

68. C₁-C₅ HYDROCARBONS FROM CORE GAS POCKETS, DEEP SEA DRILLING PROJECT LEGS 56 AND 57, JAPAN TRENCH TRANSECT

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ABSTRACT

C₁-C₅ hydrocarbons from DSDP Legs 56 and 57 sediment gas pockets were analyzed on board ship. Results suggest that the C₂-C₅ hydrocarbons accompanied biogenic methane and were generated at low temperatures — less than 50°C — either by microorganisms or by low-temperature chemical reactions. Neopentane, a rare constituent of petroleum, is the major C₅ component (about 80%) in much of the sediment at Site 438. This compound, which appeared in smaller amounts at Sites 434, 439, 440, and 441, seems to correlate with either fractured or coarse-grained sediments. Scatter in C₄ and C₅ isomer ratios and generally good correlation between C₃, C₄ and C₅ components suggest local sources for these molecules.

INTRODUCTION

Sediments from all sites on the western wall of the Japan Trench (DSDP Legs 56 and 57) proved to be unusually anaerobic considering the water depths from which they were recovered (a maximum of 5986 m for Site 434). A strong H₂S odor was present in many shallower cores (sub-bottom depth about 150–250 m). Below this depth, biogenic methane was present in small gas pockets and represented from a trace to 95 per cent of core gas. The methane was invariably accompanied by traces of C₂-C₅ hydrocarbons.

Similar occurrences have been found at many other DSDP sites containing anaerobic, organic matter-rich sediments, such as the Cariaco Trench (Site 147; Edgar, Saunder, et al., 1973), the South Atlantic Basin (Sites 360, 361; Bolli, Ryan et al., 1978), the Black Sea (Sites 379, 380, and 381; Hunt and Whelan, 1978), and the Canary Islands (Site 397/397A; Whelan, 1979). The sites at the Black Sea and the Canary Islands were the first where quantitative measurements on the traces of C₂-C₅ hydrocarbons were carried out. There seemed to be a strong correlation of these compounds with each other in fine-grained sediments. It was concluded that these compounds accompany biogenic methane and have either a biological source or are formed *in situ* by a low-temperature (less than 50°C) chemical diagenetic process. There was no evidence to suggest that these compounds resulted from migrated petroleum.

Biogenic methane was found in most of the sediments recovered from the western Japan Trench wall. This was surprising, because gassy sediments were not reported for a previous DSDP site in this area (Site 298; Karig, Ingle, et al., 1975). The reason is probably that continuous coring was not carried out previously.

The Leg 56/57 sediments generally appeared to be diatomaceous. However, there are notable differences in gas contents that reflect biological reworking of sediments and slow depositional rates, as well as the lack of anaerobic conditions. For this reason, gassy sediments from the western trench wall contrasted sharply with gas-free sediments of Site 436 on the eastern trench wall. Site 436 sediments had lower organic-carbon levels, as well as small fecal pellets, fish teeth, and small manganese nodules.

This paper examines the detailed composition of the C₁-C₅ hydrocarbons found in core gas pockets from sediments of the western Japan Trench wall. These data suggest a gas source related to bacterial activities and low-temperature chemical generation processes.

RESULTS

Core gas pocket sampling and analyses were carried out on board ship, as described previously for DSDP Leg 47A (Whelan, 1979). Qualitatively, the amount of gas present was much less than observed at the other, aforementioned DSDP sites. In some cases, the cores had to be allowed to stand at room temperature before positive gas pressure occurred, as observed by a bulge in caps on the ends of core-liner tubes.

Methane constituted a trace to 95 per cent of the core gas. However, some shallower cores showed significant gas pressure even when methane was not present. Although measurements of O₂/N₂ could be done only crudely on the shipboard Carle gas chromatography, because of overlapping of the O₂ and N₂ peaks, resolution was sufficient to indicate that all the non-methane gas is air. In soft sediment, gas cracks occurred with a continued strong pressure gradient out of the core. In harder sediment, gas bubbling out of the core was

observed. In both cases, considerable pressure built up when the core liner was capped. As a result, the predominant pressure gradient out of the core liner made extensive air contamination during sampling unlikely. During drilling, air-rich seawater is pumped down around the core barrel at higher than ambient hydrostatic pressure. Consequently, air can be driven into the sample. This is the most likely source of contaminating air. However, if this was the predominant source of air in these samples, it is not clear why *all* cores did not show high gas pressures. Secondly, it seems reasonable that interstitial-water samples should have given only surface seawater readings if drilling fluid permeated the cores. At Site 435, the cores from 67 to 163 meters posed the greatest mystery — high gas pressure, low methane content, traces of CO₂, and a predominance of air. Currently, the exact amounts of N₂ and O₂ cannot be tested from *in situ* interstitial-water samples, because oxygen reacts with the copper tubing used in sampling (see Site 436 report).

Levels of C₁–C₅ hydrocarbons found in core gas pockets are shown together with other hole parameters on the Site Summary Charts in the back pocket of Part 1 for Sites 434, 438, 439, 440, and 441, and in Figure 1 for Site 435. Levels of the trace amounts of C₂, C₃, C₄ and C₅ hydrocarbons are plotted as log of ppm by volume, normalized to 100 per cent methane. The percentages of isomeric C₄ compounds (*i*-butane to *n*-butane) and C₅ compounds (*i*-pentane, *n*-pentane, and neopentane or tetramethylmethane) are also shown.

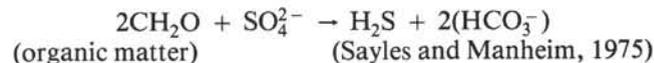
The methane is presumed to be biogenic, as is that found at other gassy DSDP sites, mentioned previously. The evidence, which is presented for each site, includes methane δ¹³C values of –67.6 to –83.75 per mill for Sites 434 and 435 (Table 1 and Figure 2), the high values of C₁/C₂ (generally 1000–300,000; shown in Figure 3), and other chemical indications of microbial activities at

each site, such as H₂S production above the methane zone and high interstitial-water alkalinities.

Site 434

Site 434 was drilled to a sub-bottom depth of 301 meters on a terrace of the landward (west) wall of the Japan Trench (water depth 5986 m). The sediments are primarily upper to lower Pliocene diatomaceous material and were recovered in a highly fractured form because of intense seismic disturbances at this site.

The strong H₂S odor which was present from the surface to 180 meters was produced by the activities of sulfate-reducing micro-organisms. Their activities can be represented simply as:



These organisms carry out oxidation of organic matter with concurrent reduction of sulfate to hydrogen sulfide and production of increased interstitial-water alkalinity, as observed at this site. Evidence of their past activities throughout the sequence is demonstrated by the sporadic presence of black iron sulfide minerals caused by sediment iron reacting with bacterial H₂S.

A small amount of gas pressure developed in most cores after standing. The quantity of methane in these cores gases was small in shallow cores, but increased to 72 per cent at 132 meters. The methane, which varied from 5 to 82 per cent throughout the rest of the hole, is assumed to be biogenic, because:

1. Its quantity increased at the approximate level where H₂S decreased. Bacterial reduction of CO₂ to CH₄ is observed in many anaerobic DSDP cores. The reduction of carbon dioxide generally occurs below the zone of bacterial reduction of SO₄²⁻ to H₂S (see, for example, Claypool and Kaplan, 1974).

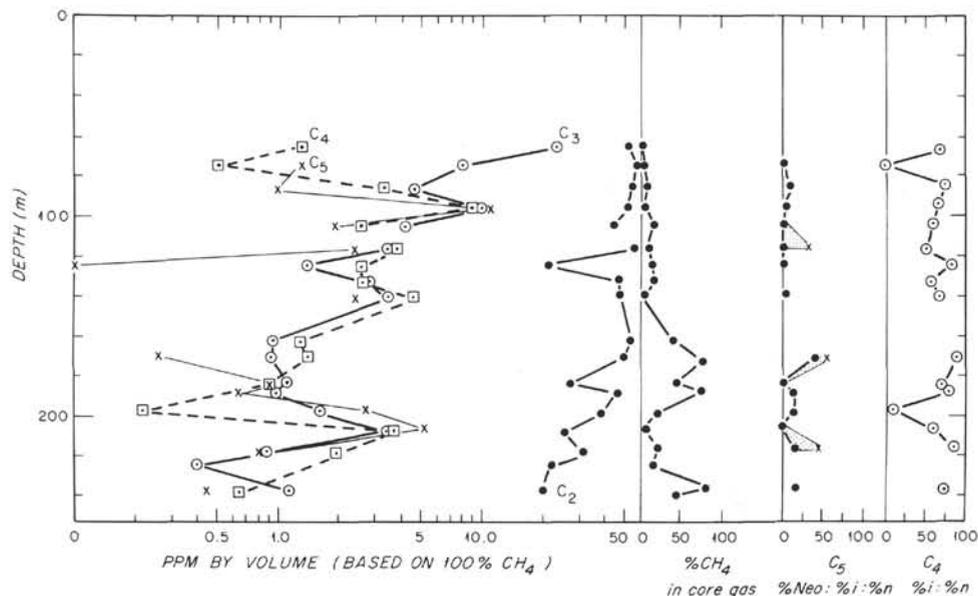


Figure 1. C₁–C₅ data, Site 435.

TABLE 1
 $\delta^{13}\text{C}$ Values, Leg 56

Sample	CH ₄ (%)	$\delta^{13}\text{C}$ (‰)	Sub-bottom Depth (m)
434-15-2, 15 cm	71.6	-80.86	132.2
434-23-1, top	48	-78.81	206.0
434B-24-2	84.1	-72.41	507.0
434B-37-1	35.1	-67.64	629.0
435A-4-3, 20 cm	77	-79.36	171.7
435A-6-2, 50 cm	75	-83.75	189.5
435A-11-2	85.4	-77.99	237.0

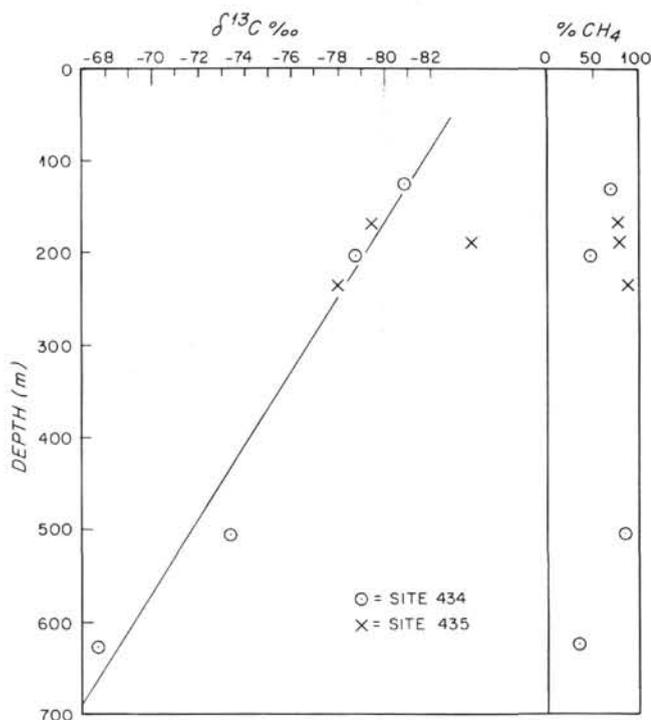


Figure 2. $\delta^{13}\text{C}$ data, Sites 434 and 435.

2. The methane $\delta^{13}\text{C}$ values of -80.86 to -67.64 per mill (Table 1) are typical of biogenic methane (Claypool, 1975). Petrogenic methane generally has values of -30 to -50 per mill.

3. The organic carbon levels in the sediment (generally about 1%) were sufficient to support bacterial growth.

4. C_1/C_2 ratios generally greater than 1000 are typical of C_2 accompanying methane production by microorganisms (see further discussion below).

5. High interstitial-water alkalinities, which are typical of anaerobic bacterial activity (Nissenbaum et al., 1972) suggest that the production of 1 mole of bacterial methane is accompanied by the production of 1 mole of carbonate:



As mentioned, the C_1/C_2 levels at this site were generally greater than 1000, which is considered charac-

teristic of bacterial methane. In spite of a considerable amount of scatter, the normal decrease in C_1/C_2 with depth is seen, as observed at other DSDP sites (Claypool, 1975). The linear regression line for these data, plotted with data from other Legs 56 and 57 sites and some other DSDP sites, is shown in Figure 3. At other sites, the slope of the line representing the linear decrease in $\log \text{C}_1/\text{C}_2$ with depth is found to depend primarily on the geothermal gradient, high-heat-flow areas, such as the Red Sea, showing higher amounts of C_2 at shallower depths than low-heat-flow areas such as the Aleutian Trench (Claypool, 1975). The intercepts of the lines on the $\log \text{C}_1/\text{C}_2$ axis in Figure 3 roughly correlated with bottom-water temperatures and the type of organic matter. Thus, more C_2 production occurred closer to the surface water interface in the Cariaco Trench (bottom-water temperature about 17°C) than in the much colder Aleutian Trench.

As shown on the Site Summary Chart, trace amounts of C_2 - C_5 hydrocarbons accompanied the biogenic methane as found at other DSDP sites. Although the amounts are less than observed in either the Black Sea (DSDP Sites 379, 380, and 381) or the Canary Islands region (DSDP Site 397), the shapes of the $\log \text{C}_2$, $\log \text{C}_3$, $\log \text{C}_4$, and $\log \text{C}_5$ curves versus depth are generally similar to each other, as found previously when these compounds accompanied biogenic methane.

It should be noted that there are many gaps in the data throughout the hole due to poor core recovery, because of the highly disturbed and fractured nature of these fine-grained sediments. There are also variations caused by difficulties in gas-sample reproducibility. In spite of these problems, the C_2 - C_5 levels are duplicated fairly well at Site 441, drilled slightly farther up the western slope (Site Summary Charts).

Variations in C_1 - C_5 due to gas losses before sampling would be expected to cause greater losses in the lighter, faster-moving C_1 than in the heavier C_5 molecules. This type of fractionation is minimal for molecules of approximately the same size, such as isomeric molecules. For example, the percentages of *i*-butane and *n*-butane can be determined with fair reliability, because gas losses affect both isomers equally. These isomeric ratios can be used to determine in what parts of the sediment column these compounds have a common or similar organic source.

The Site Summary Chart shows per cent of *i*-butane and *n*-butane plotted versus depth. Also shown are percentages of isomeric C_5 compounds — *i*-pentane, *n*-pentane, and neo-pentane (shown in the figure as per cent *i* C_5 , *n* C_5 , and neo C_5). While per cent of *i*-butane to *n*-butane (*i*- C_4 to *n*- C_4) remains approximately the same throughout the hole, the C_5 compounds vary over short distances. For example, *n*-pentane predominated over other isomers at 541 and 620 meters, while isopentane was the major component within 10 meters of each side of these samples. These large changes over short distances suggest that the sources of the absorbed C_5 hydrocarbons are local and that the hydrocarbons have not moved very far over geologic time.

The Site Summary Chart shows that neopentane constitutes up to 30 per cent of the total C_5 composition in

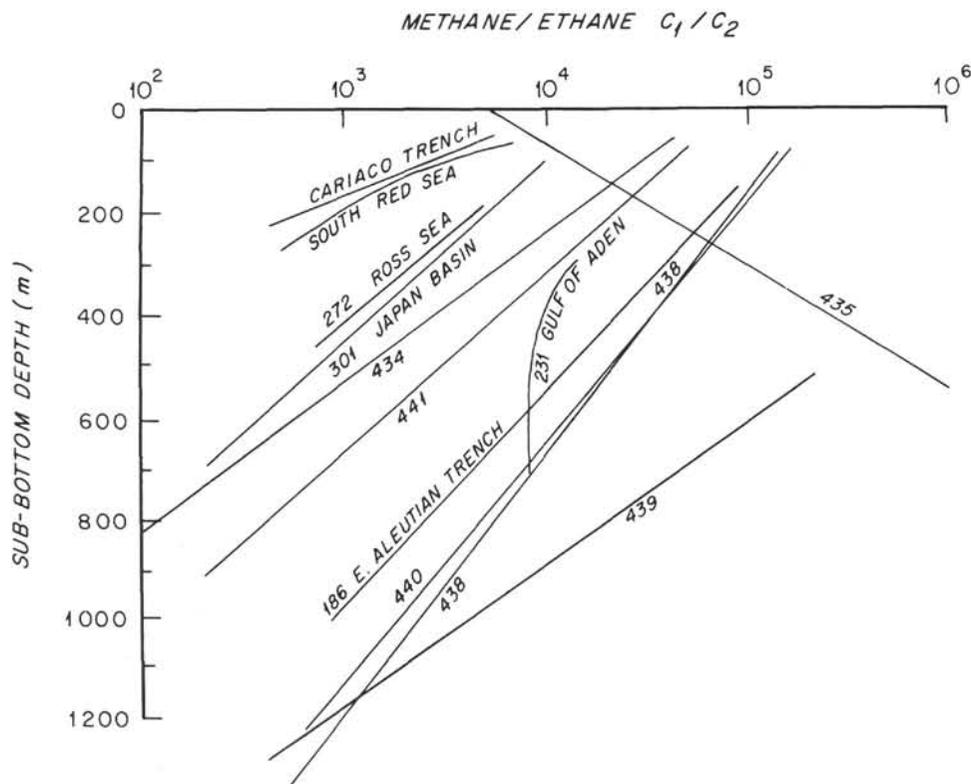


Figure 3. Summary C_1/C_2 data, many DSDP sites. (Data for sites other than Japan Trench from Claypool, 1975.)

some parts of the section. This compound is interesting because it rarely occurs in petroleum (Erdman, 1961; Hunt, in press). It is found sporadically in cores from other DSDP sites. As will be discussed, it occurs in many of the sediments drilled in this area and may have a biological source.

Site 435

Site 435 was drilled farther up the western slope than 434 — water depth 3401 m — to a sub-bottom depth of 245 meters. The sediment is primarily diatomaceous, with several interlayered ash beds, particularly in two intervals extending from 50-100 meters and from 160 to 200 meters. Core recoveries were much better than at Site 434. Fractured and disturbed sediments were generally not observed.

From 67 meters to hole bottom, varying, but in some cases substantial, gas pressure developed within the cores after standing at room temperature. This is the same depth where bulk density and thermal conductivity decreases and water content increases and shows substantial scatter. A qualitative estimate of gas content of each core is shown in Table 2. The methane content of the core gas remains low (20% or less) until Section 435A-3-3, at 136 meters.

Unlike Site 434, no H_2S odor was detected at this site. If biogenic methane is produced by anaerobic organisms, a sulfate-reduction zone normally occurs just

TABLE 2
Estimation of Gas Quantity in Holes 435 and 435A Cores with Respect to Other Cores at This Site^a

Core or Section	Gas Quantity
435-8	High
9	Low
10	Medium-Low
11	Low
12	Low-Medium
13	High
14	Medium
15	Low
16	Low
435A-3-4	High
6-2	High
7-1	Medium (poor recovery)
8-1	Low
9-2	Low (poor recovery)
10-1	Low (poor recovery)
11	High

^a“High” means enough gas to give active bubbling and to pop off end caps. “Medium” means that some gas pressure developed after the core was sectioned and stood at room temperature. “Low” means no visible signs of gas, but sampling of gas in the core liner did show the presence of methane; this often occurred with poor recovery and very fractured cores.

above the methane-production region, as discussed for Site 434. The lack of free H₂S at this site is not due to an unusually high amount of iron in the sediments. The amount of iron available for combination with sulfide is no greater than at other sites (see Murdmaa, Gordeev, et al., this volume). It is possible that the higher alkalinity at this site has kept sulfide in the form of HS⁻ rather than H₂S. It is also possible that biogenic methane was not produced *in situ*, but migrated horizontally into this region. Gas behavior, particularly in the bottom part of the hole, makes this a possibility. In addition, volcanoclastic beds are often porous and might make good migration conduits. However, these beds are thin in this section. The total amount of methane in these sediments is small throughout. Even though the source area of gas is not firmly established, the low C₂-C₅ content and methane δ¹³C values of -77.99 to -83.75 per mill (Table 1), indicate that the gas is biogenic. Deposition rates in the upper Pleistocene section (0-93 m) are calculated to be 4.0 to 6.4 cm/10³ years, and even higher through most of the Pliocene. Thus, the rates at this site were high enough to have allowed production of anaerobic sediment conditions shortly after deposition.

A semi-log plot of ppm by volume of C₂-C₄ content of the core-gas methane is shown in Figure 1. Pentane (C₅) is not shown because levels are at our detection limits. Figure 4 shows C₁/C₂ plotted versus depth. The values of 17,000 to 50,000 are typical of biogenic methane.

There are several abnormal trends in the C₂-C₅ data for this site. Most striking is that log C₁/C₂ versus depth stays approximately constant from 65 to 168 meters and then slopes in a direction opposite to that usually observed to the bottom of the hole. It is normal for C₁/C₂ to decrease with depth as the concentration of C₂ increases as a function of increasing depth and temperature (Claypool, 1975). Here the ratio increases with depth, suggesting dilution with more-"biogenic" methane with depth.

The C₂-C₄ curves in Figure 1 appear to behave independently, especially below 150 meters, where methane content was high and, consequently, the C₂-C₄ values were most reliable. This "out-of-phase" behavior is typical of porous, slumped, or disturbed sediments (Whelan, in press). In contrast, at other DSDP sites, the shapes of the log C₂-C₄ curves are the same, or "in phase", when the C₂-C₅ compounds are found at low levels in anaerobic fine-grained sediments (Hunt and Whelan, 1978).

A closer look at the data as shown in Figure 5 and 6 suggests that many of the points above 150 meters are "in phase," while a predominance of "out-of-phase" points occurred below 150 meters. Viewing the data in this way, the first three columns of Table 3 were constructed without knowing the detailed lithology of the hole. Later, the last column, indicating the sediment type, was added. It can be seen that "in-phase" gas samples correlate with fine-grained diatom ooze or muds. "Out-of-phase" behavior usually occurs in the areas of ash beds or, at 86 meters, at the location of a sand bed. The behavior of the "in-phase" and correla-

tion coefficients lends support to the idea of two types of gas distribution — "in phase" and "out of phase". Table 4 shows a weak positive correlation between log C₂ and log C₃, and between log C₃ and log C₄ at this site. When the "in-phase" points are separated and the correlation coefficients are recalculated, the positive correlation for both "in-phase" and "out-of-phase" points increases between log C₂ and log C₃. The change is more convincing between log C₃ and log C₄, where the "in-phase" values acquire a positive correlation of +0.88, while the correlation decreases for the "out-of-phase" points.

Site 438

Site 438 was drilled approximately 40 km west of the top of the Japan Trench slope (water depth 1560 m). The holes penetrate locally fractured, generally diatom-bearing siliceous strata. The deepest hole, 438B, is 1041 meters deep. Amounts of CH₄ and C₂-C₅ in the core gas, as well as compositions of C₄ isomers and C₅ isomers, are plotted on the Site Summary Chart.

In the shallowest samples, a strong H₂S odor was present. There was no appreciable amount of methane to a depth of approximately 90 meters. After methane was detected, it remained at a level of less than 50 per cent to about 175 meters and then increased to the 60 per cent range at 250 meters where the H₂S odor decreased to zero. This distribution of gases is similar to the distribution reported for Site 434. The first appearance of ethane was noted at 92 meters, but the amounts were small, as indicated by the C₁/C₂ ratio of 13,020 (Figure 4). As seen on the Site Summary Chart, the ethane content fluctuated erratically to 250 meters and was accompanied by traces of propane, butane, and pentane, which first appeared at about the same depth. The increase in methane and decrease in H₂S odor between 200 and 250 meters delineates the top of the zone of bacterial-methane production.

The levels of bacterial methane were fairly constant or increased gradually to about 800 meters. Ethane levels increased throughout the hole. Concentrations of propane, butane, and pentane all remained fairly constant, with some scatter. However, the shapes of the C₃, C₄, and C₅ curves are similar below 660 meters.

From 800 meters to the bottom of the hole, methane levels decreased (possibly due to poor core recovery and thus poor gas samples), but the C₂ content increased, so the C₁/C₂ ratio began to decrease, as at other DSDP sites (Figures 3 and 4) (Claypool, 1975). The data indicate that the methane is bacterial, as was the case for Site 434. Additional evidence for a microbial methane source is the temperature of 2°C at sea bottom and 28°C at 878 meters; 50°C is generally recognized as the minimum required for generating significant amounts of hydrocarbons.

One of the most surprising findings at this site was that neopentane is the major C₅ hydrocarbon present (around 80% of total C₅ from 580 m to hole bottom). Because neopentane is rarely found in petroleum (Erdman, 1961), the most likely source of this compound is microbiological (see below).

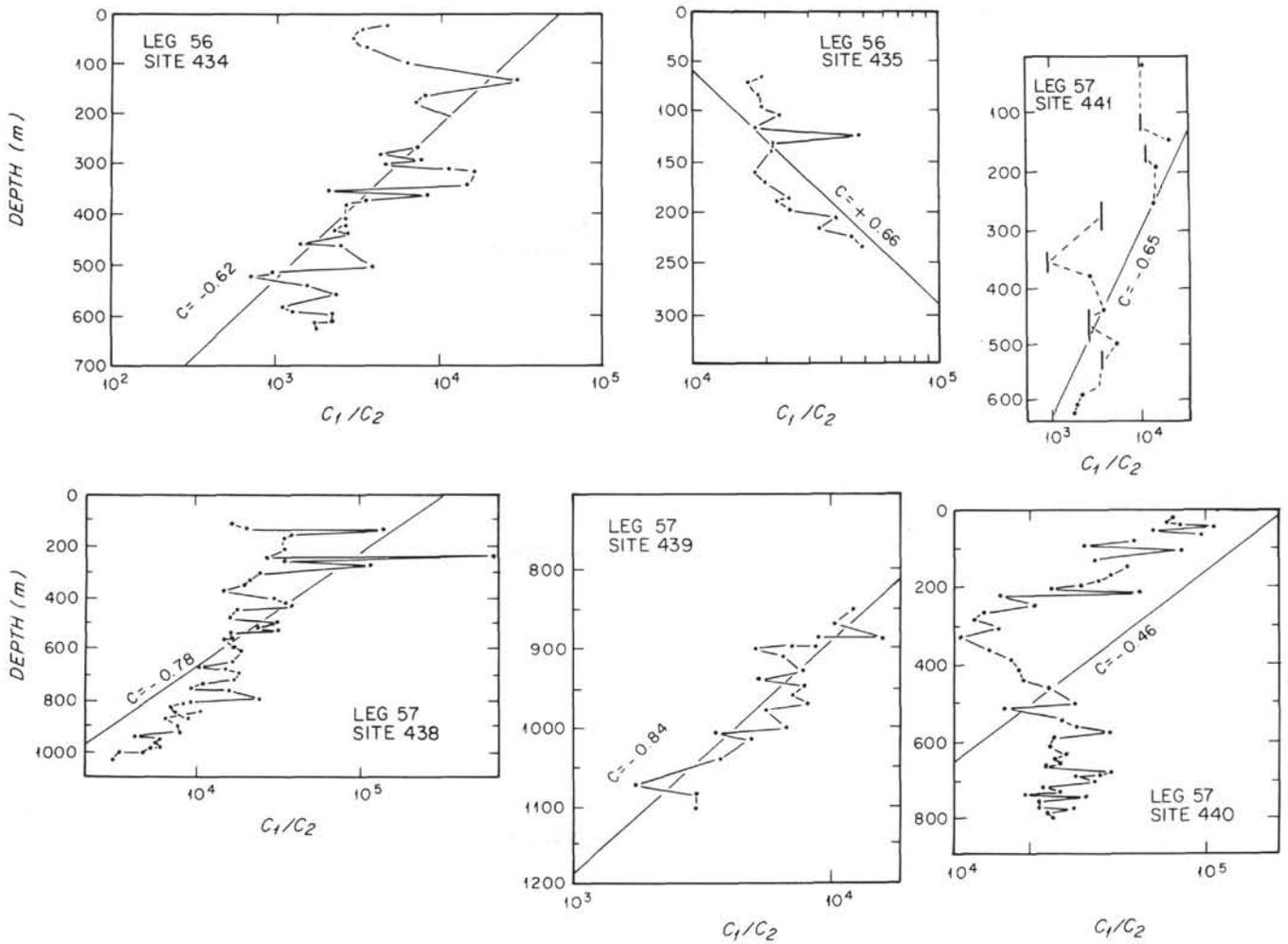


Figure 4. Least squares line of C_1/C_2 versus depth, Leg 56 and 57 sites. Correlation coefficients are shown.

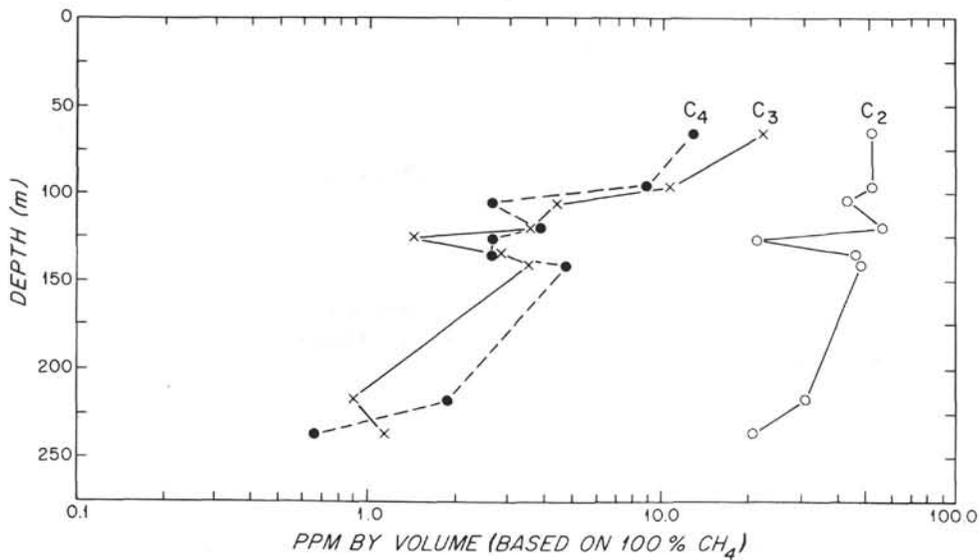


Figure 5. Holes 435 and 435A, "in-phase" C_2 - C_5 gas behavior.

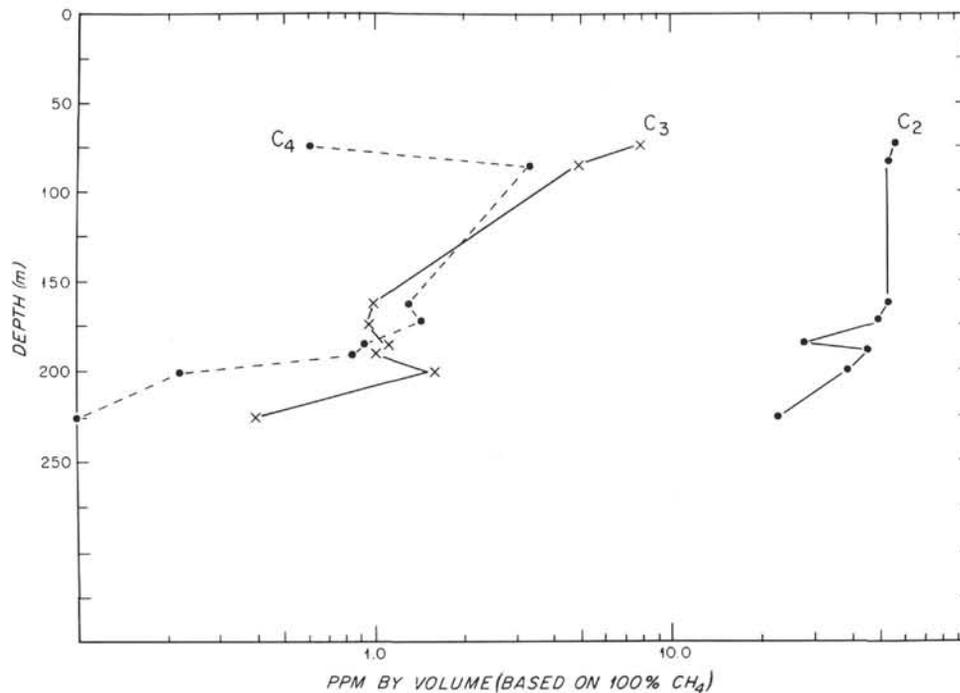


Figure 6. Holes 435 and 435A, "out-of-phase" C₂-C₅ gas behavior.

TABLE 3
Gas Behavior Versus Sediment Type, Site 435

Sub-bottom Depth (m)	Sample	Gas Behavior (log C ₂ -C ₄)	Sediment Type
65.9	435-8-1, 88 cm	In phase	Diatom ooze
74.9	9-1, 40 cm	Out of phase	Diatom ooze with sand; pumice
85.8	10-2, 32 cm	Out of phase	Sand beds
95.1	11-2, 13 cm	In phase	Diatom ooze
104.8	12-2, 30 cm	In phase	Diatom ooze
117.9	13-4, 92 cm	In phase	Diatom ooze
125.2	14-3, 20 cm	In phase	Diatom ooze
133.6	15-2, 58 cm	In phase	Diatom ooze
141.2	16-1, 15 cm	In phase	Diatom ooze
163.1	435A-3-3, 109 cm	Out of phase	Ash beds
173.2	4-3, 20 cm	Out of phase	Ash beds
185.0	5-5, 100 cm	Out of phase	Ash beds
189.5	6-2, 50 cm	Out of phase	Just above ash bed
200.0	7-1, 75 cm	Out of phase	Ash bed just above
217.5	9-2	In phase	Diatom ooze
226.0	10-1	Out of phase	Diatom ooze + nannofossils + silt
236.5	11-2	In phase	Diatom ooze + silt

The sedimentologists divided the stratigraphic section into four lithologic units (see site chapters, this volume). Unit I is a poorly sorted, sandy mud which is about 100 meters thick. Methane first occurred in amounts of 50 per cent or more of core gas at the top of unit II, which is 700 meters thick and is composed mainly of fine-grained, diatomaceous ooze. A series of rehealed faults and fractures have been analyzed in detail in the sediments from unit II (see Arthur, and Carson et al., this volume). The healed fractures first appear at about 580 meters and continue sporadically to 820 meters, the

bottom of unit II. Interestingly, neopentane constitutes about 80 per cent of total C₅ from about 580 meters to the bottom of the hole at 1040 meters (see Site Summary Chart). A high proportion of neopentane occurred throughout unit III, which is generally sandier than unit II.

As mentioned earlier, neopentane has been found periodically at other DSDP sites, but never in so consistently high a proportion with respect to the other C₅ isomers. The source of this compound is most likely microbiological (see discussion). It may reflect the activities of aerobic organisms, because it appears in coarser or fractured sediments through which water may have flowed during earlier geologic time. It has been suggested that the low interstitial-water salinities at this site are due to an artesian flow through these sediments at some time in the past (Site 438 report, this volume).

Site 439

The single hole at Site 439 was drilled in 1656 meters of water, about 35 km landward from the top of the inner west slope of the Japan Trench, and 135 km from the shoreline. It is 5 km from Site 438 and began in the same stratigraphic sequence. Spot cores were taken at several intervals to a depth of 850 meters. Below that, coring was continuous to a depth of 1157 meters.

Gas samples from Hole 439, which was drilled close to, and as a continuation of, Holes 438, 438A, and 438B, were taken from spot cores at 500, 550, 650, and 750 meters, and from each core in the continuously cored interval below 850 meters. The age of the basal claystone is Late Cretaceous; the strata above it range from Oligocene to Holocene.

TABLE 4
Correlation Coefficients for Gases

Site	Log C ₁ /C ₂ vs. Depth	Log C ₂ vs. Log C ₃	Log C ₃ vs. Log C ₄	Log C ₄ vs. Log C ₅	C ₂ vs. C ₃	C ₃ vs. C ₄	C ₄ vs. C ₅
434	-0.62	+0.19	+0.63	+0.25	+0.12	+0.64	+0.83
435	+0.66	+0.56	+0.68	+0.26	+0.44	+0.88	+0.40
438	-0.78	+0.15	+0.30	+0.62	+0.02	+0.62	+0.65
439	-0.84	+0.91	+0.80	+0.26	+0.91	+0.77	+0.91
440	-0.48	-0.42	+0.90	+0.82	-0.36	+0.96	+0.92
441	-0.65	+0.52	+0.40	+0.68	+0.46	+0.54	+0.75
435 (out of phase)	—	+0.66	+0.53	n.d.	+0.59	+0.22	—
435 (in phase)	—	+0.74	+0.88	n.d.	+0.53	+0.96	—

In the spot-cored intervals, only 1 meter of core was taken at 500 and 550 meters, and only drill cuttings at 670 meters. A 3-meter core was taken at 750 meters. Small amounts of methane were found at 500 and 550 meters (1.69% and 0.45%), and heavier hydrocarbons were not detected. At 650 and 750 meters, the methane content was 67.2 and 45.5 per cent, respectively. Traces of heavier hydrocarbons were also detected.

In the cores that were taken continuously, the methane levels varied throughout the hole, although they are lower in unit IV (fine-grained, 910–1000 m) than in the sandier sections above and below. Relatively large amounts of gas are probably lost in the coarse-grained cores by the time they arrive on deck, because of the higher permeability of sandy sediments.

C₂-C₄ hydrocarbons increased gradually with depth (Site Summary Chart). Correspondingly, the methane/ethane ratio decreases with depth (Figures 3 and 4). The slope of the ratio of methane to ethane versus depth is very similar to that for Site 438. The shapes of the C₂, C₃, and C₄ curves are not the same, in either the coarse- or fine-grained sediments. It was previously postulated that scatter of this type is characteristic of movement of these light hydrocarbons through the sediment (Whelan, in press). However, the scatter of the values — particularly of the C₅ — is more consistent with a local source for these compounds.

The C₅ composition (% neoC₅; % *i*C₅; % *n*C₅) also shows this scatter. Neopentane disappears at about 950 meters (Core 16). According to paleontologic correlation, the Miocene/Oligocene boundary occurs at 892 meters and 907 meters in Holes 438B and 439, respectively. Neopentane is a major C₅ constituent down to this depth at both sites. However, much more scatter in the C₅ data and a disappearance of neopentane below 950 meters is observed at Site 439. Assuming that the scatter in the C₅ data indicates that these compounds remained close to their site of generation, the presence of neopentane at the Miocene/Oligocene boundary in both holes is reasonable. Below this depth, neopentane remains a major component of total C₅ to the bottom of Site 438B, while neopentane disappears at 950 meters in Hole 439 and the percentage of *i*C₅ and *n*C₅ shows a great deal of scatter. Thus, if some of the deeper sediments at the two sites correlate, they must represent different parts of the same unit.

Site 440

Site 440 was drilled on a mid-slope terrace of the west, landward wall of the Japan Trench at a water depth of 4507 meters. The three holes at the site, Holes 440, 440A, and 440B, recovered a nearly continuous set of cores from the sea floor to a sub-bottom depth of 808 meters. The strata range in age from Holocene to late Miocene.

The odor of hydrogen sulfide was apparent only in the shallowest samples. In the depth interval 26 to 160 meters, the sediments were stained black — probably by iron sulfide minerals (see Site 440 report, this volume). Interstitial-water alkalinity was exceptionally high — a maximum of 92 meq/l — which is nearly 100 times the usual values. These data are consistent with the presence of very active bacterial sulfate reduction in these sediments.

The sediment at this site consists of pebbly, clayey silt, as well as fine-grained, diatomaceous deposits; much of the sediment is brecciated by intense fracturing (see Arthur, Carson et al., this volume). Many of the fractures are rehealed. However, geophysical logs and other data suggest that fractures in the interval from about 400 to 600 meters were held open by high fluid pressure.

Methane constitutes 70 per cent or more of core gas from a depth of 20 meters to the bottom of the hole. This is fairly shallow for microbiological methane production compared to the other DSDP sites mentioned above. The shallow methane zone, the high interstitial-water alkalinities, and presence of black sulfide minerals all support microbiological activity in these sediments.

The depositional rates at this site — 230 m/m.y. in the upper 230 meters and 100 m/m.y. below — were high enough to minimize aerobic bacterial oxidation of organic material. The organic-carbon content (0.5–1.2%) is high enough to support bacteria growth or petroleum generation under the right conditions. However, the shipboard pyrolysis-fluorescence measurements (see Site 440 report, this volume) qualitatively indicated values typical of reworked organic carbon, which generally occurs in more aerobic (slowly deposited) sediments. The low hole-bottom temperatures (9°C at 814 m) indicate that these sediments were too cool to have un-

dergone more than minimal petroleum generation. Thus, the refractory nature of the organic material in these sediments is probably due to the activities of microorganisms — possibly aerobic — moving with water and oxygen through the highly fractured sediments.

Levels of methane, C₂-C₅ alkanes, per cent *i*C₄ to *n*C₄, and percentages of neoC₅: *i*C₅: *n*C₅ versus depth are plotted on the Site Summary Chart. The values for these parameters are given in the appendix at the end of this volume. Again, gas is believed to be derived from micro-organisms, for reasons similar to those presented for Site 434. The shapes of the C₂-C₅ curves (plotted against depth) are generally "in phase." The levels of C₃-C₅ are one to two orders of magnitude less than C₂, as at other DSDP sites where microbial methane occurs. The ethane level increases gradually with depth, and, correspondingly, the methane/ethane ratio decreases (Figures 3 and 4).

The variations in composition of gases fit the stratigraphic units of Holes 440, 440A, and 440B fairly well. The zones were as follows:

1. Zone 1, 0 to 220 meters: silt, pebbly silt and clay, and diatomaceous ooze. The most characteristic features of the gas composition of this unit are C₃-C₅ levels higher than in deeper parts of the hole and high ratios of isobutane/*n*-butane and isopentane/*n*-pentane compared to the other Japan Trench sites. Neopentane was not detected, and the C₁/C₂ ratio decreased as expected with increasing depth (Figure 4). This zone is above the level where intense fracturing is evident in the sediments.

2. Zone 2, 220 to 340 meters: pebbly, diatomaceous claystone. In this zone, the methane level drops slightly, but ethane content increases. Thus, the methane/ethane ratios decrease. The levels of heavier hydrocarbons stay approximately constant, and neopentane first appears in Core 440B-10 (225.5 m).

3. Zone 3, 340 to 600 meters: diatomaceous claystone, intensely fractured to "brecciated," with minor faults. In this interval, gases decrease irregularly with depth, but the C₁/C₂ ratio increases, rather than decreases as is normal (Claypool, 1975). This suggests that part of the lightest hydrocarbon, methane, preferentially migrated into this area through minor faults and fractures, causing a higher C₁/C₂ ratio than normal. Neopentane occurs as 20 to 40 per cent of total C₅ through most of this zone.

4. Zone 4, 600 to 814 meters: brecciated, diatomaceous claystone and siltstone, with minor faults. Composition and the relative amounts of gases stay nearly constant with depth, although the distributions fluctuate somewhat. This irregular distribution is probably due to alternations between coarser sediment and finer-grained sediment, and to the minor faults. Neopentane is present to the extent of about 40 per cent of total C₅ in approximately half the gas samples taken within this interval.

Neopentane occurs in most of the fractured sediment zones from 385 meters to the bottom of the hole (18 samples). It is conspicuously absent in non-fractured zones throughout shallower sediments from 20 to 220

meters, and also at 778 and 840 meters. However, we do not imply that neopentane is always associated with fracturing, because seven fractured samples showed no neopentane (730 m, 646 m, 505 m, and four samples from 675 to 750 m).

Site 441

Site 441 lies on the lower part of the western slope of the Japan Trench, about 4 km from Site 434; it was drilled to a total depth of 687 meters. The cores are highly fractured, and core recovery was poor. The strata are primarily diatomaceous sediments of the late Miocene to Holocene.

Because of time constraints, the holes at Site 441 were not continuously cored. However, it is believed that a fair representation of the gas content was obtained, as the cores were systematically spaced, and all cores (including the wash cores) were sampled. The gas data also correlate reasonably well with the results obtained at Site 434. (See C₂-C₅ data plotted versus depth on the respective Site Summary Charts).

No significant correlation between type and amount of gas obtained and lithologic units is observed at this site. This is probably because of the overall-uniform sedimentary column and the high degree of fracturing (the latter may allow for greater water movement through the sediments, possibly vertical and horizontal communication of the gases, and, of course, decreased sediment recovery). The results of the gas analyses are shown on the Site Summary Chart.

Cores 441-1 through 441-4 had a very strong H₂S odor, but the lower extent of the H₂S zone could not be determined, because there was essentially no recovery in Cores 441-5 and 441-6 (83-102 m). Core 441-7 at 150 meters did not contain noticeable H₂S.

The methane content varies considerably throughout the holes, as it did at Site 434. At both sites, however, there was poor recovery. The methane/ethane ratio at Site 441 decrease normally with depth, but did not reach values as low as those encountered at Site 434 (Figure 4). The methane is believed to be microbiological, for reasons similar to those presented for Site 434.

Percentages of C₄ isomers — isobutane and *n*-butane — and the C₅ isomers — neopentane, isopentane, and *n*-pentane (Site Summary Chart) — indicate that a substantial proportion of the C₄ fraction is isobutane throughout the hole, and that a high proportion of C₅ is isopentane to about 370 meters. Neopentane occurred sporadically, as in Hole 434, to the extent of about 10 to 20 per cent of total C₅. The gradual transitions in isomer composition may indicate gas mixing. However, they are more probably due to analysis of wash cuttings which represent an average over a considerable interval in the hole. It is interesting that isopentane appears in greater quantities in deeper sections of Site 441 than Site 434. This, and the scatter in gas data which occurs at both sites, supports a very local source for C₅ hydrocarbons.

In conclusion, although local migration of biogenic gas may have taken place in some of the brecciated and

fractured lithologic units, there is no evidence that long-range vertical migration of petroleum hydrocarbons from source areas at greater depths has occurred. Perhaps this is because the fractures do not persist or are rehealed at depth, or, more likely, because proper conditions for petroleum generation may not exist in this area.

SUMMARY AND INTERPRETATIONS

As discussed for each site, all chemical evidence indicates that the methane found in the western Japan Trench wall is of microbiological rather than petrogenic origin. Other evidence against a petrogenic source is the low geothermal gradient known to exist throughout this area (30°/km for Site 439 to 17°/km for Site 440, and probably less at Sites 434 and 441; see Langseth, this volume). As mentioned earlier, microbiological methane production is found at many DSDP sites containing rapidly deposited, organic-matter-rich sediments.

The source of the traces of C_2 - C_5 alkanes is more problematical. As noted previously, these compounds usually accompany the biogenic methane (see, for example, Hunt and Whelan, 1978; Claypool, 1975). There are several reports in the literature that a mixed anaerobic bacterial culture can produce these trace compounds along with biogenic methane. No traces of C_2 - C_5 are observed when the methanogenic bacteria are cultured alone. However, preliminary work in one of our laboratories has shown that an anaerobic marine bacterial culture can produce small amounts of methane, ethane, propane, and isopentane (Miller, Hunt, and Whelan, unpublished results). Microscopic examination of the bacteria present at the end of the experiment showed small amounts of anaerobic organisms clustered around particulate matter, but none of the larger methanogenic bacteria (i.e., those capable of converting CO_2 to CH_4) were present.

In many of the fine-grained sediments, there appears to be a strong correlation among the amounts of C_2 , C_3 , C_4 , and C_5 . This can be seen at DSDP sites in the Black Sea (Hunt and Whelan, 1978) and in the Canary Islands (Whelan, 1979). Thus, when the log of the amount of each, normalized to 100 per cent methane, is plotted versus depth, the shapes of the curves are very similar. This occurs at several places in the Leg 56 and 57 sediments, as can be seen on the Site Summary Charts — namely, in most samples for Holes 434 and 434B (particularly for C_3 - C_5), for some parts of Holes 435 and 435A, as discussed earlier, in deeper sections of Site 438 (C_2 , C_3), in some places for Site 440 (C_4), and in parts of Site 441 (C_2 - C_4). It is conceivable that a low-temperature chemical process is responsible for this correlation. However, biological systems more typically show this type of specificity. A simple explanation for this correlation is that these compounds or their precursors are bacterially produced in shallow sediments in a constant ratio determined by the organisms present. Deviations from the ratio are caused then either by destruction or by movement of one or more compounds.

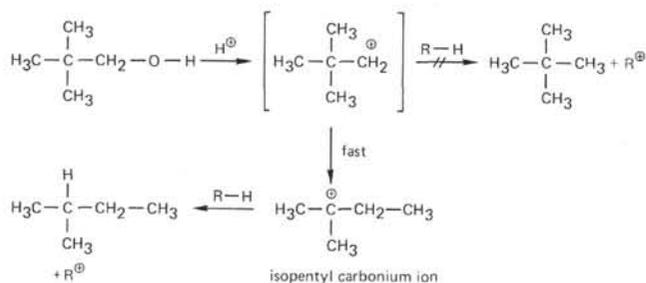
The correlation is presented in another way in Table 4 where correlation coefficients for the various gases are shown for each site. For log C_2 versus log C_3 , the only significant positive correlation is seen for Site 439. It will be remembered that data collected at this site start deeper than at any of the others. For log C_3 versus log C_4 , high positive correlations are seen at Sites 439 and 440. There also seems to be a weaker positive correlation for Sites 434 and 435. Log C_4 versus log C_5 shows little or no correlation, except for Site 440 and possibly 438 and 441. However, positive correlation improves significantly for all sites when C_4 and C_5 are plotted directly (without conversion to logs). In this case, high positive correlations are obtained for Sites 434, 439, 440, and moderate ones for Sites 438 and 441. The table also shows an improvement in correlation for all columns when only the "in-phase" values from Site 435 are used. Thus, there is a significant positive correlation for C_3 , C_4 , and C_5 at most of the sites. With the exception of Site 435, the table also shows negative correlations for log C_1/C_2 plotted against depth. As mentioned earlier, Site 435 is peculiar in this respect when compared to other DSDP sites.

The increase in the log C_1/C_2 value with depth, seen here as well as at other DSDP sites, has been used as one argument against a microbiological source for C_2 - C_5 compounds (Claypool, 1975). The slope of the line produced roughly correlates with the geothermal gradient in each area. Thus, C_1/C_2 decreases more slowly in the cold Aleutian Trench than in the warmer Red Sea. The explanation given for this behavior is that, while C_1 is biogenically produced and must decrease as bacteria die out in deeper sediments, the C_2 is produced by an inorganic chemical reaction. Thus, as temperature increases with increasing depth, C_2 increases, and the C_1/C_2 ratio decreases. This behavior can be seen for all the western Japan Trench wall sediments, except for Site 435, as shown in Figures 3 and 4.

However, it has been pointed out that bacterial activity can also increase as a function of temperature, up to a temperature optimum which varies from one species of organism to another (Farrell and Rose, 1967; Inniss, 1975). Thus, the noted temperature dependence does not rule out a bacterial source for the C_2 - C_5 compounds.

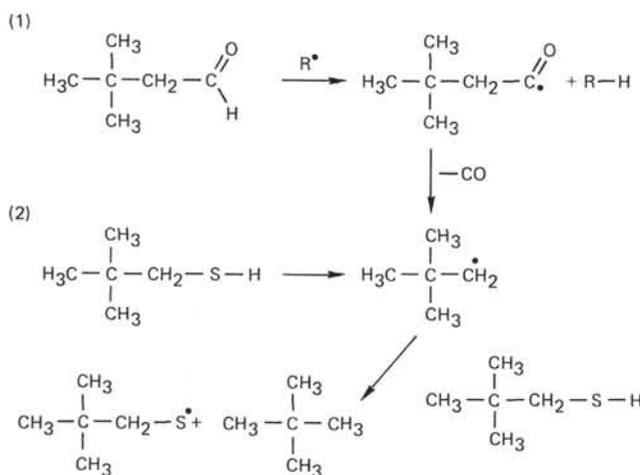
The sporadic presence of the C_5 hydrocarbon neopentane in western Japan Trench wall sediments lends some support to the idea that some or all of the C_2 - C_5 compounds found in DSDP sediments might be produced by microorganisms. This compound occurs only rarely in petroleum (Erdman, 1961; Hunt, 1978). However, it is the major C_5 hydrocarbon found in the Athabasca Tar Sands, where the petroleum initially present has been subjected to partial aerobic bacterial degradation (Strausz et al., 1977).

There is a reasonable chemical explanation for these findings. If petroleum generation occurs via a carbonium-ion process, then any potential precursor for neopentane would rearrange rapidly to the isopentyl structure (March, 1968, and references cited therein):



It is well known that primary carbonium ions rearrange rapidly and irreversibly to tertiary ones whenever possible. There is no experimental evidence for the reverse process, even under drastic conditions, such as generation of equilibrating C₅ carbonium ions in the presence of aluminum chloride and benzene (Pines, 1948).

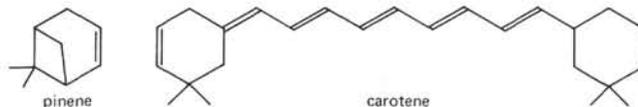
The neopentyl skeleton could be preserved chemically if generated by a free-radical process, because free radicals generally do not undergo carbon-skeleton rearrangements (March, 1968, and references cited therein). Two possible low-temperature pathways for the generation of the neopentyl radical are:



3,3-dimethylbutanal has been postulated as a possible neopentane precursor in the Athabasca Tar Sands (Strausz et al., 1977). It is well known that aldehydes and mercaptans can undergo the types of free-radical generation shown above at low temperatures. Alternatively, the neopentane might be produced microbially. There is evidence that aerobic organisms can degrade straight-chain hydrocarbons, but are stopped by branch points containing no hydrogen (McKenna and Kallio, 1971). The neopentane or its precursor might be an end product of such a biosynthetic reaction.

The arguments presented above require that the neopentyl precursor (or the precursor of any *gem* dimethyl alkane found in the sediment) must be present in the sediment, or that neopentane is produced biologically (because chemical rearrangements do not favor the *gem* dimethyl moiety). The only class of biological compounds that possesses this structural feature is the ter-

penes, examples of which are shown below. A terpene pigment such as carotene is a likely sort of precursor because it occurs very widely, for example in green plant material, although it is only one possibility.



In these sediments, neopentane is found irregularly at all the sites drilled where biogenic methane is present — namely, Sites 434, 435, 438, 439, 440, and 441. The largest amount is detected at Site 438, where it constitutes about 80 per cent of total C₅ from about 580 meters to the bottom of the hole at 1040 meters. This is the largest relative proportion found at any DSDP site to date. Neopentane makes its first appearance at about 320 meters and continues sporadically to about 450 meters. It appears again at 570 meters and then continues to hole bottom. Rehealed faults, fractures, and dewatering veins (see Arthur and Carson, this volume) are characteristic of the sediments of this site from 580 to 810 meters. Below 810 meters, sediments are sandier than in other parts of the hole. Examination of core reports also indicates intervals of coarser sediment and/or dewatering veins in the shallower part of the hole where neopentane first appears. This suggests that oxygenated water, and possibly aerobic bacteria, may have percolated through these sediments in earlier geologic time. A reasonable path for neopentane formation is via degradation of terpene organic matter by aerobic organisms. In this case, the degradation products would accumulate in the sediment as it became more anaerobic and as fractures were rehealed by the activities of anaerobic, sulfate-reducing micro-organisms. The final stages of neopentane formation might therefore have been reduction or removal of oxygenated functional groups via anaerobic organisms attacking oxygenated precursors such as 3,3-dimethylbutanal, as shown earlier.

Support for this scheme is the evidence for an artesian water system through these fractured sediments at some past time, postulated to explain the low interstitial-water salinity values at this site (see Moore and Gieskes, this volume). Such a flow gives a source of aerobic organisms required by the degradation scheme. Possible further evidence for the presence of such organisms is the appearance of a series of oxygenated and olefinic hydrocarbons which increase in sediments deeper than 580 meters (see Whelan and Hunt, this volume). These types of compounds were observed previously in surface sediments (Hunt and Whelan, 1978) where micro-organisms are very active. No other DSDP sediment below a sub-bottom depth of about 100 meters has shown the high levels or wide variety of alkenes found at these sites.

As observed previously (Hunt and Whelan, 1978), neopentane concentrations also seem to rise over other C₅ isomers in coarser-grained sediments where greater

water flow is expected. One possible explanation for this behavior is the greater diffusivity of neopentane as compared to *i*- or *n*-pentane (see Hunt, 1978; Sahores and Witherspoon, 1970). Thus, neopentane moves into coarser sediments faster than *i*- and *n*-pentane. However, a second explanation of the data is that the absorbed organic matter remains fairly close to its *in situ* formation position — possibly by hydrophobic bonding, which is known in biological systems to create very strong attraction between non-bonded and non-polar organic molecules in the presence of aqueous solutions. The absorbed hydrocarbons then remain unaltered over long periods of time unless subjected to either a water-bacterial flow (to give partially oxidized organic products, as observed here) or some other disturbance (for example, exposure to higher temperatures, causing petroleum generation via saturated hydrocarbon formation and/or cracking).

Some support for bacterial neopentane production (versus concentration by greater diffusivity) can be seen in the relative gas concentrations at Site 438, where neopentane decreases in the interval between 550 and 1040 meters (see Site Summary Chart). The first such region occurs at 570 meters — just above the neopentane zone; the second region occurs at 794 meters. In both cases, the neopentane concentration drops to zero, while C_3 – C_5 concentrations increase. In the first case, C_1 and C_2 concentrations stay approximately constant (some decrease in C_1 is evident), while in the second C_1 and C_2 increase. In both cases, it is very hard to see how diffusivity differences could discriminate *against* neopentane while allowing higher concentrations of the lighter, more-mobile C_1 – C_4 molecules. A microbiological mechanism explains these differences in a much more satisfactory way. Thus, in the two cases mentioned above, the C_1 – C_4 hydrocarbons appear in higher concentration because they have not been degraded by micro-organisms in these sediments, or because they are produced in greater quantity.

As mentioned earlier, neopentane also occurs sporadically at the other sites in this area, but not to such a large extent as observed at Site 438. One example is Site 440, where there is evidence for extensive open fractures from about 380 meters to the bottom of the hole at 800 meters. Here, neopentane constitutes up to 40 per cent of total C_5 . In addition, pyrolysis-fluorescence values for this site are very low (see Site 440 report, this volume), and C_6 – C_7 alkanes, as well as the more-oxidized compounds appearing at Site 438, are lower. In fact, a puzzle at most of the sites in this region — including 434, 440, and 441 — has been the collective evidence of refractory organic material in spite of relatively high organic-carbon content (0.5–1%). This evidence consists of low pyrolysis-fluorescence yields, low C_5 – C_7 content (relative to organic carbon present), and the generally small amounts of bacterially produced methane in the core gas in spite of geophysical evidence that these sediments have always been relatively cool. A reasonable explanation is that the intense fracturing of these sediments has allowed much more extensive bacterial degradation here than at Site 438, where the frac-

tures were rehealed and reduced organic material was locked in before degradation was complete.

The arguments given above assume that the small amounts of hydrocarbons present do not move far from their site of generation.

The most compelling argument for the minimal movement of these small alkanes, at least in fine-grained sediments, is in the relatively large changes in concentrations over very short distances — both of C_2 – C_5 species and of isomeric C_4 and C_5 species. The most spectacular example seen to date is in Site 397 sediments. At this site, a large discontinuity appeared at about 1300 meters, where sediment ages changed from Miocene to Cretaceous. The iC_5/nC_5 ratio changed by an order of magnitude from just above to just below this boundary. *Any* movement of these alkanes across this boundary over geologic time would have produced a much more gradual transition.

In the descriptions of each site presented earlier in this paper, it was pointed out that fairly abrupt changes in both amounts of C_2 – C_5 alkanes and in iC_4/nC_4 and $neoC_5/iC_5/nC_5$ ratios are very common. The most reasonable explanation for this behavior is a fairly local hydrocarbon source. It is interesting that these abrupt changes are seen in the more-fractured sediments (Sites 434, 440, and 441), as well as in the less-disturbed ones, as can be seen in the Site Summary Charts. In particular, the changes seen at Site 434 are repeated fairly well at nearby Site 441. Another interesting example, mentioned earlier, is the disappearance of neopentane at Site 439 at 950 meters. The section of Hole 438B which correlates paleontologically (between 892 meters and the bottom of the hole at 1040 meters) shows about 70 per cent neopentane (per cent of total C_5) in all samples. The difference between the two sites exists even though Site 439 is considered to be a continuation of Site 438.

Other workers have also concluded that light-hydrocarbon movement in fine-grained sediments is minimal when only small amounts of hydrocarbons are present at relatively shallow depths (less than 2000 m sub-bottom; see, for example, Young and McIver, 1977, and references cited therein).

The data here suggest that the sediment C_2 – C_5 molecules found in core gas may reflect continuing chemical and/or microbiological changes occurring as a function of depth (temperature). However, the data are also consistent with the idea that some of these molecules may be generated shortly after burial and, if undisturbed, give a “history” of the sediment and the types of micro-organisms which have populated it in past time. This hydrocarbon fingerprint then remains until petroleum-generating depths and temperatures are reached, unless some intervening event disturbs this hydrocarbon pattern — an event such as sediment fracturing and water-bacterial flow.

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