

23. C₁-C₈ HYDROCARBONS IN LEG 64 SEDIMENTS, GULF OF CALIFORNIA¹

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ABSTRACT

Sediments from the Baja California Continental Margin Transect—Sites 474 and 476—showed small amounts of C₂-C₈ hydrocarbons and functionalized compounds (alkenes) typical of organic-rich, Recent, cold (<30°C) marine sediments. In contrast, some samples from Sites 477, 478, 479, and Hole 481A in the Guaymas Basin, an active spreading center, showed the characteristics of thermally generated hydrocarbons. These include an increase (sometimes exponential) in amount and diversity of C₂-C₈ hydrocarbons and a decrease in alkenes in more thermally mature sediments. The results indicate that the injection of basaltic sills has minimal effect on C₂-C₈ hydrocarbon generation except in the immediate vicinity of the sill. The absence of light hydrocarbons close to the hottest sills suggests that the compounds distill away as they are formed in these areas of very active hydrothermal circulation. A sample of young sediment exposed to very high temperatures (>300°C) from deeper thermal sources at the hottest site, 477, showed a very limited hydrocarbon distribution, including primarily ethane, benzene, and toluene, together with smaller amounts of propane and butane.

INTRODUCTION

Samples from Sites 477, 478, 479, and 481 in the Guaymas Basin allowed investigation of organic compound production in sediments exposed to heating in an actively spreading ocean basin (Simoneit et al., this volume, Pt. 2). All of these sites provide information on C₁-C₈ hydrocarbon generation in the recent Pleistocene and younger organic-rich sediments exposed to temperatures in excess of 50°C—the minimum thought to be required for onset of intense hydrocarbon generation (Hunt, 1979; Tissot and Welte, 1978). The hottest of the sites (477) showed extensive hydrothermal alteration in all sections below a doleritic sill. The temperature at the bottom of this hole (181 m) was estimated to be about 300°C or greater (Einsele et al., 1980). Other samples included sediments of similar lithology, age, and depth from the East Pacific Rise—an area of much lower geothermal gradient. These sediments have not been exposed to temperatures in excess of 30°C, so they provide information on C₁-C₈ hydrocarbon generation in lithologically similar sediments that have not been subjected to heat.

The sediments also provide a comparison with other DSDP sediments from the geothermally “colder” and older (maximum age, Miocene) Japan Trench area (Whelan and Hunt, 1980a). The Japan Trench sediments are similar in lithology (primarily diatomaceous) and organic carbon content (typically 1-3%) to those examined here. However, the Japan Trench is an area of very low geothermal gradient (typically 2-3°/100 m or less) so that most of those sediments were exposed to temperatures less than 20°C.

METHODS

Sediments were analyzed by methods described previously (Whelan, 1979). Briefly, the procedure involves sealing a frozen sample and

distilled water in a container equipped with a septum and a helium headspace. The volatile compounds are driven out of the sediment by vigorous shaking and heating of the container to 100°C. The headspace gas is then analyzed by gas chromatography (GC). The only difference between this work and that described previously is that GC conditions were modified so that C₈ compounds could also be analyzed. This was accomplished either by maintaining the hexadecane/hexadecene capillary column at 35°C (rather than 30°) or by using columns whose retention times had shortened because of bleeding of the liquid phase.

C₁-C₈ compounds were identified by subjecting one or more samples from each site to gas chromatography-mass spectrometry and comparing spectra either to those of standards run under the same conditions or to standard reference spectra (Cornu and Massot, 1975). Percent organic carbon and total carbon were determined with a Leco carbon analyzer.

Total amounts of hydrocarbons (C₁-C₂₆) in the sediment were determined by thermal distillation-pyrolysis (TDP) as described by Whelan, Hunt, and Huc (1980). This technique involves heating wet samples in a helium stream and measuring total hydrocarbons evolved as the temperature is raised from 150 to 600°C at 60°/min. At low temperatures (about 150-250°C) the absorbed hydrocarbons present in the rock are swept out, while at high temperatures (300-600°C) the kerogen in the rock breaks apart or cracks. The analysis produces a pyrogram which records total hydrocarbons released from the sediment as a function of temperature as shown in Figures 1 and 2 for Site 477 and Hole 481A, respectively. Two peaks can be seen in each pyrogram: P₁ is related to absorbed hydrocarbons in the sediment; P₂ is related to hydrocarbons cracked from the kerogen and represents total hydrocarbon that could be generated with further exposure to time and temperature.

RESULTS AND DISCUSSION

Baja California Continental Margin Transects— Sites 474 and 476

C₁-C₈ hydrocarbon distributions, sample depths, lithologies, and geologic ages are shown in Table 1 and Figure 3. Samples include only the top sections (less than 60 m sub-bottom) or Recent (Pleistocene and younger) diatomaceous muds. Levels of several hydrocarbons including *n*-heptane, methylcyclohexane, and toluene remain relatively constant with depth. Several alkenes, including cyclohexene (seen at low levels in all sections), 1, 2- and 3T4-dimethylcyclopentene, 2-hexene, and meth-

¹ Curray, J., Moore, D. G., et al., *Init. Repts. DSDP*, 64: Washington (U.S. Govt. Printing Office).

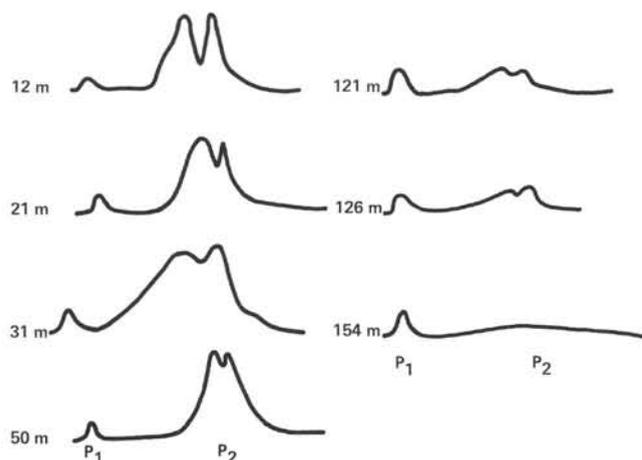


Figure 1. Pyrograms, Site 477 sediments. (Depth in meters.)

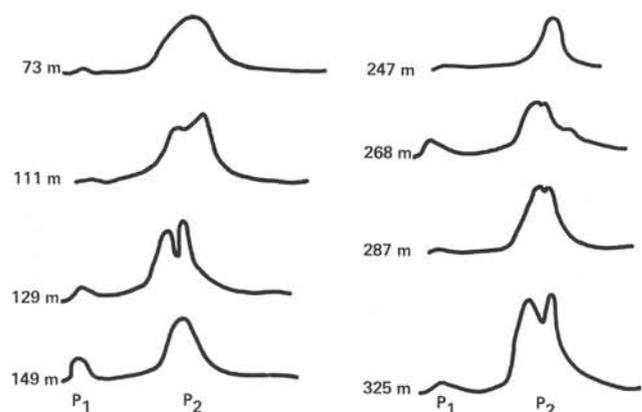


Figure 2. Pyrograms, Hole 481A sediments. (Depth in meters.)

ylpentene (which occur in specific samples) were also detected. Based on previous work, these compounds are thought to be formed by biological/low temperature chemical processes ($< 30^{\circ}\text{C}$) occurring near the sediment/water interface before sediment burial (Whelan, Hunt, and Berman, 1980). All of the compounds found here have been detected in other Recent diatomaceous sediments, including gravity cores from the Peru Shelf (Whelan, Tarafa, and Hunt, unpublished data) and Walvis Bay (S.W. Africa) (Whelan, Hunt, and Berman, 1980), as well as in older geothermally cold sediments recovered from the Japan Trench (DSDP Legs 56 and 57, Whelan and Hunt, 1980a).

The compound distribution is typical of diatomaceous organic-rich sediments that have not been subjected to temperatures much above those occurring at the sediment/water interface at the time of deposition. This pattern (see Fig. 3 and Table 1) includes: the presence of several alkenes and occasional traces of aldehyde; a limited number of saturated and aromatic hydrocarbons including *n*-heptane, methylcyclohexane, and toluene; and an absence of hydrocarbon increase with sub-bottom depth.

Some compound distributions in young cold sediments have been postulated to reflect conditions at the

time of deposition rather than diagenetic changes after burial (Whelan, Hunt, and Berman, 1980). Specifically, the occurrence of relatively high amounts of methane in Site 474 samples suggests more anoxic conditions at or shortly after deposition of the Site 474 samples as compared to those for Site 476. Levels of absorbed methane in frozen recent sediment cores can be used as a qualitative indicator of past activities of methanogenic bacteria (Whelan, Hunt, and Berman, 1980). Both 2- and 3-methylthiophene in Sample 474-4-2 at 23 meters depth were detected. These compounds are often associated with the community of sulfate-reducing bacteria in anoxic gravity cores. In contrast, the absence of thiophenes at Site 476 suggests more oxic depositional conditions for these samples.

Guaymas Basin

Site 477 is located on the south-spreading rift of the basin. The sediments recovered were all late Quaternary diatomaceous oozes (organic carbon 1–3%) intruded by magmatic sills. A very high heat flow was measured below the sill (Gieskes, et al., this volume, Pt. 2). In addition, sediments below the sill showed extensive thermal alteration attributed to effects of deeper heat sources in the sediment. The deepest sediment recovered from this site (258 m sub-bottom) was estimated to have been heated to a temperature of about 300°C (Einsele et al., 1980) on the basis of the mineral assemblage. High temperatures were indicated by the melting of a core liner at the bottom of this hole.

Hydrocarbon distributions and a summary of geological information for this site are shown in Table 1. Total C_1 – C_8 hydrocarbon levels are shown in Figure 4 where both C_1 and total C_2 – C_8 levels are shown on a log scale. The exponential increase in total C_2 – C_8 hydrocarbons with depth is typical of an increase in thermally generated hydrocarbons. The composition of the C_2 – C_8 compounds is also plotted in Figure 4 on a linear scale. The most remarkable feature of this graph is the large increase of ethane in our deepest sample from this site (at 156 m).

Hydrocarbon distributions are shown in more detail in Figure 5. Sediments above the sill show approximately the same hydrocarbon levels and distributions as detected for the Site 474 and 476 sediments, with a modest increase in several compounds just above the sill. This result suggests that sediments above the sill have not been heated to temperatures above 50°C and that the sediments were deposited after the sill had been formed. Since mineralogy and inorganic ions present in interstitial water suggest extensive hydrothermal alteration, another possibility is that all organic compounds were quickly distilled away from the sill contact. The compounds detected here might then represent compounds which formed and/or migrated after the sill had cooled.

In contrast, the sample at about 15 meters below the sill (477-16-5 at 122 m sub-bottom) shows a wide distribution of saturated and aromatic hydrocarbons at levels

about 10 times those just above the sill. The same compounds appear, but in lower levels, in Sample 477-17-1 at 126 m. Since both samples have similar organic carbon levels, it is possible that these compounds were produced by magma flowing over the sediments, with the influence of the heating falling off with increasing distance from the sill.

However, because all the sediments below the sill are described as being hydrothermally altered because of additional deeper heat sources, these would also be expected to influence thermally produced hydrocarbon levels throughout the hole. This influence can be seen most dramatically in the deepest sample from this site (477-20-1, 154 m). The distribution of compounds in this sample is very different from that of any other DSDP sample investigated to date. The lightest hydrocarbons predominate, with ethane, propane, and butane being present in levels of 1046, 140, and 8 ng hydrocarbon per gram dry weight of sediment, respectively. The fact that the relative level of the lightest compound, ethane, is about 10 times higher than the next heavier homolog, propane, is consistent either with preferential migration of the smallest compound or with thermal cracking of longer hydrocarbon chains to give predominantly small fragments. The latter process is postulated to occur in deeper, hotter sections of sediments (>250°C) undergoing active petroleum generation (Hunt, 1979). Consistent with this hypothesis is the relatively high level of methane in the section (see Fig. 4).

A relatively hot hydrothermal source for the hydrocarbons in this deepest section is supported by several other observations. First, the methane $\delta^{13}\text{C}$ values of -40 to -44‰ support a thermogenic rather than a biogenic methane source in deeper sections of this hole (Galimov and Simoneit, this volume, Pt. 2). Secondly, the ethane is accompanied by moderate levels of the aromatic hydrocarbons benzene and toluene, but by no other C₅-C₇ hydrocarbons—very unusual in comparison to other DSDP sediments studied. It has been reported that in petroleum source rocks, benzene and toluene migrate preferentially over other C₆ and C₇ hydrocarbons (Thompson, 1979). It is well known that aromatic hydrocarbons can be produced by thermal degradation of many organic materials. For example, both benzene and toluene result from the thermal degradation of the amino acid phenylalanine (Vallentyne, 1964). Toluene also forms from the thermal degradation of β -carotene (Day and Erdman, 1963). Finally, the sediment at 154 meters depth is described as being a brecciated silty claystone containing coaly fragments. Thus, this section may be more porous and migration-prone than the sections at 122-126 m, which are described as more clayey.

Below the sill, several compounds appear in much lower levels or not at all. These include the alkenes (2-hexene and methylpentene in Fig. 5). The explanation is that these compounds probably do not survive in sediments exposed to even mild heating (>30°C) since they are not generally detected below the surface in DSDP sediments. However, they have been detected at depth in the geothermally cold sediments recovered from the

Japan Trench (DSDP Legs 56 and 57; Whelan and Hunt, 1980a).

Thermal distillation-pyrolysis analyses are consistent with the thermal history of the sediment as described. Figure 1 shows a very small P₁ peak as compared to P₂ for the shallower sediments (12-50 m), which is typical of immature sediments. Below the sill, sediments from 121 and 126 meters show P₁ and P₂ becoming more equal as would be expected if the sediment was undergoing maturation or heating, with P₂—the measure of hydrocarbon-generating potential—decreasing as more hydrocarbons are cracked off the kerogen matrix and contribute to an increase in P₁. Finally, P₂ disappears almost entirely in the 154-meter sample because of exposure of the sediment to temperatures high enough to crack much of the kerogen present.

The relationship has been quantified via the Production Index (P.I.), defined by the relationship $\text{P.I.} = \text{P}_1 / (\text{P}_1 + \text{P}_2)$ as suggested by Espitalié et al. (1977) and used in this laboratory (Huc and Hunt, 1980). Thus, this index is related to the relative increase of free absorbed hydrocarbons in the rock as a result of natural breakdown of the kerogen during maturation and is shown for sediments from Sites 477 and 481 in Table 4. The low P.I. values (<0.1) are typical of immature sediments (Huc and Hunt, 1980), while the higher values (0.17-0.71) from 121 to 154 meters are typical of more thermally mature sediments (those exposed to temperatures in excess of 100°C).

Table 4 also shows the maximum temperature of the P₂ peaks. In several samples, P₂ is actually split into two distinctive peaks (see Fig. 1). The two peaks may represent two types of kerogen (with different resistance to cracking) that are dominant in the sediments. Kerogens are classified into various types (for a summary, see Hunt, 1979, p. 274). The sapropelic types of kerogen tend to decompose at lower temperatures than do the humic types. In ancient sediments, such as South Padre formation in the Gulf of Mexico (Huc and Hunt, 1980), these differences tend to blend together during catagenesis. In recent young sediments, however, they show up clearly on the P₂ peaks. If the kerogen has been subjected to such external sources of heat as magmatic sills or hydrothermal alteration, the maximum temperature of the P₂ peak (T_{max}) will shift to a higher range.

The effect of hydrothermal alteration in Hole 477 shows up in both the P.I. and T_{max} . Above the dolerite sill (Table 4) there is almost no change in P.I., but a noticeable increase in T_{max} of the first P₂ peak. Below the sill, the P.I. increases by a factor of more than 10 and T_{max} reaches a maximum reading of 460°C. At the sediment depth of 154 meters at Site 477, the P.I. is higher than at 4877 meters in a mature source rock taken from the Texas Gulf Coast at South Padre (Huc and Hunt, 1980). This comparison once again shows that temperature is more important than time and pressure for the conversion of kerogen to hydrocarbons.

Site 478 is 12 km from Site 477 in the southern Guaymas Basin and represents an older flanking site. Heat flow was about six times lower than at Site 477. C₁-C₈ hydrocarbon levels, organic carbon levels, and

Table 1. C₁-C₈ volatile compounds in Leg 64 sediments.

Sample (interval in cm)	474-4-2, 40-49	474-5-3, 115-120	476-2-2, 73-79	476-3-4, 37-41	476-7-2, 113-117	477-3-1, 135-140	477-4-1, 145-150	477-5-1, 115-120	477-7-1, 132-137	477-16-5, 62-68	477-17-1, 140-145	477-20-1, 155-122	478-2-1, 7-18	
Water Depth (m)	3033	3033	2413	2413	2413	2013	2013	2013	2013	2013	2013	2013	1899	
Sediment Depth (m)	23	35	12	23	59	11.5	21	30.5	49.8	122	125.9	154	3.6	
Lithology	Diatomaceous Ooze, H ₂ S-rich	Diatom Ooze, H ₂ S-rich	Nannofossil Diatom Ooze	Nannofossil Diatom Ooze	Silty Clay Sand	Diatom Ooze, Diatom Clayey Silt, Mud Turbidite	Sandy Silt, Diatom Ooze, Turbidite Cycle	Diatom Ooze to Mud, High H ₂ S	Diatom Ooze (above sill)	Hydrothermally Altered (just below sill)	Hydrothermally Altered Clayey Siltstone (coarser than Core 16)	Brecciated Pyrite, Coaly Fragments, Carbonaceous/Silty Claystone	Muddy Diatom Ooze (sand just below)	
Age	Quaternary	Quaternary	Pleistocene	L. Pleistocene	E. Pleistocene	L. Pleistocene	L. Pleistocene	L. Pleistocene	Quaternary	Quaternary	Quaternary	Quaternary	L. Pleistocene	
Packed Column (ng/g dry wt. sediment)														
Methane	C ₁	464	285	7.6	6.2	5.6	858	157	587	73	153	703	522	7
Ethane	C ₂	1.58	2.0	1.7	0.86	1.08	0.41	2.5	2.0	23	117	258	1046	1.94
Propane	C ₃	1.76	2.9	2.6	0.85	1.22	0.45	2.7	2.99	7.6	162	222	140	1.92
<i>i</i> -Butane	<i>i</i> -C ₄	0.39	1.1	0	0	0	0	0.3	1.03	0.9	23	19	4.5	0
<i>n</i> -Butane	<i>n</i> -C ₄	0.50	1.13	1.5	0.22	0	0.26	1.6	1.11	3.8	52	50	3.2	0
neo-Pentane	neoC ₅	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>i</i> -Pentane	<i>i</i> -C ₅	4.0	5.4	0	0	0	0	4.0	4.34	1.8	7.2	6.4	0	0
<i>n</i> -Pentane	<i>n</i> -C ₅	0.43	2.1	0	0	0	0	0.4	1.36	1.7	6.3	5.3	0	0.01
Cyclopentane	CP	0	0.7	0	0	0	0	0	0.77	1.5	3.3	2.0	0	0
Capillary Column														
2,2DiMeButane	22DMB	2.9	0	0	0.1	0	0.2	0.2	0	0	0	0	0	0
2,3DiMeButane	23DMB	0.8	0.1	0	0.2	0.15	1.7	0.3	1.0	0.1	0.83	0.43	0	0.7
2MePentane	2MP	4.6	0.1	0.4	0.4	0.40	1.2	0.1	1.0	1.0	3.8	1.9	0	1.0
3MePentane	3MP	0.4	0.83	0.1	n.d.	0.2	0.1	0	0.7	3.4	6.9	1.0	0	0.2
<i>n</i> -Hexane	<i>n</i> -C ₆	1.8	0	0.5	0.6	3.0	0.56	0.1	0	2.1	8.1	4.4	0	0.94
MeCycloPentane	MCP	0.82	0	0.1	0.01	0.46	0.1	0	2.0	0.88	14	6.6	0	0.1
2,2DiMePentane	22DMP	0.65	0	0	0.14	0.15	0	0	0	1.5	0.4	0	0	0.1
Benzene + 2,4DiMePentane	Benz + 24DMP	1.2	0	0.2	0.25	0.37	0.26	0.1	1.00	1.5	151	88	170	0
2,2,3TriMeButane	2,2,3TMB	0	0	0	0	0	0	0	0.6	0.6	0	0	0	0
CycloHexane	CH	0.32	0	0	0.13	0.2	0.01	0	0.2	1.7	3.7	1.9	0	0
3,3DiMePentane	3,3DMP	0.1	0	0	0	0	0	0	0.1	0	0	0	0	0.1
1,1DiMeCycloPentane	1,1DMCP	0	0.16	0	0	0	0	0.8	0	0	0	0.2	0	0.1
2MeHexane	2MH	0	0	0.3	0	0	0	0	0.1	0.3	4.0	1.8	0	0
2,3DiMePentane	2,3DMP	0.77	0	0	1.09	0.2	0	0	0	0.3	0.3	0.7	0	0
1C3DiMeCycloPentane	1C3DMCP	0	0.32	0	0	0	0	0	0	1.4	12	2	0	0
3MeHexane	3MH	0.13	0.32	0	0	0	0.1	0	0	0	0	0	0	0
1T3DMCPentane	1T3DMCP	0	0	0	0	0.1	0.1	0	0.1	1.4	3.0	1.0	0	0
1T2DMCPentane	1T2DMCP	0.2	0	0	0	0.1	0.1	0	0.1	0.9	4.0	1.5	0	0
3EthylPentane	3EP	0.1	0	0.1	0.1	0.1	0.1	0	0	0.9	0	0	0	0
C ₈	2,2,4TMP	0	0	0	0	0	0	0	0	0.01	0	0	0	0
<i>n</i> -Heptane	<i>n</i> -C ₇	1.1	0.62	0.38	0.73	0.2	0.33	0.1	0.1	1.6	21	8.3	0	3
1C2DMCycloPentane	1C2DMCP	0	0	0	0	0	0	0	0	0	2.6	0.4	0	0
MethylCycloHexane	MCH	0.5	0	0	0.1	0	0	0	0.1	2.1	12	3.1	0	0.1
EthylCycloPentane	ECP	0	0	0	0	0	0	0	0	0.1	2.2	0	0	0
C ₈	2,5DMH	0	0	0	0	0	0	0	0	0.1	2.0	0.4	0	0
C ₈	2,4DMH	0	0	0	0	0	0	0	0	0.1	2.0	0.4	0	0
C ₈	1T2C4TMCP	0	0	0	0	0	0	0	0	0	0	0	0	0
Toluene	Tol	2.9	1.2	1.5	3.81	1.98	0	0	0.38	0.6	2.4	6.4	18	4.7
C ₈	1,1,3TMP	0	0	0	0	0	0	0	0	14	25	0	0	0
C ₈	2,3,4TMP	0.4	0	0	0.1	0.2	0	0	0	0	0	0	0	0
C ₈	1,1,2TMP	0	0	0	0	0	0	0	0	0.5	0.1	0	0	0
C ₈	1C2T4TMCP	0.5	0	0	0.1	0.15	0	0	0	0	10	2.5	0	1.0
C ₈	1C2T3TMCP	0	0	0	0.1	0	0	0	0	0	0	0	0	0
C ₈	3MHept	0	0	0	0	0	0	0	0	0	10	2.5	0	0
C ₈	1,1DMCH	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₈ (A)	1T4DMCH	0	0	0	0.15	0.15	0	0	0.5	6	1.8	0	0	0
C ₈	2,2,5TMH	0.4	0	0	0	0	0	0	0	0	0	0	0	0
C ₈	MECP(A) ^a	0	0	0	0	0	0	0	0	1.0	0	0	0	0
C ₈	MECP(B) ^a	0	0	0	0	0	0	0	0	0	2	0	0	0
C ₈	1T2DMCH	0	0	0	0	0	0	0	0	0	3	0	0	0
C ₈ (B)	1C4DMCH	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₈	<i>i</i> -PropCP	0	0	0	0	0	0	0	0	0.28	30	25	0	0
C ₈	<i>n</i> -C ₈	0.2	0	0.1	0	0	0	0	0	0	1	0	0	1.0
C ₈	Tetra MCP	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₈	MECP(C) ^a	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₈	1C2DMCH	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₈	MECP(D) ^a	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₈	MECP(E) ^a	0	0	0	0	0	0	0	0	0.5	0	0	0	0
EthylBenzene		0.2	0	0	0	0	0	0	0	n.d.	0	0	0	0
Xylenes		0.4	0	0	0	0	0	0	0	3.4	0	0	0	0.4
MePentene		0	3.2	0	0	0.15	0	0	0	n.d.	1.3	0	0	0
2-MePentene		0	0	0	0	—	0	0	0	0	0	0	0	0
3-MePentene		0	0	0	0	—	0	0	0	0	0	0	0	0.2
4-MePentene		0	0	0	0	—	0	0	0	1.11	0	0	0	0.34
2-Hexene		0	0	0	0	0	0.1	0	0	0.1	0	0	0	0
1 MeCyclopentene		—	0	—	0	—	0	0	0	0	0	0	0	0
DMCPenes		0.17	0	0	0	0	0	0	0	—	—	—	—	—
1,2-DMCPene		0	0	0.1	0	0.15	0	0	0	—	—	—	—	—
1,3-DMCPene		0	0	0	0	0	0	0	0	—	—	—	—	—
1,5-DMCPene		0	0	0	0	0	0	0	0	—	—	—	—	—
Cyclohexene		0.15	0	0	0.1	0.1	0	0	0	0	0	0	0	0.4
2-MeButanal		0	0.7	0	0	0	0	0	0	0	0	0	0	0
3-MeButanal		0	0.8	0	0	0	0	0	0	0	0	0	0	0
2-Methiophene		0.97	0	0	0	0	0	0	0	0.1	0	0	0	0
3-Methiophene		0.14	0	0	0	0	0	0	0	0	0	0	0	0
Ethylcyclohexane		0	0	0	0	0	0	0	0	0	0	0	0	0
Totals														
Total Carbon ^b		5.39±0.04	3.84±0.01	4.43±0	5.09±0.04	3.82±0.3	1.92±0.1	3.82±0.03	4.02±0.01	3.22±0.1	0.89±0.01	0.91±0.01	1.56 ^d	4.57±0.04
Organic Carbon ^b		3.65±0.03	2.63±0.03	2.50±0.01	3.91±0.02	2.16±0.02	1.41±0.3	2.88±0.01	2.97±0.01	2.23±0.02	0.99±0.01	0.96±0.04	0.95 ^d	3.63±0.04
Hydrocarbons ^c		464	285	7.6	6.2	5.6	858	157	587.0	73	153	703	522	7
C ₁		—	—	—	—	—	—	—	—	—	—	—	—	—
C ₂ -C ₃		3.34	4.9	4.3	1.71	2.3	0.86	5.2	5	31	280	480	1186	3.9
C ₄ -C ₇		25	13.8	5.1	7.9	7.6	6.8	6.6	16	32	344	212	196	11
C ₈		2.1	0	0	0.55	0.5	0.0	0.0	0.0	17	90	33	0	2
Other Compounds		1.4	4.7	0.1	0.51	0.4	0.1	0.0	0.0	4.7	1.3	0.0	0	1.3

Note: n.d. = not determined.
^a Represent different positional and cis-/trans-isomers. Exact stereochemical assignments not known.
^b Standard deviations given for duplicate samples.
^c Saturated and aromatic hydrocarbons.
^d Shipboard values.
^e Identified as either ethylbenzene or another unknown C₈ with about the same retention time.

Table 1. (Continued).

Sample (interval in cm)	479-29-5, 130-134	479-34-5, 135-140	479-39-4, 135-140	479-43-1, 120-125	479-47-4, 137-140	481-P3-2, 31-46	481-P10-2, 45-55	481A-4-2, 110-125	481A-8-2, 115-125	481A-10-2, 137-150	481A-12-2, 120-135	481A-22-4, 122-150	481A-24-5, 121-131	481A-26-5, 120-131	481A-30-5, 117-122		
Water Depth (m)	757	757	757	757	2008	2008	2008	1998	1998	1998	1998	1998	1998	1998	1998		
Sediment Depth (m)	266.8	314.3	360.3	393.7	436.3	6.6	44.7	73.1	111.2	130.4	149.2	247.7	267.7	286.7	324.7		
Lithology																	
	Muddy Diatom Ooze	Muddy Diatom Ooze	Muddy Diatom Ooze	Muddy Diatom Ooze	Dolostone	Diatom Silty Clay	Diatom Silty Clay	Diatom Clay	Diatom Clay	Diatom Clay	Silty Clay Carbonate	Diatom Clay Carbonate	Diatom Silty Clay	Diatom Silty Clay	Diatom Silty Clay		
Age	E. Pleistocene	E. Pleistocene	E. Pleistocene	E. Pleistocene	Pleistocene	Quaternary	Quaternary	Quaternary	Quaternary	Quaternary	Quaternary	Quaternary	L. Pleistocene	L. Pleistocene	L. Pleistocene		
Packed Column																	
Methane	C ₁	667	2085	1809	1053	27	304	198	469	739	188	157	490	257	157	309	
Ethane	C ₂	16	64	101	103	8.3	1.1	0.16	22	9.3	10	199	9.7	6.8	5.4	33	
Propane	C ₃	8.9	16	88	56	14	1.1	0.55	5.0	17	16	31	18	4.1	5.1	25	
i-Butane	i-C ₄	1.9	3.9	56	196	75	0.52	0	6.7	175	112	143	66	8.5	9.2	173	
n-Butane	n-C ₄	0.4	1.6	12	7	3	0.11	0	3.2	224	100	31	17	2.0	3.9	18	
neo-Pentane	neo-C ₅	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
i-Pentane	i-C ₅	1.0	1.7	33	24	28	0.2	0	23	388	176	707	78	16	24	86	
n-Pentane	n-C ₅	2.5	1.1	14	5.1	6.7	0	0	2.5	123	92	73	19	3.50	4.3	20	
Cyclopentane	CP	35	4.7	41	24	37	0	0	0.0	7.0	5.8	4.1	0.0	0.0	0.0	0.0	
Capillary Column																	
2,2DiMethButane	22DMB	0.2	0.3	2.0	1.6	1.2	0.8	0.6	0.5	1.4	0.66	1.0	0.55	0.20	0.10	1.7	
2,3DiMethButane	23DMB	2.2	2.3	7.8	8.4	6.4	0	0	1.8	12	8.0	23	2.8	1.3	0.60	44	
2MePentane	2MP	0.74	1.5	7.9	6.3	6.8	0	0	2.8	33	33	44	12	2.6	3.3	12	
3MePentane	3MP	0.71	0.59	2.8	2.2	2.7	0.15	0.1	1.8	31	25	100	5.0	3.6	1.5	23	
n-Hexane	n-C ₆	2.1	1.2	9.2	3.3	3.2	0	0.2	2.6	30	44	9.8	10	3.9	2.8	14	
MeCycloPentane	MCP	1.8	2.5	81	58	35	0	0.3	1.1	54	88	84	20	2.0	8.1	85	
2,2DiMethPentane	22DMP	1.9	0.1	0.4	0.7	1.4	0	0.9	0.0	1.5	0.2	0.5	0	0	0	2.6	
Benzene + 2,4DiMethPentane	Benz + 24DMP	4.3	2.4	4.4	4.1	2.6	3.41	0.1	1.0	25	26	15	107	18.0	52	6.7	
2,2,3TriMethButane	2,2,3TMB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.16	0	0	0	0	2.4	5.1	0	0.77	
CycloHexane	CH	4.7	4.2	12	7.7	4.5	0	0	1.0	13	27	33	2.4	1.5	0.59	38	
3,3DiMethPentane	3,3DMP	0.2	0.78	0.6	1.2	0.2	0	0	0	0	0	0	0	0	0	0	
1,1DiMethCycloPentane	1,1DMCP	0.21	0.1	0.66	0.1	0.2	0.6	0	0	1.4	1.3	4.2	0.50	0.20	0	3.3	
2MeHexane	2MH	0.1	0.1	0.1	0.1	0.6	0	0	0.5	1.9	3.2	3.2	1.1	0	0	4.8	
2,3DiMethPentane	2,3DMP	3.4	2.3	6.6	4.4	5.2	0	0	0.5	1.9	2.6	4.8	1.9	0.72	0.79	9.6	
1C3DiMethCycloPentane	1C3DMCP	9.3			13	0	0	0									
3MeHexane	3MH		8.5	27	18	0.3	0	0	0.91	11.4	14	70	8.0	6.8	1.6	54	
1T3DiMethCycloPentane	1T3DMCP	9.8	9.5	32	14	9.8	0	0	0	10.5	9.62	57	4.8	2.9	1.0	56	
1T2DiMethCycloPentane	1T2DMCP	6.9	11	58	43	28	0	0	0	14.7	15	90	7.7	4.8	2.2	110	
3EthylPentane	3EP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
C ₈	2,2,4TMP	0.1	0.1	0.1	0	0.2	0	0	0	0	0	0	0	0	0	0	
n-Heptane	n-C ₇	1.5	0.84	2.4	2.0	3.6	0.2	0.1	0.85	4.4	12	7.3	8.1	2.2	2.6	8.4	
1C2DiMethCycloPentane	1C2DMCP	1.1	1.2	7.6	8.3	8.0	0	0	0	3.7	4.79	43	3.8	1.6	1.1	51	
MethylCycloHexane	MCH	8.4	7.8	28	15	19.6	0	-1.0	12.7	20	85	12	4.8	8.3	81	81	
2,2DiMethHexane	2,2DMH	0	0	0.1	0	0.86	0	0	0	0	0	0	0	0	0	0	
EthylCycloPentane	ECP	1.2	2.8	11	5.4	3.5	0	0	2.7	4.5	20	3.7	1.4	0.67	14	14	
C ₉	2,5DMH	0.18	0	0	0.4	0	0	0	0	0	0	0.2	0	0	0	0	
C ₉	2,4DMH	0.33	0.35	0.77	0.6	0.5	0	0	0	0	0	0.2	0	0	0	0	
C ₉	1T2C4TMCP	2.2	4.0	16	8.7	7.2	0	-1.4	-1	-1.3	36	1.7	0	0	0	20	
Toluene	Tol				18	11.5	-10	3.2	2.0	0	11	7.1	41	23	5.7	0	20
C ₈	1,1,3TMP		6.4	18	5.7	-22	0	0	0	0	0	0	0	0	0	0	
C ₈	2,3,4TMP	2.5	4.5	4.7	1.3	4.0	0	0	0	0	0	0	0	0	0	0	
C ₈	1,1,2TMP	0.7	2.0	4.2	3.3	2.83	0	0	0	0	0	6.3	0.96	0	0	10.3	
C ₈	1C2T4TMCP	1.4	0.86	3.9	0.4	2.2	0	0	0	0	0	16	0.88	0	0	10	
C ₈	1C2T3TMCP	2.1	2.3	6.6	3.9	2.8	0	0	0	0	0	0	0	0	0	0	
C ₈	3MHepi	1.6	0	0.5	0	1.0	0	0	0	0	0	9.9	0	0	0	0	
C ₈	1,1DMCH	0.5	0	0.4	0	0	0	0	0	0	0	0	0	0	0	0	
C ₈ (A)	1T4DMCH	11	28	15	16.5	0	0	0	0	0	0	0	0	0	0	0	
C ₈	2,2,5TMH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
C ₈	MECP(A) ^h	2.8	1.0	8.2	3.3	3.3	0	0	0	0	0	12	5.8	0	0	9.3	
C ₈	MECP(B) ^h	4.2	14	23	10	11	0	0	0	0	0	26	2.5	0	0	30	
C ₈	1T2DMCH	0.5	0	16	3.0	8.5	0	0	0	0	0	0	0	0	0	0	
C ₈ (B)	1C4DMCH	1.8	3.4	23	10	7.0	0	0	0	0	0	0	0	0	0	0	
C ₈	i-PropCP	1.8	12	3.7	1.6	2.9	0	0	0	0	0	6.1	0	0	0	0	
C ₈	n-C ₈	0.92	2.6	4.4	1.5	2.0	0	0	0	0	1.0	0	0	1.0	0	0	
C ₈	Tetra MCP	0	0	0	0	2.9	0	0	0	0	0	0	0	0	0	0	
C ₈	MECP(C) ^h	0	0	1.2	1	2.0	0	0	0	0	0	6.1	0	0	0	0	
C ₈	1C2DMCH	0	0	3.2	0.96	2.6	0	0	0	0	0	6.0	7.11	0	0	0	
C ₈	MECP(D) ^h	0	0	0	0	9.6	0	0	0	0	0	0	0	0	0	0	
C ₈	MECP(E) ^h	1.8		5.0	0.1	0	0	0	0	0	0	0	0	0	0	0	
EthylBenzene		40 ^c	71 ^c	606 ^c	110 ^c	74	0	0	0	-15	-40	-500	-62	-30.0	0	0	
Xylenes		20	17	-20	-5	0	0	0	0	0	-80	-490	684	-60.0	0	0	
MePentane		0.42	0.42	0.99	0.1	0	0	0	0	0	0	0	0	0	0	0	
2-MePentane																	
3-MePentane																	
4-MePentane																	
2-Hexene		0.4	1.6	0.5	1.4	0	0	0	0	0	0	0	0	0	0	0	
1 MeCyclopentene																	
DMCPenes		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1,2-DMCPene																	
1,3-DMCPene																	
1,4-DMCPene						0.2	0.2										
Cyclohexene		0	0	0	0	0	0.8	0.15	0	0	0	0	0	0	0	0	
2-MeButanal		0	0	0	0	0	0	0.2	0	0	0	0	0	0	0	0	
3-MeButanal		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
2-Methiophene		0	0	0	0	0	-1	0	0	0	0	0	0	0	0	0	
3-Methiophene		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Ethylcyclohexane		2.0	0	0	0.8	0.98	0	0	0	0	0	0	0	0	0	0	
Totals																	
Total Carbon ^b		3.04 ± 0.01	3.66 ± 0.01	4.55 ± 0.02	3.64 ± 0.02	2.70 ± 0.03	3.61 ± 0.02	4.76 ± 0.04	3.49 ± 0.02	2.63 ± 0.0	1.81 ± 0.03						

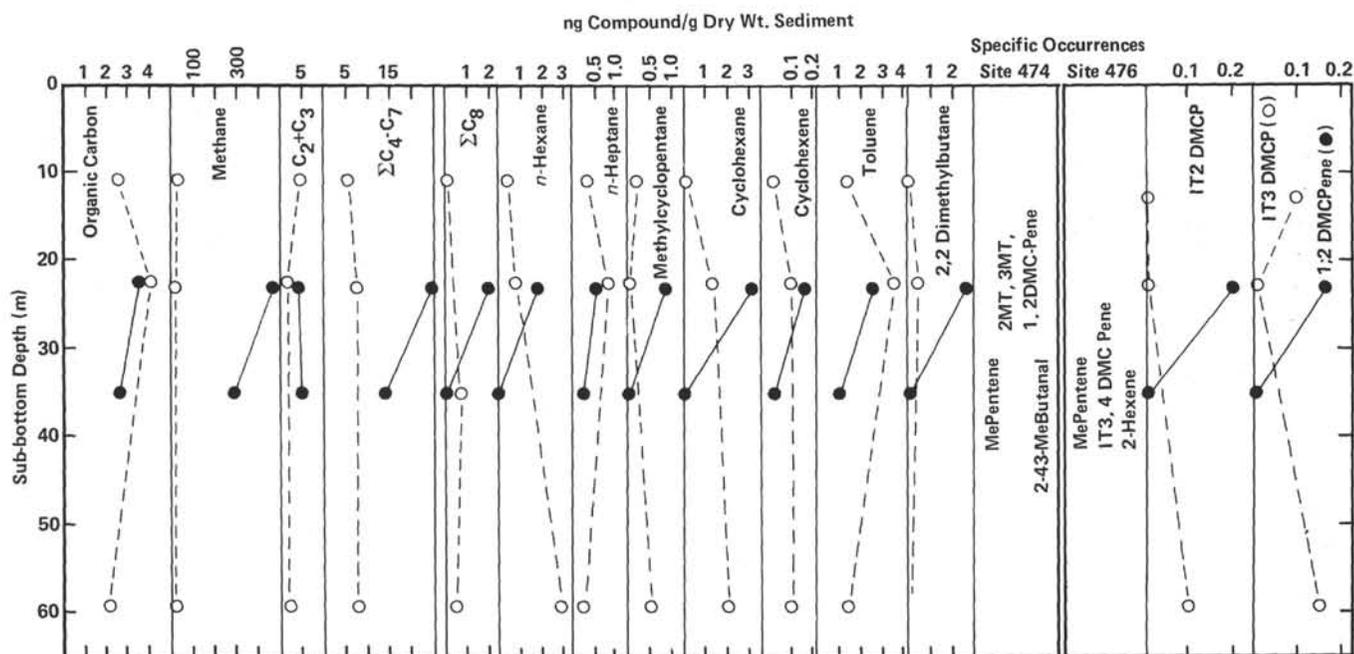


Figure 3. Compound distributions at Sites 474 (closed circles) and 476 (open circles). (See Table 1 for abbreviations; 2MT and 3MT are 2-methyl- and 3-methylthiophene; DMC is dimethylcyclopentene.)

other sediment parameters are shown in Table 1 and in Figures 6 and 7. Two dolerite sills were penetrated at 220 to 241 meters and at 250 to 256 meters. One of our samples (478-28-4 at 248 m) came from the sediment 7 meters below the upper sill contact and 2 meters above the bottom sill contact. The most interesting feature of these samples is that the sills appear to have had minimal influence on production of C₂-C₈ hydrocarbons. Similar effects were noted in hydrothermally generated ions such as lithium (Einsele et al., 1980). Total hydrocarbon levels are somewhat higher than for other DSDP legs, but are not spectacularly high in comparison with other sediments from this area.

A number of alkenes (for example, see 2-hexene in Fig. 7) occur throughout the sediment column, suggesting that the sediment has not undergone extensive heating—an idea supported by several other observations. First of all, the sediments are generally not described as hydrothermally altered as in the case of lower sections of Site 477. The C/N ratios generally do not increase on approaching the sill/sediment contact as would be expected for a sediment subjected to a localized "hot spot" (see Simoneit, this volume, Pt. 2). Alkenes, such as 2-hexene, are typical of recent geothermally cold sediments (Hunt and Whelan, 1979). In addition, there are no unusual increases in ethane or the aromatic hydrocarbons as observed for the deepest sample from Site 477. Levels of most of the C₂-C₈ hydrocarbons appear to correlate with organic carbon in all samples deeper than 50 meters. Such a correlation is unusual in DSDP samples examined previously. It does seem to hold for deeper samples from areas with a moderate (4–5%/100 m) geothermal gradient (see, for example, the Moroccan Basin, Leg 50, Whelan and Hunt, 1980b).

The deepest sediment/sill contact, shown in Figures 6 and 7 at 256 meters, is described as displaying sediment thermal alteration effects. However, the sediment alteration is very limited in extent—continuing for a depth of only 1.5 meters (site chapter, this volume, Pt. 1). The sample from below this sill (Sample 478-35-5, 305 m) is much deeper and shows no increase in hydrocarbon generation from the heating 50 meters above. In fact, there is a decrease in total hydrocarbon levels for this sample. The increase in several compounds, including C₂-C₃ and toluene in the sample from between the two sills (478-28-4 at 248 m), could be from some contribution of heat produced as the sills were formed. However, the higher level of organic carbon as compared to levels in samples just above and below, may also explain the increase in concentration of these compounds.

Site 479 is located on the northwest continental slope of the Guaymas Basin within the oxygen minimum zone. Measured heat flow was lower than at Sites 477 and 478. However, in terms of C₂-C₈ hydrocarbon levels, this site shows characteristics of a sediment undergoing active (catagenic) hydrocarbon generation at temperatures greater than 50°C. For example, many C₂-C₈ hydrocarbons—in particular the cycloalkanes—show an exponential increase in deeper sections as shown in Figures 8, 9, and 10 and Table 1. This behavior is reminiscent of Sites 467 and 471 of Leg 63 (Whelan and Hunt, 1981) on the other side of the Baja Peninsula. A maximum in several C₅-C₈ compounds occurs at 360 meters at Site 479, where organic carbon also shows a maximum.

Piston cores were taken to obtain some undisturbed shallow cores from this site. The letters "V" and "B" in Figure 8 indicate the "varved" and "bioturbated" sediments, respectively. It can be seen in Figure 8 that total

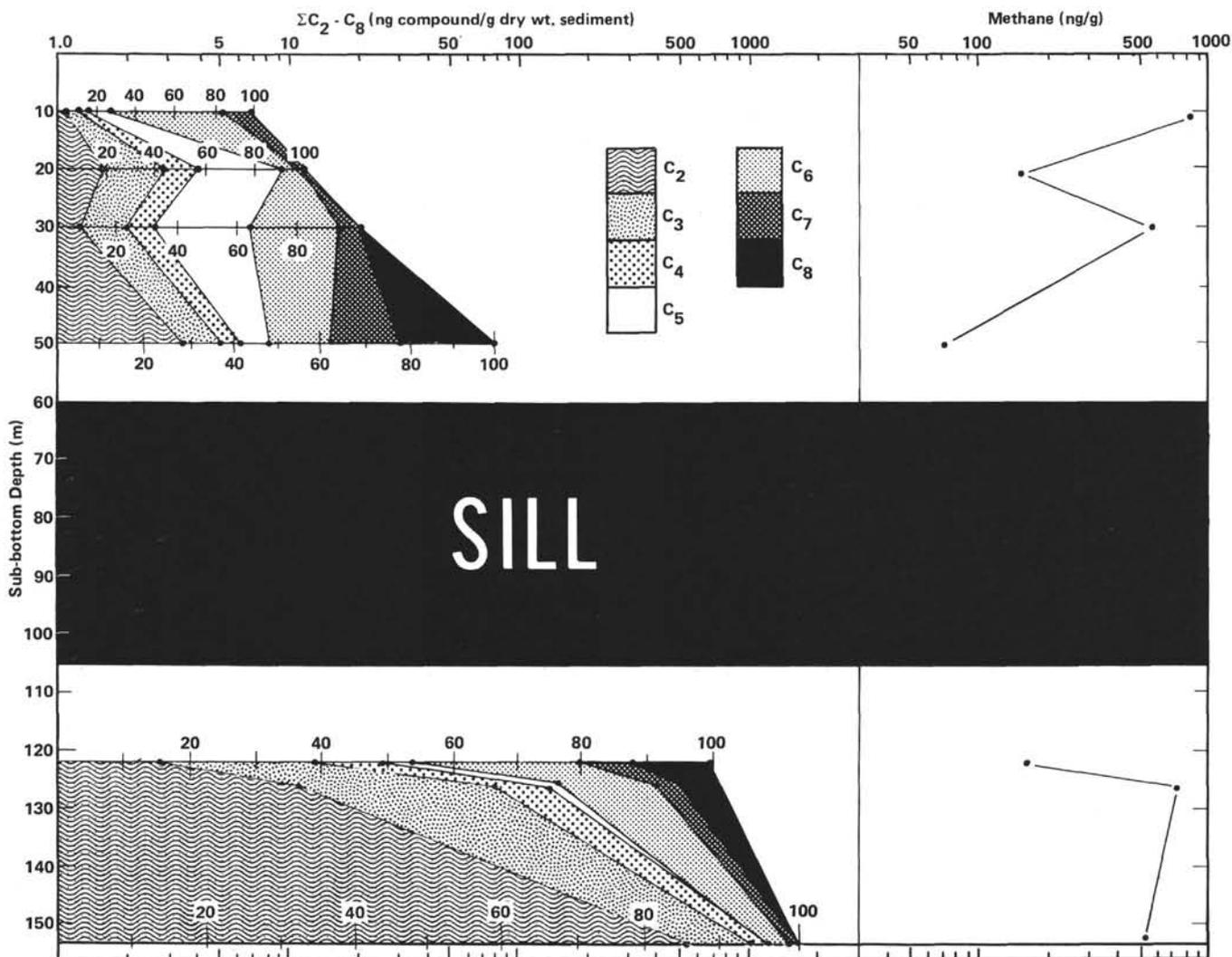


Figure 4. Total amounts of C_1 and C_2 - C_8 (log scales), Site 477. (Also shown are proportions of C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , and C_8 , shown as percent of the total on a linear scale.)

levels of C_2 - C_8 hydrocarbons seem to decrease in the bioturbated sediments and to increase somewhat in the varved sediments. Since varved sediments indicate periods of anoxic sediment deposition, methane and organic carbon might also be expected to fit this pattern—that is, an increase in anoxic sediments and a decrease in bioturbated sediments. Figure 9 shows that such a correlation is not found. Thus, at this site, C_2 - C_8 hydrocarbon minima and maxima appear to be better indicators of oxic versus anoxic depositional conditions than either organic carbon or methane.

Two compounds, 3,3-dimethylpentane and 2-hexene, show an inverse correlation with most other C_4 - C_8 compounds in deeper sections (> 150 m) of this site. It has previously been suggested that some gem-dimethylalkanes and alkenes (or their precursors) may be formed by aerobic biological processes occurring near the sediment/water interface at the time of sediment deposition (Hunt and Whelan, 1979; Whelan, Hunt, and Berman, 1980). If this hypothesis is correct, it suggests that sev-

eral other gem-dimethyl compounds—including 1,1-dimethylcyclopentane and 2,2-dimethylbutane—must be formed under different conditions since they do not correlate with the 3,3-dimethylpentane. The 1,1-dimethylcyclopentane and 2,2-dimethylbutane correlate well with most of the other hydrocarbon profiles shown in Figure 9 and may be associated with sediments deposited under anoxic conditions. Such a correlation fits with gravity core data from Walvis Bay (West Africa) (Whelan, Hunt, and Berman, 1980) where 2,2-dimethylbutane was found in an organic-rich anoxic diatomaceous sediment recovered from an upwelling area.

A rise in isopentane to n -pentane (i - C_5/n - C_5) with depth has been noted at many DSDP sites (Hunt et al., 1980) and is thought to reflect the increasing contribution of thermally generated i - C_5 at increasing depths. A similar trend is found here as shown in Figure 10. An unusual feature of this site is the relatively high amount of cyclopentane in most sections deeper than 100 meters. Changes in cyclopentane as percent of total C_5

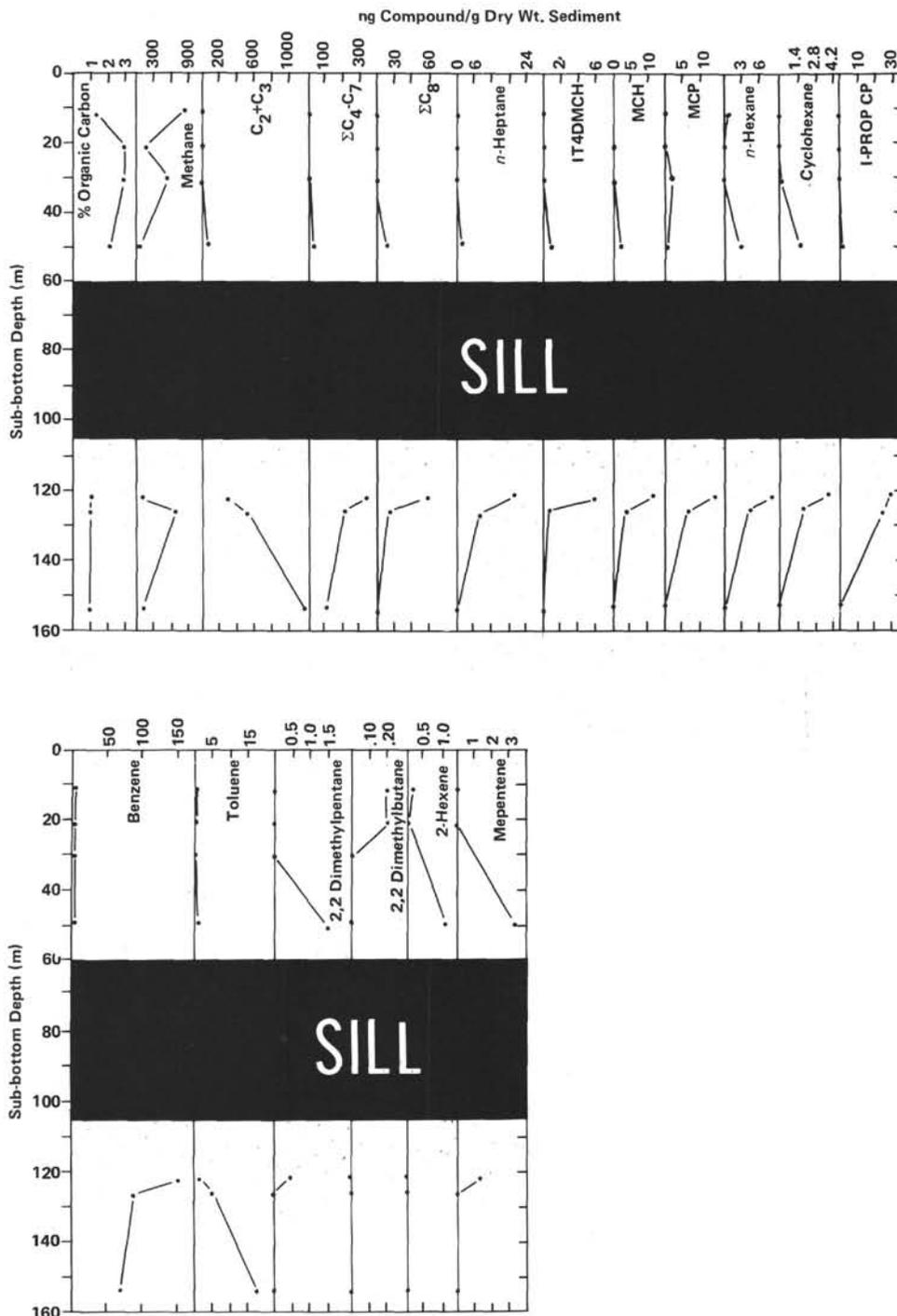


Figure 5. Distributions of organic carbon and organic compounds as a function of depth, Site 477. (See Table 1 for abbreviations.)

(Fig. 10) correlate well with lithology changes at this site. For example, the change from diatomaceous sediment to a more calcareous dolomitic mudstone at 314 meters is accompanied by a decrease in CP and in total C₅ as a percent of total C₂-C₈ (Fig. 8).

Site 481 is on the north rift of the active spreading basin. Two shallow piston core samples from this area, 481-P3-2 at 6.2 meters and 481-P10-2 at 44.7 meters, show hydrocarbon compositions similar to those

found at Sites 474 and 476 (Table 1). The low amounts of C₁-C₇ hydrocarbons together with small amounts of alkenes suggest only biological/low-temperature (< 30° C) sources for these compounds. The virtual absence of a P₁ peak in pyrograms of these sediments (P.I. of zero) is also consistent with a low thermal history.

This result is in marked contrast to a gravity core (30G) from about the same area (8 km to the northeast), which was examined by Simoneit et al. (1979). They

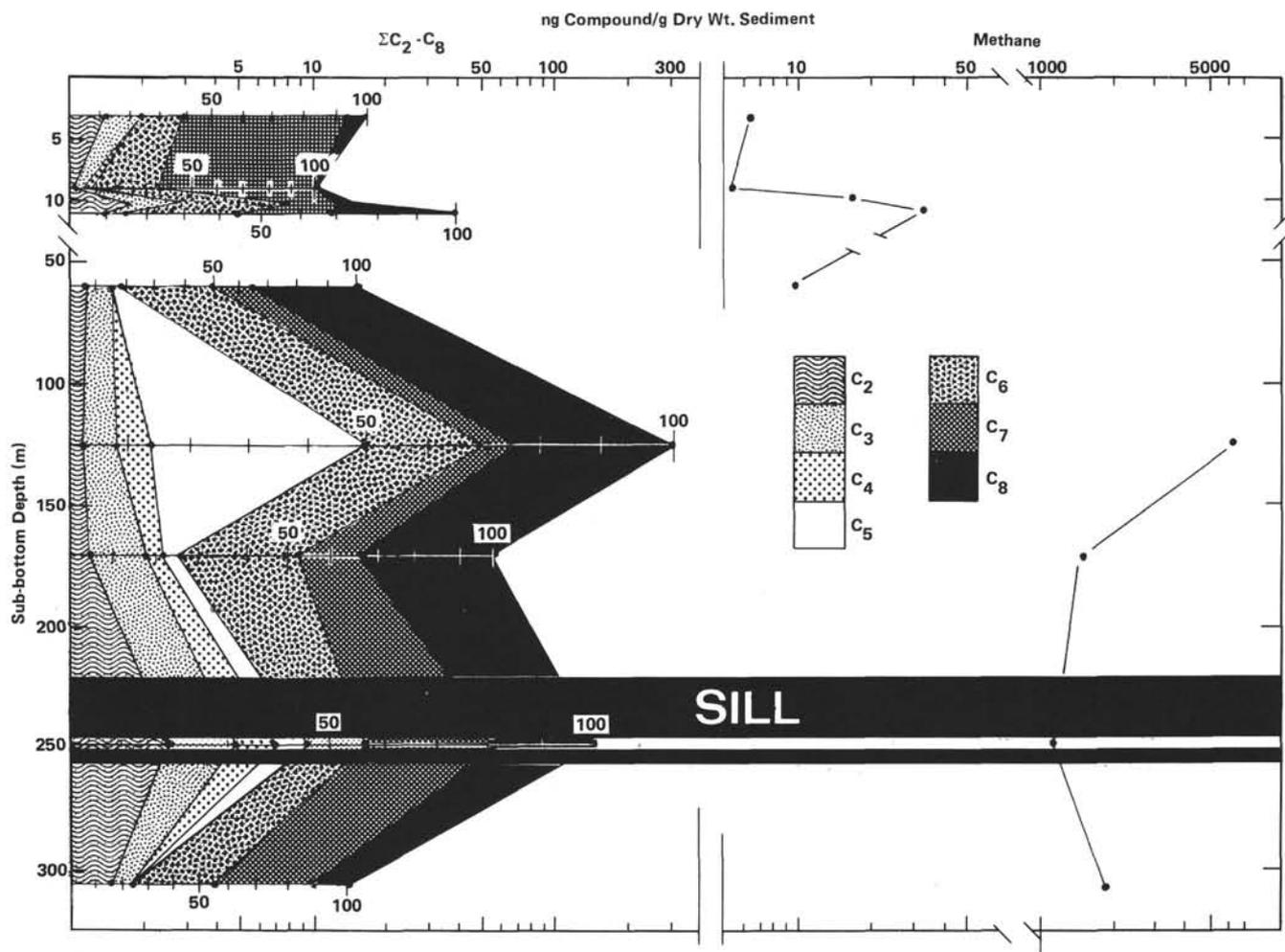


Figure 6. Total amounts of C_1 and C_2 - C_6 (log scales) and percentages of C_2 through C_8 (linear scale), Site 478.

found very high levels (2000-7000 ng C_2 - C_8 hydrocarbon per gram dry weight of sediment) in the lower sections (sub-bottom depth 2.5-3.5 m). Sections of the same core were analyzed in this laboratory and gave similar results, as shown in Tables 2 and 3 and Figure 11. The levels of C_2 - C_7 compounds are among the highest found in any sample analyzed in this laboratory (16,000 ng/g) including petroleum source rock cuttings (Huc and Hunt, 1980). The other surprise from this analysis was the almost total absence of these compounds in the shallower sections of the core (1.2-1.3 m). Since Simoneit and coworkers found that the bulk of organic matter in these sediments is autochthonous and thermally immature, they concluded that the C_2 - C_8 compounds must have migrated into these sediments. Considering the very abrupt vertical changes in hydrocarbon composition (compare, for example, the differences in all hydrocarbon isomers as shown in Table 3 and Figures 12 and 13) from the sediment at 1.2 to 1.3 meters with samples from 2.5 to 3.4 meters, such migration must be occurring in an irregular fashion. Also, the fine-grained nature of the sediments and the rather limited distance over which sporadic magmatic heating is effective (1.5 meters at Site 478—as previously discussed)

suggests that the heat source may have been fairly close (within a few meters) of these sediments in order to produce the rather localized hydrocarbon distributions observed.²

Analysis of sediments deeper than 50 meters from Hole 481A showed high levels of C_2 - C_8 hydrocarbons similar to those found in deeper sections of gravity core 30G. Levels increased significantly in samples taken closest to sills—namely Samples 481A-12-2, 149 m, 481A-22-4, 248 m, and 481A-30-5, 325 m—because of localized heating at both the lower and upper sill contact. Also, localized heating resulted in very high i - C_5/n - C_5 values in the 149 meter section just above the sill contact (Fig. 13). Although the i - C_5/n - C_5 ratio below the contact shows no such maximum, all the i - C_5/n - C_5 values below the contact are relatively high. We have found in previous work that high values of i - C_5/n - C_5 correlate well with an increasing thermal contribution for the C_5 hydrocarbons in shallow sediments (Hunt et al., in press) and that this trend reverses in more deeply

² A surface dredge sample recently taken from the area of Hole 481A also shows very high levels of C_2 - C_8 hydrocarbons. It is believed that this sample was recovered very near an active spreading center (B. Simoneit, unpublished results).

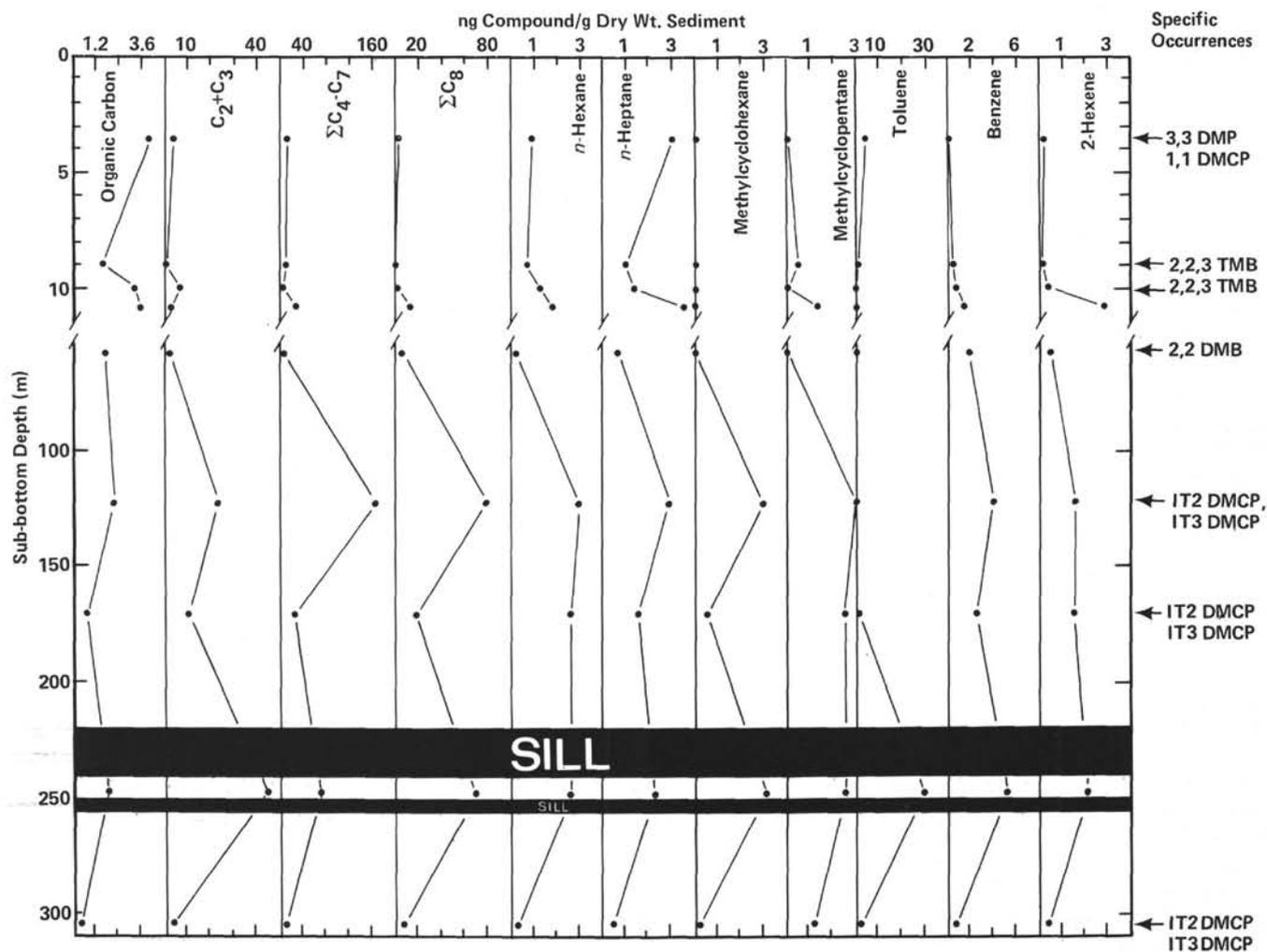


Figure 7. Distributions of organic carbon and some C₁-C₈ hydrocarbons, Site 478. (See Table 1 for abbreviations.)

buried sediments. The maximum in the $i\text{-C}_5/n\text{-C}_5$ ratio at 70 meters may also reflect thermally generated C₅ compounds.

The thermal distillation-pyrolysis results support a thermal contribution to hydrocarbon generation in the sediments at 149 meters, just above the sill contact, but present a confusing picture for sediments below the contact (Fig. 2 and Table 4). The P₁ and P₂ profiles are quite different than at Site 477. The P.I. values are low throughout the hole except for the sample at 149 meters just above the dolerite sill. This showed a small amount of thermal alteration (maximum in P.I. and a P.I. value > 0.1) and the highest T_{\max} for the first P₂ peak (405°C) of all the samples from this site. Sediments from below the sill show low P. I. values (0.01-0.05), characteristic of young nonthermally altered sediments. However, the first P₂ peak is completely absent from the sample closest to the sill. In deeper samples, T_{\max} of both P₂ peaks then generally decrease with increasing depth and distance from the sill. The T_{\max} data are consistent with the sediments closest to the sill having been exposed to the highest thermal regime. However, the high T_{\max}

values do not necessarily indicate only thermal alteration—they can represent a high contribution of coaly or carbonized organic matter in the original sediment deposition—sometimes from small amounts of recycled carbon in the sediment. Such a source here would explain inconsistencies between the P.I. values on the one hand and the T_{\max} and C₁-C₈ values on the other. Initial core descriptions do record “long black carbonaceous fragments” in this core but not in deeper sections. Alternatively, both P.I. and C₁-C₈ values would be expected to be low in a sediment exposed to sufficiently high temperatures to volatilize away or decompose any hydrocarbons produced.

An attempt was made to correlate hydrocarbon compositions between gravity core 30G and Hole 481A since both were taken from approximately the same location. This was attempted in two ways. First, distributions of total amounts of C₂-C₈ components were plotted as shown in Figure 12. A marked similarity in the distributions of C₂-C₈ hydrocarbons can be seen between the bottom section of 30G and the 111-meter section of Hole 481A. Both have a maximum at C₅. Deeper sec-

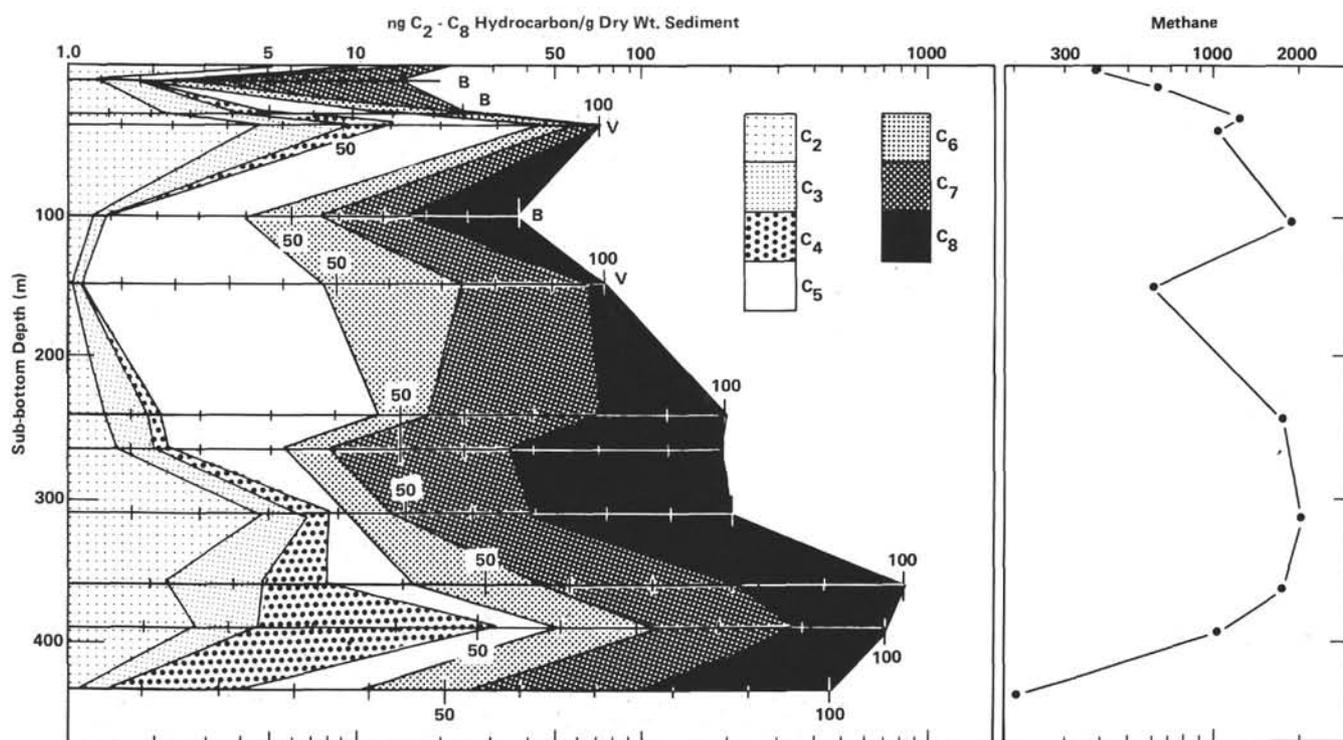


Figure 8. Total amounts of C₁-C₈ components, Site 479. (Same scales as Figs. 4 and 6.)

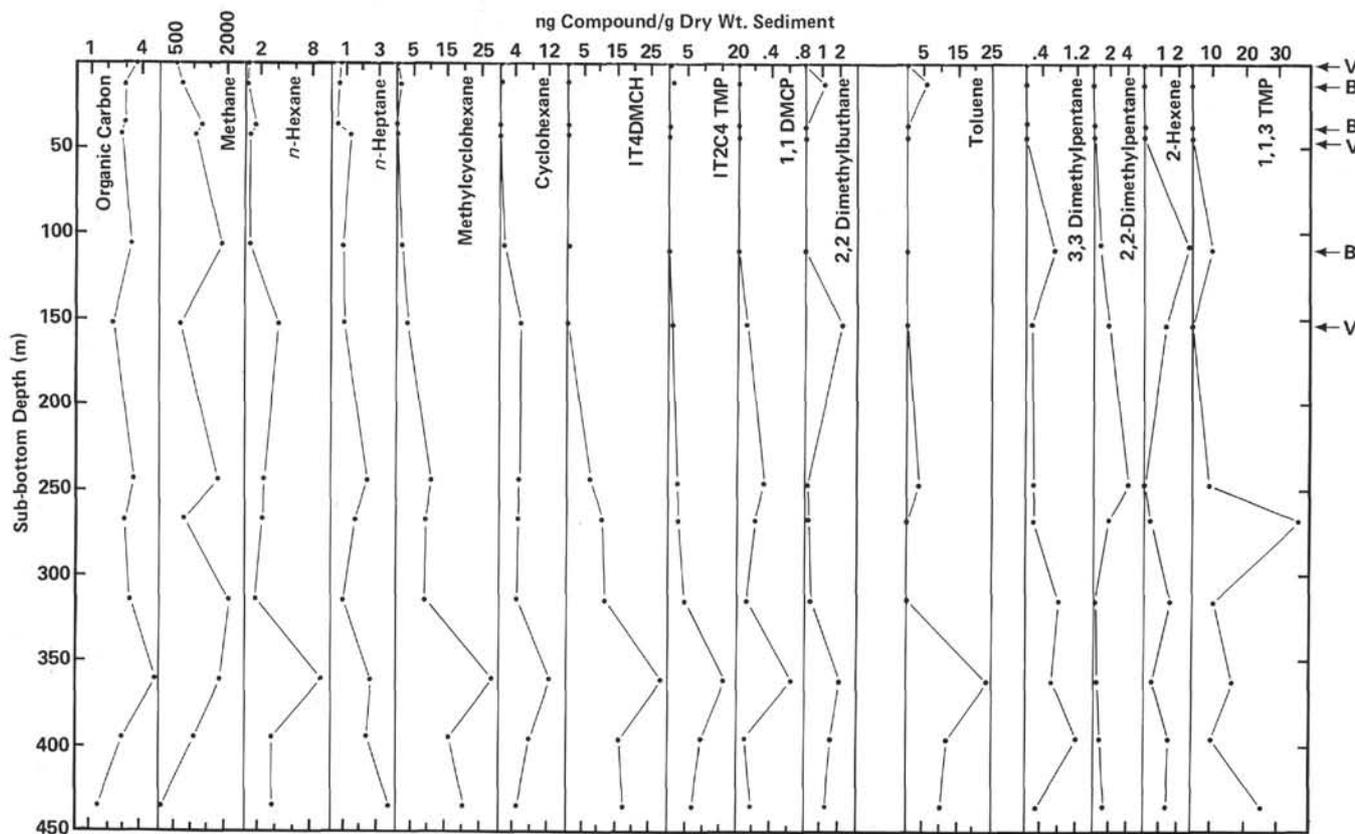


Figure 9. Distributions of organic carbon and C₁-C₈ hydrocarbons, Site 479. (Abbreviations: V = varved sediment, B = bioturbated. For compound abbreviations, see Table 1.)

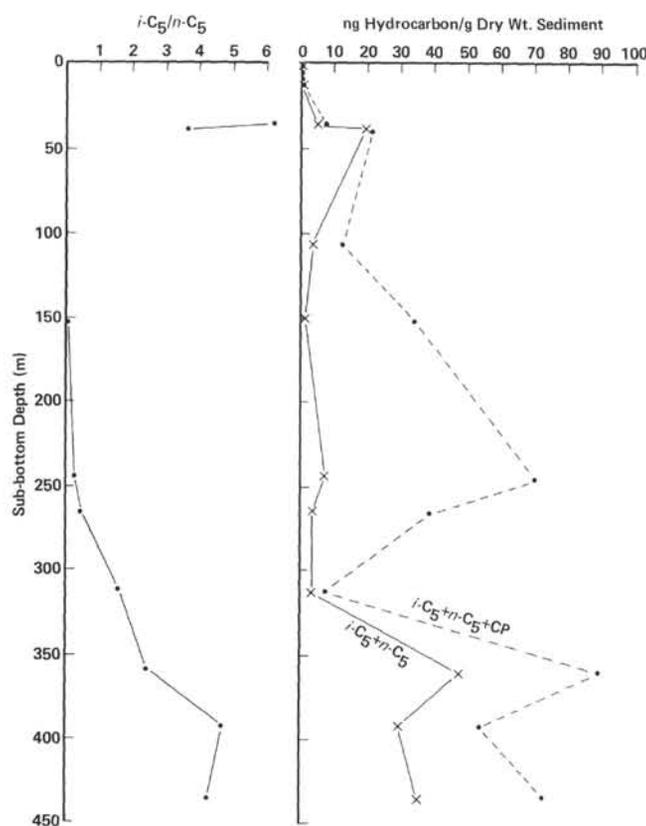


Figure 10. Distribution of C₅ isomers, Site 479. (See Table 1 for abbreviations.)

tions of Hole 481A show an increase in C₈, which also occurs in the middle section of 30G.

However, the distribution of individual C₆ and C₇ components (Fig. 14), indicates that the correlations mentioned above may be an oversimplification. The C₆ composition of the bottom section of 30G is most like the 73-meter section of Hole 481A, with the proportion of benzene being slightly higher for the latter. Deeper sections of 481A to 130 meters show similar patterns except for an increase in the MCP/CH ratio. Thus, the correlation of the bottom section of 30G with the 111-meter section of Hole 481A is roughly supported by the individual C₆ distributions. In sections of Hole 481A below the 185 to 195 meter basaltic sill, the amount of benzene increases dramatically in all sections except in the deepest at 325 meters. It seems very likely that increased thermal stress is responsible for some of the increased benzene production in some sections (as found for the deepest sediments from Site 477). However, it is also possible that the benzene may have migrated after generation since, of all the C₆ hydrocarbons, benzene is the most prone to movement (Thompson, 1979).

The C₇ distribution presents a somewhat different picture. The 111-meter section of Hole 481A is most similar to the *middle* section of 30G. In fact, the C₇ composition of the bottom of 30G is dominated by the dimethylcyclopentanes and is therefore unlike any sample from Hole 481A. However, large amounts of MCH and DMCP can be seen to predominate in the 111-me-

Table 2. Volatile compounds from Gravity Core 30G from Guaymas Basin.

Sample		Gravity Core ^a	Gravity Core ^a	Gravity Core ^a
Sediment Depth (cm)		123-129	259-265	331-337
Lithology		Diatom Ooze	Diatom Ooze	Diatom Ooze
Age		Quaternary	Quaternary	Quaternary
Packed Column		(ng/g dry wt. sediment)		
Methane	C ₁	9	72	4104
Ethane	C ₂	0.65	34	61
Propane	C ₃	0.36	19	174
<i>i</i> -Butane	<i>i</i> -C ₄	0	32	1774
<i>n</i> -Butane	<i>n</i> -C ₄	0	6.0	1224
neopentane	neoC ₅	0	16	27
<i>i</i> -Pentane	<i>i</i> -C ₅	0	40	4762
<i>n</i> -Pentane	<i>n</i> -C ₅	0	4.2	2371
Cyclopentane	CP	0	0.2	319
Capillary Column				
2,2DiMeButane	22DMB	0.42	57	49
2,3DiMeButane	23DMB	0.01	396	345
2MePentane	2MP	0.01	3.0	547
3MePentane	3MP	0.01	17.4	1020
<i>n</i> -Hexane	<i>n</i> -C ₆	0.52	1.8	1080
MeCycloPentane	MCP	0.01 (trace)	5.0	549
2,2DiMePentane	22DMP	0	30	20
Benzene	Benz	0.10	47	34.4
2,4DiMePentane	24DMP	0	2	2
2,2,3TriMeButane	2,2,3TMB	0	6.2	0
CycloHexane	CH	0.01	43	782
3,3DiMePentane	3,3DMP	0	10	0
1,1DiMeCycloPentane	1,1DMCP	0	78	54
2MeHexane	2MH	0	0	9.2
2,3DiMePentane	2,3DMP	0	85	15
1C3DiMeCycloPentane	1C3DMCP	0	25	275
3MeHexane	3MH	0	57	392
1T3DMCPentane	1T3DMCP	0	25	634
1T2DMCPentane	1T2DMCP	0	26	0
3EthylPentane	3EP	0	8.4	23
<i>n</i> -Heptane	<i>n</i> -C ₇	0.01	85	160
1C2DMCycloPentane	1C2DMCP	0	32	5
MethylCycloHexane	MCH	0	5.8	146
EthylCycloPentane	ECP	0	11	96
Toluene		0		
Other Compounds				
C ₅ -C ₇ Alkenes		6.0	20	70
2,5-Dimethylfuran		0	6	0
3-Methylbutanal		0	14	0
2-Methylbutanal		0	2	5
Ethylfuran		0	0	53
Totals				
C ₁		9	72	4104
C ₂ and C ₃		1.0	53	235
C ₄ -C ₇		1.1	1153	16,715
C ₈		0	450	113

^a Simoneit et al., 1979.

Table 3. Isomer composition—Gravity Core from Guaymas Basin.

Sample Depth ^a (m)	<i>i</i> -C ₄ / <i>n</i> -C ₄	<i>i</i> -C ₅ / <i>n</i> -C ₅	NeoC ₅ /C ₅	CP/C ₅	2,3DNB/2MP	<i>n</i> -C ₇ /MCH
1.23-1.29 ^a	(no C ₄)	(no C ₅)	—	—	1	(no MCH)
2.51-2.58	7.4	12.7	0.37	0.008	40	nd
2.59-2.65 ^a	5.4	9.4	0.27	0.003	132	0.26
2.94-2.99	1.8	2.2	0.005	0.02	0.76	nd
3.31-3.37 ^a	1.4	2.0	0.004	0.04	0.63	4.6
3.38-3.45	1.8	2.2	0.0001	0.001	0.41	nd

^a Samples analyzed in laboratory of Whelan and Hunt; others analyzed in laboratory of Simoneit et al.

ter, 130-meter, and 149-meter zones. Toluene increases proportionately with benzene, suggesting in some sections that the source of both compounds in these sediments may be primarily thermal.

HYDROCARBON MIGRATION VERSUS IN SITU GENERATION

Most DSDP sediments examined to date are younger, less deeply buried, geothermally colder, and less hydrocarbon-rich than typical petroleum source rocks. Consequently, it has been assumed that most of the C₄-C₈

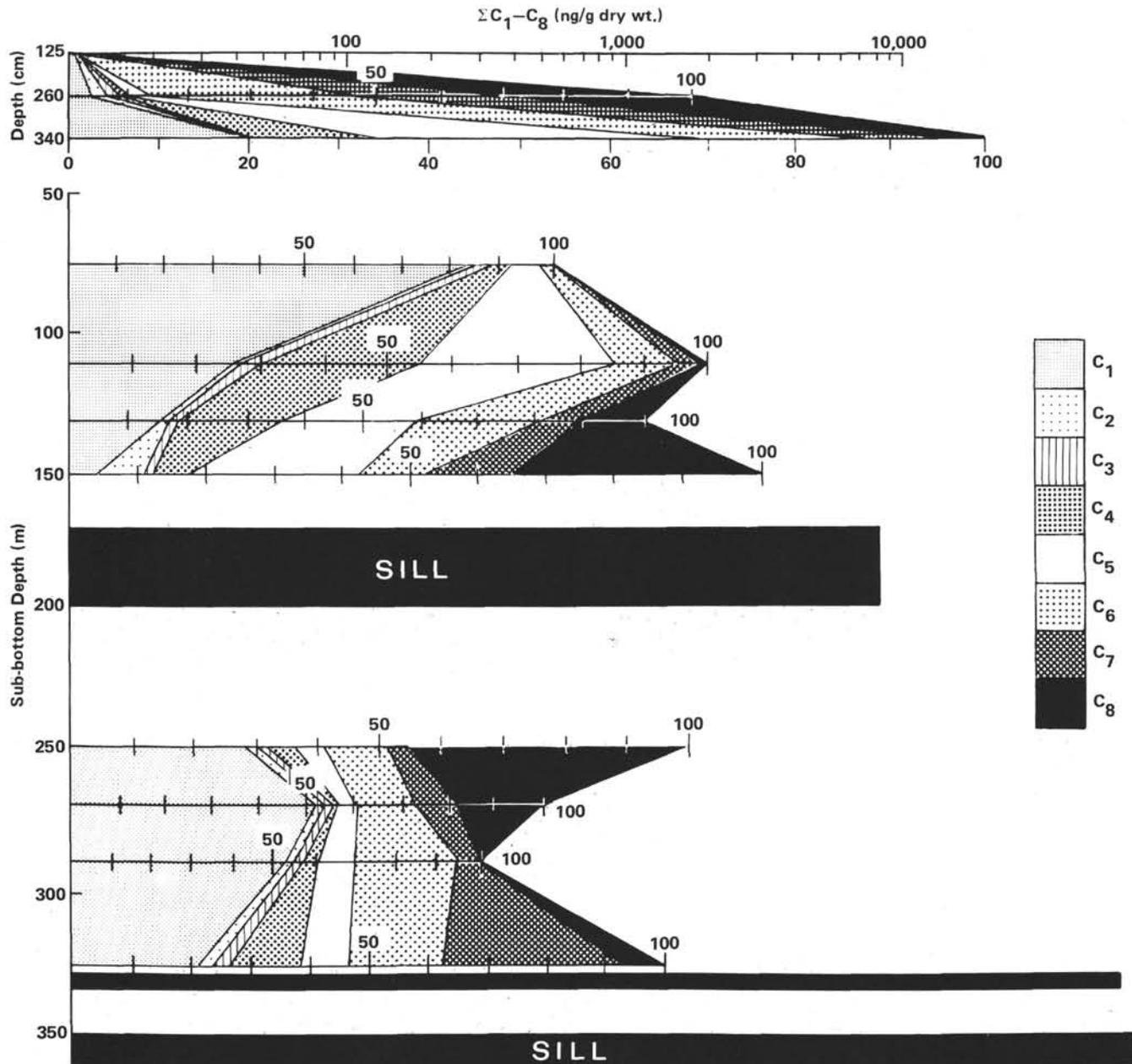


Figure 11. Total amounts of C_1 - C_8 components, Hole 481A and Core 30G. (Same scales as for Figs. 4 and 6.) Note that data from 481A and Core 30G are plotted together, even though they are from slightly different locations (see text).

(and to a smaller extent C_1 - C_3) hydrocarbons present (generally < 1500 ng hydrocarbon/g dry weight of sediment) represent absorbed³ hydrocarbons in fine-grained sediments. That is, the hydrocarbons are generated in the organic matrix of the sediment and then remain absorbed in this organic phase as long as water is present. This hypothesis is based on several lines of evidence, including the following: (1) the methane absorption capacity of various sediments and soils has been found to be 150 to 7000 ng methane/g dry weight of sediment (0°C , 1 atmosphere pressure using 1% methane in air), with the higher values corresponding to sediments with

higher organic carbon content (Kartsev et al., 1959). Absorption of higher molecular-weight compounds, such as propane and hexane, is considerably higher. Secondly, measurements from this laboratory and others (Leythaeuser, 1979) have shown good correlations of C_4 - C_8 hydrocarbon levels with lithology. The clearest example is a Miocene/Cretaceous discontinuity at Site 397 (Canary Islands, Whelan, 1979) where the $i\text{-}C_5/n\text{-}C_5$ ratio shows an abrupt change by an order of magnitude at the discontinuity. The ratio is 5 above the discontinuity and 0.5 below.

However, the sediments examined at Sites 477, 478, and Hole 481A are unlike those described above. It is thought, in all of these cases, that the magma intruded into the sediments, distilling water and light hydrocar-

³ The terms absorption and adsorption are used interchangeably here.

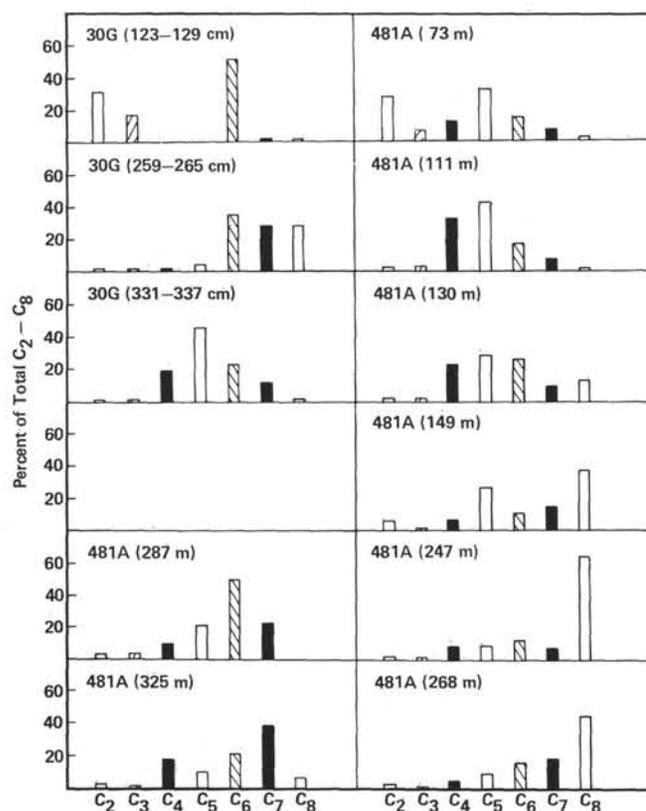


Figure 12. Bar graph of C₂-C₈ components as a percent of C₂-C₈, Hole 481A and Core 30G.

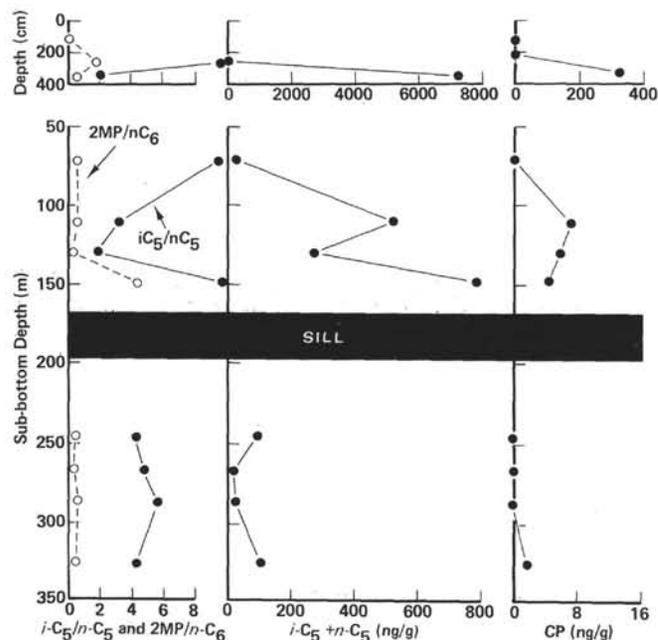


Figure 13. Changes in C₅ and C₆ isomer distributions with depth; Hole 481A and Core 30G.

bons away from the source of heat (Einsele et al., 1980). The effect can be seen in high concentrations of lithium in sediments closest to the sill contacts—particularly at Site 477 and Hole 481A. It is interesting that total C₁-C₈

Table 4. Thermal distillation-pyrolysis data, Gulf of California.

Sample (interval in cm)	Sediment Depth (m)	Production Index	T_{\max} of P ₂ Peaks	
Site 477				
3-1, 135-140	12	0.016	330	400
4-1, 145-150	21	0.035	348	460
5-1, 129-135	31	0.021	355 ^a	440 ^a
7-1, 132-137	50	0.020	395	460
(Dolerite sill, 60-105 m; hydrothermally altered muds below.)				
16-5, 62-68	121	0.24	405	>460
17-1, 140-145	126	0.17	420	>460
20-1, 115-122	154	0.71		>460
Hole 481A				
4-2, 110-125	73	<0.1		>460
8-2, 115-125	111	<0.01	400	>460
10-2, 137-150	129	0.015	355	425
12-2, 120-135	149	0.12	405	435
(Dolerite sills interbedded with chert; no hydrothermal effects.)				
22-4, 121-130	247	<0.01		>460
24-5, 121-131	268	0.046	375	420
26-5, 120-131	287	<0.01	385	420
30-5, 117-122	325	<0.01	330	435

^a Heating rate, 60°/min.; all others, 120°/min.

profiles are very similar to the lithium profiles at all three sites. Thus, even though very little is known about hydrocarbon movements in sediments of this type, a good first approximation appears to be that C₁-C₈ hydrocarbons and inorganic ions generated by interaction of hot magma with water (for example, Li⁺) have moved in the same way. Hydrocarbon generation and migration in these hydrothermally altered sediments can also be seen in the large concentrations of the most water-soluble hydrocarbons (ethane, propane, benzene, toluene, and probably some methane) at the bottom of the hottest site, 477. It has been shown that deep heat sources at this site (deeper than 150 m) have produced temperatures of at least 300°C (Einsele et al., 1980). It is also known that when migration of these light hydrocarbons does occur, benzene and toluene move faster than the saturated hydrocarbons (Thompson, 1979).

CONCLUSIONS

1. Very hot (estimated 350°C) hydrothermally altered sediment from Site 477 (depth 154 m) shows only a very limited hydrocarbon distribution, including primarily ethane, benzene, and toluene.

2. Sediments from Sites 474, 476, and shallow sections from other sites show low levels and a limited distribution of C₂-C₈ hydrocarbons. Small amounts of functionalized molecules, such as alkenes, were also present. These are typically present in sediments which have been subjected only to low (<30°C) temperatures.

3. Deeper sections of Sites 478 and 479 showed higher levels and a wide diversity of C₂-C₈ hydrocarbons, suggesting sediment subjected to moderate heating (50-100°C). This conclusion is supported by the general increase of alkanes with depth.

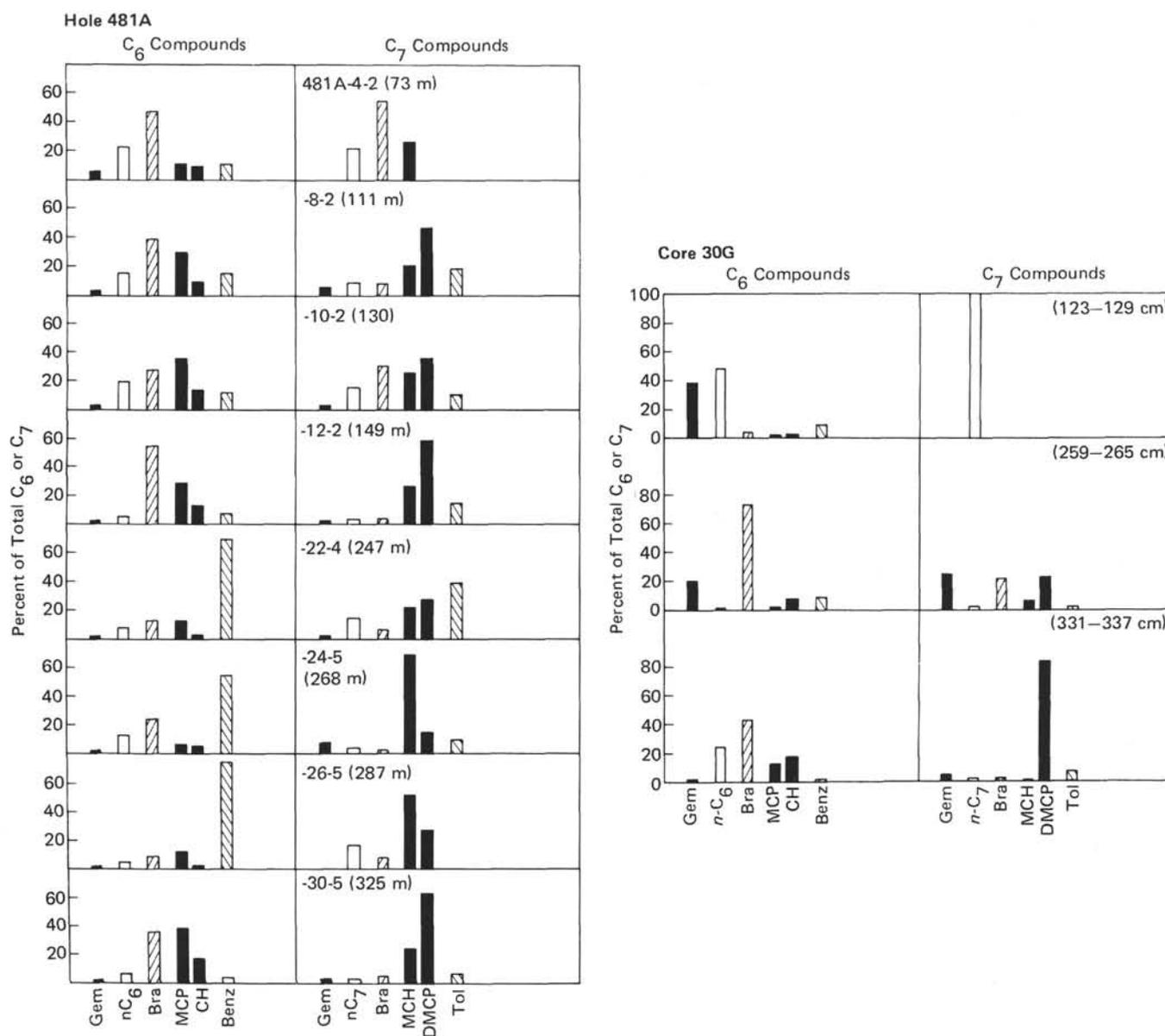


Figure 14. Changes in C_6 and C_7 isomer distribution with depth, Hole 481A and Core 30G. (Abbreviations: Gem = gemdimethyl alkanes; Bra = branched alkanes.)

4. The ratio of $i-C_5/n-C_5$ increases with depth at Site 479 as found in other DSDP sites where $i-C_5$ increases at moderate temperatures. In contrast, the ratio of ($i-C_5 + n-C_5$) to cyclopentane correlates well with a lithology change at 314 meters.

5. Abrupt increases in C_2-C_8 levels occur in bottom sections of a gravity core taken in the vicinity of Site 481. The thermal immaturity of the sediment suggests lateral movement of gasoline range hydrocarbons into the sediment. Deeper sections of Hole 481A show that C_8 , benzene, and toluene increase in the vicinity of a dolerite sill, suggesting a pyrolytic source for these compounds as lava intruded into the sediments.

6. Comparison of thermal distillation-pyrolysis data for Site 477 and Hole 481A indicates that extensive thermal alteration of kerogen requires a widespread heat source as observed below the sill at Site 477.

7. The sills themselves do not appear to have extensively altered the organic matter except in the immediate vicinity of the sills.

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