-150	183.6	42,000	34,000	7.2	7.9	4.5	2.4	0.31	0.26	0.081	0.047
-644-22-4,145-150	192.7	14,000	18,000	4.9	4.9	3.1	1.7	0.29	0.25	0.071	0.047
-644-23-4,145-150	200.0	5,900	15,000	3.2	4.9	1.6	1.8	0.38	0.29	0.13	0.065
-644-25-2,145-150	208.9	140,000	35,000	6.8	2.1	4.9	2.3	0.41	0.29	0.088	0.076
-644-28-2,145-150	219.0	190,000	44,000	6.9	12	3.5	4.2	0.61	0.42	0.12	0.11
-644-29-2,145-150	224.0	84,000	22,000	5.6	5.6	3.7	2.1	0.45	0.29	0.035	0.03
-644-31-2,145-150	235.0	24,000	62,000	12	12	6.4	3.7	0.65	0.35	0.065	nd
-644-34-4,145-150	251.9	161,000	na	9.8	na	5.8	na	na	na	na	na

¹mbsf = meters below the seafloor to the top of the interval; ²ODP = results from shipboard laboratory;
³USGS = results from USGS shore-based laboratory after long-term storage of samples for 1 yr.
na = not analyzed; nd = not detected

The higher molecular-weight gases C₂, C₃, i-C₄, and n-C₄ are present at all 10 sites and probably represent products of early thermal and microbial diagenesis; C_{2:1} and C_{3:1} are probably biological products. Bottom samples from Sites 679, 682, 683, and 685 have anomalous concentrations of hydrocarbon gas that are believed to represent an artifact of drilling, i.e., hydrocarbons generated from the breakdown of lubricants of drilling parts. The amounts of gas in the lowermost samples at Site 688 are also anomalous, but these higher concentrations may represent thermogenic (catagenic) hydrocarbons.

Comparison of shipboard with shore-based analyses of the same samples from Leg 112 generally yielded comparable results, with some exceptions, the most notable of which occurred in samples from Site 688. Reanalysis of gas samples from Site 644 of ODP Leg 104 after 1 yr of storage showed large differences between C₁ concentrations measured at the shipboard and shore-based laboratories; these differences are attributed to shipboard procedural problems. Concentrations of C₂ are in reasonable agreement, as measured at the two laboratories. Reanalyses of samples from DSDP Legs 76 and 84 provided an opportunity to investigate the effects of long-term storage over a period of 8 and 6 yr, respectively. Although these results lack consistency, they show that the procedure, using sealed metal cans containing sediment, does retain hydrocarbon gases during long-term frozen storage in a qualitative, but not quantitative, manner.

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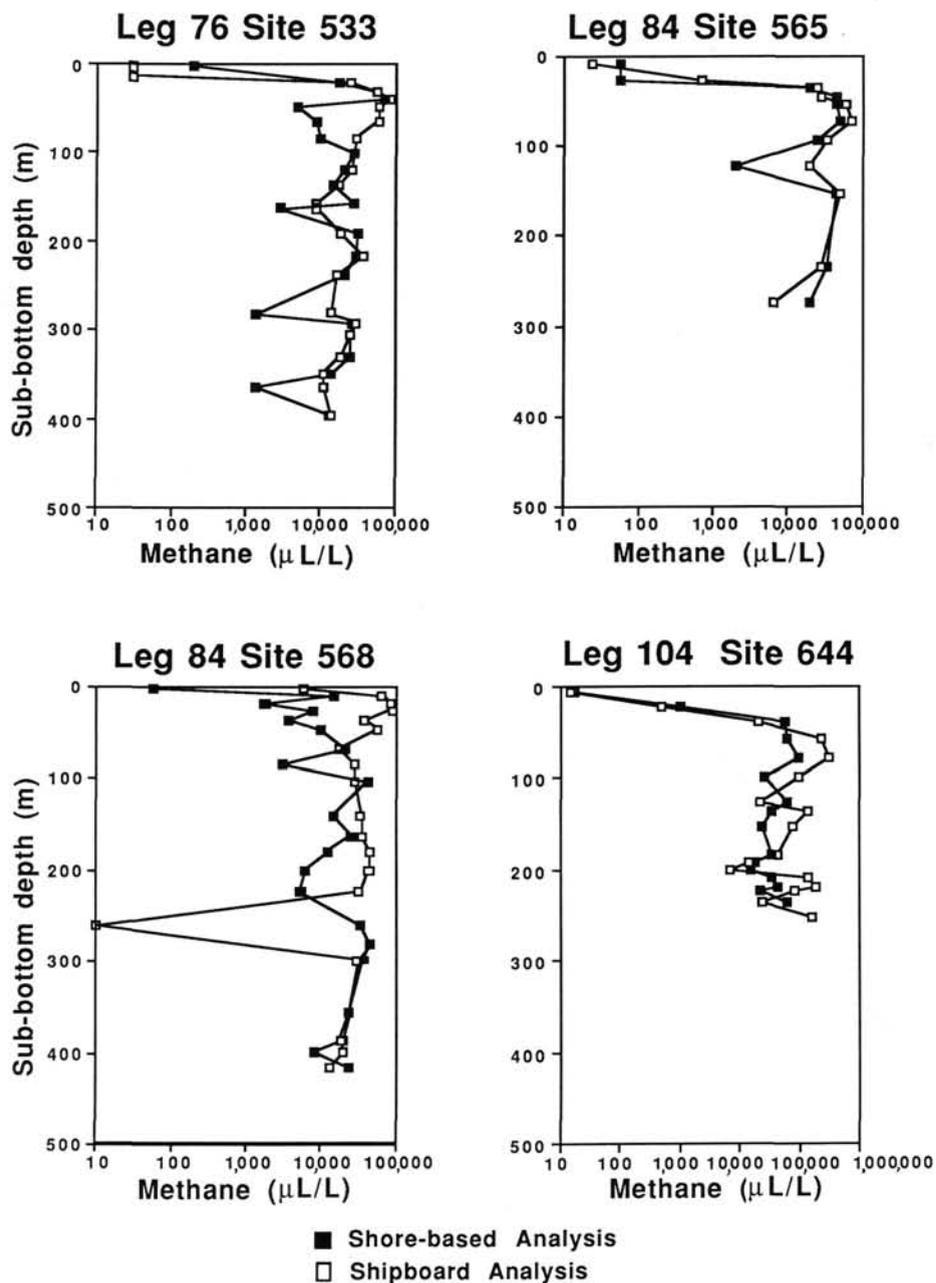


Figure 5. Comparison of C_1 concentrations with depth, as determined at shipboard and shore-based laboratories, for Site 533, DSDP Leg 76 (Blake Outer Ridge, Atlantic Ocean), and Sites 565 and 568, DSDP Leg 84 (Middle America Trench, Pacific Ocean), and Site 644, ODP Leg 104 (Vøring Plateau, Norwegian Sea). Shore-based analyses of thawed samples were performed after frozen storage times of 8, 6, and 1 yr, respectively.

Table 4. Comparison of hydrocarbon gas concentrations ($\mu\text{L/L}$ of wet sediment) at Site 533, Leg 76 (Blake Outer Ridge, Atlantic Ocean) and Sites 565 and 568, Leg 84 (Middle America Trench, Pacific Ocean).

Leg-Core-Section Interval (cm)	Depth (mbsf) ¹	C ₁		C ₂		C ₃		i-C ₄	n-C ₄	C ₂ :1 USGS $\mu\text{L/L}$	C ₃ :1
		DSDP $\mu\text{L/L}$	USGS $\mu\text{L/L}$	DSDP $\mu\text{L/L}$	USGS $\mu\text{L/L}$	DSDP $\mu\text{L/L}$	USGS $\mu\text{L/L}$				
76-533-1-1,145-150	1.5	30	200	0.018	0.12	0.02	0.08	0.02	0.05	0.14	0.06
-533-2-1,80-85	3.5	30	nd	0.018	nd	0.01	nd	nd	nd	nd	nd
-533-6-2,140-145	14.3	30	nd	0.047	0.19	0.04	0.15	nd	nd	0.44	0.15
-533-8-1,145-150	21.6	24,000	17,000	0.94	0.84	0.24	1.1	0.05	0.07	0.62	0.22
-533-10-2,140-145	32.3	57,000	56,000	1.7	2.4	0.53	9.6	0.96	0.78	1.0	1.36
-533-12-1,140-145	39.8	82,000	69,000	2.1	2.4	0.53	11.3	1.0	0.00	3.0	1.36
-533-14-1,140-145	48.4	59,000	4,800	2.1	0.48	0.65	0.85	0.07	0.08	0.35	0.12
-533-18-1,135-140	65.4	58,000	8,400	1.9	0.80	0.59	0.88	0.08	0.11	0.54	0.22
-533-22-1,135-140	83.4	29,000	9,500	1.2	1.3	0.47	0.85	0.12	0.15	1.0	0.35
-533-26-1,145-150	100.5	27,000	27,000	1.4	1.8	0.47	1.8	0.16	0.09	0.25	0.14
-533-30-1,135-140	119.4	26,000	21,000	1.7	2.4	0.88	2.8	0.49	0.27	0.69	0.25
-533-34-1,135-140	137.4	17,000	15,000	0.77	1.3	0.35	0.93	0.22	0.19	0.28	0.14
-533-39,CC,0-5	158.5	8,800	27,000	0.64	3.8	0.47	4.8	1.2	0.84	0.59	0.32
-533-41-1,145-150	164.5	8,800	2,800	0.88	2.1	0.88	2.2	1.1	0.22	0.85	0.42
-533A-8-2,135-140	192.9	18,000	31,000	1.2	4.0	1.0	3.6	3.7	2.2	1.3	0.74
-533A-10-6,0-5	216.5	37,000	30,000	3.7	4.4	3.2	9.1	3.9	2.4	0.20	0.79
-533A-13-1,31-37	237.8	16,000	21,000	2.7	3.8	0.70	2.0	0.76	0.51	0.12	0.12
-533A-16-4,145-150	272.0	14,000	1,300	1.4	1.9	1.9	3.2	1.6	1.2	0.21	0.11
-533A-18-6,135-140	293.0	29,000	26,000	5.2	6.4	2.9	6.9	2.2	2.0	0.38	0.23
-533A-20-2,135-140	306.9	24,000	24,000	3.8	3.8	2.6	3.5	1.2	1.1	0.09	0.07
-533A-22-6,145-150	332.0	18,000	24,000	4.4	6.2	2.7	5.2	1.5	1.9	0.17	0.13
-533A-24-5,135-140	349.4	11,000	14,000	2.5	3.4	2.8	2.7	1.3	1.7	0.52	0.14
-533A-26-3,135-140	365.4	11,000	1,300	2.8	1.5	2.1	0.53	0.33	0.71	1.1	0.78
-533A-29-3,135-140	396.6	14,000	14,000	5.1	6.5	0.65	1.0	0.19	0.45	0.27	0.22
84-565-1-2,140-145	7.45	24	59	0.006	0.38	0.006	0.14	nd	nd	nd	0.49
-565-3-5,145-150	27.45	710	59	0.33	0.63	0.065	0.29	nd	nd	0.25	0.37
-565-4-4,145-150	34.45	24,000	20,000	1.1	2.4	0.90	0.71	0.41	0.12	0.47	0.24
-565-5-5,145-150	46.45	27,000	44,000	2.1	3.4	0.57	0.92	0.56	nd	nd	0.12
-565-6-4,145-150	54.45	59,000	45,000	2.7	4.0	0.83	1.1	0.65	0.12	nd	0.24
-565-8-4,145-150	73.45	72,000	49,000	5.0	5.9	1.8	nd	0.71	0.24	0.24	nd
-565-10-5,145-150	92.45	34,000	24,000	3.1	3.7	1.3	1.3	0.29	0.18	0.18	1.51
-565-13-5,145-150	122.45	19,000	2,000	2.4	1.1	1.8	0.88	0.29	0.21	0.47	0.52
-565-17-1,145-150	154.45	50,000	44,000	4.4	6.5	2.5	3.2	1.2	0.29	nd	nd
-565-25-5,145-150	234.95	27,000	33,000	6.6	9.6	1.5	2.4	1.1	0.41	nd	0.30
-565-29-5,145-150	274.45	6,600	19,000	3.1	10	1.3	5.6	3.5	1.0	nd	nd
84-568-1-2,140-145	2.9	6,000	60	0.32	0.27	0.19	0.17	nd	nd	0.12	0.12
-568-2-4,140-145	9.3	65,000	15,000	0.57	0.27	0.36	0.21	nd	0.19	nd	nd
-568-3-4,140-145	18.9	90,000	1,800	0.58	0.38	0.62	0.44	0.10	nd	0.17	0.11
-568-4-3,140-145	27.1	90,000	8,200	0.69	0.78	0.80	0.64	0.38	nd	nd	nd
-568-5-4,140-145	38.2	40,000	3,800	0.31	0.58	0.45	0.47	0.12	0.12	0.27	0.24
-568-6-4,140-145	47.9	55,000	10,000	0.35	1.4	1.8	2.0	0.93	nd	0.57	0.29
-568-8-5,140-145	68.5	17,000	22,000	0.66	1.7	1.2	nd	1.9	0.56	0.39	nd
-568-10-3,140-145	84.5	27,000	3,000	0.64	1.1	0.92	1.4	0.41	0.29	0.65	0.35
-568-12-3,140-145	103.2	27,000	41,000	1.1	2.2	1.9	3.7	4.2	0.95	nd	nd
-568-16-2,145-150	140.2	36,000	15,000	4.8	2.7	1.3	0.92	1.4	0.45	nd	0.65
-568-18-4,145-150	162.5	35,000	26,000	7.4	8.6	1.1	1.5	1.9	0.53	0.41	0.18
-568-20-3,145-150	180.5	44,000	13,000	14	0.7	1.1	1.2	0.88	0.47	0.29	0.24
-568-22-4,145-150	201.4	45,000	6,000	14	4.5	0.42	0.76	nd	0.12	0.12	0.24
-568-24-5,145-150	222.3	33,000	5,300	11	3.6	0.21	0.19	nd	0.07	nd	0.12
-568-28-4,145-150	259.4	?	35,000	11	14	0.15	0.12	0.12	nd	nd	0.28
-568-30-5,145-150	280.1	47,000	46,000	18	19	0.15	0.18	0.11	0.50	nd	0.37
-568-32-5,145-150	299.5	31,000	37,000	18	6.1	0.21	0.09	0.28	nd	0.14	0.41
-568-38-3,145-150	354.7	25,000	25,000	35	44	0.26	0.48	1.8	0.06	0.12	0.18
-568-41-4,145-150	385.5	18,000	20,000	22	33	0.56	1.24	1.2	0.35	0.12	0.35
-568-42-6,145-150	398.0	19,000	8,000	21	nd	0.16	nd	nd	0.32	nd	0.12
-568-44-4,145-150	414.4	13,000	23,000	20	37	0.19	0.30	1.1	nd	nd	0.44

¹mbsf = meters below the seafloor to top of the interval; ²DSDP = results from shipboard laboratory;

³USGS = results from USGS shore-based laboratory after long-term storage of samples for 8 yr (Leg 76) and 6 yr (Leg 84).

na = not analyzed; nd = not detected; ? = questionable analysis.