

## 16. SEARCH FOR TERRIGENOUS LIPIDS IN CARBONATE-RICH SAMPLES FROM SITE 39-354<sup>1</sup>

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### ABSTRACT

The lipids extracted from carbonate-rich samples from the Ceará Rise (Site 354) were examined for terrigenous components, which could be derived by potamic influx from the Amazon. The total lipid yields were low (~ 1 ppm) and consisted mainly of marine autochthonous components. Minor amounts of lipids attributable to a terrigenous origin were also present. These consisted of *n*-alkanes in the range *n*-C<sub>25</sub> to *n*-C<sub>35</sub> with an odd-to-even predominance (*n*-C<sub>31</sub> maximum), *n*-fatty acids in the range *n*-C<sub>22</sub> to *n*-C<sub>32</sub> with an even-to-odd predominance, and the diterpenoid dehydroabietic acid. Thus, a minor potamic influx of terrigenous lipids has probably occurred to these sediments at this site.

### INTRODUCTION

Samples from various DSDP drill sites have been examined for their content of terrigenous lipids (e.g., Simoneit, 1975; Aizenshtat et al., 1973). Such analyses permitted the assessment of the sources of the lipid matter, i.e., autochthonous marine versus allochthonous terrigenous (e.g., Simoneit, 1975; Aizenshtat et al., 1973) and some inferences about the paleoenvironmental conditions of sedimentation could also be proposed (e.g., Didyk et al., in press; Aizenshtat et al., 1973). Thus, it was of interest to determine if the potamic outflow from the Amazon River system could be detected in the core samples from Site 354. The only samples taken for organic geochemical analyses were carbonate sediments, usually extremely poor in organic lipids.

Site 39-354 is located on the Ceará Rise (5°54'N, 44°11.8'W; water depth 4052 m) and the sediments recovered all consist of nanno ooze or chalk (Perch-Nielsen, Supko et al., 1975). The organic carbon content does not frequently exceed the average of 0.1% (Bode, 1975).

### EXPERIMENTAL

The core samples were extracted wet with Dole's mixture (isopropanol and heptane, 4:1) and then with toluene and methanol (4:1). The extracts for each sample were combined, then concentrated on a rotary evaporator and subjected to gas chromatographic analysis (GC). The extracts were then treated with diazomethane in ether and subjected to silica gel thin-layer chromatography (TLC) using methylene chloride as eluent. The bands corresponding to hydrocarbons

and esters were scraped off the TLC plate and eluted with ether or ethyl acetate. These fractions were subjected to GC and GC/MS analyses.

The GC analyses were carried out on a Hewlett-Packard Model 5830 gas chromatograph using a 16 m × 0.75 mm stainless steel SCOT column coated with OV-101, programmed from 110-280°C at 4°C per minute using He carrier gas at a flow rate of 3 ml/min.

The GC/MS analyses were carried out on a DuPont Model 21-492-1 mass spectrometer interfaced with a Varian Aerograph Model 204 gas chromatograph equipped with a 10 m × 0.75 mm glass capillary column packed with Gas chrom Q (80-100 mesh) coated with 1% OV-1.

The mass spectrometric data were acquired and processed using a DuPont Model 21-094 data system.

### RESULTS AND DISCUSSION

The sample descriptions, carbon analyses and lipid yields are found in Table 1. The yields of lipid components were low, as is typical for sediments with high carbonate contents. The *n*-fatty acids were present in greater abundance than *n*-alkanes. The distribution diagrams for the *n*-alkanes and *n*-fatty acids are shown in Figure 1.

The *n*-alkanes of both samples maximize at *n*-C<sub>17</sub> and at *n*-C<sub>31</sub>, this second maximum is, however, not as distinct in the case of Sample 39-354-10-0. The alkanes in the range *n*-C<sub>13</sub> to *n*-C<sub>21</sub> show no carbon number predominance, and coupled with the maximum at *n*-C<sub>17</sub> are typical of autochthonous marine lipids (Simoneit, 1975). The alkanes in the range *n*-C<sub>22</sub> to *n*-C<sub>35</sub> exhibit a strong carbon number predominance, and coupled with the maximum at *n*-C<sub>31</sub> are typical of terrigenous plant waxes (Simoneit 1975; in press). The abundance of *n*-C<sub>31</sub> > *n*-C<sub>29</sub> and *n*-C<sub>27</sub> is similar to peaty-swamp vegetation (i.e., less forest plants—Cranwell, 1973; Gaskell,

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TABLE 1  
Sample Descriptions, Carbon Analyses, and Extract Yields for the Core Sections Examined

Samples	Depth Below Seabed (m)	Lithology	Geologic Age	Total Carbon (%) <sup>a</sup>	Organic Carbon (%) <sup>a</sup>	Carbonate (%) <sup>a</sup>	Lipid Yield	
							<i>n</i> -alkanes (μg/g)	<i>n</i> -fatty Acids (μg/g)
39-354-10-0, 0-10 cm	452.6	Diatom, nanno chalk	Lower Oligocene	9.5	0.1	79	0.05	0.14
39-354-12-0, 0-10 cm	605.5	Foram, nanno chalk	Eocene	7.7	0.1	63	0.07	0.16

<sup>a</sup>Data supplied by G. Bode, Deep Sea Drilling Project, Scripps Institution of Oceanography, University of California, La Jolla.

1974). The ratios of pristane to phytane are 0.8 for Sample 39-354-10-0 and 2.9 for Sample 39-354-12-0. A ratio of < 1 may indicate anoxic paleoenvironmental conditions in the sediment (Didyk et al., in press; Simoneit, 1975), whereas a ratio > 1 indicates oxic conditions during sedimentation.

The *n*-fatty acids of both samples exhibit maxima at *n*-C<sub>16</sub> and *n*-C<sub>26</sub>, with a strong even-to-odd carbon number predominance. The large amounts of *n*-C<sub>16</sub> and *n*-C<sub>18</sub> acids are typical of a marine origin (Boon et al., 1975; Simoneit, 1975). The maximum at *n*-C<sub>26</sub> acid is probably due to terrigenous higher plants (Hitchcock and Nicholls, 1971; Simoneit, 1975). Dehydroabiatic acid (Structure 1) was found in minor amounts in both samples and was the only polycyclic diterpenoid detected. Dehydroabiatic acid was always the major component in other sediments where diterpenoids have been detected (Simoneit, in press). Such diterpenoids are unambiguous terrigenous marker compounds (Simoneit, 1975; in press). Triterpenoids were not detected.

It is not certain whether these terrigenous lipids represent early Amazon drainage, since other

In view of the low lipid yields, a blank was also analyzed and was found to contain butyl and octyl phthalates. Plasticizers from the core tubes, consisting mainly of dioctyl-2,3-dimethylsuccinate and other dibutyl esters (Simoneit, 1975), were also found in these samples.

## CONCLUSION

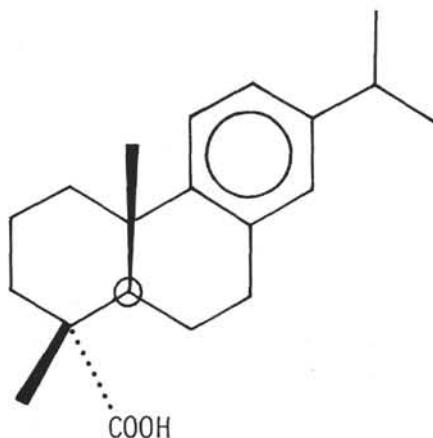
The lipids that were extracted from the carbonate sediments of Site 354 consisted mainly of marine autochthonous components. Minor amounts of lipids attributable to a terrigenous origin were also present in both samples. These consisted of *n*-alkanes ranging from *n*-C<sub>25</sub> to *n*-C<sub>35</sub> with an odd-to-even predominance and *n*-C<sub>31</sub> maximum, *n*-fatty acids ranging from *n*-C<sub>22</sub> to *n*-C<sub>32</sub> with an even-to-odd predominance, and *n*-C<sub>26</sub> maximum and dehydroabiatic acid. No triterpenoids were detected. Thus, a minor potamic influx of terrigenous lipids from the Amazon system has probably occurred during sediment accumulation at this site in the Oligocene and Eocene.

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I dehydroabiatic acid, C<sub>20</sub>H<sub>28</sub>O<sub>2</sub>

parameters indicate that such drainage did not start until the Miocene (Supko, private communication, 1976). Lipid analyses of samples above the mid-Miocene hiatus should further clarify this point.

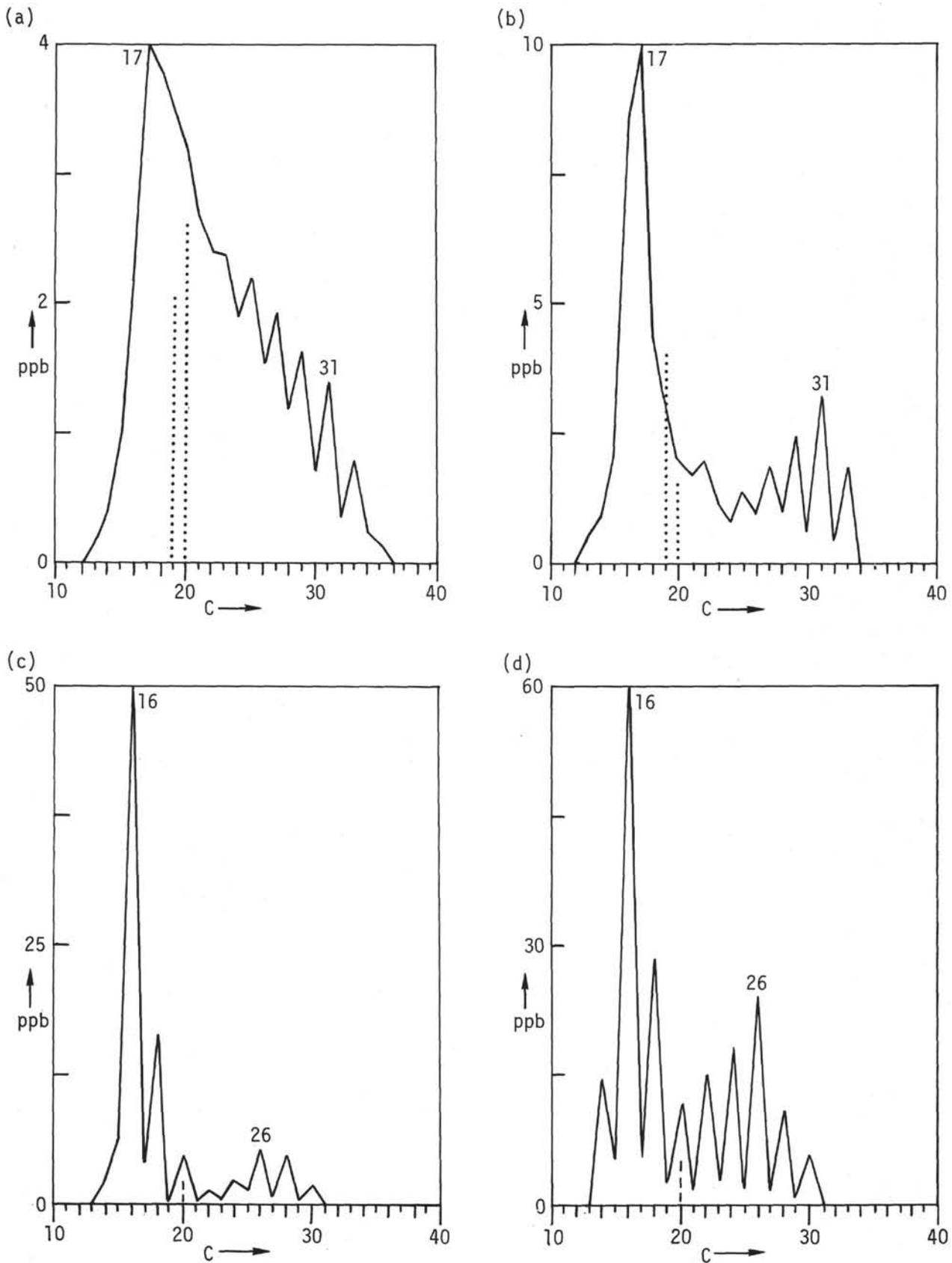


Figure 1. Distribution diagrams for the *n*-alkanes and *n*-fatty acids (. . . isoprenoid hydrocarbons—pristane and phytane, - - - dehydroabiatic acid). *n*-Alkanes: (a) 39-354-10-0, 0-10 cm; (b) 39-354-12-0, 0-10 cm; *n*-Fatty acids: (c) 39-354-10-0, 0-10 cm; (d) 39-354-12-0, 0-10 cm.

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