# 36. PRELIMINARY ORGANIC GEOCHEMICAL ANALYSES OF THE SITE 217 CORE SAMPLES IN THE BENGAL BASIN, DSDP LEG 22<sup>1</sup>

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#### ABSTRACT

Four core samples from Site 217 were extracted, and the solvent soluble organic matter was characterized by GC (gas chromatography) and GC/MS (gas chromatography/mass spectrometry). The samples range in age from the Quaternary to the Upper Cretaceous and contain only traces of organic carbon. The normal alkanes are the major homologous series present in all the samples. They do not exhibit a carbon number preference. Unresolved cyclic and aromatic compounds comprise the bulk of the extracts. The Quaternary sample may be contaminated by drill pipe joint grease. The other samples appear to be matured sediments.

## INTRODUCTION

The samples discussed herein were taken from Site 217, situated on the northern end of Ninetyeast Ridge (8°55.6'N, 90°32.3'E) in 3020 meters of water. The stratigraphy at this site is comprised predominantly of calcareous ooze and chalk as detailed by von der Borch, Sclater, et al. (1971). All the samples are low in organic carbon content (average about 0.1%). The details of each sample are given in Table 1.

#### EXPERIMENTAL

Analyses using GC/MS were carried out on a modified Varian MAT model 311 GC/MS linked on-line to an XDS Sigma 2 computer (Smith et al., 1971). The column conditions used in the GC and GC/MS analyses are cited in the respective figure legends, and the mass spectrometric and computer operating parameters are analogous to those reported by Smith et al. (1971). Certain mass spectra from the various GC/MS analyses were identified by using a compound classifier (Smith, 1972; Chang et al., in preparation).

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.

All solvents used, e.g., toluene, benzene, methanol, and *n*-heptane were Mallinckrodt nanograde quality. The toluene, benzene, and methanol were redistilled in an all-glass apparatus prior to use.

The samples were dried under vacuum (60°C and 25 cm Hg pressure) and then extracted in a sealed ball mill jar with benzene or toluene and methanol solvent mixture (3:1) according to the method of Rittenberg et al. (1963). After

filtration through a fine-glass frit, the extracts were concentrated on a rotary evaporator (bath at 30-40°C) and then repartitioned into a heptane-diethyl-ether-soluble fraction and a toluené or benzene-methanol-soluble fraction. The heptane-soluble fraction of Sample 217-1-3, 0-20 cm, was subjected for further separation using silica gel chromatography. A 15 mm X 15 cm glass column was packed with 10-g conditioned SiO<sub>2</sub> (washed with methanol, dried at 100°C overnight, and conditioned with heptane) and the sample eluted into 13 fractions. Each cut was analyzed by GC and similar fractions were combined.

#### RESULTS

The extraction yields for the Site 217 preliminary analysis are given in Table 1. The gas chromatographic traces for the total extract fractions are shown in Figure 1. Each extract is a complex unresolved mixture. The total fractions were then partitioned between heptane and benzene and methanol (3:1). Most of each fraction was soluble in heptane (cf. Table 1) which is unlike previous results from other DSDP samples (Simoneit and Burlingame, 1972; in press a). The GC traces of these fractions are shown in Figures 2 through 5. The total fractions were also subjected to GC/MS analysis, and the salient features of those data are shown in Figures 6, 7, and 8. The GC/MS results for the total extracts are summarized in Table 2.

The predominant components in all four samples are normal alkanes. The series  $C_nH_{2n+2}$  ranges from n = 13 to 29, with a maximum at n = 17 and essentially no carbon number preference for Sample 217-1-3, 0-20 cm. The *n*-alkanes amount to 6 ppm of the dry weight for this sample. It should be noted that total ion current suppression occurs in these capillary GC/MS analyses when a large unresolved hump is injected. For example, in the data for Sample 217-1-3 (cf. Figure 6a) the scans 120-170 are detuned, resulting in the minimum observed. The normal paraffins,  $C_nH_{2n+2}$ , in Sample 217-6-5, 10-30 cm, are also equivalent to about 6 ppm and range from n = 14to 34, with a maximum at n = 24 and essentially no carbon

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Sample	Descrip	otions	and	Extract	Yields,	Site	217

Sample <sup>a</sup>	Depth Below Sea Floor (m)	Age	Description	Organic Carbon <sup>b</sup> (%)	Total Extract (µg/g)	Heptane Extract (µg/g)	Benzene/Methanol Extract (µg/g)	H <sub>2</sub> O (%)
217-1-3,	3.1	Quaternary	Pale gray green	0.3	193	180	13	51
0-20 cm			clay-rich nannofossil ooze					
217-6-5, 10-30 cm	188.6	Upper Oligocene	Yellowish gray nannofossil ooze	0.1	26	16	10	37
217-14-4, 20-40 cm	397.3	Paleocene	Very pale orange nannofossil chalk	0.0	14	12	2	26
217-30-3, 0-20 cm	547.1	Upper Cretaceous	Greenish gray and light gray biomicrite and chert	0.1	42	24	18	11

<sup>a</sup>Location 8°55.6'N, 90°32.3'E, water depth 3020 m.

<sup>b</sup>Data provided by G. Bode, DSDP staff.

number preference. Sample 217-14-4, 20-40 cm, has a normal alkane distribution rnaging from n = 17 to 33 for  $C_nH_{2n+2}$ , with a maximum at n = 22 and no carbon number preference. The alkanes account for approximately 4 ppm of the dry sample. The series  $C_nH_{2n+2}$  ranges from n = 17 to 35, with a maximum at n = 22 and again no carbon number preference in Sample 217-30-3, 0-20 cm. The *n*-alkanes amount to approximately 8 ppm of the dry weight of this sample.

Possible contaminants from core tube material, mainly the compound dioctyl 2,3-dimethylsuccinate (Simoneit et al., 1973; Simoneit and Burlingame, in press (b), were found in all of the samples. Phthalate esters were detected in two samples (cf. Figures 6d and f). The Cretaceous sample (217-30-3) had a suite of unknown compounds of short GC retention times (cf. Figures 7d and 8a,b) and two peaks probably due to dipentylbenzene (Structure I). The scan 112 spectrum (Figure 7c) fits the fragmentation pattern of probably the ortho isomer of Structure I. The compound classifier matched the spectrum to an alkylbenzene. The scan 88 spectrum (Figure 8b) is a mixture of a dipentylbenzene and an unknown of molecular weight 220.

The recombined extract fractions from Sample 217-1-3, 0-20 cm, were subjected to liquid chromatography on silica gel. The fraction yields and descriptions are listed in Table 3. Representative GC traces for this separation are found in Figure 9. Fraction 1 (cf. Figure 9a) closely resembles the initial heptane extract. Fractions 2 through 4 consist of a highly unresolved mixture of cyclic and aromatic hydrocarbons (cf. Figure 9b). Fractions 5 through 11 have the same unresolved GC traces as is the case for fractions 2 through 4. Fractions 12 and 13 consist of the more polar compounds. A GC/MS analysis of this cut was carried out. The major peaks are phthalate esters and dioctyl 2,3-dimethylsuccinate.

## DISCUSSION AND CONCLUSION

The distribution histograms for the *n*-alkanes in these samples are shown in Figure 10. No carbon number preference is evident. The Quaternary sample has a maximum at  $C_{17}$ , the Oligocene sample at  $C_{24}$ , the Paleocene at  $C_{22}$ , and the Cretaceous is bimodal with maxima at  $C_{22}$ and  $C_{27}$ . These alkane distributions indicate matured sediments (Bray and Evans, 1961). This distribution for the Quaternary sediment seems peculiar, especially since the GC trace closely resembles that for drill pipe joint grease (Simoneit et al., 1972). In view of the low extract yields, contamination by drilling oils must be considered. Samples 217-14-4, 20-40 cm, and 217-30-3, 0-20 cm, exhibit a predominance of the  $C_{22}$  *n*-alkane.Schenck(1969) observed this predominance in a large number of terrestrial sediments ranging in age from Miocene to Permian. Such a predominance has not been observed in crude oils (Schenck, 1969).

The contaminants such as phthalate esters and dioctyl 2,3-dimethylsuccinate were minor in all samples, indicating that the bulk of the solvent-soluble organic matter is indigenous to the sediments. The anomaly in the case of the Quaternary sample may be due to drilling lubricants or possibly petroliferous sediments of terrigenous origin eroded and brought in by the Ganges River system.

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Figure 1. Gas chromatograms of the total extract fractions from core samples: (a) 217-1-3, 0-20 cm; (b) 217-6-5, 10-30 cm; (c) 217-14-4, 20-40 cm; (d) 217-30-3, 0-20 cm. (GC conditions: 10 ft × 1/8 in. stainless steel column, packed with 3% OV-1 on 100-120 mesh Gaschrom Q, programmed from 100-270°C at 6°/min, and using He carrier gas at 40 ml/min).

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Figure 2. GC traces of two solvent extract fractions from Sample 217-1-3, 0-20 cm: (a) heptane-soluble material; (b) benzene and methanol-soluble material (GC conditions as cited in Figure 1).

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Figure 3. GC traces of two solvent extract fractions from Sample 217-6-5, 10-30 cm: (a) heptane-soluble material; (b) benzene and methanol-soluble material. (GC conditions as cited in Figure 1).



Figure 4. GC traces of two solvent extract fractions from Sample 217-14-4, 20-40 cm: (a) heptane-soluble material; (b) benzene and methanol-soluble material. (GC conditions as cited in Figure 1).



Figure 5. GC traces of two solvent extract fractions from Sample 217-30-3, 0-20 cm: (a) heptane-soluble material; (b) benzene and methanol-soluble material. (GC conditions as cited in Figure 1).



Figure 6. (a) Sample 217A-17-1, 83 cm. Euhedral dolomite rhombs of Stage 3 (Figure 2) showing dolomite zone. Matrix , possibly cristobalite. Innermost calcite zone appears to be corroding dolomite core. Calcite zone retouched in black. (b) Sample 217A-17-1, 65 cm. Euhedral dolomite rhombs of Stage 3 (Figure 2) showing corroded dolomite nuclei, followed by calcite-dolomite-calcite-dolomite zones. Slide stained, calcite zones retouched in black. (c) Sample 217A-17-1, 65 cm. Similar to (b).



Figure 7. Selected GC/MS data for the total extract of Sample 217-30-3, 0-20 cm: (a) total ionization sum plot; (b) m/e 41 and 57 sum plot; (c) mass spectrum scan 112 (dipentylbenzene, MW 218); (d) mass spectrum scan 129 (unknown, MW 234). (GC conditions as cited in Figure 6).



Figure 8. Selected GC/MS data for the total extract of Sample 217-30-3, 0-20 cm): (a) mass spectrum scan 69 (unknown, MW 165); (b) mass spectrum scan 88 (dipentylbenzene, MW 218; unknown, MW 220); (c) mass spectrum scan 174 (n-heptacosane, MW 380); (d) mass spectrum scan 180 (n-octacosane, MW 394); (e) mass spectrum scan 188 (n-nonacosane, MW 408).

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			217-1-3, 0-20 cm	217-6-5, 10-30 cm	217-14-4, 20-40 cm	217-30-3, 0-20 cm
Compound	Compositio Molecular W	n and /eight	Spectrum Scan No. (cf. Fig. 6a)	Spectrum Scan No. (cf. Fig. 6c)	Spectrum Scan No. (cf. Fig. 6e)	Spectrum Scan No. (cf. Fig. 7a)
Tridecane	C13H28	184	52	n.d.	n.d.	n.d.
Tetradecane	C14H30	198	70	95	n.d.	n.d.
Pentadecane	C15H32	212	86	101	n.d.	n.d.
Diethyl phthalate <sup>a</sup>	C12H14O4	222	n.d. <sup>b</sup>	104	105	n.d.
n-Hexadecane	C16H34	226	97	109	n.d.	108
Dipentylbenzene	C16H26	218	n.d.	n.d.	n.d.	112
n-Heptadecane	C17H36	240	104	116	116	117
n-Octadecane	C18H38	254	112	123	123	124
n-Nonadecane	C19H40	268	119	130	130	130
Dibutyl phthalate <sup>a</sup>	C16H22O4	278	n.d.	132,138	132,138	n.d.
iso-Eicosane	C <sub>20</sub> H <sub>42</sub>	282	n.d.	n.d.	135	n.d.
n-Eicosane	C20H42	282	126	136	137	136
iso-Heneicosane	C21H44	296	n.d.	140	n.d.	n.d.
n-Heneicosane	C21H44	296	134	142	142	142
n-Docosane	C22H46	310	141	148	147	148
n-Tricosane	C23H48	324	148	153	153	153
iso-Tetracosane	C24H50	338	n.d.	158	n.d.	n.d.
Dioctyl 2,3-di- methylsuccinate <sup>C</sup>	C <sub>24</sub> H <sub>42</sub> O <sub>4</sub>	370	153	159	157	156
n-Tetracosane	C24H50	338	155	160	159	159
n-Pentacosane	C25H52	352	162	164	165	164
Dioctyl phthalate <sup>a</sup>	C24H38O4	390	n.d.	169	169	n.d.
n-Hexacosane	C26H54	366	170	168	170	169
n-Heptacosane	C27H56	380	178	173	175	174
n-Octacosane	C28H58	394	187	180	181	179
n-Nonacosane	C29H60	408	199	187	189	188
n-Triacontane	C30H62	422	n.d.	197	198	197
n-Hentriacontane	C31H64	436	n.d.	208	210	209
n-Dotriacontane	C32H66	450	n.d.	222	225	223
n-Tritriacontane	C33H68	464	n.d.	240	n.d.	238
n-Tetratriacontane	C34H70	478	n.d.	254	n.d.	255

TABLE 2 Major Components of the Total Benzene-Methanol-Soluble Extracts from the Core Samples of Site 217, Determined by GC/MS

<sup>a</sup>Probably plasticizer and bagging contamination. <sup>b</sup>n.d. = not detected. <sup>c</sup>Probably core tube contamination.



Figure 9. Representative GC traces of various fractions separated by silica gel chromatography of the extract from Sample 217-1-3, 0-20 cm: (a) fraction 1; (b) combined fractions 2, 3, and 4; (c) combined fractions 12 and 13. (GC conditions as cited in Figure 1).

TABLE 3 Column Chromatographic Separation of the Total Solvent-Soluble Fractions from Sample 217-1-3, 0-20 cm

Fraction	Weight (mg)	Eluent	Description
1	54	15 ml heptane	Yellow liquid
2,3,4	11	60 ml heptane	Yellow oil
5,6,7	1.2	90 ml heptane	Light green oily solid
8,9	1.3	60 ml heptane/5% benzene	Yellow residue
10,11	4.7	60 ml heptane/20% benzene	Greenish solid
12,13	16.5	60 ml benzene to benzene/ 50% methanol	Dark green residue



Figure 10. Normal alkane distribution histograms for the core samples from Site 217: (a) 217-1-3, 0-20 cm;
(b) 217-6-5, 10-30 cm;
(c) 217-14-4, 20-40 cm;
(d) 217-30-3, 0-20 cm. (Concentrations are approximate as determined by GC).