

## 16. HYDROCARBONS IN SEDIMENT OF THE WEDDELL SEA, ANTARCTICA<sup>1</sup>

Keith A. Kvenvolden,<sup>2</sup> Frances D. Hostettler,<sup>2</sup> and Tamara J. Frank<sup>3</sup>

### ABSTRACT

Heavy hydrocarbons ( $\sim C_{15+}$ ) are ubiquitous but minor components in sediment from three sites (692, 693, and 694) drilled during Ocean Drilling Program (ODP) Leg 113. This preliminary report is the first to describe the distribution of some of these hydrocarbons in sediment of the Weddell Sea. Samples from Sites 692 and 693, located on a mid-slope bench along the margin of Dronning Maud Land, span a time interval from Early Cretaceous to Pleistocene. In our samples from the Tertiary portion of the record, having an average organic-carbon content of about 0.2%, *n*-alkanes are common and are characterized by populations that indicate both marine and terrigenous sources. The  $\alpha\beta$ -hopanes and  $\alpha\alpha\alpha$ -steranes are minor components with isomer ratios indicating partial to full maturity. In contrast, our samples from the Cretaceous portion of the record, having an average organic carbon content of about 4%, contain mixtures of hydrocarbons in which *n*-alkanes are secondary in abundance to the isoprenoid hydrocarbons, pristane and phytane. Diasterenes, sterenes, and hopenes are present in anomalously high concentrations and indicate immaturity. The Cretaceous hydrocarbons appear to be mainly primary, whereas the Tertiary hydrocarbons contain compounds that indicate that the sediment, along with its organic content, has been recycled. Our samples from Site 694, located in the Weddell Sea on the abyssal plain, range in age from late Miocene to early Pliocene, have an average organic-carbon content of about 0.2%, and contain *n*-alkanes with a strong terrigenous signature. Isomer ratios of  $\alpha\beta$ -hopanes and  $\alpha\alpha\alpha$ -steranes indicate intermediate maturity; diasterenes, sterenes, and hopenes are absent. The hydrocarbons at this site are mainly recycled and indicate erosion of previously buried sediment from the continent of Antarctica.

### INTRODUCTION

During the last 5 years, interest in the heavy-hydrocarbon ( $\sim C_{15+}$ ) geochemistry of ocean sediment offshore from Antarctica has significantly increased. This increase is the result of (1) a greater availability of samples due to more marine surveys being undertaken by various nations in Antarctic waters, (2) an awareness that the isolation of Antarctica provides an offshore environment that has been relatively shielded from modern pollution, and (3) a desire by some to ascertain the petroleum potential of this vast offshore region. For example, in 1984 a marine geological and geophysical investigation was undertaken offshore from Wilkes Land and in the Ross Sea (Fig. 1) by the U.S. Geological Survey (Eittrheim et al., 1984). Sediment samples from this investigation have been studied and the hydrocarbon geochemistry described (Kvenvolden et al., 1987a, b; Rapp et al., 1987). These studies concluded that hydrocarbons came from both marine and terrigenous sources and that the terrigenous component probably represents recycled sediment. Later Venkatesan (1988a) described the lipid geochemistry, including hydrocarbons, of some sediment samples collected in 1983 by a team from New Zealand, and she also concluded that the organic matter is mainly recycled and mixed with some modern marine material. Other related studies of Ross Sea sediment are those of McIver (1975), who analyzed hydrocarbon gases from Deep Sea Drilling Project sites, Sackett et al. (1974), who first recognized the importance of organic matter recycling in Antarctic sediment, and Matsumoto et al. (1979), who studied a dumpsite at McMurdo Station.

The Alfred Wegener Institute for Polar Research of Germany conducted a marine geological survey in 1984 in the Bransfield Strait, on the opposite side of the continent of Antarctica (Fig. 1). Geochemical studies of sediment samples from this area

have indicated that (1) thermogenic hydrocarbons are present locally (Whiticar et al., 1985), and (2) both marine and lesser amounts of recycled terrigenous hydrocarbons are dispersed in the sediment (Venkatesan and Kaplan, 1987).

In addition to these studies, Mackie et al. (1978) described hydrocarbons in sediment from King Edward Cove on the island of South Georgia (Fig. 1) in the subantarctic region, and Matsumoto et al. (1979, 1984) and Volkman et al. (1986) reported on hydrocarbons (attributed mainly to bacterial and algal sources) in lake water, sediment, and soil on the continent of Antarctica. Also, Matsumoto et al. (1987) described steranes and triterpanes from outcrop samples collected in southern Victoria Land (Fig. 1); their results show variable maturities reflecting the effects of the intrusion of basaltic dikes on sedimentary organic matter.

With this background of hydrocarbon-geochemical information, Ocean Drilling Program (ODP) Leg 113 provided an unprecedented opportunity to extend investigations of hydrocarbons in sediment offshore from Antarctica to include the Weddell Sea (Fig. 1). Although nine sites were drilled on Leg 113, we were able to obtain samples (Table 1) from only three sites (692, 693, and 694). Site 692 is located on a mid-slope bench on the continental margin of Antarctica offshore from Dronning Maud Land (Fig. 1) at a water depth of 2875 m. From this site we obtained two samples of Early Cretaceous, probably Berriasian to Aptian or Albian age, organic-rich mudstone. The Early Cretaceous sediment at this site was encountered at a very shallow sub-bottom depth of about 53 m. Much of the overlying Mesozoic and Cenozoic section is missing because of unconformities and erosion by canyon cutting. About 30 km southwest of Site 692, and still on the mid-slope bench at a water depth of 2359 m, the stratigraphic section is more complete, and holes drilled here (Site 693) cored sediment that ranges in age from Early Cretaceous to Pleistocene. The Early Cretaceous sediment at Site 693 is slightly younger (Aptian-Albian age) than the sediment found at Site 692. Unfortunately, no sample of this unit from Site 693 was collected for us. Nevertheless, from this site we obtained six samples of sediment ranging in age from early Oligocene to Pleistocene (Table 1). Site 694 is located on the

<sup>1</sup> Barker, P. F., Kennett, J. P., et al., 1990. *Proc. ODP, Sci. Results*, 113: College Station, TX (Ocean Drilling Program).

<sup>2</sup> U.S. Geological Survey, Menlo Park, CA 94025.

<sup>3</sup> Present address: Surface Science Laboratories, Mountain View, CA.

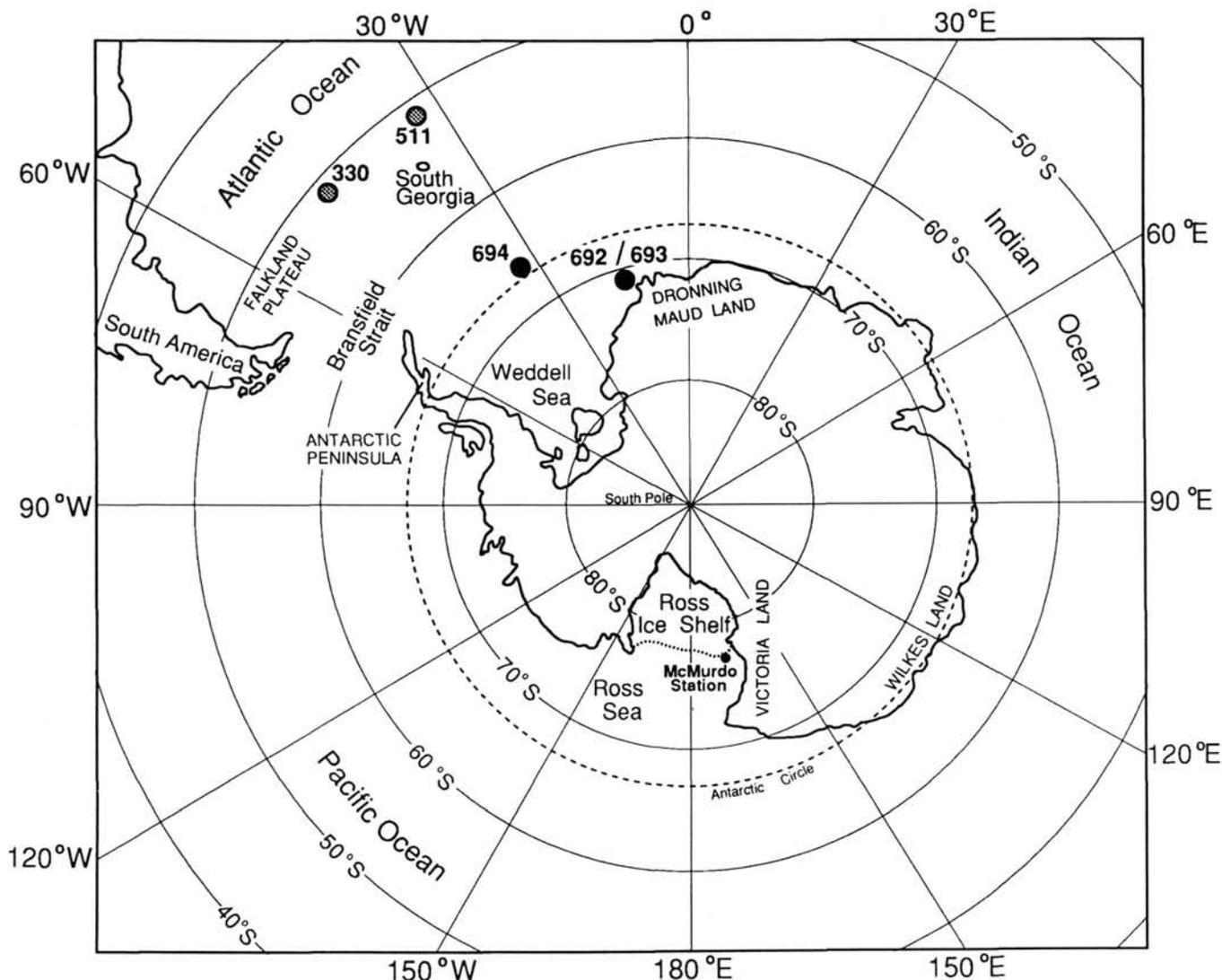


Figure 1. Map of Antarctica showing sampling Sites 692, 693, 694 from ODP Leg 113 in the Weddell Sea and regions where other organic-geochemical studies have been done, including DSDP Sites 330 and 511.

**Table 1. Descriptions of sediment samples from the Weddell Sea, Antarctica.**

Core, Sample, Number	Core interval (cm)	Sample depth (mbsf)	Geologic age	Water depth (m)	Organic carbon (%)	EOM ( $\mu\text{g/g}$ )
Dronning Maud Land margin — Sites 693 and 692						
693A-4R-3	129-132	26.2	Pleistocene	2359	0.15	4.5
693A-9R-4	125-128	75.9	e. Pliocene	2359	0.17	5.3
693A-12R-4	125-128	104.7	e. Pliocene	2359	0.31	7.1
693A-18R-3	125-128	161.2	e. Pliocene	2359	0.14	5.1
693A-25R-2	129-132	227.4	l. Miocene	2359	0.27	7.9
693A-40R-2	143-146	371.8	e. Oligocene	2359	0.23	11
692B9R-2	60-63	70.9	E. Cretaceous	2875	3.57	160
692B-12R-1	118-121	89.4	E. Cretaceous	2875	4.84	120
Weddell Abyssal plain — Site 694						
694B-3H-3	125-128	19.4	e. Pliocene	4653	0.34	4.5
694B-24X-2	125-128	172.4	l. Miocene	4653	0.15	0.4
694C-6X-3	125-128	222.2	l. Miocene	4653	0.16	3.4

abyssal plain of the Weddell Sea, remote from continental areas (Fig. 1). From this very deep-water site (4653 m), we obtained three sediment samples ranging in age from late Miocene to early Pliocene. These 11 samples provided material for us to prepare this preliminary report, which is the first to describe the hydrocarbon geochemistry of sediments of the Weddell Sea.

## PROCEDURES

The 11 sediment samples described here were collected on board ODP's *JOIDES Resolution*. An attempt was made to collect samples at approximately equal intervals down a hole, but sampling could only be done in intervals of undisturbed sediment that contained enough material to provide for both sedimentological control and organic-geochemical analyses.

The geochemical procedures were described previously (Kvenvolden et al., 1987a, b) and are only summarized here. The sediment samples, collected shipboard, had been carefully wrapped in cleaned aluminum foil and frozen immediately in plastic bags for storage. When we were ready to analyze the samples, water was removed by freeze-drying, and the samples were gently pulverized and sieved through a 32-mesh screen. We analyzed a small portion of the sieved sediment for organic carbon by wet combustion (Bush, 1970). For extraction and identification of hydrocarbons, we used 50–75 g of pulverized and sieved sediment. Each sample was triple extracted with dichloromethane by shaking on a wrist-action shaker. The combined filtered extracts were concentrated by rotary evaporation. Any sulfur was removed by filtration through activated copper. We used a portion of the filtrate to determine the weight of the extract—the extractable organic matter (EOM). The dichloromethane solvent was then exchanged for *n*-hexane.

The extracts in *n*-hexane were fractionated by liquid-solid chromatography using a column packed with activated silica gel and deactivated alumina. The column was sequentially eluted with *n*-hexane, benzene, and methanol to yield fractions containing mainly aliphatic hydrocarbon, aromatic hydrocarbons, and N, S, O-containing compounds, respectively. Only the aliphatic hydrocarbons were studied in detail by high resolution gas chromatography using a 30-m by 0.3-mm, DB-1 bonded phase, fused-silica capillary column; aromatic hydrocarbons were analyzed only in selected samples. Identification of *n*-alkanes, isoprenoid hydrocarbons (pristane and phytane), and aromatic hydrocarbons was based on retention times and comparison with standards. Relative proportions of the individual compounds were determined by integrator peak heights. Portions of all hexane fractions and some benzene fractions were examined by gas chromatography-mass spectrometry using a 30-m by 0.3-mm DB-5 bonded phase, fused-silica column. Single-ion monitoring (SIM) of *m/z* 191 and 217 produced mass fragmentograms from which terpanes and steranes/diasteranes, respectively, were identified. In addition, SIM of *m/z* 57, 243, and 257 produced mass fragmentograms of *n*-alkanes, fernenes, and diasterenes, respectively.

## RESULTS

Geochemical results for 11 samples are shown in Tables 1 and 2; samples from proximal Sites 692 and 693 are arranged in stratigraphic sequence, and the results from these sites are listed separately from the results obtained at the remote Site 694. At Site 693 the organic-carbon contents of the Cenozoic samples are low (0.14%–0.31%) whereas the two Mesozoic (Early Cretaceous) samples (Site 692) are organic-rich (3.57% and 4.84%); at Site 694 the organic-carbon values of the Cenozoic samples are also low (0.15%–0.34%). Likewise, the EOM values follow the same trend as the organic carbon with highest amounts found in the two Early Cretaceous samples at Site 692 and much lower amounts in the Cenozoic samples from Sites 693 and 694.

The aliphatic hydrocarbon fractions all contain *n*-alkanes ranging from about *n*-C<sub>13</sub> to about *n*-C<sub>36</sub>. Representative chromatograms of the *n*-alkanes are shown in Figure 2; in addition, pristane and phytane are shown along with other isoprenoid hydrocarbons. To illustrate the relations among *n*-alkanes and the isoprenoid compounds pristane and phytane, various ratios are listed in Table 2. The odd-even carbon number predominance (OEP<sub>x</sub>) for the *n*-alkanes was calculated by the method of Scalan and Smith (1970); OEP<sub>17</sub> and OEP<sub>27</sub> correspond to the *n*-alkane ranges C<sub>17±2</sub> and C<sub>27±2</sub> over which the calculations are made. Values of OEP<sub>17</sub> are variable and, except for one sample, show odd-carbon-number predominances. OEP<sub>27</sub> values usually indicate large odd-carbon-number predominances for the high-molecular-weight *n*-alkanes. In the Early Cretaceous samples, in which high-molecular-weight *n*-alkanes are partially masked chromatographically by polycyclic-aliphatic hydrocarbons (Fig. 2D), relative proportions of individual compounds were estimated from chromatographic and mass spectral information; these *n*-alkanes have an odd-carbon-number predominance (Table 2).

Pristane/phytane ratios increase with depth from 1.0 to 2.1 at Site 693 (Table 2); but at Site 692 the ratios of these compounds are about 1 (0.96 and 1.07), and they are the dominant aliphatic hydrocarbons in the Early Cretaceous samples as indicated by average values of the ratios Pr/C<sub>17</sub> and Ph/C<sub>18</sub> (2.6 and 5.4, respectively). The isoprenoid hydrocarbons also become increasingly significant with depth relative to the *n*-alkanes at Site 694. The complexity of the relative distributions of aliphatic hydrocarbons—*n*-alkanes and pristane and phytane—at the three sites is illustrated by representative chromatograms in Figure 2. The differences in distribution patterns between Cenozoic (Site 693) and Mesozoic (Site 692) samples are dramatic (Fig. 2A–D). Besides the identified *n*-alkanes and isoprenoid hydrocarbons, all samples contain minor to significant branched and cyclic compounds. Particularly interesting are the high-molecular-weight aliphatics in the Early Cretaceous samples (Site 692), some of which were identified by gas chromatography-mass spectrometry.

A portion of the aliphatic hydrocarbons in all samples is composed of terpenoid and steroid compounds (Figs. 3 and 4). At Site 693, the identified terpenoid compounds (Fig. 3A–C) are principally a series of 17 $\alpha$ (H),21 $\beta$ (H)-hopanes, including Tm [17 $\alpha$ (H)-22,29,30-trisnorhopane], and Ts [18 $\alpha$ (H)-22,29,30-trisnorhopane]. Tm/Ts ratios are variable at this site; however, in three samples, Tm greatly exceeds Ts (Table 2). The 17 $\beta$ (H),21 $\alpha$ (H)-hopane series (moretanenes) becomes increasingly important with depth, and the 17 $\beta$ (H),21 $\beta$ (H)-hopanes are present in only three of the six samples from this site (Table 2). Both 22S and 22R epimers of 17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane and of 17 $\alpha$ (H),21 $\beta$ (H)-30,31-bishomohopane are present. The values of the epimer ratios 22S/(22S + 22R) for three samples from Site 693 (Table 2) are at or near the equilibrium value of full maturity of about 0.6 (Mackenzie, 1984), whereas in three samples the ratios are not at equilibrium. At this site, steranes (Fig. 4A–C) include the C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub>-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane series with both the 20R and 20S isomers present. Only two of the 20S/(20S + 20R) ratios of the C<sub>29</sub> $\alpha\alpha\alpha$  sterane (Table 2) are at the equilibrium value of 0.5 (Mackenzie, 1984). Individually, these compounds are present in lower concentrations than the diasteranes, 13 $\beta$ (H),17 $\alpha$ (H)-diacholestane (20S) and 13 $\beta$ (H),17 $\alpha$ (H)-diacholestane (20R) as illustrated in Figure 4A–C. Hopanes, steranes, and diasterenes were not observed.

The terpenoid and steroid hydrocarbons in the Early Cretaceous samples at Site 692 (Figs. 3D and 4D) are in almost complete contrast to the compounds seen in the Cenozoic section at Site 693. Although 17 $\alpha$ (H),21 $\beta$ (H)-hopanes are present, they are minor compared to 17 $\beta$ (H),21 $\beta$ (H)-hopanes and the ho-

Table 2. Organic geochemical parameters in sediment samples from the Weddell Sea, Antarctica.

Sample	Ratios of alkanes and isoprenoids					m/z 191				m/z 217	
	OEP <sub>17</sub>	OEP <sub>27</sub>	Pr Ph	Pr C <sub>17</sub>	Ph C <sub>18</sub>	C <sub>30</sub> $\frac{\beta\beta}{\alpha\beta}$	C <sub>30</sub> $\frac{\alpha\beta}{\beta\alpha}$	C <sub>31</sub> $\frac{\alpha\beta}{S}$ S+R	Tm Ts	C <sub>29</sub> $\frac{\alpha\alpha}{S}$ S+R	Dominant Steroid Hydrocarbon
Dronning Maud Land margin:											
693A-4R-3	1.1	1.6	1.01	0.42	0.46	0(no $\beta\beta$ )	12.2	0.59	0.85	0.50	D
693A-9R-4	0.98	2.2	1.11	0.42	0.60	0(no $\beta\beta$ )	10.6	0.56	0.86	0.39	D
693A-12R-4	1.3	2.4	1.23	0.36	0.47	0.38	2.6	0.35	1.6	0.37	D
693A-18R-3	1.1	1.7	1.19	0.33	0.44	0(no $\beta\beta$ )	9.4	0.55	0.91	0.49	D
693A-25R-2	2.3	2.3	1.70	0.21	0.34	0.64	2.1	0.38	3.6	0.25	D
693A-40R-2	1.4	2.9	2.05	0.46	0.34	0.38	2.9	0.39	6.6	0.33	D=St
692B-9R-2	1.9	1.7	0.96	2.1	4.4	1.6	1.5	0(no S)	nc(no Ts)	0(no S)	St(no D)
692B-12R-1	1.8	1.9	1.07	3.1	6.4	1.3	1.5	0(no S)	nc(no Ts)	0(no S)	St(no D)
Weddell Abyssal plain:											
694B-3H-3	1.4	2.2	1.63	0.57	0.70	0(no $\beta\beta$ )	2.2	.31	4.1	0.13	St
694B-24X-2	1.5	2.5	1.73	0.59	0.85	0(no $\beta\beta$ )	7.3	.47	0.87	0.47	D
694C-6X-3	1.8	1.8	1.33	0.91	1.6	0(no $\beta\beta$ )	5.7	.48	1.1	0.34	D

Explanation: OEP, a measure of odd-even carbon number predominance (see text); Pr, pristane; Ph, phytane; C<sub>x</sub>, carbon number of molecule;  $\alpha\beta$ ,  $\beta\alpha$ ,  $\beta\beta$ , hopanes; Tm and Ts, terpanes (see text);  $\alpha\alpha\alpha$ ,  $\alpha\alpha\alpha$ -sterane; R and S, epimer configuration; m/z, mass to charge ratio of fragment ion; St, sterane; D, diasterane; nc, not calculated.

penes. In addition, fernenes (m/z 243) were tentatively identified. The 22R-epimer of 17 $\alpha$ (H),21 $\beta$ (H)-30-homohopane and of 17 $\alpha$ (H),21 $\beta$ (H)-30,31-bishomohopane greatly exceeds the 22S epimer. Tm is also present but not Ts. Only the 20R epimers of C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub>-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane series and the 5 $\beta$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane series can be identified (Fig. 4D) along with possible 4-methyl steranes. The 13 $\beta$ (H), 17 $\alpha$ (H)-diasteranes were not observed. Diasterenes (C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub>) are also present as identified by single ion monitoring of m/z 257 (Brassell et al., 1986); the 20R epimer is more abundant than the 20S epimer.

At Site 694 the dominant terpanes (Fig. 3E, F) are the 17 $\alpha$ (H),21 $\beta$ (H)-hopane series and to a lesser extent the 17 $\beta$ (H), 21 $\alpha$ (H)-hopane series (moretanens). Both Tm and Ts are present with Tm/Ts ratios ranging from 0.9 to 4.1 (Table 2). The 17 $\beta$ (H),21 $\alpha$ (H)-hopanes are not present in significant amounts. The epimer ratios 22S/(22S + 22R) of the 17 $\alpha$ (H),21 $\beta$ (H)-homohopanes range from 0.31 to 0.48, indicating intermediate maturity. Values of 0.13 to 0.47 for the epimer ratios 20S/(20S + 20R) of the C<sub>29</sub>-sterane [24-ethyl-5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-cholestane], the dominant sterane in the hydrocarbon mixtures, also indicate intermediate maturity (Table 2). Diasteranes are also present (Fig. 4E, F).

Identifiable aromatic hydrocarbons were found only in the organic-rich Early Cretaceous mudstone at Site 692. In both samples, perylene is the dominant aromatic compound, and it constitutes at least 90% of the aromatic fraction of the deepest sample. The remainder of this fraction contains a complex mixture of unidentified alkylated compounds. The aromatic fractions of the other samples from Sites 693 and 694 are composed of very minor amounts of methylated and regular polycyclic aromatic hydrocarbons including traces of phenanthrene.

## DISCUSSION

Our results show that *n*-alkanes, isoprenoid (pristane and phytane), terpenoid, and steroid hydrocarbons are common, but minor, components of Cenozoic sediment of the Weddell Sea at least on the continental slope and abyssal plain. These sediments are organic-poor, characterized by low amounts of organic carbon and EOM, apparently resembling sediments offshore from Wilkes Land and in the Ross Sea (Fig. 1; see Kvenvolden et al., 1987b). In striking contrast are the results from the Mesozoic sediment sampled from the continental slope; two samples contain the same general classes of hydrocarbons but different concentrations, distributions, and structural configurations. These sediments are organic-rich and, therefore, were likely deposited under conditions where organic matter was abundant and preservation was efficient.

### Cenozoic Section

Although the Cenozoic sediments from Sites 693 and 694 share the common characteristic of being organic-poor, their hydrocarbon geochemistries reveal slight differences at the two sites. For example, in most cases the distributions of aliphatic hydrocarbons at Site 693 on the continental slope are more complex, having more unidentified components and relatively more *n*-alkanes of lower molecular weights (Fig. 2A-C). Except for one sample, *n*-C<sub>15</sub> or *n*-C<sub>17</sub> dominates the low-molecular-weight mixtures, and the heavy *n*-alkanes show a variable odd-carbon-number predominance (OEP<sub>27</sub> = 1.6-2.9). Pristane/phytane ratios are always greater than one, and, with one exception, *n*-C<sub>17</sub> and *n*-C<sub>18</sub> are always more abundant than the accompanying isoprenoid hydrocarbons. The *n*-alkane distributions of the abyssal plain sediments (Site 694) show two distinct modes (Fig. 2E,

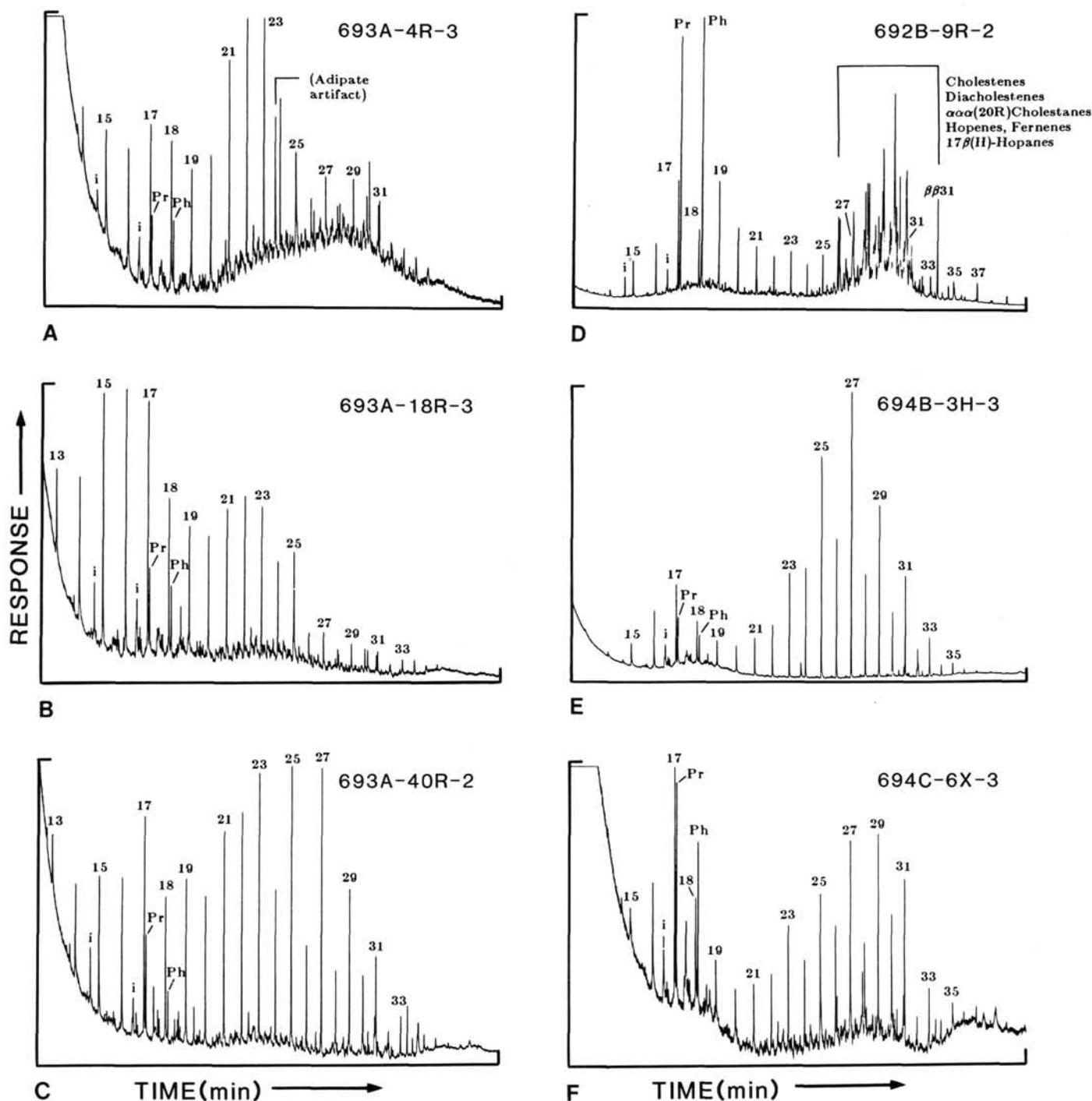


Figure 2. Gas chromatograms of the aliphatic hydrocarbons in six sediment samples from the Weddell Sea, Antarctica. The *n*-alkanes are indicated by carbon number; the carbon number of unnumbered peaks can be inferred from the carbon number of nearby homologs. Pr = pristane; Ph = phytane; and i = other isoprenoid hydrocarbons.

-F), one at *n*-C<sub>17</sub> and the other at high molecular weights where OEP<sub>27</sub> values of 1.8–2.5 indicate a significant odd-carbon-number dominance. Pristane and phytane become increasingly important with depth relative to *n*-C<sub>17</sub> and *n*-C<sub>18</sub> (Table 2).

The lower molecular weight *n*-alkanes at both Sites 693 and 694 likely represent marine sources, an interpretation supported by Clark and Blumer (1967), Han and Calvin (1969), and Simoneit (1978). The higher-molecular-weight *n*-alkanes with the

odd-carbon-number dominances likely represent contributions of waxes from vascular plants of terrigenous (continental) origin (Eglinton et al., 1962). This interpretation is based on many observations of marine sediments worldwide and summarized by Simoneit (1978).

The cyclic biomarkers show contrasting maturities at the Sites 693 and 694 with the sediments at Site 693 having both mature and intermediate-maturity mixtures. At Site 693, the

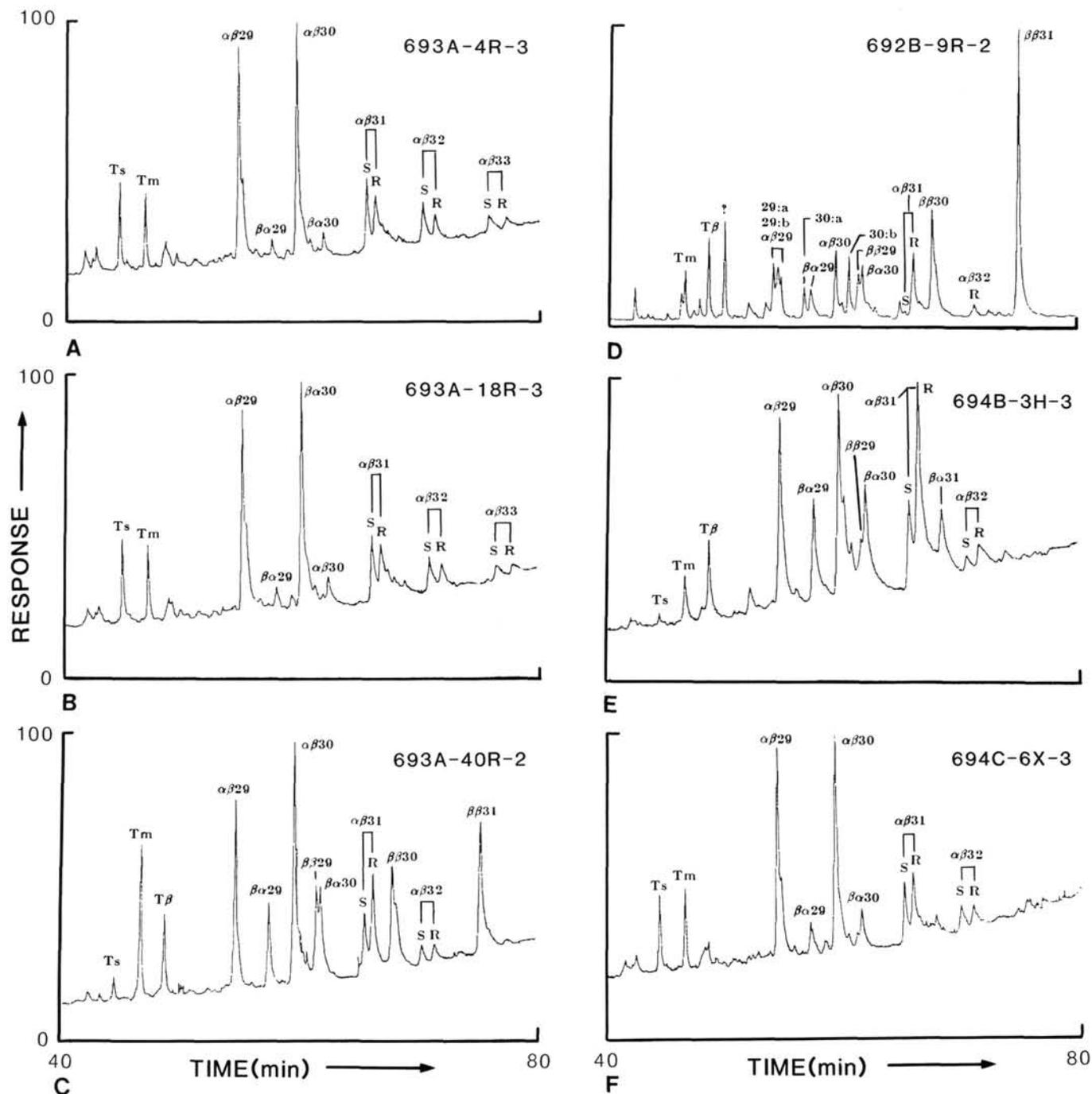


Figure 3. Mass fragmentograms ( $m/z$  191) of terpenoid hydrocarbons in six sediment samples from the Weddell Sea, Antarctica. Carbon numbers are indicated near peaks.  $\alpha\beta$  =  $\alpha\beta$ -hopanes;  $\beta\beta$  =  $\beta\beta$ -hopanes;  $\beta\alpha$  =  $\beta\alpha$ -hopanes (moretanes); a =  $\Delta^{17(21)}$ -hopene; b =  $\Delta^{13(18)}$ -neohopene; R and S =  $C_{22}$  epimers; Ts and Tm, defined in text; T $\beta$  = 17 $\beta$ (H)-22,29,30-trisnorhopane.

panes are dominated by the highly stable  $\alpha\beta$ -hopane series. The  $\alpha\beta$ -homohopane epimers in three samples are at equilibrium (full maturity). Tm/Ts ratios range from 0.85 to 6.6, with the largest value found in the sediment sampled at the greatest depth below the seafloor (Tables 1, 2). The  $\beta\alpha$ -hopanes (moretanes) of intermediate stability increase in importance with depth. The unstable  $\beta\beta$ -hopanes are present in three of the six samples. Although the  $\alpha\beta$ -hopanes are dominant at Site 694, the  $\beta\alpha$ -hopanes (moretanes) are present in significant amounts. The  $\alpha\beta$ -homohopanes are only partially isomerized; that is, the epimers are not at equilibrium. At Site 694, ratios of Tm/Ts vary from

0.9 to 4.1 (Table 2). No hopenes could be identified at this site. Epimer ratios of the  $C_{29}\alpha\alpha\alpha$ -steranes provide further support for the relative maturities at Sites 693 and 694 (Table 2). Thus the cyclic-biomarker evidence, based on considerations of the stability of structural isomers and the epimer ratios, clearly demonstrates that Site 694 has intermediate-maturity mixtures, similar to those observed in Ross Sea sediment (Kvenvolden et al., 1987b), and that both intermediate and fully mature mixtures occur at Site 693.

Of course, the question arises as to how unconsolidated Cenozoic sediment, which has not been deeply buried and which

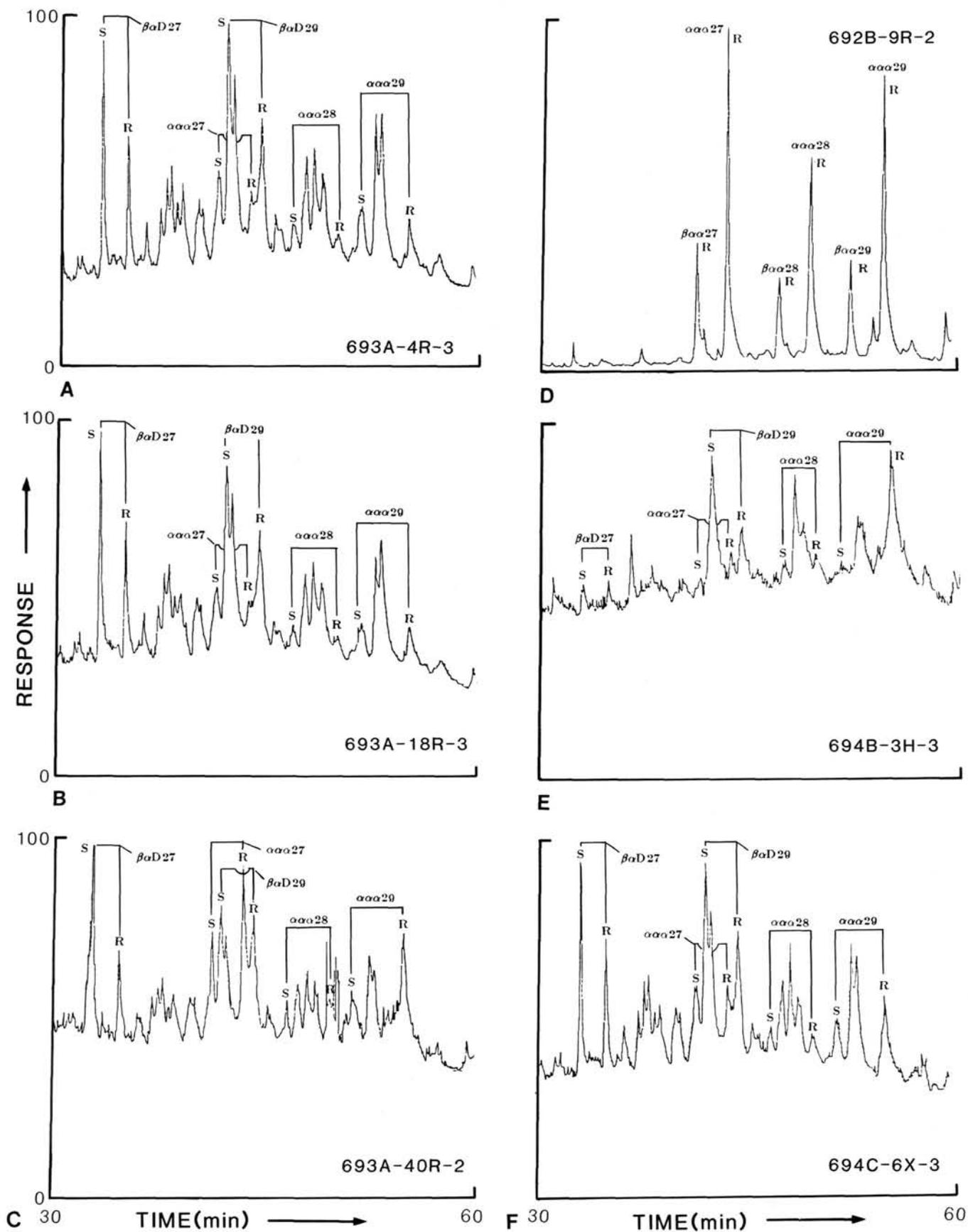


Figure 4. Mass fragmentograms ( $m/z$  217) of steroid hydrocarbons in six sediment samples from the Weddell Sea, Antarctica. Carbon numbers are indicated near peaks.  $\alpha\alpha\alpha$  =  $\alpha\alpha\alpha$ -steranes;  $\beta\alpha\alpha$  =  $\beta\alpha\alpha$  steranes;  $\beta\alpha D$  = diasteranes; R and S =  $C_{20}$  epimers.

has not obviously been subjected to high temperatures, can contain some hydrocarbons signaling intermediate to full maturity. The answer to this question was previously proposed in other investigations in the Antarctic (Sackett et al., 1974; Kvenvolden et al., 1987b; Venkatesan, 1988a). Much of the sediment, containing hydrocarbons from both marine and terrigenous sources, must have been recycled; that is, the sediment constituents must be older than the Cenozoic time of sedimentation. Perhaps the sediment had been eroded earlier from exposed rock that were previously buried on the continent of Antarctica. Ice-rafted debris from multiple sources may have been involved. This scenario would help explain (1) the terrigenous signature of *n*-alkanes which may have come from vascular plants that were once present on Antarctica but are now absent, and (2) the range of maturities shown by the cyclic biomarkers.

### Mesozoic Section

The hydrocarbon geochemistry of the two Early Cretaceous (possibly Berriasian to Albian age) samples at Site 692 reveals a paleohistory in which the organic-rich sediment has undergone little diagenetic change since the time of deposition more than 130 million years ago. In general, our results are comparable to the observation of Brassell et al. (1983), who pointed out that deep-sea sediments of Cretaceous age commonly show little evidence of diagenetic change. Apparently these sediments have never been deeply buried and have never been subjected to anomalous thermal stress.

The distributions of *n*-alkanes (Fig. 2D) show predominance of odd-carbon-numbers in the low-molecular-weight region (OEP<sub>17</sub> = 1.8 and 1.9). The source of these compounds is believed to be mainly aquatic algae. This interpretation is supported by the extensive compilation by Clark and Blumer (1967) in which they showed that the distributions of *n*-alkanes in marine phytoplankton comprises mainly *n*-C<sub>14</sub> through *n*-C<sub>20</sub> with an odd-carbon-number dominance. For carbon numbers greater than C<sub>25</sub>, the *n*-alkanes are partially masked on the gas chromatograms (Fig. 2D) by a complex mixture of polycyclic hydrocarbons; therefore, the distributions of *n*-alkanes in this complex region were not determined chromatographically with great confidence, but SIM of *m/z* 57 showed an odd-carbon-number predominance suggesting some terrigenous input. Between *n*-alkanes identified as *n*-C<sub>33</sub> and *n*-C<sub>34</sub> (Fig. 2D) is a distinctive compound whose retention time suggested diploptene, previously identified in sediment of the Bransfield Strait and the Ross Sea by Venkatesan (1988b). However, mass spectra and comparison with a known standard indicate that the compound in our samples is 17β(H),21β(H)-30-homohopane; no diploptene was detected.

The isoprenoid hydrocarbons pristane and phytane are about equally abundant and dominate the *n*-alkanes (Fig. 2D). The very large Pr/C<sub>17</sub> and Ph/C<sub>18</sub> ratios (Table 2) emphasize this dominance. Pristane/phytane ratios have been used to assess paleoenvironments (Didyk et al., 1978), but the application has restricted use (ten Haven et al., 1987), and Pr/Ph ratios near one are difficult to interpret (Powell, 1988). The Mesozoic sediment samples, which contain these isoprenoid hydrocarbons have organic carbon contents of 3.6% and 4.8%. This large amount of organic matter strongly suggests that the paleoenvironment of these sediments was anoxic. Under such conditions, a Pr/Ph ratio much less than one would be expected if the general model of Didyk et al. (1978) is accepted; however, we believe that our data brings the utility of this model into question (see also ten Haven et al., 1987). Although the specific source for these isoprenoid hydrocarbons is not known, they likely represent mainly marine sources such as algae and bacteria. We believe that our observed Pr/Ph ratios were established mainly by the contributing sources and that the ratios have changed very

little during the course of time because these sediments have undergone minimal diagenesis.

The hopanoid and steroid hydrocarbons in our Early Cretaceous samples comprise mixtures that are diagenetically very immature. Hopane isomers exemplify this interpretation. For instance, ββ-hopanes are least stable and have the stereochemistry of their biological, bacterial precursors (Ourisson et al., 1984), whereas, βα-hopanes are of intermediate stability, and αβ-hopanes are most stable (Seifert and Moldowan, 1978). In our two samples, the least stable ββ-hopane isomers dominate (Fig. 3D). The more-stable hopane isomer configurations are present but are relatively unimportant. Ts, the more stable of the Tm-Ts pair, is not present. The 22R epimer greatly exceeds the 22S epimer of the αβ-homohopane, showing that the extent of epimerization, which normally results in a mixture of 22R-22S, is very small. In addition to the foregoing evidence of immaturity, the presence of significant amounts of unsaturated hopenes (Fig. 3D) supports the interpretation of immaturity.

The steranes in these two Early Cretaceous samples compose a very simple mixture (Fig. 4D) compared to the complex mixtures observed in the Cenozoic samples (Fig. 4A-C, E, F). The 20Rααα-steranes are the dominant steranes followed by the 20Rβαα-steranes. The 20Rααα-steranes have undergone little or no isomerization because the 20Sααα-steranes were not detected. This lack of isomerization, the presence of the unstable 20Rβαα-steranes, and the fact that diasteranes were not observed provide additional evidence that these samples have undergone little diagenesis and are immature. The presence of diasteranes also indicates immaturity.

Perylene is the major aromatic compound in these Early Cretaceous sediments. Its source is uncertain, but the compound probably represents the very early diagenetic product from a single source, possibly diatoms. Venkatesan (1988c) reviewed the possible sources of perylene in sediments and concluded that perylene is common in anoxic marine sediments and that diatoms are major potential precursors. Our data appear to support these conclusions. Also of interest is the fact that perylene is the dominant polycyclic aromatic hydrocarbon in sediment of the Bransfield Strait (Venkatesan and Kaplan, 1987), which is near the Weddell Sea (Fig. 1).

The Mesozoic sediment at Site 692 represents a paleoenvironment that favored both the production and preservation of organic material. The extent of this paleoenvironment is not known, but the same or similar organic-rich facies are found on the Falkland Plateau (Fig. 1) (Barker, Dalziel, et al., 1977; Ludwig, Krashennnikov, et al., 1983), which in the Early Cretaceous was close to Site 692 (Norton and Sclater, 1979; Lawver et al., 1985). The molecular organic geochemistry of our samples from Site 692 is similar in many aspects to the results obtained on Early Cretaceous samples from the Deep Sea Drilling Project at Site 330 (Simoneit, 1980) and, in particular, Site 511 (von der Dick et al., 1983) on the Falkland Plateau (Fig. 1). At Site 511 similarities include the dominance of pristane and phytane relative to the *n*-alkanes, the striking abundance of unsaturated terpenoid and steroid hydrocarbons, and the unusually high amounts of 17β(H),21β(H)-30-homohopane.

The depositional setting of these organic-rich sediments has been separated by plate-tectonic movement so that similar facies are now found near to the Antarctic continent as well as in the region of the Falkland Plateau. Apparently, not much has happened diagenetically since these sediments became part of the geologic record; hydrocarbon mixtures are immature, indicating that the post-depositional diagenetic history has been uneventful although the tectonic history has involved major rifting. More mature facies of such organic-rich sediments would be excellent sources of petroleum and may have developed elsewhere, for example, through deeper burial. The petroleum potential of

Mesozoic sediment of the Falkland Plateau was recognized earlier by Comer and Littlejohn (1977). Our report shows that potential source beds of Mesozoic age are also located very close to the Antarctic continent.

### CONCLUSIONS

During this preliminary study of the hydrocarbon geochemistry of Weddell Sea sediment, we found immature mixtures of hydrocarbons in organic-rich Mesozoic sediment and mature mixtures of hydrocarbons in Cenozoic sediment. The Cenozoic sediment apparently contains only a small amount of primary marine organic material. Most of this kind of organic material must have been lost through oxidation; what remains is mostly secondary and recycled. The small amounts of organic matter in the Cenozoic sediments originally may have come from the erosion of older sedimentary rocks of the continent of Antarctica. This source seems to explain much of the hydrocarbon geochemistry of Cenozoic sediment not only of the Weddell Sea but elsewhere offshore from Antarctica.

The organic material in the Mesozoic samples is mainly primary, and the hydrocarbons apparently have undergone little change during the history of the sediment, assuming minimal burial depths and minimal thermal stress. If any recycled organic matter is present in these samples, it is masked by the abundant primary organic material. The Mesozoic sediment studied here represents a paleoenvironment that favored the production and preservation of organic matter and where diagenetic processes have had little impact. More mature facies of this sediment could be considered potential sources of petroleum.

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