36. PRELIMINARY ORGANIC ANALYSES OF THE DEEP SEA DRILLING PROJECT CORES, LEG 11¹

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ABSTRACT

Two core samples from the DSDP Leg 11 were analyzed and further studies made on sources of possible organic contamination.

A small sample derived from approximately 130 meters below the seabed and of mid-Cretaceous age was solvent extracted. The acetone soluble fraction of the extract is dominated by the presence of an amine $C_8H_{19}N$ and contains a substantial amount of palmitic acid. The heptane soluble fraction contains a series of saturated alkanes (C_nH_{2n+2} for n = 15-50) and palmitic and stearic acids as the principal components.

Also examined was a large sample (Site 105 at northern end of Hatteras Abyssal Plain) from 310 meters below the seabed and derived from the thick section of black lower Cretaceous clay. The sample consists mainly of zeolitic clays, some foraminifera and significant amounts of carbonate, but despite the terrestrial source of the clays the sample is very low in terrigenous plant detritus. An extract of the sample was divided into acidic, basic and neutral fractions. Using urea clathration the acids, after methylation, and the neutral fraction were subdivided into normal and branched/cyclic fractions. All fractions were analyzed by high resolution mass spectrometry and GC/MS.

The clathrated acid ester fraction contains saturated normal esters ($C_nH_{2n}O_2$ for n = 12-31), with even carbon values of the acids predominating over odd values. Mono-unsaturated esters are present in low concentration as are α , ω -dicarboxylic acid esters.

The branched/cyclic acid-fraction contains saturated branched acid esters, aromatic esters, benzene dicarboxylic esters, and esters substituted with methyl groups in the α , β and γ positions. The basic fraction contains pyridines, phenylpyridines, carbazoles and acridines. Also present are oxygenated cycloalkanopyridines or quinolones, and hydroxyindoles or dihydroquinolones.

Normal components from the neutral fraction contain straight chain esters probably formed during the initial extraction. Normal alkanedioic acid esters from core barrel

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plasticizer contamination are also present. The branched/ cyclic fraction of the neutrals contains biphenyls (or acenaphthenes) and tetracyclic terpanes.

Most of the extract of the cellulose butyrate polymer used as core tube material consists of dibutyl esters of α , ω -alkanedioic acids. Only trace amounts of phthalates were detected, indicating the core tubes are not the major source of this contaminant. Further possible sources of contamination from bearing lubricant and pipe joint grease were considered. A suite of normal and iso-alkanes from C₁₁ to C₃₁ was identified in the bearing lubricant. The pipe joint grease contains acetone soluble neutral components, and semiquantitative emission spectrographic analysis showed that zinc is the principal metallic element present.

INTRODUCTION

Two core samples from the DSDP Leg 11 have been analyzed. A small sample of high carbonate sediment (0.3 per cent organic carbon) from Site 98 was analyzed first. This site is in the Northeast Providence Channel on the Bahama Banks (water depth 2769 meters). The sample is derived from approximately 130 meters below the seabed and is of mid-Cretaceous age. A large sample from Site 105, which was drilled near the northern end of the Hatteras Abyssal Plain in a water depth of 5251 meters, was analyzed next. The sample is derived from the thick section of black lower Cretaceous clay (extremely rich in carbonaceous material) situated below the hiatus where the sediment age changes from Oligocene-Miocene to lower Cretaceous (that is, 310 meters below the seabed). The total carbon content is 5.72 per cent, carbonate 17.7 per cent and organic carbon 3.60 per cent. The sample consists mainly of zeolitic clays, some foraminifera and significant amounts of carbonate ooze; but is very low in terrigenous plant detritus, despite the terrestrial source of the clays.

The continuing analyses of potential organic contamination sources are also updated. The bearing lubricant and pipe joint grease have been analyzed and further data on the plasticizers in the core tubes is also presented.

EXPERIMENTAL

High resolution mass spectrometric analyses of the acetone and heptane extracts were carried out on a GEC-AEI MS-902 mass spectrometer on-line to an XDS Sigma 7 computer (described by Burlingame, 1968 and 1970, and Burlingame *et al.*, 1970). The samples were introduced *via* a ceramic direct inlet probe into the ion source, operated at the following conditions: resolution 10,000 to 12,000; ionizing current 500 μ A; ionizing voltage 50 eV; and temperature 200 to 220°C. The scan rate was 16 seconds per decade with a clock rate of 24 kHz. Multiple scans were taken during each analysis and then sum averaged together during data

reduction. Selected high resolution mass spectral data are presented as heteroatomic plots (Burlingame and Smith, 1968) in various figures in the text.

Gas chromatographic analyses were carried out using a Perkin-Elmer Model 900 gas chromatograph fitted with a flame ionization detector and operating under the conditions stated in the respective figure legends. Analyses using gas chromatography-mass spectrometry were carried out on a modified Perkin-Elmer Model 270 GC/MS linked on-line to an XDS Sigma 2 computer (Smith *et al.*, 1971). The GC conditions used in the GC/MS analyses are cited in the respective figure legends, and the mass spectrometric and computer operating parameters are as reported (Smith *et al.*, 1971).

All solvents used, for example, acetone, benzene, methanol, toluene, and *n*-heptane were Matheson Coleman and Bell Pesticide quality and/or Mallinckrodt Nanograde quality. Benzene and methanol were redistilled prior to use.

Leg 11, Site 98 - 6-4

The sample (8.08 grams) was extracted (Soxhlet apparatus) with acetone (200 milliliters) for 2 days. The extract was concentrated to approximately 5 milliliters using a rotary evaporator and then filtered through an ultra-fine fritted disc. Removal of solvent from the filtrate gave a product which appeared inhomogeneous because of the presence of water. The water was removed by azeotropic distillation with 1:1 acetone/toluene (8×1 milliliter) yielding 1.1 milligrams of extract. Heptane was added to the extract and the heptane soluble portion carefully removed and stripped of solvent furnishing 0.1 milligram of material. Similar treatment of the extract residue with acetone afforded 0.5 milligram of acetone extract.

The acetone and heptane extracts were redissolved in 29.1 μ l acetone and 8.1 μ l heptane, respectively, and 2.0 μ l of each subjected to GC analysis.

Leg 11, Site 105 - 11-2 (10-138)

The methodology used for the separations and the yields of the various fractions are summarized in Figure 1 and are essentially the same as discussed in earlier reports (Simoneit and Burlingame, 1971 a-c).

Wet chemical separation methods previously described (Burlingame *et al.*, 1969) were used to divide the heptane/ether soluble material into acids (17 per cent, 18 milligrams), bases (less than 1 per cent, 1 milligram), and a neutral fraction (82 per cent, 89.1 milligrams). As indicated in Figure 1, the ester fraction and the neutral fraction were separated into normal and branched/cyclic fractions by urea clathration and the yields of each fraction are given in Figure 1.

Results: 11-98-6-4

The GC traces of the acetone and heptane soluble fractions from Core 11-98-6-4 are shown in Figure 2a and b, respectively. The major peak in Figure 2b has the retention time of palmitic acid. The high resolution mass spectrometric data for the acetone soluble fraction is shown in Figure 3.¹ The low amounts of hydrocarbons of the series C_nH_{2n+2} to C_nH_{2n-10} for n = 4.10 (not all homologs were detected) attest to the efficiency of the separation procedure. In the C/H O data, significant amounts of acetone condensation products are indicated, such as, mesityl oxide (Structure I) and a minor amount of phorone (Structure II).

¹In this report, all high resolution mass spectra are presented as heteroatomic plots (Burlingame and Smith, 1968) with the masses plotted in methylene units. On the abscissa, each principal division marker corresponds to the saturated alkyl fragment (even-electron ion), for example, CnH2n+1, with the number of carbon and hydrogen atoms given subsequently. Each principal division of the abscissa is further divided into seven units. The number of hydrogen atoms of an unsaturated or cyclic-fragment ion is obtained by subtracting the number of units (two hydrogen atoms) or half units from the 2n+1 hydrogen atoms of the respective saturated principal division, CnH2n+1. Fragments which have more than seven degrees of unsaturation are plotted as heteroatomic plots where each principal division marker on the abscissa corresponds to the fragment ion CnH2n-14. Each principal division is again further divided into seven units, and the number of hydrogen atoms of a fragment ion is derived as discussed above. The origin of the abscissas is the same m/e ratio for each plot; thus the nominal masses from plot to plot lie directly above one another, and a superposition of the plots yields a "low" resolution mass spectrum of the sample. (In some of the data such a plot is presented first.) The nominal masses are indicated in 50 mass unit intervals below the carbon/hydrogen ratio scale. All plots are normalized to a base peak (usually the base peak of the entire spectrum, unless otherwise specified) on the relative intensity scale. In order to make high mass, low intensity features of the spectrum observable, the whole spectrum or any region thereof can be multiplied by a scale factor. This factor is indicated by X00 at the point of scale expansion.

Phenols of the series $C_nH_{2n-6}O$ were detected in minor amounts for n = 6-9. The C/H O_2



I m/e 98, C₆H₁₀O II m/e 133, C₉H₁₄O

data consist of trace polar components less than C₉. A minor amount of phthalate esters is indicated by the peak of composition $C_8H_5O_3$ (Structure III), probably diethyl and dibutyl phthalate (peaks of compositions $C_{10}H_{11}O_4$ and



III $m/e 149, C_8H_5O_3$

 $C_{12}H_{15}O_4$ respectively). The base peak of the data has the composition C_2H_6N and suppresses the whole spectrum. It is probably derived from an amine of composition $C_8H_{19}N$. The fragment ion series $C_nH_{2n+2}N$ for n = 2-7 is probably also derived from this compound.

The heptane extracted residue from Core 11-98-6-4 was examined by high resolution mass spectrometry and the data are shown in Figure 4. The principal components of this fraction are saturated alkanes C_nH_{2n+2} for n = 15-50. Molecular ions are found for all values of n except 16, 17, 19, 25, 27, 36, 38, 41 and 44+; and, the fragment ions C_nH_{2n+1} range from n = 3-47. Also present are alkylnaphthalene M-1 fragments as exemplified by $C_{11}H_9$, that is, naphthylmethyl cation (or benzotropylium ion-Structure IV), and the series



IV m/e 141, C11Ho

 C_nH_{2n-13} ranges from n = 11-19. Other more aromatic fragment ions are also found. A series C_nH_{2n-15} occurs with values of n = 9 and 11-18. Carboxylic acids of the compositional series $C_nH_{2n}O_2$ are indicated present for n = 10 and 12-22. The principal homologs of this series are $C_{16}H_{32}O_2$ (palmitic acid) and $C_{18}H_{36}O_2$ (stearic acid) which is also corroborated by the GC data (see Figure 2b). The fragment ions corresponding to loss of an OH radical, that is, the series $C_nH_{2n-1}O$, are also present for values of n ranging to 37, with n = 16 and 18 standing out quite prominently.

A series of fragments, formula $C_nH_{2n-13}O_2$, occurs at n = 9-20. Four prominent peaks with formula $C_nH_{2n-25}O_2$ occur at n = 28, 29, 30 and 32. The CH/O₃ plot indicates a trace of phthalate esters (peak of composition CgH₅O₃-Structure III).

Results: 11-105-11-2 (10-138)

The GC traces of the acid fractions (as methyl esters) are shown in Figure 5 a-c. The high resolution mass spectral data and the GC/MS data of the normal acid ester fraction are shown in Figures 6 and 7, respectively. The GC/MS results, listed in Table 1, indicate saturated normal esters, CnH2nO2. On the basis of these data (GC peak heights), even carbon values of the acids predominate over odd values. The series ranges to n = 32 and $C_{17}H_{34}O_2$ (methyl palmitate) is most intense. A series of mono-unsaturated esters, $C_nH_{2n-2}O_2$ was detected with values of n = 4-16, 18,20 and 22, but was of low concentration. Minor amounts of dicarboxylic acid esters, CnH2n-2O4, are present. The nature of urea clathration suggests that these acids are a, ω substituted. The M-CH₃O fragments, $C_nH_{2n-3}O_3$, used in deducing the dicarboxylic esters range from n = 14-18. An oxoacid ester series, CnH2n-2O3, was determined to be present in minor amounts, with even numbered acids predominating over odd, in the ranges n = 5-11 and n = 13-17.

A small amount of saturated alkanes ranging from C_{6} - C_{17} is also present in the normal ester fraction. They probably occur in this fraction from a less than perfect extraction of the heptane/ether soluble fraction with aqueous KOH (Figure 1). Since they are derived from urea clathration they must have a normal or *iso*-alkane structure. A more ideal separation of acidic and non-acidic components should be possible by use of aqueous ethanolic KOH for extraction (Seifert and Howells, 1969). The ethanol will prevent emulsification which probably caused entrainment of the hydrocarbons in an oil in water emulsion system.

The branched/cyclic acid ester fraction was analyzed by GC/MS and high resolution mass spectrometry and the data are shown in Figures 8 and 9, respectively. The major components determined by GC/MS are listed in Table 2 and consist of a series of saturated branched acid esters. The m/e 74 sum plot (Figure 8b) indicates a series of methyl esters buried in the mixture. The high resolution data (Figure 9) confirm the range of the carboxylic acid esters to C₂₀. There are minor peaks attributable to sterols or steranes in the C₂₇ to C₂₉ skeletal range (compositions: C/HO, C/HO₂ and C/HO₃). There are indications of minor amounts of benzene dicarboxylic acid esters, $C_nH_{2n-10}O_4$, for n = 8-10, 12 and the respective M-CH₃O fragments, $C_nH_{2n-11}O_3$, for n = 8-17, 19-23 and 26. Also evident is the series $C_nH_{2n-12}O_4$ for n = 10-15 and 18. Trace amounts of the aromatic ester series, $C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$ are present for values of n = 7-19 and 9-21, respectively. It should also be noted that the peak of composition C14H₂₃ (Structure V) is significantly above background.



The low intensity of major steroid fragment ions such as $C_{16}H_{25}$ at m/e 217 for example indicates that the molecular ions in the C_{27} - C_{29} range may have an A-B ring system as indicated by Structure V and not the steroidal A-B configuration.

The GC traces of the neutral fractions are shown in Figure 10. The GC/MS data of the normal components are shown in Figure 11 and the high resolution mass spectral data for the same sample appear in Figure 12. The components isolated from the urea clathration of this neutral fraction (see Figure 1) did not, as expected, consist of straight chain and iso-alkane structures. Instead the components were found to be acid esters. It is suspected that these esters were formed, at least in part, from the free acids present in the original core. Methylation during the course of Soxhlet extraction with benzene and methanol may well have been catalyzed by slightly acidic core material. To ascertain whether this is the case, sequential aliquots will be withdrawn from the extract of a similar core and determination of ester contents carried out. The findings of the GC/MS run are summarized in Table 3, and indicate mainly the same suite of esters as were found in the normal ester fraction above. The same even-over-odd predominance is also found. In addition the plasticizer from the core tube barrel, which consists of dicarboxylic acid dibutyl esters (see contamination section), was extracted into this neutral fraction. Dibutyl azelate (scan 90 in the GC/MS data -Figure 11d) is the major constituent in this fraction.

The GC/MS data for the branched/cyclic components in the neutral fraction are shown in Figure 13 and the salient results are summarized as follows. The mixture is very complex and unresolved (see Figure 13a). Isoprenoid and cycloalkanes were not detected. The m/e 191 sum plot (Figure 13b) indicates the presence of possible tetracyclic triterpane structures and the scan 117 spectrum shows a molecular ion at m/e 410 with loss of a methyl radical to yield the peak at m/e 395. The peak at m/e 191 (Structure V) is significantly

Spectrum at scan number	Compound Name	Molecular Weight and	
	compound traine		
20	Methyl laurate	214	С13H26O2
34	Methyl tridecanoate	228	C ₁₄ H ₂₈ O ₂
52	Methyl myristate	242	C ₁₅ H ₃₀ O ₂
65	Methyl pentadecanoate	256	C ₁₆ H ₃₂ O ₂
74	Methyl hexadecenoate	268	$C_{17}H_{32}O_2$
76	Methyl palmitate	270	C ₁₇ H ₃₄ O ₂
85	Methyl margarate	284	C ₁₈ H ₃₆ O ₂
91	Methyl octadecenoate	296	C19H36O2
92	Methyl stearate	298	C19H38O2
100	Methyl nonadecanoate	312	C ₂₀ H ₄₀ O ₂
105	Methyl eicosenoate	324	C ₂₁ H ₄₀ O ₂
106	Methyl arachidate	326	$C_{21}H_{42}O_2$
113	Methyl heneicosanoate	340	C ₂₂ H ₄₄ O ₂
117	Methyl docosenoate	352	C ₂₃ H ₄₄ O ₂
119	Methyl behenate	354	C ₂₃ H ₄₆ O ₂
124	Methyl tricosanoate	368	C24H48O2
130	Methyl lignocerate	382	C ₂₅ H ₅₀ O ₂
135	Methyl pentacosanoate	396	C ₂₆ H ₅₂ O ₂
140	Methyl cerotate	410	C ₂₇ H ₅₄ O ₂
147	Methyl heptacosanoate	424	C ₂₈ H ₅₆ O ₂
155	Methyl octacosanoate	438	C29H58O2
166	Methyl nonacosanoate	452	C ₃₀ H ₆₀ O ₂
177	Methyl triacontanoate	466	C ₃₁ H ₆₂ O ₂

TABLE 1 Major Components of the Normal Acid Ester Fraction from Core 11-105-11-2 (10-138) as Determined by GC/MS

intense. The high resolution mass spectral data for this fraction are shown in Figure 14. The peak of composition $C_{14}H_{23}$ (Structure V) is again above the general background fragmentation. The hydrocarbon fragments range to C_{30} for the more saturated series and to C_{37} for the more aromatic series. Significantly intense peaks are present in the C_{20} to C_{30} range with one to four oxygen atoms. However, no structure suggestions can be made at this time.

The basic compounds isolated from the non-acid fraction of the exhaustive extract of Core 11-105-11-2 were subjected to GF (Figure 15) and high resolution

mass spectrometric analyses (Figure 16). The compound series found are listed in Table 4. The series $C_nH_{2n-5}N$ (pyridines) for n = 4.7, 9, 10; $C_nH_{2n-13}N$ (phenyl pyridines) for n = 10, 13, 15, 19; $C_nH_{2n-15}N$ (carbazoles) for n = 16-18; and, $C_nH_{2n-17}N$ (acridines) for n = 14-19 are the most abundant. The other series listed in Table 4 are found in minor amounts. The oxygenated series are of interest since their relative abundance is significant. The major series are $C_nH_{2n-7}NO$ (oxygenated cycloalkanopyridines or quinolones) for n = 8-10, 14 and 15, $C_nH_{2n-9}NO$ (hydroxyindoles or dihydroquinolones) for n = 10, 11, 13, 15-17, and $C_nH_{2n-11}NO$ (hydroxyquinolines) for

Spectrum at scan number (see Figure 7a) 157	Compound Name	Molecular Weight and Composition	
	Dimethyl phthalate $(m \text{ or } p)$	194	C10H10O4
174	Methyl 2-methyltridecanoate	242	C ₁₅ H ₃₀ O ₂
183	C13 branched ester	228	C14H28O2
189	Methyl 3-methyltetradecanoate	256	C ₁₆ H ₃₂ O ₂
204	Methyl 4-methylpentadecanoate	270	C17H34O2
211	C15 branched ester	256	C ₁₆ H ₃₂ O ₂
213	Unknown	250	C ₁₆ H ₂₆ O ₂
218	C17 branched ester	284	C18H36O2
225	C ₁₆ branched ester	270	C ₁₇ H ₃₄ O ₂
234	C ₁₉ branched ester	312	C ₂₀ H ₄₀ O ₂

TABLE 2 Major Components of the Branched/Cyclic Acid Ester Fraction from Core 11-105-11-2 (10-138) as Determined by GC/MS

n = 12, 14, 15. At lower mass a group of substituted morpholines are present, as for example C4H9NO (morpholine), C4H5NO (isoxazine), C5H5NO (hydroxypyridine), C5H7NO (methylisoxazine), and a group with six carbons. No species of compositions C/H N₂, C/H N₃, C/H N₄ and C/H N₂O were detected. The general distribution of the C/H N species is analogous to that reported for the Green River Formation Oil Shale (Simoneit *et al.*, 1970 and 1971) and for Core 5-35-6-3 (Simoneit and Burlingame 1971a). Most of the C/H NO species are analogous to those found in the shale mentioned above, but were not found in Core 5-35-6-3.

Analysis of Bearing Lubricants

Bearing lubricant (136.2 milligrams) dissolved in benzene (1 milliliter) was added to a magnetically stirred solution of urea (3.79 grams) in boiling methanol (15 milliliters) to which 2 drops each of *n*-heptane and *n*-decane had previously been added. After refluxing for one hour the mixture was allowed to stir overnight at room temperature. Solvent was then removed using a rotary evaporator and the solid clathrate transferred to a filter funnel and washed with ice-cold *n*-heptane (4 \times 6 milliliters).

Removal of *n*-heptane from the filtrate afforded 92.4 milligrams of non-adducted components. The urea clathrate was decomposed with water and extractions carried out with a mixture of 1:1 diethyl ether/n-heptane (3 X 20 milliliters). The organic extract was washed with water and evaporated using toluene for azeotropic removal of water. This furnished 26.3

milligrams of urea adducted organic material. Material recovery from the clathration procedure was 87 per cent.

Gas chromatographic traces of the original bearing lubricant, the urea clathrated components and the non-clathrated fraction are shown in Figure 17. It is evident from these chromatograms that, although clathration with urea reduced the complexity of the bearing lubricant mixture, the non-clathrated fraction still contains a large number of components most of which are unresolved and buried beneath the few prominent peaks (see Figure 17c).

Combined GC/MS analysis of the urea adducted fraction showed the principal components to be n-alkanes ranging from C11 to C31. The salient GC/MS data are given in Figures 18 and 19. The scan 44 spectrum fits the fragmentation pattern of n-tetradecane and the scan 173 spectrum fits for n-tricosane. An additional series of compounds besides the n-alkanes can be discerned in the GC trace of Figure 17b. The mass spectra indicate this series to be iso-alkanes, C_nH_{2n+2} , ranging from approximately n = 13 to 23. A few selected mass spectra are shown in Figure 19. The scan 56 spectrum fits the fragmentation pattern of iso-pentadecane (M⁺ at m/e 212 and m/e 169 due to M - 43) and the scan 72, 87 and 130 spectra fit iso-hexadecane (M⁺ at m/e 226), iso-heptadecane (M⁺ at m/e 240) and iso-eicosane (M⁺ at m/e 282), respectively. Interpretation of the mass spectra corresponding to the components eluting just prior to the iso-compounds was not possible due to their low intensities.

Spectrum at scan number (see Figure 11a)	Compound Name	Molecu	lar Weight and
(see rigure ria)	compound Name		
57	Dibutyl glutarate*	244	C ₁₃ H ₂₄ O ₄
63	Methyl tetradecanoate	242	C ₁₅ H ₃₀ O ₂
66	Dibutyl adipate*	258	C ₁₄ H ₂₆ O ₄
72	Methyl pentadecanoate	256	C ₁₆ H ₃₂ O ₂
74	Dibutyl pimelate*	272	C ₁₅ H ₂₈ O ₄
79	Methyl palmitate	270	C ₁₇ H ₃₄ O ₂
86	Methyl heptadecenoate	282	C ₁₈ H ₃₄ O ₂
87	Methyl margarate	284	C ₁₈ H ₃₆ O ₂
90	Dibutyl azelate*	300	C ₁₇ H ₃₂ O ₄
93	Methyl octadecenoate	296	C19H36O2
94	Methyl stearate	298	C19H38O2
100	Methyl nonadecanoate	312	C ₂₀ H ₄₀ O ₂
106	Methyl eicosenoate	324	C ₂₁ H ₄₀ O ₂
107	Methyl arachidate	326	C ₂₁ H ₄₂ O ₂
112	Methyl heneicosenoate	338	C22H42O2
113	Methyl heneicosanoate	340	C22H44O2
118	Methyl behenate	354	C ₂₃ H ₄₆ O ₂
123	Methyl tricosenoate	366	C24H46O2
124	Methyl tricosanoate	368	C24H48O2
128	Methyl tetracosenoate	380	C ₂₅ H ₄₈ O ₂
129	Methyl lignocerate	382	C ₂₅ H ₅₀ O ₂
134	Methyl pentacosenoate	394	C ₂₆ H ₅₀ O ₂
139	Methyl pentacosanoate	396	C ₂₆ H ₅₂ O ₂
140	Methyl hexacosenoate	408	C ₂₇ H ₅₂ O ₂
146	Methyl heptacosanoate	424	C ₂₈ H ₅₆ O ₂

TABLE 3 Major Constituents of the Normal Components in the Neutral Fraction from Core 11-105-11-2 (10-138) as Determined by GC/MS

*Contamination from the core tube.

The partial GC/MS data for the urea non-adducted fraction is shown in Figure 20. Unfortunately, as can be seen from the GC trace of this material (Figure 17c), a very high proportion of the components are buried and consequently interpretation of the mass spectra of the peaks that are evident is not possible. Further separation procedures will be necessary, such as chromatography on silica gel, prior to conducting GC/MS analyses for structure determination. The m/e

83 sum plot indicates the presence of a series of alkyl cyclohexanes and the m/e 191 sum plot indicates the possible presence of polycylic hydrocarbons.

Pipe Joint Grease

The grease was extracted with acetone and the GC trace of the extract is shown in Figure 21, indicating the presence of neutral organic compounds. The grease

TABLE 4 General Nitrogen Compound Distribution Found in the Base Extract of Core 11-105-11-2 (10-138)

Skeletal Examples	Series	n found
1) (N)	$C_nH_{2n-5}N$	4-7, 9, 10
	C _n H _{2n-7} N	6, 10
$3)$ N_{H} N_{N}	C _n H _{2n-9} N	8, 12
4) $\bigcirc \bigcirc_N$ $\bigcirc \bigcirc_N$	$C_n H_{2n-11} N$	10, 21
5)	C _n H _{2n-13} N	10, 13, 15, 19
	^C _n H _{2n-15} N	16, 17, 18
7) $\bigcirc \bigcirc \bigcirc$	^C _n H _{2n-17} N	14-19, 21, 23 (max 17)
	C _n H _{2n-19} N	13, 20, 21
	C _n H _{2n-7} NO	8, 9, 10, 14, 15
10) $\underset{HO}{\bigcirc}$ $\underset{HO}{\bigcirc}$ $\underset{HO}{\bigvee}$ $\underset{HO}{\lor}$ $\underset{HO}{\lor}$ \underset{HO}	C _n H _{2n-9} NO	10, 11, 13, 15-1 7
11) $\operatorname{OO}_{N}^{OH} \operatorname{OO}_{N}^{H}$	с _n H _{2n-11} NO	12, 14, 15

12) Various substituted morpholines

sample was also analyzed for metallic elements and silicon by emission spectrography. Prior to the analysis a sample was heated at 600 to 700°C in the electrode of the spectrograph where it underwent a 60 per cent weight loss. The results of the semi-quantitative emission spectrographic analysis conducted on the 40 wt % residue indicated the following elements were present (as oxides): zinc-principal constituent; lead-1.5 per cent; calcium-1.75 per cent; and, silica-0.1 per cent.

Other elements (also as oxides) present in less than 0.1 wt % included copper, cadmium, aluminum, iron, magnesium, barium and strontium. No molybdenum or lithium, which are quite frequently compounded in greases, were detected. This pipe joint grease will be subjected to further analysis to determine its composition in more detail.

Core Tube Contamination

The cellulose acetate butyrate polymer used as core tube material, which had been extracted with benzene and methanol (3:1), was further analyzed by GC/MS. The high resolution mass spectral data and GC trace were discussed in the previous report (Simoneit and Burlingame, 1971c). The bulk of the plasticizer in the polymer consists of dibutyl esters of dicarboxylic acids $(C_nH_{2n-2}O_4 \text{ ranging from } n = 5-15)$. The salient features of the GC/MS data are shown in Figure 22, and the major peaks identified are listed in Table 5. The characteristic fragmentation pattern of these esters is illustrated by the following example. Scan 142 fits the fragmentation pattern of dibutyl glutarate (Structure VI, molecular ion at m/e 244). All these esters exhibit a strong loss of butoxy radical yielding in this example the peak at m/e 171 (Structure VII), followed by loss of the elements of butene yielding in this example the base peak at m/e 115 (Structure VIII).



The m/e 149 sum plot indicates only trace amounts of phthalate esters, showing that the core tubes are not the major source of phthalate contamination found in many samples. Abalyn (methyl esters of rosin acids) was not detected in the core tube extract.

CONCLUSIONS

The high carbonate sample (11-98-6-4) exhibited an alkane distribution ranging to about C50, showing no carbon number predominance and as the major constituents carboxylic acids, especially palmitic and stearic acids. The yield of extractable organic material was low (12 ppm heptane soluble and 62 ppm acetone soluble) as was observed for other high carbonate cores from the Pacific Ocean (Simoneit and Burlingame, 1971 a-c).

The large sample (11-105-11-2, 10-138 centimeters) with the high organic carbon content yielded relatively low amounts of solvent soluble organic material (total heptane/ether \cdot soluble material-315 ppm). This indicates that the bulk of the organic carbon consists of

Peak at scan number (see Figure 22a)	Compound Name	Molecular Weight and Composition		Figure Reference
142	Dibutyl glutarate	244	C ₁₃ H ₂₄ O ₄	22c
147	Dibutyl adipate	258	C14H26O4	22d
152	Dibutyl pimelate	272	C ₁₅ H ₂₈ O ₄	22e
157	Dibutyl suberate	286	C ₁₆ H ₃₀ O ₄	22f
160	Dibutyl azelate	300	C17H32O4	
163	Dibutyl sebacate	314	C18H34O4	-
166	Dibutyl hendecanedioate	328	C19H36O4	_
171	Dibutyl dodecanedioate	342	C20H38O4	

TABLE 5 Major Components of the Benzene and Methanol Extract of the Core Tubes (Determined by GC/MS)

adsorbed and entrapped organic material and probably a significant amount of kerogen. The nature of the carbon in the extracted residue of this sample is under further investigation. The acid fraction consisted of 52 ppm of the total extract, and the normal to branched/ cyclic ratio was essentially 1:1. The normal acids exhibit an even/odd carbon number predominance and range to C32 with palmitic and lignoceric acids as maxima. Approximately 10 per cent of the normal esters consist of unsaturated (mainly one double bond) material of the series $C_nH_{2n-2}O_2$ for n = 13-26. The branched/cyclic acid ester fraction consists mainly of α , β and γ -methylalkanoic acid esters of the series $C_nH_{2n}O_2$ for n = 14-19. Such acids with a methyl branch close to the carboxyl group are of interest, since geochemically iso- and anteiso-acids are more prevalent. Isoprenoidal acid esters, especially phytanic and pristanic acid esters were not detected in this mixture. In Recent Sediments from the Black Sea (Simoneit, 1971) there were indications of the presence of traces of isoprenoidal acids and significant amounts of isoprenoid alkanes.

The neutral fraction (254 ppm) was clathrated with urea and yielded 74 ppm normal components and 114 ppm branched/cyclic material. Analysis of these fractions showed them to be esters, contaminants and complex oxygenated polycyclic material, but essentially non-hydrocarbons. This absence of normal and iso-alkanes in this sample with such a high organic carbon content is quite intriguing. For comparison, the Core 5-35-6-3 sample (Simoneit and Burlingame, 1971 a and b), which yielded similar amounts of extractable material and also contained significant amounts of terrigenous organic matter, exhibited a large alkane fraction ranging from C17 to C32 in both the exhaustive and the demineralization extracts. We feel that the methyl esters in this neutral fraction were formed for the most part during the extraction with benzene/methanol, possibly catalyzed by acidic components of the clay. The distribution of these esters essentially matches the distribution of the esters from the acid fraction, strongly indicating a common source. The absence of alkanes in the extract may indicate that either a strong adsorption process is holding them mainly to the clay matrices or they are just absent. The acids are probably also "bound" to the mineral matrices by adsorption and as salts and are solubilized by the slow esterification during Soxhlet extraction with benzene and methanol. A demineralization of this sample with acid (HCl and HF) should liberate any adsorbed and entrapped organic matter other than kerogen. This analytical step is planned next for this sample. The series of dibutyl alkanedioates $(C_nH_{2n-2}O_4, \text{ for } n=13-17)$ derived from the core tube plasticizer were found in this neutral fraction. As butyl esters, these compounds were easily recognized as contaminants, but if hydrolysis occurs then the presence of such a series of dicarboxylic acids could be

very misleading. This is another example of potential problems caused by organic contamination.

The basic compounds isolated from this sample exhibited a general distribution analogous to that reported (Simoneit *et al.*, 1970 and 1971, and Simoneit and Burlingame, 1971a).

Further analyses of potential organic contamination sources are continuing. The shipboard bearing lubricant was examined and found to consist of *n*-alkanes ranging from C₁₁ to C₃₁, *iso*-alkanes (C₁₃ to C₂₃) and a significant unresolvable branched/cyclic fraction. The drilling-pipe joint grease contains solvent soluble neutral material, and semiquantitative emission spectrography showed zinc as the major metallic element present. The extract of the cellulose butyrate polymer used as core tube material was shown to consist of dibutyl esters of α , ω -alkanedioic acids.

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Figure 1. Separation Scheme of Sample 11-105-11-2 (10-138 cm).



Figure 2a. Gas chromatogram of the acetone soluble extract from Core 11-98-6-4. (Conditions: 10 ft \times 1/8 in. stainless steel column, packed with 3% OV-1 on 100-120 mesh gaschrom Q, programmed from 100-275° at 8°/min and using helium carrier gas at 90 ml/min.)



Figure 2b. Gas chromatogram of the heptane soluble extract from Core 11-98-6-4. (Conditions as cited in Figure 2a.) The arrows indicate the positions at which n-hexadecane and n-tetracosane elute under the same chromatographic conditions (by coinjection), and the lower trace is the background.



Figure 3. Partial high resolution mass spectral data for the acetone soluble extract from Core 11-98-6-4.







Figure 5. Gas chromatograms of the acid ester fraction isolated from Core 11-105-11-2 (10-138 cm). (Conditions as cited in Figure 2a.) a) Total acid methyl esters. b) Normal acid methyl esters. c) Branched/cyclic acid methyl esters.



Figure 6. Partial high resolution mass spectral data for the normal acid esters from Core 11-105-11-2 (10-138 cm). (The first plot is a low resolution spectrum as described in Figure 4.)



Figure 7. GC/MS data for the normal acid esters from Core 11-105-11-2 (10-138 cm). (GC column conditions as cited in Figure 2a.) a) Total ionization sum plot. b) m/e 74 sum plot. c) m/e 87 sum plot. d) Mass spectrum scan 91. e) Mass spectrum scan 92.



Figure 8. GC/MS data for the branched/cyclic esters from Core 11-105-11-2 (10-138 cm). (GC column conditions as cited in Figure 2a.) a) Total ionization sum plot. b) m/e 74 sum plot. c) Mass spectrum scan 174. d) Mass spectrum scan 189. e) Mass spectrum scan 204.



Figure 9. Partial high resolution mass spectral data for the branched/cyclic esters from Core 11-105-11-2 (10-138 cm). (The first plot is a low resolution mass spectrum as described in Figure 4.)



Figure 10. GC traces of the neutral fraction isolated from Core 11-105-11-2 (10-138 cm). (Conditions as cited in Figure 2a.) a) Total neutral fraction. b) Normal neutral fraction. c) Branched/cyclic neutral fraction.



Figure 11. GC/MS data for the normal components of the neutral fraction from Core 11-105-11-2 (10-138 cm). (GC conditions as cited in Figure 2a.) a) Total ionization sum plot. b) m/e 74 sum plot. c) Mass spectrum scan 57. d) Mass spectrum scan 90.

RLKANES N 1 X1 105-11-2/10-138









010 020 020 040 060 060 070 020 030 100 100 120 020 050 060 070 170 180 070 050 050 050 050 050 050

SUMM M/E=131 ALMANES+8+XI MAX TI = EE131



Figure 13. GC/MS data for the branched/cyclic components in the neutral fraction from Core 11-105-11-2 (10-138 cm). (GC conditions as cited in Figure 2a.) a) Total ionization sum plot. b) m/e 191 sum plot. c) Mass spectrum scan 5.d) Mass spectrum scan 45.e) Mass spectrum scan 117.



Figure 14. Partial high resolution mass spectral data for the branched/cyclic components in the neutral fraction from Core 11-105-11-2 (10-138 cm). (The first plot is a low resolution mass spectrum as described in Figure 4.)



Figure 15. Gas chromatogram of the base fraction from Core 11-105-11-2 (10-138 cm). (Conditions as cited in Figure 2a.)



Figure 16. Partial high resolution mass spectral data for the base fraction from Core 11-105-11-2 (10-138 cm).

CORE X1 105-11-2/10



Figure 17. Gas chromatogram of the bearing lubricant. (Conditions as cited in Figure 2a.) a) Total sample. b) Normal fraction (urea clathrated). c) Branched/cyclic fraction (non-urea clathrated).





Figure 18. GC/MS data for the normal fraction of the bearing lubricant (GC conditions as cited in Figure 2a.) a) Total ionization sum plot. b) Mass spectrum scan 44. c) Mass spectrum scan 173.





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Figure 20. GC/MS data for the branched/cyclic fraction of the bearing lubricant. (GC conditions as cited in Figure 2a.) a) Total ionization sum plot. b) m/e 83 sum plot. c) m/e 191 sum plot. d) Mass spectrum scan 54. e) Mass spectrum scan 70.



Figure 21. Gas chromatogram of the acetone extract of pipe joint grease. (Conditions as cited in Figure 2a.)



Figure 22. GC/MS data for the benzene/methanol extract of the core tube material. (GC conditions as cited in Figure 2a.) a) Total ionization sum plot. b) m/e 149 sum plot. c) Mass spectrum scan 142. d) Mass spectrum scan 147. e) Mass spectrum scan 152. f) Mass spectrum scan 157.