# 22. C<sub>1</sub> TO C<sub>7</sub> HYDROCARBONS FROM IPOD HOLES 397 AND 397A

Jean K. Whelan, Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

### ABSTRACT

Gases from sediment pockets were monitored onboard ship during continuous coring to a depth of 1453 meters. Gas pockets first appeared at a sediment depth of 80 meters (Hole 397) and continued irregularly to the bottom of Hole 397A. The gas contained small quantities (0.1 to 1.3%) of methane from 30 to 124 meters, with major components of air and CO2. The odor of H2S was noted in the cores from 9 to 151 meters. Starting at 196 meters, methane became a significant component (43%) and then varied irregularly from 1 to 81 per cent of the gas throughout the rest of the hole. A gas chromatograph installed on board ship at the beginning of Leg 47A allowed monitoring of traces of C2 to C5 hydrocarbons in gas pockets. These hydrocarbons, found along with the methane throughout the hole, included 3 to 2000 ppm of C2 by volume, 1 to 140 ppm of  $C_3$ , 0.1 to 25 ppm of  $C_4$ , and 0.1 to 4 ppm of  $C_5$ . The C1 to C5 hydrocarbon levels followed lithologic changes to a remarkable degree with proportions of C2:C3:C4:C5 staying relatively constant in fine-grained sediments and with the  $(C_1 + C_2)/(C_3 + C_2)$  $C_4 + C_5$ ) ratio increasing erratically in coarser grained sediments and at most of the unconformities. This indicates hydrocarbons were migrating from fine-grained source beds to coarse-grained reservoir beds and along the more permeable unconformities throughout the hole. Ratios of  $i-C_5/n-C_5$  and  $i-C_4/n-C_4$ , appeared to vary with changes in organic source material. Traces of neopentane occurred irregularly and are probably indicative of terpene-derived material. Sediment C1 to C7, analysis showed that only traces of C6 and C7 hydrocarbons were present above 800 meters. Below 800 meters, the C6 and C7 hydrocarbons generally increased with sediment depth and age.

### INTRODUCTION

Biogenic methane, in concentrations high enough to form gas pockets in cores brought on deck and to blow sediments forcibly out of core tubes, has been found at several DSDP sites from areas of high productivity and high deposition rate. These sites include the Cariaco Trench at Site 147 (Edgar et al., 1973); the South Atlantic Basin at Sites 360 and 361 (Ryan et al., 1978); and the Black Sea at Sites 379, 380, and 381 (Hunt and Whelan, 1978). Small amounts of ethane and occasionally traces of propane and butane have been detected with the methane.

The origin of  $C_2$  to  $C_4$  hydrocarbons is not clear. Even though they are ubiquitous with biogenic methane in deeper DSDP cores, it is generally believed that these compounds are not biogenic and, therefore, are diagnostic of petroleum formation and possibly migration from deeper horizons. Thus, the presence of these compounds has been used as one criterion to cease drilling because of the possibility of encountering a pressured oil or gas deposit.

In subjecting the Black Sea gases to  $C_2$  to  $C_5$  hydrocarbon analyses at Woods Hole via methods more sensitive than those used onboard ship, we noted (Hunt and Whelan, 1978) that most samples, composed primarily of the biogenic methane, contained small amounts of C2 to C5 hydrocarbons which dropped by about one order of magnitude for each increased carbon number. However, the gases showed a remarkable correlation with each other in that when logs of the  $C_2$ ,  $C_3$ ,  $C_4$ , and  $C_5$  curves were plotted as a function of depth, the shapes of the curves were very similar. This behavior was observed in all three holes of the Black Sea. We postulated that this "in phase" behavior of the C<sub>2</sub> to C<sub>5</sub> hydrocarbons was diagnostic of these compounds being formed either biologically or by low temperature chemical reactions associated with biogenic methane production. If this hypothesis proved to be true, then the "in phase" behavior of C2 to C5 hydrocarbons could be used for hydrocarbon monitoring aboard ship to show that petrogenic gas was not present. Site 397 was drilled on the first DSDP cruise having a gas chromatograph aboard ship that was sensitive enough to measure quantitative levels of C2 to C5 hydrocarbons. The results from this hole, through much greater lithologic variations than encountered in the Black Sea, gave remarkable confirmation to the

suggestion that the  $C_2$  to  $C_5$  hydrocarbons are somehow associated with biogenic methane production in fine-grained sediments. The results also raised many intriguing questions about low molecular weight hydrocarbon production and migration in sediments.

# METHODOLOGY

Samples were collected in "vacutainers" from core gas pockets through the core liner immediately after the cores were brought on deck. A rubber septum was pressed between the gas sampler and the core liner to minimize air contamination of the sample. If possible, the sample was taken from a gas pocket in the middle of the core where a sediment "seal" and/or active gas bubbling could be observed. For gasier cores, sample withdrawal was accompanied by vigorous spraying of gas and water from the hole. Analysis of these samples for hydrocarbons of higher molecular weight than  $C_5H_{12}$  was not possible because of contamination from the rubber stopper in the vacutainer.

Shipboard analysis of C1-C5 hydrocarbons was conducted routinely on two gas chromatographs (GC's): C<sub>1</sub> analysis on an Exploration Logging GC (3 minutes of analysis time), and C<sub>2</sub> to C<sub>5</sub> analyses on a dual column Hewlett Packard 5711A instrument equipped with temperature programming and dual flame ionization detectors used in the compensation mode as described below (15 minutes of analysis time). Analyses of both  $C_1$  and  $C_2$  to  $C_5$  on the same sample in a reasonable time were not possible because of the appearance of the small  $C_2$  to  $C_5$  peaks on the tail of the much larger methane peak. Amounts were measured via peak height for C1 and via peak areas measured with an electronic integrator (CSI Model 38) for C<sub>2</sub> to C<sub>5</sub>. For several cores, core liner gas was taken from two different positions within the same core. Methane determinations on the two samples were generally the same within  $\pm 5$  per cent.

Sample introduction into the Hewlett Packard GC was via a  $1/8'' \times 8''$  loop packed with 60/80 mesh alumina (Analabs, Activated Alumina F-1) attached to a Carle sampling valve (microvolume valve 2014 or minivolume valve 2818) as described by Swinnerton and Linnenbom (1976). A stream of dry helium, flow rate adjusted to 15 cc/minute via a fine metering valve, was passed through the alumina-filled loop. The sample to be analyzed (1 to 5 ml depending on CH<sub>4</sub> content detected) was withdrawn from the vacutainer and injected through a silicone rubber septum into the helium stream flowing through the sample loop. The loop had been previously cooled in a 2-propanol bath cooled to between -72°C and -68°C via a portable refrigeration unit (FTS Systems Model 80). Methane was stripped from the sample before analysis by allowing helium to flow through the loop (1 cc/3 sec) for 2 minutes before analysis. After stripping, the sample loop was shut off via toggle valves from helium flow and injection port, than heated for 1 minute in a 90° to 100°C water bath; the sample was injected by turning the sample valve. GC analysis was carried out on a column of  $1/8'' \times 6'$  Sherosil (40-100 mesh microns, Superlo, Inc.) attached to  $1/8'' \times 12' 20\%$  OV-101 on Analabs AS (100/110 mesh) as described by Durand and Espetalie (1971) via temperature programming from 60 to 200°C at 8°/min. The loop was left in the carrier gas stream during GC analysis as described above.

Occasionally, no  $C_3$  to  $C_5$  hydrocarbons would elute from the GC using the conditions described above. This usually indicated that the alumina loop had become too "active" and was decomposing the compounds. The situation was remedied by injecting about 10  $\mu$ l of distilled water into the loop to deactivate the alumina.

The sampling and GC conditions described above allowed separation of methane, ethane, ethylene, propane, propylene, isobutane, *n*-butane, neopentane, isopentane, *n*-pentane, and cyclopentane in order of increasing retention time.

The absolute sensitivity achieved with the system on gas samples was about 2.0  $\times$  10<sup>-11</sup> moles for C<sub>2</sub> and 7  $\times$  10<sup>-12</sup> moles for C<sub>5</sub>. This is equivalent to detection of 50 ppb by volume of C<sub>2</sub> and 17 ppb by volume of C<sub>5</sub> using a 10-ml gas sample. Reproducibility is within 10 per cent at this level. Qualitative detection of gas is possible to about 10 ppb of C<sub>2</sub> and 3 ppb of C<sub>5</sub>. These results were attained without optimizing H<sub>2</sub>, air, and carrier gas flows for maximum GC sensitivity.

Sediment C1-C7 hydrocarbon analyses were obtained at Woods Hole on frozen core samples sealed in Kopak bags. The total hydrocarbon levels reported here may be low since the samples were stored for 3 weeks at 4°C during transit. Briefly, the procedure involves placing the frozen sample in a 600-ml can equipped with a silicone rubber septum. The can is filled with distilled water and sealed. A headspace is then made by injecting 150 ml of helium and withdrawing 150 ml of water from the can. The sediment is allowed to thaw, the can shaken vigorously, and 5 ml of gas from the headspace analyzed for C1 to C5 hydrocarbons via the procedure described above for C2 to  $C_5$  analysis with the modification that the loop is frozen in liquid nitrogen before sample injection. Depending on the quantity of gas detected on the packed column, a 5 to 50-ml gas sample then is analyzed by capillary gas chromatography for C5 to C7 hydrocarbons as described by Schwartz and Brasseaux (1963). The sample is concentrated on a 10 inch  $\times$  0.01 inch stainless steel loop cooled in liquid nitrogen before injection into the column via a Carle microvolume valve (no. 2014). Peak areas are measured with a CSI Supergrator 3 electronic integrator.

## **RESULTS AND DISCUSSION**

Pressured gas pockets began to appear in chalky marly fine-grained sediments at about 80 meters. Methane was a minor component of this gas (0.1 to 1.3%) until a depth of 196 meters, where the methane concentration increased to 43 per cent (Whelan, foldout diagram at the end of this volume). The methane concentration in gas pockets then varied widely from 1 to 81 per cent throughout the rest of the hole. The odor of  $H_2S$  was detected in the cores from 9 to 151 meters. This  $H_2S$  results from sulfate-reducing bacteria which generally predominate in anoxic sediments above the zone of methane producing microorganisms (Claypool and Kaplan, 1974).

Measurements of other non-hydrocarbon gases at Woods Hole indicated that constituent gases were air, N2, and CO2 above 200 meters. Below this depth, N2/ O<sub>2</sub> ratios indicated that the non-hydrocarbon gases at predominantly air. In fact, all gas samples analyzed contained some quantity of air as determined by No:Oo ratios. The source of this air is probably from gas dissolved in the sea-water drilling fluid which is effectively "headspaced" by methane. This methane is initially dissolved at in situ bottom temperatures and pressures, then forms gas pockets as the sediment is brought to the surface. Air contamination of gas samples during sampling is not believed to be a problem for several reasons. Firstly, gas pressure in many pockets (particularly in fine-grained marly chalks above 550 meters) was high enough to forcibly extrude sediment and water from core barrels or through gas sampling holes. Here, sediment plugs probably sealed the gas pockets. In deeper, more compacted sediments, cores fitted loosely into barrels so that gas pockets were more open to air contamination. Yet, even in these sediments, active gas bubbling out of a particular spot was often observed. In both cases, the prevailing gas flow out of the sediment during gas sampling would minimize air contamination during actual sampling. Secondly, duplicate methane measurements on a particular core, even a compacted one where gas samples were taken at different locations in the core tube, were usually within  $\pm 5$  per cent. Thus, the gas collecting procedure seems to provide representative samples of gas in the core barrel.

The methane throughout the hole is biogenic as shown by values (Figure 1) of -60 to  $-80 \delta C^{13}$ . Petrogenic methane values are generally in the range of -20 to  $-50 \delta C^{13}$ . The  $\delta C^{13}$  curves show an almost linear change with depth, with deeper methane becoming more enriched in C13. This trend is somewhat surprising when one considers the large variations in lithology throughout the hole and their probable influence on methane diffusion within the sediment. There are several possible explanations for this behavior. The first, which seems unlikely in these predominantly finegrained sediments, is that lighter methane produced in shallower sediments is diluted with heavier petrogenic methane migrating up with depth. The second is that biogenic methane production occurs to considerable depth in the sediment and that the deeper methane becomes heavier as the lighter CO<sub>2</sub> used to form methane is preferentially depleted. There is no direct evidence that methane bacteria live in deep marine sediments; sampling bacteria in such sediments without contamination is extremely difficult (H. Jannasch, C. Taylor, private communication). Since methane bacteria are anaerobic, there is no theoretical reason that they cannot exist to any depth where CO<sub>2</sub> and a food supply exists up to their temperature limit of about 65° to



Figure 1.  $C^{13}$  (°/  $_{\circ\circ}$ ) for gas pocket methane in Holes 397 and 397A.

75°C. A third possibility is that some methane is formed by low temperature ( $\leq 50$ °C) diagenetic processes in the sediment and that the contribution of this diagenetic methane increases with depth. As depth increases, the biogenic methane then would be diluted increasingly with diagenetic methane, with  $\delta C^{13}$  values similar to petrogenic methane. In addition, any slow upward movement of methane by diffusion would favor lighter methane at shallower depths. However, if preferential movement of lighter methane is occurring, it is difficult to see why this does not show up as "spikes" of lighter methane in more porous sections such as those occurring between 600 and 800 meters.

Due to variations in methane values, levels of ethane (C<sub>2</sub>); propane (C<sub>3</sub>); iso- and *n*-butane (C<sub>4</sub>); and iso-, *n*-, and neo-pentane (C<sub>5</sub>) were calculated in ppm by volume assuming all of the non-C<sub>2</sub> to C<sub>5</sub> gas was methane. The C<sub>2</sub> to C<sub>5</sub> levels are plotted on a log scale as a function of depth (Whelan, foldout diagram). Several areas can be seen where the shapes of the curves are very similar, or travel "in phase" even though the levels of  $C_2$ ,  $C_3$ ,  $C_4$ , and  $C_5$  compounds decrease by about an order of magnitude for each increase in carbon number. This behavior prevails in fine-grained sediments, from 190 to 350 meters through wide variations in  $C_2$  to  $C_5$  levels, from 420 to 530 meters and from 840 meters to the bottom of the hole at 1453 meters. In more porous sections representative of discontinuities, volcaniclastics, sandstone, or higher proportions of silt, the concentrations of  $C_3$  to  $C_5$  compounds decrease with respect to  $C_2$  and the curves no longer travel "in phase." These areas include a section with irregular layers of sand, sandstone, and volcaniclastics from 550 to 825 meters, as well as several other narrower sand/silt bands shown in Table 1.

One interpretation of these results which is consistent with the data is that the  $C_2$  to  $C_5$  hydrocarbons are formed by a low temperature ( $<50^{\circ}C$ ) chemical or biological process and move upward very slowly (a few cm to several m/m.y.) with compaction water in fine-grained sediments (Magara, 1976). Since the hydrocarbons are soluble in the water at these low concentrations, they move together without fractionation. At discontinuities, all the gases were washed out of the sediments. Reburial then led to coarse-grained sediment layers, whereupon there occurred rapid horizontal movement of light hydrocarbons. This type of lateral gaseous movement, usually referred to as "diffusion," is believed to occur very rapidly (distances up to 175 km/m.y. are not uncommon) and favors the lighter hydrocarbons. Thus, the process would concentrate lighter molecules, such as methane and ethane, in the coarser grained sediments. It would explain the relatively high concentrations of  $C_1$  and  $C_2$  in coarser grained sediments and discontinuities such as the section between 700 and 750 meters where sand layers predominate and where  $C_3$  to  $C_5$  hydrocarbons drop to their lowest levels. It would also explain why both carbon isotope values and log  $(C_1/C_2)$  values change linearly with depth in spite of large variations in lithology as shown in Figures 1 and 2, respectively. Predominantly horizontal movement of methane and ethane would not affect this linearity.

It might be expected that isomeric alkanes, such as iso-butane and *n*-butane or isopentane, *n*-pentane, and neopentane, might move together by either vertical or horizontal migration since their sizes are approximately the same. Figure 3 shows that  $iC_4/nC_4$  values stay approximately constant in predominantly fine-grained sediments from 190 to 550 meters and from 830 to 1453 meters. In contrast, the  $iC_5/nC_5$  values show more variability over short sections, which probably reflects local variation in organic precursors to these compounds rather than a result of exposure to temperatures greater than 60 °C. This non-uniformity of  $iC_5/$ nC<sub>5</sub> ratios is consistent with low temperature in-situ hydrocarbon production in these sediments. In particular, a large change in this ratio occurs at the Miocene-Cretaceous uncomformity at 1300 meters.

Neopentane (or tetramethyl methane) occurred sporadically in this hole, particularly in deeper sections. It is plotted as percentage of total  $C_5$  in Figure 4. One

Core (Depth in m)	Hydrocarbon Concentrations With Respect to Adjacent Samples	Grain Size With Respect to Adjacent Samples	Neopentane-Per Cent of C5 With Respect to Adjacent Samples Higher Irregularly higher Slightly higher		
397-36 (340)	C1 increases; C2 to C5 decrease	Higher per cent sand			
397-58 to 397-86 (550-825)	$C_1$ and $C_2$ stay approximately constant; $C_3$ to $C_5$ gradually decrease with depth and no longer travel "in phase"	Irregular sand, silt, volcaniclastics throughout			
397-90 (860)	$C_4$ and $C_5$ increase with respect to $C_1$ and $C_2$	Less sandy than section just above			
397-92 (875) 93 (890)	$C_4$ and $C_5$ low; $C_1$ , $C_2$ and $C_3$ increases	Per cent sand higher than in section above	No change		
397-94 (894)	C <sub>1</sub> high; C <sub>4</sub> and C <sub>5</sub> low	Sand = 90%	No change		
397-94 (903)	$C_1$ low; $C_2$ to $C_5$ high	Finer grained than in sec- tion just above	No change		
397A-18 (1090)	$C_1 \text{ high}; C_3 \text{ to } C_5 \text{ low}$	Sandier and siltier than adjacent sections	Higher		
397A-19 (1105)	C <sub>1</sub> less; C <sub>5</sub> higher	Finer grained sediment than just above	Lower		
397A-21 (1128)	$C_1$ high; $C_5$ low	60% sand (compared to 10% in samples just above and below)	Higher		
397A-24 (1192)	$C_5$ decreases a little with respect to $C_2$ to $C_4$	Slightly siltier	No change		
397A-36 (1318)	$C_1$ high; $C_5$ low	Small wedge of sandy sediment	Slightly higher		

TABLE 1 Gas Samples Showing Changes in Gas Pocket C1-C5 Hydrocarbons Correlating With Grain Size



Figure 2. Log  $C_1/C_2$  gas pocket gas in Holes 397 and 397A.

very interesting trend appearing in this graph is that the portion of total  $C_5$  represented by neopentane often increases in porous sections where total  $C_5$  levels are very low, e.g., at 330, 820, and at 1130 meters. It has been calculated that the diffusivity of neopentane is higher than for i- and *n*-petane (Sahares and Witherspoon, 1970). Thus, any diffusion of  $C_5$  hydrocarbons into coarse-grained sediments should favor neopentane as observed in this hole.

The picture of sediment hydrocarbon movement presented above is consistent with many features of the data as summarized in Table 1. However, there are several samples which do not neatly fit the general pattern. These are outlined in Table 2 with a brief description of the sediment grain size in the vicinity of a particular gas pocket. In general, these samples showed a drop in total  $C_5$  with respect to  $C_2$  even though there was no obvious change in lithology.

As mentioned earlier, the exact source of the  $C_2$  to  $C_5$  hydrocarbons in this and other DSDP holes is not clear. However, examination of data from this hole and from sites in the Black Sea, Leg 42B (Hunt and Whelan, 1978) strongly suggest that most of this material is generated by a low temperature ( $\leq 50^{\circ}$ C) diagenetic process. Several lines of evidence support this hypothesis. First, hydrocarbon migration through fine-grained sediment (where the highest concentrations of these



Figure 3. Logs of ratios of iso-butane/n-butane ( $iC_4/nC_4$ ) (shown as circles) and iso-pentane/n-pentane ( $iC_5/nC_5$ ) (shown as squares).

hydrocarbons occur) is known to be very slow (Magara, 1976) while their concentration in coarse-grained beds (where migration rates should be much faster) is lower even though methane concentrations are irregularly high throughout the hole. This argues strongly for in situ generation of the  $C_2$  to  $C_5$  compounds in finegrained sediments followed by no movement or slow upward movement of all the compounds together with compaction water. Any in situ process responsible for the creation of these compounds must occur at low temperatures, because sediments above 1100 meters were not exposed to temperatures above 50 °C. Estimated temperature at the hole bottom was about  $60^{\circ}C$ .

It is possible that bacteria produce traces of  $C_2$  to  $C_5$ hydrocarbons along with methane. However, this has never been demonstrated in pure culture despite numerous attempts (Stone and Zobell, 1952). If bacterial production of these compounds is occurring, it must happen either only in mixed culture or when the organisms encounter stress, such as a limited food supply; it has been noted sporadically in the literature that  $C_2$  to  $C_5$  hydrocarbons, in the approximate relative concentrations encountered in this hole, are occasionally asso-



Figure 4. Per cent of total C<sub>5</sub> hydrocarbon represented by neopentane (tetramethyl methane).

ciated with anoxic mud and sewage sludge (Davis and Squires, 1954; Bokova, 1959; Malyshek, 1962; Stone and Zobell, 1952; Weber and Maximov, 1976).

A second possibility is that the  $C_2$  to  $C_5$  compounds arise from a low temperature chemical process using remains from the bacterial community as source material. There are several lines of evidence that support this hypothesis. First, a linear decrease in log  $C_1/C_2$ with depth has been observed in many gaseous DSDP holes (Claypool et al. 1976; Claypool and Kaplan, 1974; Hunt and Whelan, 1978) including this one (Figure 2). This type of change is characteristic of a chemical reaction generating an increasing proportion of  $C_2$  as a function of increasing temperature (depth). The  $C_3$ ,  $C_4$  and  $C_5$  curves correlate well with the  $C_2$ curve in fine-grained sediments; similar arguments may apply to their generation.

Analysis of C1 to C7 hydrocarbons in frozen sediment sections (Table 3) shows that C2 to C5 hydrocarbon levels in upper marly nannofossil ooze sections are very low in contrast to gas pocket C2 to C5 levels and deeper Miocene pebbly mudstone samples. Levels of sediment C<sub>6</sub> and C<sub>7</sub> hydrocarbons also show distinct differences between the top marly nannofossil ooze section and the deeper pebbly mudstone. In the deeper strata, Sections 397A-11-5, 397A-16-4, and the tops of 397A-23-4 and 397A-33-2 all show the wide distribution of C<sub>6</sub> and C<sub>7</sub> isomers seen in other DSDP cores (Hunt, 1975). Total levels of C<sub>6</sub> and C<sub>7</sub> generally increase with depth and increasing organic carbon content as observed in other DSDP cores with immature organic carbon in very early stages of petroleum generation. The trend continues into the Cretaceous section, but with total levels of  $(C_6 + C_7)/C_0$  being lower. In contrast, the shallower marly nannofossil ooze sections (including 397-2-5, 397-6-3, 397-9-2, 397-10-6, 397-12-2, 397-18-5, 397-29-3, 397-32-2, and 397-45-4) all show lower levels of  $C_6 + C_7$  with limited compound distribution. In these cases, a major proportion of the total  $C_6 + C_7$  is contributed by one or two compounds, with toluene usually being a major component. The same pattern holds for Section 397-83-1 which comes from the middle volcaniclastic sandstone section.

It has been observed for other organic geochemical mixtures, e.g., higher molecular weight aromatic and straight carbon hydrocarbons, that the complexity of the mixture increases with geochemical alteration (Blumer, 1974; Blumer et al., 1971; Youngblood et al., 1971). Thus, the limited hydrocarbon distribution from the shallower nannofossil ooze sediments is typical of carbon skeletons generated from fairly specific biogenic debris under mild conditions. In the deeper samples, the increased amounts and/or wider spectrum of light hydrocarbons may reflect generation from a more complex organic matrix that results from more varied organic source material, higher temperatures, and longer burial times.

The results are intriguing since they suggest that the processes for generation of gas pocket  $C_2$  to  $C_5$  hydrocarbons are different from those for generation of most of the  $C_6$  and  $C_7$  compounds. A similar result was suggested by subjecting  $C_2$  to  $C_7$  sediment hydrocarbon analyses from the Black Sea to factor analysis (Whelan, unpuslished results). The analysis showed a strong correlation of  $C_2$  to  $C_5$  hydrocarbons and strong correlation of many  $C_6$  and  $C_7$  hydrocarbon isomers. However, there was a strong inverse correlation between the two sets of compounds.

One way to interpret these results is that the  $C_2$  to  $C_5$  hydrocarbons result from a low temperature diagenetic process utilizing bacterial remains as starting material, while the wide  $C_6$  to  $C_7$  distributions seen both here and in the Black Sea (Whelan and Hunt, 1978)

Core (Depth in m)	Hydrocarbon Concentrations With Respect to Adjacent Samples	Grain Size With Respect to Adjacent Samples	Neopentane-Per Cent of C <sub>5</sub> With Respect to Adjacent Samples		
397-26 (243)	C <sub>1</sub> increases; C <sub>2</sub> to C <sub>5</sub> de- creases	No change	No change		
397-41 (384)	$C_1$ and $C_2$ low; $C_3$ to $C_5$ curves normal, but out of phase	No change (Pliocene-Miocene bounday at 398.5 m;	Higher		
397-43 (407)	$C_1$ and $C_2$ increase; $\Sigma C_3$ to $C_5$ decrease	Miocene climate warmer, Pliocene cooler)	No change		
397-95 (912)	$C_5$ decreases more than $C_2$ to $C_4$	Siltier; coarser than be- low; finer than above	Slightly higher		
397A-33 (1292)	$C_1$ and $C_2$ increase; $C_4$ and $C_5$ decrease	Less sand than in sedi- ment just above	Slightly higher than sec- tion above		
397A-39 (1337)	$C_1$ increases; large decrease in $C_5$	No change	Lower		
397A-47 (1404)	C <sub>1</sub> and C <sub>2</sub> increase slightly; C <sub>5</sub> decreases slightly	No change	No change		

TABLE 2 Gas Samples Showing Changes in Gas Pocket C1-C5 Hydrocarbons Not Correlating With Grain Size

come from a process more akin to early stages of petroleum formation using the whole organic matrix as starting material. The narrow spectrum of  $C_6$  to  $C_7$ compounds seen in upper sections then might be characteristic diagenetic processes operating on remains of either sulfate-reducing or methane-producing bacteria, or both. Evidence for the former comes from work of J. Boon (unpublished data), who has identified cyclic terpenes produced by sulfate-reducing bacteria both in the marine environment and in laboratory cultures. He noted high levels of toluene in sediments where chemical rearrangement of these materials is possible. Toluene and benzene probably form in many goechemical settings. However, it is well-known to organic chemists that acid-catalyzed rearrangement of many terpenes leads to aromatic structures. A strong H<sub>2</sub>S odor characteristic of sulfate reduction was noted in Cores 397-2 through 397-10 with traces of pyrite noted irregularly throughout the hole. Pyrite usually forms when iron in sediments reacts with sulfide produced by sulfate-reducing microorganisms. Even after active sulfate reduction ceases, the organic compounds derived from these communities would remain in the sediment.

The presence of neopentane as a major contributor to total C<sub>5</sub> content of the gases was mentioned earlier (Figure 4). The source of this compound is unknown. However, its presence is very interesting since its carbon skeleton must be derived from terpenes. Kinetically, there are many organic chemical processes which would cause rearrangement of the neopentyl to the isopentyl skeleton, but there is no low temperature kinetically controlled organic reaction known to produce a neopentyl carbon skeleton from other C<sub>5</sub> skeletons. The compound could be a breakdown product of terrigenous terpenes or of the terpenes of marine origin which have recently been discovered in sulfate-reducing microorganisms and diatoms (J. Boon, unpublished results) and other marine derived material (Ensminger et al., 1973; Simoneit and Burlingame, 1973; Simoneit,

1977; Gaskell and Eglington, 1976; Vandenbrouke et al., 1976). Its appearance does not seem to correlate with lithology or any particular type of organism in this hole or in Hole 381 of the Black Sea.

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#### REFERENCES

- Blumer, M., 1973. Chemical fossils: trends in organic geochemistry. Woods Hole Oceanographic Institution Collected Reprints, Part I, Contribution No. 2898.
- Blumer, M., Guillard, R. R. L., and Chase, T., 1971. Hydrocarbons of marine phytoplankton, *Marine Biology*, v. 8, p. 183-189.
- Bokova, E. N., 1959. Formation of heavy gaseous hydrocarbons during anaerobic decomposition of organic matter, *Petroleum Geology*, v. 3, p. 490-494.
- Claypool, G. E., et al., 1976. Manual on Pollution-Prevention and Safety, JOIDES Journal, no. 4, p. C1-C11a.
- Claypool, G. E. and Kaplan, I. R., 1974. The origin and distribution of methane in marine sediments: In Kaplan, I. R., (Ed.), Natural gases in marine sediments: New York (Plenum Press), p. 99-139.
- Davis, J. B. and Squires, R. M., 1954. Detection of microbially produced gaseous hydrocarbons other than methane, *Science*, v. 119, p. 381-382.
- Durand, B. and Espitalie, J., 1971. Formation et Evolution des Hydrocarbures, de  $C_1$  a  $C_{15}$  et des Gaz Permanents Dans les Argiles du Toarcien du Bassin de Paris, *Advances in organic geochemistry*, p. 455-468.
- Edgar, N. T., Saunders, J. B., et al., 1973. Initial Reports of the Deep Sea Drilling Project, v. 15: Washington (U.S. Government Printing Office), p. 169-216.
- Ensminger, A., et al., 1973. Pentacyclic triterpenes of the hopane type as ubiquitous geochemical markers: origin and significance. In Tissot B. and Bienner F. (Eds.), Advances in organic geochemistry: Paris (Technip), p. 245-260.

Sample (Interval in cm)	397-2-5, 120-130	397-6-3, 135-150	397-9-2 (Top)	397-10-6, 10-35	397-12-2	397-18-5, 100	397-29-3	397-32-2
Lithology	Marly Nanno Ooze	Siliceous Nanno Ooze	Siliceous Nanno Ooze	Marly Nanno Ooze	Marly foram Nanno Ooze	Marly Nanno Ooze	Nanno Ooze	Marly Nanno Ooze
Depth (m)	16.2	51.3	77.0	92.6	105.5	168.0	269.5	296.5
Age	Pleistocene	Pleistocene	Pleistocene	Pleistocene	Pleistocene	Pliocene	Pliocene	Pliocene
Hydrocarbon	ng/g dry weight sediment							
Methane	1.32	30.2	75.2	17.7	19.7	Trace	7.8	3.9
Ethane	0.23	0.96	0.53	0.21	0.61	Trace	0.23	0.15
Propane	0.35	1 34	0.62	0.28	0.73	Trace	0.16	0.18
<i>i</i> -Butane	0.06	0	0.10	0.02	0.14	0	0.09	0
n-Butane	0.00	1.07	0.10	0.02	0.40	0	0.05	õ
neo-Pentane	0.24	1.07	0.50	0.15	0.40	0	0.05	0
<i>i</i> -Pentane	0.09	0	Traca	0	0 31	0	0	0
n-Pentane	0.09	0	Trace	0	0.31	0	0.5	0
Cyclopentane	0.54	0	nace	0	0.20	0	0	õ
2 2-Dimethylbutane	nda	0 nd	0	U	o	o	od	0
2. 3-Dimethylbutane	nue	nu	nu	nu	nu	nu	nu	0.01
2. Mathylbutane	0	0 20	0 02	0	0	0	0	0.01
2 Methylpontane	0	0.29	0.02	0	0	0	0	0.01
-Methylpentalle	0.24	0.90	0.06	0.08	4.2	0.24	0 20	0.10
Mathylevelopantana	0.24	0.02	0.24	0.08	4.5	0.54	0.20	0.19
2 2 Dimethylpontono	0	0.50	0.03	0	2.5	0.17	0.03	0.01
Papzapa	0	0.50	0.21	0.04	0 1	0.14	0 08	0.08
2 4 Dimethylpentene	0	0.59	0.21	0.04	0.1	0.14	0.08	0.08
2, 2 2 Trimothylbutane	0	0	0	0	0	0	0	0
Cyclobayana	0	0	0 10	0 10	0.26	0 11	0 02	0
2 2 Dimethylasates	0	0	0.10	0.10	0.20	1.04	0.02	0
1. 1. Dimethylpentane	0.05	0	0	0	0	1.84	0.69	0
2 Mathylhavana	0.05	0	0	0	0	0	0.05	0
2. 3 Dimethylaentee	0	0.55	0	0.11	0	0	0.05	0
2. S-Differingipentane	0	0.17	0	0	0 (2	0 12	0	0
1 + 2 Dimothylavalamentana	0	0.17	0	0	0.65	0.15	0	0
1 + 2 Dimethylevelopentane	0	0 00	0	0	0	0	0	0
2 Ethylpontono	0	0.09	0	0	0	0	0	0
-Eurypentane	0 (7	0 1 5	0	0 00	0	0 50	0 12	0 21
1 a 2 Dimathulaualanantana	0.67	0.15	0	0.09	0	0.59	0.15	0.21
Mathylayalahayana	0.53	0	0	0	0 12	0.25	0	0 01
Ethylovolopontono	0	0	0	0.04	0.13	0.35	0	0.01
Tabaaa	0	0	0	0	20.0	10.0	0	0
Cation	0 60	5.54	0	0.54	39.8	12.8	0.01	2.50
$C_2 + C_3$	0.58	2.3	1.15	0.49	1.5	Trace	0.39	0.33
$C_4 + C_5$	0.73	1.1	0.46	0.17	1.1	16.6	0.64	2.0
Corton (C)	1.49	9.1	0.66	1.00	47.5	10.5	1.81	3.0
$\log (C_1 + C_2)/\log C_1 + 107$	2.0	1.4	0.78	0.92	2.8	1.3	0.68	0.83
$[\ln g (C_4 + C_5)/\ln g C_0] \times 10^7$	0.36	0.75	0.59	0.18	0.39	10.7	0.94	0
[ng (C6 + C7)/ngC0] × 10/	0.75	6.4	0.85	1.09	17.0	12.7	2.7	3.0

TABLE 3 C1-C7 Hydrocarbons in Holes 397 and 397A

\*nd means not determined

- Gaskell, S. J. and Eglington, G., 1976. Sterols of a contemporary lacustrine sediment, *Geochimica et Cosmochimica Acta*, v. 40, p. 1221-1228.
- Hunt, J. M., 1975. Origin of gasoline range alkanes in the deep sea, *Nature*, v. 254, p. 411-413.
  Hunt, J. M. and Whelan, J. K., 1978. Dissolved gases in
- Hunt, J. M. and Whelan, J. K., 1978. Dissolved gases in Black Sea sediments. In Ross, D., Neprochnov, Y., et al., Initial Reports of the Deep Sea Drilling Project, v. 42, Part 2: Washington (U.S. Government Printing Office), 661-666.
- Magara, K., 1976. Water expulsion from clastic sediments during compaction-directions and volumes, Bulletin of the American Association of Petroleum Geologists, v. 60, p. 543-553.
- Malyshek, V. T., 1962. The biogenic formation of the higher gaseous hydrocarbons in bottom sediments, *Izvestiya Aka*damie Nauk Azerbaidzhanian SSR, Ser. Geolog.-Geograf. Nauk i Nefti, v. 1, p. 63-72.

- Ryan, W. B. F., et al., 1978. *Initial Reports of the Deep Sea Drilling Project*, v. 40: Washington (U.S. Government Printing Office).
- Sahores, J. J. and Witherspoon, P., 1970. Diffusion of light hydrocarbons in water from 2°C to 80°C. In Hobson G. D. and Speers G. C. (Eds.), Advances in organic geochemistry: New York (Pergamon Press), p. 219-230.
- Schwartz, R. D. and Brasseaux, D. J., 1963. Resolution of complex hydrocarbon mixtures by capillary column gas liquid chromatogrphy. Composition of the 28° to 114°C portion of petroleum, *Analytical Chemistry*, v. 35, p. 1375-1382.
- Simoneit, B. R. T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance, *Geochimica et Cosmochimica Acta*, v. 41, p. 463-476.

Marly no Ooze; Chalk 48.2 ocene 3.2 0.07 0.05 0 0 0 0	Calcareous Mudstone; Siltstone; Sandstone 788 Miocene 35.1 2.6	Breccia 40% CaC0 <sub>3</sub> 40% Clay 865.5 Miocene	Pebbly Mudstone 1026.5 Miocene	Pebbly Mudstone (slumped) 1072.8 Miocene	Calcareous Sandy Mudstone 1158	Pebbly Mudstone 1288	Quartz- Mudstone- Siderite Layers 1308.5	Mudstone + Siderite Layers
3.2 0.07 0.05 0 0	788 Miocene 35.1 2.6	865.5 Miocene	1026.5 Miocene	1072.8 Miocene	1158 Mi	1288	1308.5	
3.2 0.07 0.05 0 0	Miocene 35.1 2.6	Miocene	Miocene	Miocene	Minute			1421
3.2 0.07 0.05 0 0 0	35.1 2.6	9.7			Miocene	Miocene	Cretaceous	Cretaceous
3.2 0.07 0.05 0 0	35.1 2.6	9.7		ng/g dry weig	ht sediment			
0 0 nd 0 0.04 0.03 0.24	$2.4 \\ 0.45 \\ 1.51 \\ 0 \\ 0.89 \\ 0.93 \\ 0 \\ 1.4 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	0.71 3.30 1.64 1.53 0.01 2.30 0.98 0.01 0.24 0 0 0 0 0	333 7.04 11.1 15.2 9.3 0.25 12.2 5.7 0.28 9.2 4.64 1.58 6.73	93.7 230.5 194.0 73.8 38.3 0.99 35.0 13.0 0.7 17.7 1.69 9.04 1.98 8.11	26.0 14.8 58.5 47.0 24.9 1.5 37.8 6.4 0.09 0.65 0.72 1.76 0.95 1.87	344 7.0 12.9 8.3 2.9 1.0 3.4 0.9 0 nd 1.94 3.24 2.9 17.3	75.2 29.2 30.7 11.0 3.1 1.1 2.48 0.28 0.02 0.09 0.43 0.48 0.47 1.73	2.7 Trace Trace 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.11 0.03 0 0 0.09 0 0	0.64 0 1.24 0 0 0 0 0	0 0.23 0 0 0.43 0	4.80 0 4.44 0 2.78 0 0	$\begin{array}{c} 8.48 \\ 0.10 \\ 5.11 \\ 0 \\ 0.56 \\ 1.5 \\ 0.03 \\ 0.05 \\ 0.32 \end{array}$	$ \begin{array}{c} 1.95 \\ 0.03 \\ 0.41 \\ 0 \\ 0.08 \\ 0.86 \\ 0 \\ 0 \\ 0.21 \\ \end{array} $	$20.4 \\ 0.03 \\ 1.68 \\ 0 \\ 0.25 \\ 0.28 \\ 0.04 \\ 0.09 \\ 0.44$	2.75 0 3.90 0 0.1 0.14 0 0	7.27 0.02 0.47 0 0.10 0.17 0.03 0.03 0.70
0.10 0.01 0.01 0.01 0.07 0.07 0.170 0.12 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0 0.06 0.34 0 0 0.08 4.0 6.5 1.4 0.93 7.0	1.69 2.47 0 2.05 0.34 2.63 0 27.2 18.1 42.9 72.0 2.2 19.5	0.80 3.03 1.84 0.63 Trace 1.28 0.26 1.93 0.15 7.10 424 162 71.7 5.16 31.4	$\begin{array}{c} 0.38\\ 1.0\\ 1.18\\ 2.04\\ 0.07\\ 0.68\\ 0.36\\ 1.98\\ 0.22\\ 0.26\\ 73.3\\ 118\\ 17.7\\ 2.34\\ 50.3 \end{array}$	$\begin{array}{c} 0.82\\ 1.01\\ 0.62\\ 1.82\\ 0.11\\ 1.37\\ 1.15\\ 0.76\\ 0.24\\ 10.3\\ 19.9\\ 16.5\\ 66.8\\ 0.73\\ 22.6 \end{array}$	0.33 0.29 0.20 0 0.08 0 0.24 0 0.2 59.9 18.0 11.7 0.57 31.6	$\begin{array}{c} 0.71\\ 0.46\\ 1.40\\ 0.1\\ 0.69\\ 0.17\\ 1.23\\ 0.26\\ 0.74\\ 0.1\\ 0.1\\ 27.5\\ 0.56\\ 0.18\\ \end{array}$
0 0. 0 1. 0	10 07 70 12 6 64 02	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE 3 – Continued

- Simoneit, R. T. and Burlingame, A. L., 1973. Study of the organic matter in the DSDP (JOIDES) cores, Legs 10-15. In Tissot B. and Bienner, F. (Eds.), Advances in organic geochemistry: Paris (Technip.), p. 629-648.
- Stone, R. W. and Zobell, C. E., 1952. Bacterial aspects of the origin of petroleum, *Industrial and Engineering Chemistry*, v. 44, p. 2564-2567.
- Swinnerton, J. W. and Linnenborn, V. J., 1967. Determination of C<sub>1</sub>-C<sub>4</sub> hydrocarbons in sea water by gas chromatography, *Journal of Gas Chromatography*, v. 5, p. 570-573.
- Vandenbroucke, M., Albrecht, P., and Durand, B., 1976. Geochemical studies on the organic matter from the Douala Basin (Cameroon). III. Comparison with early Toarcian

shales, Paris Basin, France, Geochimica et Cosmochimica Acta, v. 40, p. 1241-1249.

- Weber, V. V. and Maximov, S. P., 1976. Early diagenetic generation of hydrocarbon gases and their variations dependent on initial carbon composition, *Bulletin of the* Project, v. 42, Part 2: Washington (U.S. Government Printing Office), p. 673-678.
- Printing Office), p. 673-678.
  Youngblood, W. W., Blumer, M., Guillard, R. L., and Fiore,
  F., 1971. Saturated and unsaturated hydrocarbons in marine benthic algae, *Marine Biology*, v. 8, p. 190-201.
  American Association of Petroleum Geologists, v. 60, p. 287-293.
- Whelan, J. K. and Hunt, J. M., 1978. C<sub>1</sub>-C<sub>7</sub> hydrocarbons in Holes 379A, 380/380A and 381. In Ross, D., Neprochnov, Y., et al., Initial Reports of the Deep Sea Drilling