

SOURCE OF ORGANIC MATTER IN THE SINKING PARTICLES
COLLECTED FROM THE PACIFIC SECTOR OF THE
ANTARCTIC OCEAN BY SEDIMENT
TRAP EXPERIMENT

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Abstract: Sediment trap experiment was conducted at Stn. 3 (61°34.1'S, 150°23.3'E) in the Pacific Sector of the Antarctic Ocean for 23 days from December 20, 1983 to January 13, 1984. Sinking particles from 630, 1430 and 3230 m depths, suspended particles from 1, 30, 80 and 500 m depths and bottom sediment were analyzed for hydrocarbons, which consisted of n-alkanes with the carbon atoms ranging from 14 to 32 (n-alkane, n-C₁₄-C₃₂), heneicosahexaene (n-C_{21:6}), isoprenoid hydrocarbons and branched C₂₅ and cyclic C₃₀ alkenes (br-C₂₅ and c-C₃₀).

Hydrocarbons were quantified by gas chromatography and identified and/or elucidated by combined gas chromatography and mass spectrometry. Isoprenoid hydrocarbons consisted of squalene, pristane and phytane, while branched C₂₅ and C₃₀ alkenes were composed of br-C_{25:3}, br-C_{25:4}, br-C_{25:3'} (isomer of br-C_{25:3}), c-C_{30:4:1} and c-C_{30:4:2}.

Hydrocarbon composition was characteristic to each of the particle and sediment samples. Thus, the hydrocarbon composition gives us a clue to clarify the source of organic matter in the sinking particles collected from the intermediate and deep waters. Heneicosahexaene widely occurring in diatoms and coccolithophores, was found in the suspended and sinking particles, indicating that organic matter in the sinking particles was derived from diatoms and/or coccolithophores living in the surface waters. br-C₂₅ and C₃₀ alkenes commonly found in the fecal pellets, were abundant in the sinking particles collected from the intermediate through deep waters. Thus, these findings indicate that large part of the organic materials in the sinking particles are derived from phytoplankton growing in the surface waters through fecal pellets of zooplankton. Occurrence of br-C₂₅ and C₃₀ alkenes even in the suspended particles of the euphotic layers indicates that these particles are contaminated by zooplankton fecal pellets and/or their debris. Further discussions will be conducted on the source materials of the sinking particles on the basis of the hydrocarbon compositions of the suspended and sinking particles.

1. Introduction

Organic matter in the sinking particles which are transported from the surface water toward the ocean floor is an important food source for the deep sea organisms (WIEBE *et al.*, 1976; HINGA *et al.*, 1979). However, the organic matter is also degraded by deep sea inhabitants to regenerate various nutrients with the consumption of dissolved oxygen (SUESS, 1980; KNAUER *et al.*, 1979). Thus, the vertical transport

and degradation processes of organic matter in the sinking particles give a great influence on the geochemical cycles of biologically limited elements in the oceanic environments.

Several studies on the sinking particles collected by sediment traps indicated that organic materials of the particles consisted of lipids (CRISP *et al.*, 1979; TANOUE and HANDA, 1980; WAKEHAM *et al.*, 1980; GAGOSIAN *et al.*, 1982), amino acids and proteins (LEE and CRONIN, 1982) and carbohydrates (ITTEKOT *et al.*, 1984a, b).

Recently, the sinking particles were extensively analyzed for n-alkanes, n-alkenes and isoprenoid hydrocarbons (CRISP *et al.*, 1979; PRAHL *et al.*, 1980; WAKEHAM *et al.*, 1980; BURNS and VILLENEUVE, 1983) and the results suggested that isoprenoid hydrocarbons of C₂₀, C₂₅ and C₃₀ with several unsaturations found only in the surface layer of the marine sediments (BARRICK *et al.*, 1980; PRAHL *et al.*, 1980; REQUEJO and QUINN, 1983; VOLKMAN *et al.*, 1983) might be the key substances to clarify the source of the organic matter in the sinking particles (MATSUEDA *et al.*, 1986). However, no direct evidences have been available to solve this problem.

During the BIOMASS cruise of the R. V. HAKUHO MARU, Ocean Research Institute, University of Tokyo, from November 1983 to February 1984, the sediment trap system was deployed in the Antarctic Ocean to collect the sinking particles from the various water depths. The collection of the suspended particles from various depths and the bottom sediment was also conducted at the trap site. All of these samples were analyzed for hydrocarbons. An aim of this work is to clarify the source of organic matter in the sinking particles on the basis of hydrocarbon compositions of those samples collected in the Antarctic Ocean.

2. Materials and Methods

2.1. Sampling

Sinking particles: Sinking particles were collected from the water depths of 630, 1430 and 3230m by the sediment trap, which was deployed at Stn. 3 (61°34.1'S, 150°23.3'E, 3750m depth) in the Pacific Sector of the Antarctic Ocean, for 23 days from December 20, 1983 to January 13, 1984 (Fig. 1). Each of the sediment traps consisted of six polyvinyl chloride (PVC) cylinders (25cm i.d. × 50cm height). Each of the cylinders was equipped with a cup (8cm i.d. × 10cm height) to collect sinking particles in the presence of antiseptics. After recovery of the sediment trap, each of the samples of the sinking particles was transferred to a glass bottle, then a few drops of saturated mercuric chloride solution were added and the sample was allowed to stand in a refrigerator at 2°C until analyses.

Suspended particles: Sea water samples (200l) were collected from the depths of 1, 30, and 80m by the submersible impeller pumping system at Stn. 3 on December 26, 1983 and filtered through the preliminarily combusted glass fiber filter (Whatman GF/C, 285 × 420mm) to obtain particles suspended in seawater (suspended particles). Large volume *in situ* filtration system (LVFS) was applied to collect suspended particles from 759l of sea water at 500m depth on December 25, 1983. All of the suspended particles were kept frozen at -20°C in the dark until analysis.

Size fractionation of suspended particles: Surface sea water (400l) was collected

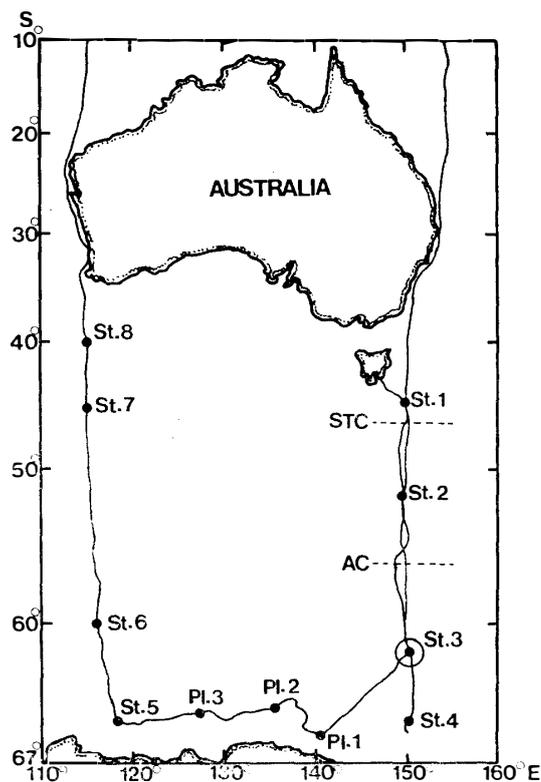


Fig. 1. Track chart of the BIOMASS cruise of the R. V. HAKUHO MARU to the Antarctic Ocean.

from the depth of 1 m by the pumping system on December 26, 1983 and passed through a series of the plankton nets of 20, 47 and 100 μm mesh under hydraulic pressure. Each of the plankton nets was washed with the sea water free from particles and the washings were filtered through glass fiber filter to collect suspended particles. Three particle size fractions of the suspended matter obtained (1–20, 20–100, > 100 μm) were kept frozen at -20°C until analysis.

Bottom sediment: Bottom sediment was collected at Stn. 3 by the box corer on December 15, 1983. A stainless steel tube (10 \times 10 \times 50 cm) was inserted into the sediment in the box corer to obtain a core sample of the sediment without any disturbance of the sedimentary layers. The core sample was sectioned every 1 cm in thickness on board and kept frozen at -20°C until analysis. Only surface sediment (0–1 cm) was analyzed for organic materials in the present study.

2.2. Analytical procedures

2.2.1. C, N analyses

Sinking particles, suspended particles and bottom sediment were analyzed for total organic carbon and nitrogen by a CHN-Corder (Yanaco, MTD-1S) after removal of inorganic carbonate by the addition of diluted HCl as reported by TANOUE and HANDA (1979). Analytical errors of the organic carbon and nitrogen measurements were within $\pm 5\%$.

2.2.2. Hydrocarbon analysis

Extraction: Lipids were extracted from the sinking particles (2g wet weight), suspended particles (200 l) and surface bottom sediment (36g wet weight) with chloroform/methanol (2/1, v/v, 50–200 ml) thrice by stirring vigorously under nitrogen at room temperature overnight in the dark. Combined extracts were gently stirred after addition of distilled water and then allowed to stand at room temperature for 5 min. Organic solvent phase was washed with distilled water twice and dried over anhydrous sodium sulfate to obtain chloroform extract.

Separation: Lipid extract was evaporated to dryness under nitrogen gas using a rotary evaporator at $<30^{\circ}\text{C}$. The residue was redissolved in hexane (5 ml), and an aliquot of which was separated into individual classes of compounds by column chromatography. Fractionation of lipids was performed by using a small glass column (0.8 cm i.d. \times 9 cm) packed with activated silica gel (Merk Kiesel Gel 60, 240–400 mesh, 1 g). Six fractions were collected by elution with a series of solvents increasing its polarity stepwisely as described by MATSUEDA *et al.* (1986). Hydrocarbon fraction was eluted first with 5 ml of hexane. Methyl ester of $\text{C}_{20:0}$ acid ($\text{C}_{20:0}$ FAME) was added to the eluate as an internal standard. The sample was analyzed for hydrocarbons by gas chromatography (GC) and combined gas chromatography and mass spectrometry (GC-MS).

Reduction: Hydrogenation of unsaturated hydrocarbon was conducted by the method described by BARRICK *et al.* (1980). Hydrocarbon fractions were moderately hydrogenated in ethyl acetate solution (5 ml) with H_2/PtO_2 (1 mg) at room temperature for 30 min after complete removal of elemental sulfur by passing through a column of activated copper (1 g). Saturated hydrocarbons treated by this reaction were analyzed by GC and GC-MS.

GC and GC-MS analysis: GC analysis was conducted on a Shimadzu 9A gas chromatograph equipped with a hydrogen flame ionization detector (FID), solvent cut system and a fused silica capillary column (25 m \times 0.25 mm i.d.) coated with SE-52. Nitrogen was used as carrier gas in 1 ml/min of the flow rate. Column was programmed from 120 to 280°C at $4^{\circ}\text{C}/\text{min}$ for hydrocarbon analysis. The detection and injection ports were operated both at 285°C . Hydrocarbons were quantified by peak areas using a microcalculator (Shimadzu Chromatopac C-R1B). Whole analytical precision for the determination of hydrocarbons in GC was within $\pm 15\%$.

Structural information of these hydrocarbons was obtained by their mass spectra of the electron impact (EI) and chemical ionization (CI) modes using a JEOL D-300 coupled with a JEOL JMA-200 data analysis system. The ion sources were kept at 30 eV with $200\ \mu\text{A}$ ionization current for EI mode and 70 eV with $200\ \mu\text{A}$ for CI mode.

3. Results

3.1. Vertical flux of organic matter

Vertical fluxes of dry mass and organic carbon and nitrogen tended to decrease toward deep (Table 1).

Organic carbon and nitrogen contents in the sinking particles also tended to decrease with depth, while no vertical change in C/N ratio was found in the values ranging

Table 1. Bulk flux data and concentrations of organic carbon and nitrogen in the sinking particles collected at Stn. 3.

Depth (m)	Total mass	Flux		Concentration		C/N
		C mg/(m ² ·day)	N	C %	N	
630	1350	51.8	8.13	3.84	0.602	6.38
1430	1150	32.9	5.15	2.86	0.448	6.38
3230	555	15.8	2.48	2.85	0.446	6.39

from 6.38 to 6.39, which were much larger than that of the surface sediment (0–1 cm layer) of the ocean floor at the sediment trap site.

3.2. Characterization of unsaturated long-chain hydrocarbons (ULCH)

Unsaturated long-chain hydrocarbons were found in the samples of the sinking particle by GC analyses (Fig. 2). Several alkenes (peaks-a~j and peak-A) with some isoprenoid hydrocarbons occurred in the hydrocarbon fraction of the sinking particles, while only small amounts of n-alkanes with the carbon atoms ranging from 15 to 32

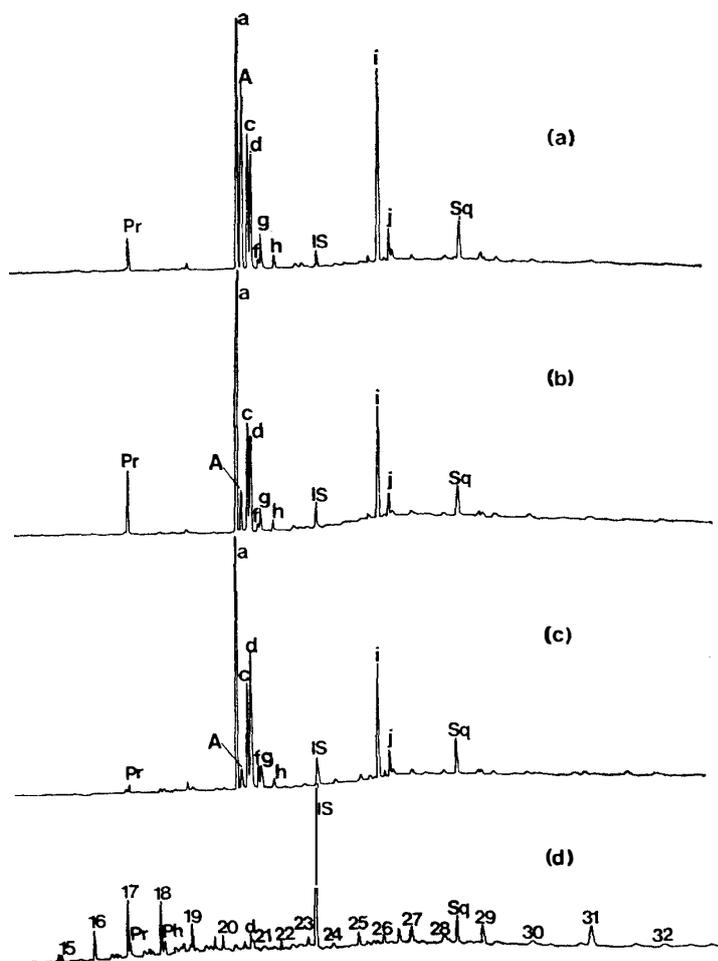


Fig. 2. Gas chromatograms of hydrocarbons of the sinking particles collected from 630 (a), 1430 (b) and 3230 (c) m depths, and bottom sediment (d) respectively in the Antarctic Ocean.

were detected. Some of these hydrocarbons were also found in the suspended particles and bottom sediment. Thus, characterization of these hydrocarbons before and after hydrogenation of H_2/PtO_2 -ethyl acetate system was conducted by GC-MS.

Peaks-a, c and d with their Kovat's indices (I) of 2047, 2083 and 2092 respectively on SE-52 were found in the sinking particles as the predominant components. These hydrocarbons were determined with their chemical structure (Fig. 3). Peaks-a and d exhibited the same molecular ion (m/z 346) and fragmentation pattern in the EI mode before hydrogenation, indicating that these compounds are isomers. The molecular ion of peak-c was found at m/z 344 in the EI mode. After hydrogenation, peaks-a, c and d were converted to an identical saturated compound with the molecular ion of m/z 352. The shift of the mass number of the molecular ion before and after hydrogenation indicated that peaks-a, c and d were acyclic C_{25} alkenes having three, four and three of the double bonds in their molecules' respectively. However, full hydrogenation of the alkenes gave sole alkane which had much lower value of the retention time in GC compared with that of $n-C_{25}$ (MW 352). This finding indicated that peaks-a, c and d were tentatively identified as branched C_{25} with three double bonds (br- $C_{25:3}$), branched C_{25} with four double bonds (br- $C_{25:4}$) and branched C_{25} with three double bonds (br- $C_{25:3}'$) respectively on the basis of mass spectra of the EI mode for hydrocarbon samples before and after hydrogenation. Hydrocarbons of the peaks-a and c were positional isomers which had three double bonds in their molecules.

Unsaturated hydrocarbons which appeared at peaks-f~j were also analyzed for their mass numbers of the molecular weights before and after hydrogenation by GC-MS (Table 2). Peak-f, and peaks-g, h, i and j increased in their molecular weights by two to eight after hydrogenation, respectively. Peak-f was converted by the hydrogenation

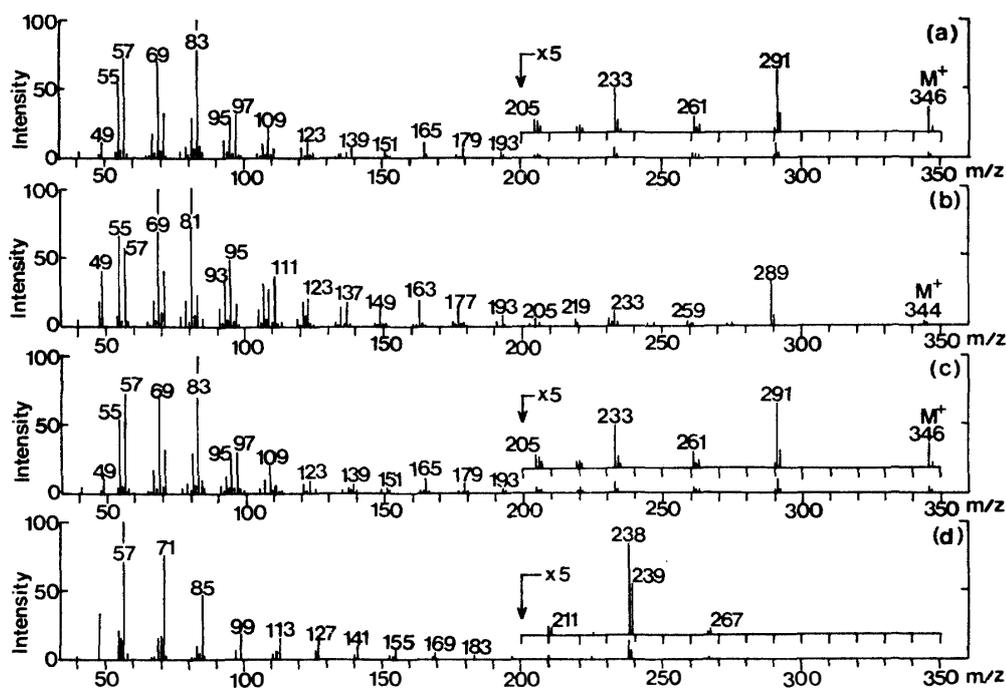


Fig. 3. EI mass spectra of peak-a (a), peak-c (b), peak-d (c) and the hydrogenation product of peaks-a, c and d (d).

Table 2. Kovat's indices (*I*) and molecular weights (*MW*) before and after hydrogenation of unsaturated hydrocarbons.

Peaks	Hydrocarbons	<i>I</i>	MW before hydrogenation	MW after hydrogenation
a	b _r -C ₂₅ :3	2047	346	352
c	b _r -C ₂₅ :4	2083	344	352
d	b _r -C ₂₅ :3'	2092	346	352
f	n-C ₂₁ :1	2120	294	296
g	c-C ₂₅ :4:1	2128	342	350
h	c-C ₂₅ :4:1'	2176	342	350
i	c-C ₃₀ :4:1	2576	412	420
j	c-C ₃₀ :4:2	2621	410	418

to a n-C₂₁ alkane without any rings in the molecule, while the hydrogenation products of peaks-g ~ j were not identical to acyclic C₂₅ and C₃₀ alkenes in terms of the molecular weight, suggesting the presence of ring structure in all of these molecules. From these results, it can be seen that peak-f is n-C₂₁ with only one double bond, while peaks-g ~ j are cyclic C₂₅ or C₃₀ alkenes containing four double bonds as well as some rings as shown in Table 2.

Hydrocarbon of peak-A (*I*=2062) revealed a marked shift in the retention time of GC before and after hydrogenation. Peak-A gave the molecular ion at *m/z* 284 in the EI mode of GC-MS analysis (Fig. 4). After hydrogenation, reduced peak-A gave the molecular ion at *m/z* 296 with a series of fragment ions from *m/z* 43 to *m/z* 269 increasing every 14 amu in mass number. From these results, it can be seen that peak-A is a heneicosahexaene (n-C_{21:6}). The positions and steric configurations of six double bonds of this hydrocarbon are still not known. However, the EI mass spectrum of peak-A gave the characteristic fragment ions at *m/z* 255 (M⁺-CH₃CH₂-) and *m/z* 55 (CH₃CH₂=CH⁺), suggesting no occurrence of the terminal double bonds of the molecule. The EI fragmentation pattern of this compound was much like that of all-cis-3, 6, 9, 12, 15, 18-heneicosahexaene in *Skeletonema costatum* reported by LEE *et al.* (1970).

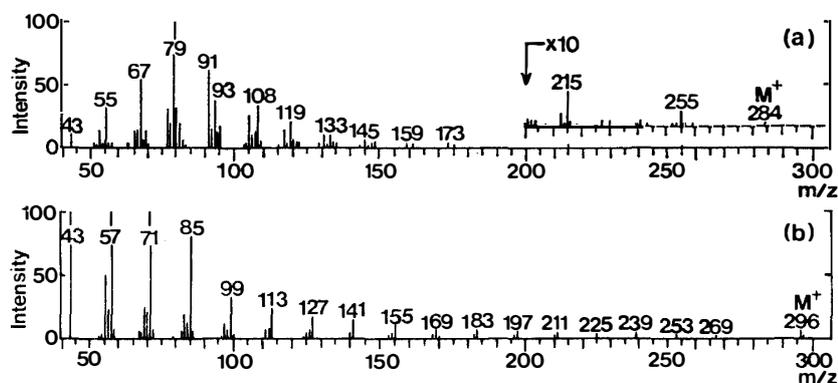


Fig. 4. EI mass spectra of peak-A (a) and its hydrogenation product (b).

3.3. Hydrocarbon composition of sinking particle

Table 3 shows the concentrations and compositions of hydrocarbons in the sinking particles from the water depths of 630, 1430 and 3230 m. Total hydrocarbon of the sinking particles did not significantly change vertically and its carbon accounted for 0.09 to 0.12% of the total organic carbon. All of the C₂₅ and C₃₀ alkenes were found in the sinking particles without any significant changes in their concentrations toward deep, while pristane and n-C_{21:6} tended to significantly decrease with depth. Squalene tended slightly to decrease with depth, while phytane and n-alkanes tended to increase with depth. From these findings, it can be seen that degradation and transformation of hydrocarbons occur during the sinking of the particles in the water column to some extent.

Table 3. Hydrocarbon compositions of the sinking particles from 630, 1430 and 3230 m at Stn. 3.

Peaks	Hydrocarbons	Depth (m)		
		630	1430 ($\mu\text{g/g}$)	3230
Peak-a	br-C _{25:3}	11	12	13
-c	br-C _{25:4}	3.8	4.1	3.1
-d	br-C _{25:3'}	3.0	4.0	4.0
-f	n-C _{21:1}	0.29	0.38	0.68
-g	c-C _{25:4:1}	1.5	1.5	1.2
-h	c-C _{25:4:1'}	0.34	0.38	0.31
-i	c-C _{30:4:1}	4.8	4.4	3.3
-j	c-C _{30:4:2}	0.96	1.1	0.92
Peak-A	n-C _{21:6}	4.4	1.6	0.68
Pr	pristane	1.0	2.9	1.20
Ph	phytane	0.02	0.0	0.06
Sq	squalene	1.4	1.5	1.1
15	n-alkane	0.01	0.0	0.0
16	"	0.02	0.0	0.04
17	"	0.06	0.04	0.07
18	"	0.03	0.05	0.09
19	"	0.03	0.03	0.09
20	"	0.02	0.0	0.07
21	"	0.10	0.14	0.16
22	"	0.01	0.0	0.0
23	"	0.02	0.0	0.05
24	"	0.03	0.0	0.12
25	"	0.08	0.05	0.21
26	"	0.12	0.07	0.21
27	"	0.16	0.15	0.34
28	"	0.14	0.19	0.30
29	"	0.18	0.34	0.24
30	"	0.15	0.27	0.23
31	"	0.11	0.0	0.0
32	"	0.0	0.0	0.0
Total		34	35	30

The most characteristic feature of hydrocarbon composition in all of the samples of the sinking particles was the abundance of br-C₂₅ and C₃₀ alkenes consisting of br-C_{25:3} with br-C_{25:4}, br-C_{25:3'} and c-C_{30:4:1}. The alkenes in all of the samples accounted for more than half of the total hydrocarbons, while n-C_{21:6} tended to be much less abundant toward deep. Pristane, squalene and phytane were identified as isoprenoid hydrocarbons in the sinking particles, which accounted for 4 to 14% of the total hydrocarbons. Long-chain n-alkanes (n-C₂₄-C₃₂) without any odd carbon predominance occurred and each of the n-alkanes accounted for far less than 1% of total hydrocarbon throughout the samples of the sinking particles.

3.4. Hydrocarbon composition of the suspended particles

Total hydrocarbon-carbon of the suspended particles from 1, 30, 80 and 500m

Table 4. Hydrocarbon compositions of the suspended particles from 1, 30, 80 and 500 m at Stn 3.

Peaks	Hydrocarbons	Depth (m)			
		1	30	80	500
		(µg/1000L)			
Peak-a	br-C _{25:3}	2.2	3.2	3.4	0.0
-c	br-C _{25:4}	0.72	1.2	1.1	0.0
-d	br-C _{25:3'}	1.5	1.8	1.6	0.0
-f	n-C _{21:1}	0.51	0.27	0.38	0.0
-g	c-C _{25:4:1}	0.0	0.18	0.17	0.0
-h	c-C _{25:4:1'}	0.0	0.0	0.0	0.0
-i	c-C _{30:4:1}	4.6	4.9	3.3	0.0
-j	c-C _{30:4:2}	2.2	0.64	0.54	0.0
Peak-A	n-C _{21:6}	9.7	32	23	0.0
Pr	pristane	3.2	4.4	1.3	0.0
Ph	phytane	0.58	0.33	0.15	0.01
Sq	squalene	14	12	18	0.55
15	n-alkane	0.56	0.13	0.03	0.0
16	"	0.45	0.36	0.11	0.04
17	"	1.4	0.94	0.55	0.08
18	"	1.0	0.92	0.22	0.05
19	"	1.1	0.44	0.28	0.0
20	"	1.2	0.31	0.21	0.0
21	"	1.1	0.0	0.26	0.0
22	"	1.2	0.22	0.24	0.08
23	"	2.3	0.40	0.42	0.40
24	"	4.7	0.72	0.79	1.3
25	"	9.1	1.5	1.5	2.5
26	"	13	2.4	2.1	4.0
27	"	14	2.8	2.7	5.1
28	"	14	2.8	2.3	5.5
29	"	15	3.0	2.2	5.4
30	"	13	2.7	1.9	4.0
31	"	13	1.8	1.9	2.7
32	"	10	1.3	1.4	1.3
Total		160	84	72	33

depths accounted for 0.19, 0.06, 0.09 and 0.35% of the total organic carbons, respectively. Hydrocarbon compositions of suspended particles from five depths are shown in Table 4.

The striking features of the hydrocarbon composition of the suspended particles from the euphotic layer (<100m) were as follows; firstly two hydrocarbons of $n\text{-C}_{21:6}$ and squalene were extremely predominant relative to other hydrocarbons, secondly long-chain n -alkanes ($n\text{-C}_{24}\text{--C}_{32}$) were much more abundant than short-chain n -alkanes ($n\text{-C}_{15}\text{--C}_{23}$), and thirdly no significant odd-chain carbon predominance of n -alkanes was observed in these samples of the suspended particles. It is of interest that $br\text{-C}_{25}$ and C_{30} alkenes were also found in the suspended particles from the euphotic layer, even though they were only minor components accounting for less than 7% of the total hydrocarbons, while any $n\text{-C}_{21:6}$, $br\text{-C}_{25}$ and C_{30} alkenes were not detected in the suspended particles from the aphotic layer (>200 m). n -Alkane composition, however, did not much change throughout the samples from the euphotic and aphotic layers. These findings clearly indicated that unsaturated long-chain hydrocarbons were more labile than saturated hydrocarbons during the translocation of the suspended particles from the euphotic to the aphotic zones. This result indicates that several alkenes occurring in the suspended particles are more rapidly degraded compared with long-chain n -alkanes.

3.5. Hydrocarbon composition of the size-fractionated suspended particles

The suspended particles from the surface water were fractionated according to their sizes. The particle fractions with 0–20, 20–100 and >100 μm diameters were analyzed for hydrocarbon by GC and GC-MS (Fig. 5) to search the particles which had the hydrocarbon composition closest to that of the sinking particles. Two small-sized fractions of suspended particles (0–20 and 20–100 μm) showed a similar hydro-

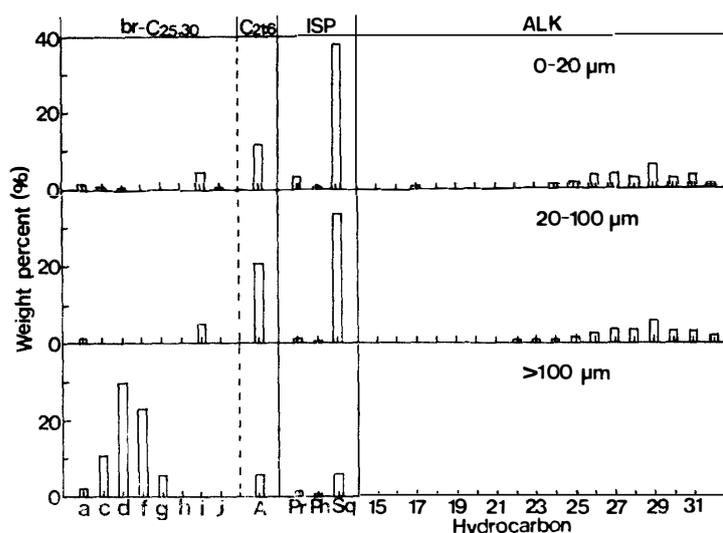


Fig. 5. Percent composition of hydrocarbons in ALK (n -alkanes), $n\text{-C}_{21:6}$ (peak-A), ISP (isoprenoid hydrocarbons) and $br\text{-C}_{25,30}$ ($br\text{-C}_{25}$ and C_{30} alkenes) in the particle size fractions of the suspended particles from 1m depth at Stn. 3 of the Antarctic Ocean.

carbon composition to each other, but the composition was markedly different from that of large-sized suspended particles ($>100\ \mu\text{m}$).

The major hydrocarbons in two small-sized suspended particles were $n\text{-C}_{21:6}$ and squalene, which accounted for more than half of total hydrocarbons. All of C_{25} and C_{30} alkenes and long-chain n-alkanes were found in these small-sized suspended particles as only minor components. These hydrocarbon compositions were quite similar to those of whole surface suspended particles, indicating that the main fractions of hydrocarbons occur in the small-sized suspended particles ($<100\ \mu\text{m}$) from the surface water.

br-C_{25} and C_{30} alkenes, however, were abundantly found in the hydrocarbon of the large-sized suspended particles as observed in the sinking particles. These alkenes consisting mainly of $\text{br-C}_{25:3}'$ with $\text{br-C}_{25:3}$, $\text{br-C}_{25:4}$, $n\text{-C}_{21:1}$ and $c\text{-C}_{25:4:1}$ accounted for about 60% of the total hydrocarbons in the large-sized particles, while $n\text{-C}_{21:6}$ and squalene in this fraction were less predominant compared with hydrocarbon compositions in small-sized fractions. These results indicate that hydrocarbons in large-sized fraction are not derived simply from the aggregates of small-sized suspended particles.

3.6. Hydrocarbon composition of the bottom sediment

Figure 6 shows the hydrocarbon composition of the bottom sediment (0–1 cm) at Stn. 3. The hydrocarbon composition was different from those of the sinking particles as well as suspended particles from the same location. The concentration of total hydrocarbons was determined to be $0.14\ \mu\text{g/g}$, which accounted for 0.0035% of total sedimentary organic carbon.

Hydrocarbons in the bottom sediment consisted mainly of n-alkanes with the bimodal distribution at maxima of $n\text{-C}_{17}$ or $n\text{-C}_{18}$ and $n\text{-C}_{31}$, accounting for more than 80% of the total hydrocarbon. The long-chain n-alkanes ($n\text{-C}_{24}\text{--}\text{C}_{32}$) in the sedimentary samples showed a high odd carbon predominance, which was different from long-chain n-alkanes of both the sinking particles and suspended particles. However, no predominance of odd carbons was found in the short-chain n-alkanes ($n\text{-C}_{15}\text{--}\text{C}_{23}$). Several isoprenoid hydrocarbons and $\text{br-C}_{25:3}'$ also occurred in the sedimentary sample, but they were only minor hydrocarbon components.

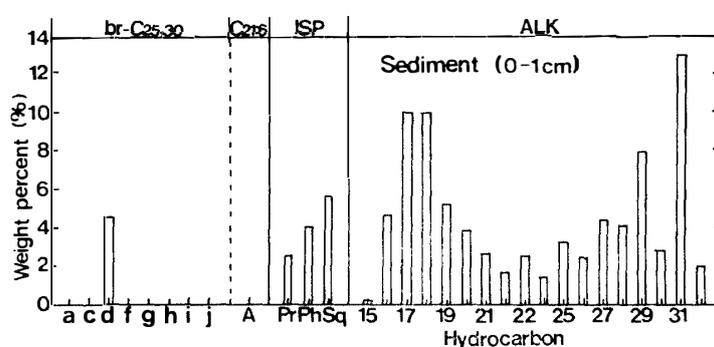


Fig. 6. Percent composition of hydrocarbons in ALK, $n\text{-C}_{21:6}$, ISP and $\text{br-C}_{25,30}$ in the bottom sediment from Stn. 3 of the Antarctic Ocean.

4. Discussion

4.1. Vertical flux of organic matter

Total organic carbon fluxes at Stn. 3 in the Antarctic Ocean were measured with the range from 15.8 to 51.8 mgC/(m²·day) through 630 to 3230 m depths. WEFER *et al.* (1982) reported that slightly lower values of the organic carbon flux ranging from 13.1 to 14.8 mgC/(m²·day) were found in the Antarctic Circumpolar Water. However, these values were among the highest values compared with those from world oceans compiled by SUESS (1980) and HANDA and TANOUE (1980).

Recently, several workers found that the seasonal fluctuation of vertical flux of organic matter into the deep sea is governed by the temporal change in the primary productivity in the euphotic layer (DEUSER and ROSS, 1980; DEUSER *et al.*, 1981; HONJO, 1982). High flux of organic carbon observed at Stn. 3 is most likely due to high primary productivity in the Antarctic Ocean (EL-SAYED, 1968; NIENHUIS, 1981), although the primary productivity is sometimes changing with time and space of the oceanic areas. During this BIOMASS cruise, a marked change in the standing stocks of particulate organic carbon and chl. *a* in the euphotic layer was observed for only five days in this study area. TANOUE and HANDA (1982) found a significant regional variability of the concentrations of surface particulate organic carbon in the Southern Ocean south of 40°S, and pointed out that their variability may coincide with a temporal change in the distribution of phytoplankton. Thus, it is most likely that high values of the vertical flux of organic matter to the deep sea found at Stn. 3 in the Antarctic Ocean are caused by high level of the primary productivity in the oceanic area, even if temporal and regional changes in the primary productivity occur in the area near Stn. 3 to a large extent.

4.2. Source materials of organic matter of the sinking particles

Hydrocarbons of the sinking particles, suspended particles and bottom sediment consisted of several types of saturated and unsaturated hydrocarbons, such as n-alkanes with carbon atoms ranging from 15 to 32 (ALK), heneicosahexaene (n-C_{21:6}), isoprenoid hydrocarbons (ISP), and branched C₂₅ (br-C₂₅). The distribution pattern of these alkanes and alkenes is characteristic to each of those samples (Fig. 7), which result in to give us the information on the source materials of organic matter of the sinking particles.

n-C_{21:6} was found in the suspended particles of the euphotic layer but not in those of the aphotic layer. SCHULTZ and QUINN (1977) and OSTERROHT *et al.* (1983) reported that concentration of n-C_{21:6} in the suspended particles of the surface waters was largely dependent on the abundance of diatoms. No report, however, has been available for n-C_{21:6} to occur in both zooplankton and marine bacteria (SALIOT, 1981). Thus, it can be concluded that n-C_{21:6} of the sinking particles was derived from diatoms growing in the euphotic layer.

Squalene and pristane were major isoprenoid hydrocarbons found in both the sinking particles and the suspended particles. Squalene was one of the most predominant hydrocarbons in the suspended particles from the euphotic layers and in the particles with the diameter of 0–20 and 20–100 μm. This hydrocarbon was found in diatom culture (VOLKMAN *et al.*, 1980) and in diatom population of the coastal waters (OSTERROHT and PETRICK, 1982; OSTERROHT *et al.*, 1983) together with n-C_{21:6}. Thus,

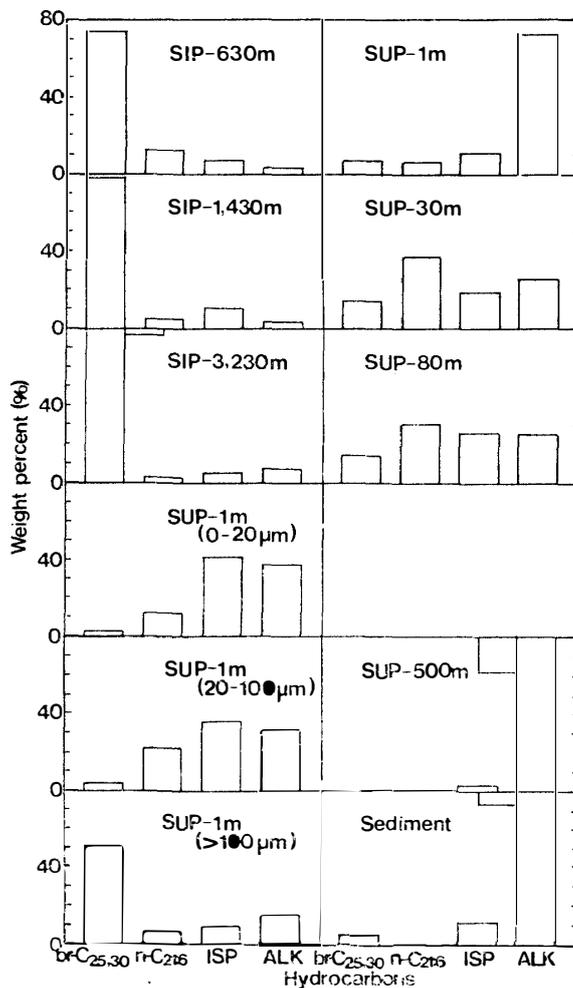


Fig. 7. Percent composition of *br-C*_{25,30}, *n-C*_{21,6}, *ISP* and *ALK* in the sinking particles (*SIP*), suspended particles (*SUP*) and bottom sediment from Stn. 3 in the Antarctic Ocean.

distribution of squalene in the suspended particles through the sinking particles supports the conclusion based on the *n-C*_{21,6} distribution that both of the suspended and sinking particles were mostly derived from diatoms.

Zooplankton is a primary source of pristane, which is derived from chlorophylls through its biochemical decay (AVIGAN and BLUMER, 1968). Pristane is distributed throughout the suspended and sinking particles as shown in Fig. 7. This indicates that suspended particles in the euphotic layers are contaminated by zooplankton fecal pellets to some extent. This is supported by the distribution of *br-C*₂₅ alkenes in the suspended particles of the euphotic layers, which occur characteristically in the zooplankton fecal pellets as will be stated later.

*br-C*₂₅ alkenes were extremely abundant in the sinking particles, while they were much less abundant in the suspended particles in the euphotic layers, and none in those of the aphotic layer. Suspended particles with $>100\ \mu\text{m}$ in particle diameter, however, showed abundance of *br-C*₂₅ alkenes, indicating that the particles of this size are more

likely the direct source of the sinking particles collected from the intermediate and deep waters.

br-C₂₅ alkenes have never been found in marine bacteria (ORO *et al.*, 1967; HAN *et al.*, 1968; HAN and CALVIN, 1969) and in airborne and riverborne particles to the ocean (BARRICK *et al.*, 1980), while a series of the alkenes were found widely to occur in the fecal pellets of zooplankton (PRAHL *et al.*, 1980; VOLKMAN *et al.*, 1983; MATSUEDA *et al.*, 1986). MATSUEDA *et al.* (1986) reported that these alkenes were a biological marker characteristic to the particulate matter excreted by zooplankton as a fecal pellet. Thus, these findings indicate that large particles with >100 μm diameter must be zooplankton fecal pellets and/or their debris, of which organic matter was derived from diatoms growing in the surface water layers through zooplankton grazing.

The sinking particles collected by the sediment trap experiment were fractionated into a series of the particles with different diameters by the wet sieving, and it was found that small-sized particles with 0–20 μm diameter consisting mostly of diatoms with some coccolithophores accounted for more than 85% of the total mass of the sinking particles. However, much less abundance of the debris of large-sized phytoplankton was found in this fraction by microscopic observation.

The small-sized particles which may be mostly disintegrated product of the large particles with >100 μm during the sieving, were distinctively characterized by lowering the proportions of n-C_{21:6}, isoprenoid hydrocarbons and n-alkanes, which were exclusively derived from zooplankton (MATSUEDA *et al.*, 1986).

Small-sized particles of 0–20 μm in diameter consisting mostly of diatoms with some coccolithophores were also found to occur abundantly in the suspended particles of the surface waters near the sediment trap site in the Antarctic Ocean and accounted for 32–95% of the total mass of the suspended particles (MATSUEDA and HANDA, in preparation). However, these small-sized particles were relatively rich in n-C_{21:6}, isoprenoid hydrocarbon and n-alkanes but very poor in br-C₂₅ alkenes.

Considering the distribution pattern of the hydrocarbons as well as the particle size and phytoplankton composition, grazing models of the suspended particles for the formation of the sinking particles near the sediment trap site of the Antarctic Ocean can be explained as follows; zooplankton excrete large size particles with a diameter of >100 μm by grazing small-sized particles with a diameter of 0–20 μm suspending in the euphotic zone. During the course of the grazing, the small-sized particles are infected with br-C₂₅ alkenes produced by zooplankton as observed in salp fecal pellets collected from the intermediate through deep waters in the eastern North Pacific (MATSUEDA *et al.*, 1986).

Consequently, results obtained in this work strongly suggest that br-C₂₅ alkenes are extremely important organic compounds to diagnose the particles which have been grazed by zooplankton in the marine environment and such diagnostic br-C₂₅ alkenes are retained even in the small-sized particles produced in the disintegration processes of the large particles by any mechanical causes. Thus, more works are needed to confirm br-C₂₅ alkenes as a biological marker for the particles grazed by zooplankton in the various marine environments.

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(Received June 21, 1985; Revised manuscript received September 10, 1985)