CHARACTERIZATION OF ORGANIC MATTER IN SEDIMENTS FROM GULF OF ALASKA, BERING SEA, AND BEAUFORT SEA

by

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

INDEX OF DATA SUBMITTED IN PREVIOUS ANNUAL REPORTS

April 1976

Tables:

1 Elemental Analysis of Eastern Bering Sea, Western Gulf of Alaska and Eastern Gulf of Alaska sediments

2. Characterization of sediment organic fractions determined by gravimetric analysis of extracts

3. Gas chromatographic data - high molecular weight hydrocarbons

4. Gas chromatographic data - low molecular weight hydrocarbons

Figures:

1. Locations of stations occupied during Legs III (EBBS) and Iv (GASS) Of NOAA Ship, DISCOVERER

2. Locations of stations during Leg IV (GASS) of NOAA Ship, DISCOVERER

3-10. Gas chromatographic traces of aliphatic fractions from GASS sediments

11. _n_-Alkane standard, gas chromatogram)

12. Low molecular weight hydrocarbon standard (gas chromatogram)

April 1977

Tables:

1. Elemental analysis of sediments from Eastern Bering Sea and Western Gulf of Alaska

2. Gravimetric analysis of hydrocarbons extracted from Eastern Bering Sea (EBBS) stations

3. Gravimetric analysis of hydrocarbons extracted from Western Gulf of Alaska (GASS) stations

4. Gravimetric analysis of benzene fractions of extracts after thin-layer chromatography

5. Gas chromatographic analysis of hexane fraction of hydrocarbons extracted from Eastern Bering Sea (EBBS) surface sediments

6. Gas chromatographic analysis of hexane fraction of hydrocarbons from Western Gulf of Alaska(GASS) surface sediments

Figures:

April 1978

Figures:

Tables:

3. Gravimetric data for 1977 samples

4. Aliphatic hydrocarbon concentrations in 1976 samples

5. Aliphatic hydrocarbon concentrations in 1977 samples

6. Characteristic parameters for Cook Inlet hydrocarbons

7. Major aromatic hydrocarbons from GC/MS data

April 1979

Tables:

1. Beaufort sea samples (1976 cruises)

2. Aliphatic hydrocarbon concentrations in Beaufort Sea sediment samples, 1976 curises

3. Characteristic parameters for Beaufort Sea hydrocarbons (1976 cruise)

4. Norton Sound sediment samples (1976 cruises)

5. Aliphatic hydrocarbon concentrations in Norton Sound sediment samples (1976 cruise)

6. Characteristic parameters for Norton Sound hydrocarbons (1976)

7. Norton sound sediment samples (1977 cruises)

8. Aliphatic hydrocarbon concentrations in Norton Sound sediment samples (1977 cruise)

9. Characteristic parameters for Norton Sound hydrocarbons (1977 cruise)

10. Kodiak shelf sediment samples (1976 cruises)

11. Aliphatic hydrocarbon concentrations in Kodiak Shelf sediment samples, 1976 cruise

12. Characteristic parameters for Kodiak Shelf hydrocarbons (1976 cruise)

13. Cook Inlet sediment samples (1978, Spring Cruise)

14. Aliphatic hydrocarbon concentrations in Cook Inlet sediment samples, Spring, 1978 Cruise

15. Characteristic parameters for Cook Inlet hydrocarbons (Spring, 1978)

16. Cook inlet sediment samples (1978 - Summer Cruise)

17. Aliphatic hydrocarbons concentrations in Cook Inlet samples (Summer, 1978)

Figures:

April 1980

Tables:

Figures:

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SPECIAL NOTE

This is the final report of our investigations of the high molecular weight hydrocarbons in the Alaskan continental shelf. Most of the data presented here also have been presented in our earlier annual reports. Because of refinements and revisions in the analytical procedures, numbers presented in the text, tables and figures of this final report may differ from and supersede those in the earlier versions.

SUMMARY

The distribution and concentration of high molecular weight hydrocarbons in surficial sediments from the outer continental shelf of Alaska were determined as part of an environmental survey. Sediments were collected from the proposed lease areas of Beaufort Sea, southeastern Bering Sea, Norton Sound, Navarin Basin, Gulf of Alaska, Kodiak Shelf and Cook Inlet. The objectives of the investigation were: 1) to establish the baseline hydrocarbon levels of sediment samples in the areas, 2) to characterize the distribution and nature of these hydrocarbons, 3) to assess the possible source of the hydrocarbons in surface sediments, whether biogenic or anthropogenic, and 4) to understand the probable pathways of hydrocarbon transport in the area in case of an oil spill. The sediment samples were analyzed for total carbon, organic carbon, aliphatic and aromatic hydrocarbon contents. Capillary gas chromatography and gas chromatography-mass spectrometry techniques were utilized to study the hydrocarbon components. Our extensive investigations indicate that the sediment in the study areas is generally unpolluted with a very few exceptions. Beaufort Sea sediments have the highest hydrocarbon budget while Kodiak Shelf sediments have the lowest. The characteristics of the aliphatic hydrocarbons are typical of a mixture of marine autochthonous and terrestrial allochthonous components. Norton Sound and Cook Inlet sediments contain the highest and Kodiak Shelf, the lowest levels of terrigenous input while the other areas shown intermediate trend. The distribution of polycyclic aromatic hydrocarbons (PAH) is complex and shows a pyrolytic source in all the study areas. Bioaccumulation of PAH is probably prevalent in Gulf of Alaska and Kodiak Shelf areas.

Two stations, north of Kalgin Island, in lower Cook Inlet and one station in southeastern Bering Sea show typical weathered petroleum distribution of

n-alkanes and triterpenoids. The hydrocarbons distribution pattern in the sediments suggest that petroleum hydrocarbons released from any major spill, tank or pipeline blowout in upper Cook Inlet would be dispersed and redeposited eventually in Shelikof Strait and possibly in Gulf of Alaska, west of Kodiak Shelf. The distribution profile of especially n-alkanes and perylene in Navarin Basin would indicate that any petroleum contaminant from production activities in Norton Sound or southeastern Bering Sea could affect Navarin Basin equally or more than the other two areas.

Presence in large amounts of the relatively labile polyolefins in a few stations in southeastern Bering Sea and Gulf of Alaska, and, in all the stations in Kodiak Shelf and Navarin Basin implies relatively less oxidizing depositional environment. Such areas where sediments apparently accumulate and preserve labile lipids would be most affected by pollutants introduced into the marine environment.

The above-mentioned sensitive areas should therefore be the main target of any future environmental monitoring program whenever fossil fuel developments are carried out in the vicinity.

INTRODUCTION

General Nature and Scope of Study

This final report describes the progress made during the period July 1975 through December 1980 in a study of the abundance and dynamics of hydrocarbons in the surface sediments from the Alaskan continental shelf. A knowledge of the baseline levels of classes of hydrocarbons and specific hydrocarbon pollution indicators in the marine sediments is very important in order to assess any environmental impact by petroleum development on the outer continental shelf.

The first year cruise experience (1975-1976), emphasized the importance of proper sampling devices and the methods of collection. The objectives of the 1976-1977 studies were to develop a set of experimental conditions that would yield reproducible results in the trace analysis so that it could be used on a routine basis for several samples. After this goal was reached, the samples were analyzed and the hydrocarbons were quantitatively estimated in the sediments from different parts of the Alaskan area.

From 1977 to 1979, the emphasis was diverted to the Lower Cook Inlet area and several cruises were conducted to collect sediment samples in view of the oil development in Upper Cook Inlet.

The objectives of the 1979-1980 programs were to provide more information on the sediments from Norton Sound and Navarin Basin.

Specific Objectives

The objectives of this investigation were to achieve the following results:

1. To establish the baseline hydrocarbon levels in the sediments from the proposed lease areas in the Alaskan continental shelf by measuring aliphatic and aromatic hydrocarbons.

2. To characterize the distribution and nature of these hydrocarbons.

3. To assess the possible source of the hydrocarbons, in surface sediments; whether biogenic or anthropogenic.

4. To understand the probable pathways of hydrocarbon transport in the event of oil spill in the areas.

Relevance to Problems of Petroleum Development

Sediment samples were collected from proposed lease areas in the Alaskan Seas. Oil production and transport is well established in Beaufort Sea and it had started in upper Cook Inlet. Exploratory drilling has been performed on six out of 87 blocks leased in lower Cook Inlet from October, 1977. The second part of the sale in lower Cook Inlet, with Shelikof Strait, is scheduled for September, 1981 (Wright, 1980). Information on the present level of hydrocarbons in these areas is required to assess, in the future, any chronic pollution arising from offshore drilling for oil and gas, or any residual effect resulting from an accidental spill or blow-out. The baseline data should therefore be helpful in monitoring the cleanliness of the future Alaskan marine environment.

Current State of Knowledge

Studies on the Alaskan Seas are relatively scant to date. Hydrocarbons and their possible precursors were investigated in the few samples in Beaufort Sea by Peake _et al_. (1972). Aliphatic and aromatic hydrocarbons have been analyzed by Shaw _et al_. (1979) in Beaufort Sea nearshore sediments. Aromatic hydrocarbons in fish and sediment in Prince William Sound, northeast Gulf of Alaska, have also been reported (Chester _et al_., 1976). An extensive and informative study on hydrocarbons in sediments, water, organisms and fish in Beaufort Sea, along the Canadian border, was published by Wong _et al_. (1976).

Studies undertaken by our group on organic constituents of sediments from different parts of the Alaskan Seas are probably the most extensive investigations of hydrocarbons in this area as far as we know. Our data from analyses of sediments from the study area indicate that the Alaskan continental shelf is generally unpolluted except in a very few stations.

STUDY AREA AND CRUISES

We have analyzed samples from all regions of interest to NOAA/OCSEAP: the Beaufort Sea, the Bering Sea, the Gulf of Alaska, Kodiak Shelf, Norton Sound, Cook Inlet and Navarin Basin. The details of when, where and how samples were collected are specified in Table 1. Station locations are presented in Figures 1-8.

METHODS

Sediment samples were kept frozen from the time of collection until the beginning of anlaysis.

Elemental Analysis*

Elemental sulfur analysis was carried out on freeze-dried sediment samples. Twenty to forty milligrams of the powdered sample was combusted with the accelerator (Cu chips and Fe filings) in a LECO (Laboratory Equipment Corporation) induction furnace (Model No. 523). The resulting sulfur gases were titrated according to ASTM procedure E30-47, using a LECO (Model No. 517) titrator. The total sulfur content was corrected for sea salt sulfate content. Total carbon and organic carbon (that remaining after treatment with 3N HCl) were measured with a LECO acid-base semi-automate carbon determinator or on a LECO No. 589-600 Low Carbon Analyzer.

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* The details of the procedures are given in the respective manuals of LECO, 3000 Lakeview Avenue, St. Joseph, Michigan 49085

Analysis of High Molecular Weight Hydrocarbons

Initially, a methodology recommended by BLM was followed to analyze the sediment samples from the eastern Bering Sea and Gulf of Alaska. These samples had to be cleaned by thin-layer chromatography to remove the methyl esters from aromatic compounds eluted by benzene (Kaplan et al., 1977). This methodology was Improved subsequently to avoid contamination from freeze drying and to obtain ester-free aromatic hydrocarbons. Freeze-drying was replaced by wet extraction with methanol. Based upon a suggestion by R. Bieri (Virginia Institute of Marine Science), only silica gel was used instead of the original silica gel--alumina column chromatography. The solvent mixture, hexane: benzene (3:2 V/V} was found to elute only the aromatic hydrocarbons, leaving behind the esters in the column. The following methodology incorporating these modifications was adopted for all the samples in our program except for the above-mentioned two areas.

A pre-cleaned cellulose thimble of known weight was filled to approximately 2/3 of its capacity with a thawed sediment sample and placed in a beaker-like funnel. The interstitial water was allowed to drain into an Erlenmeyer flask. The sediment was then washed with about 150 ml of organically clean double-distilled water to remove salts. The filtrate and the interstitial water was extracted three times with" 25 ml of hexane and saved for later analysis (A).

The wet sample in the thimble was extracted in a Soxhlet extractor with 500 ml of methanol for 24 hours and then with 500 ml of toluene:methanol (3:7) for 76 hours. The methanol extract was concentrated to 100 ml, added to a separatory funnel with clean water and extracted with 100 ml of hexane three times (B). If an emulsion formed, saturated NaCl solution was added before extracting into hexane. The hexane fractions (A and B) were combined with the toluene: methanol extract and concentrated to about 5 ml.

Activated copper wire was dipped into the extract to test for sulfur. If a blackening of the wire was observed, the sulfur was removed by passing the extract through a column of activated fine copper granules (J.T. Baker). The eluate was concentrated to 5 ml and saponified by refluxing for four hours with 40 ml of IN KOH in 1:1 water:methanol. A 5Å molecular sieve trap on top of the condenser prevented contamination from external sources. The mixture was then diluted with an equal volume of saturated sodium chloride solution. If no emulsion was observed, the mixture was extracted three or four times with hexane and concentrated with a rotary evaporator. If an emulsion did occur, the extract was centrifuged three times with hexane in a glass jar with a teflon-lined cap. The organic phases were combined and back-extracted with an equal volume of saturated sodium chloride solution. The aqueous solution was then re-extracted once with hexane and all the organic phases combined and concentrated to 2 ml. This non-saponifiable fraction was transferred to a 2 ml vial using a glass syringe and the solvent was removed on a sand bath at 40”C under a stream of nitrogen. A subsample of about 5 µℓ was transferred onto the pan of a Mettler ME22 electrobalance and the residue after evaporation of the solvent was weighed. The weight was extrapolated to the total volume of the fraction.

Pre-cleaned silica gel was activated at 235*C for 16 hours and packed with hexane in a column with a length-to-id. ratio of 20. A weight ratio of 200 parts of silica gel to one part of the sample was used. Aliphatic hydrocarbons were eluted with ∿ 1 column volume of hexane, after the void volume was discarded. Alkenes containing less than four double bonds were also eluted by hexane. Aromatic hydrocarbons were eluted with ∿ two column volumes of 3:2 hexane:benzene mixture. Highly unsaturated alkenes and cycloalkenes eluted along with 2- to 7-ring aromatic hydrocarbons. The fractions were reduced to 100-150 µℓ and weighed on the Mettler as before, prior to gas chromatography.

The amount of hexane extractable lipids (nonsaponifiable) determined the size of column used in column chromatography. The conditions of column operations as standardized in our laboratory are given in the following table:

Total mg Non-saponifiable lipid	Column Internal Diameter	Silica gel for column (9)	Height of silica column (cm)	Hexane		Hexane:Benzene 3:2	
				Reject volume (ml)	Elution volume (ml)	Reject volume (ml)	Elution volume (ml)
0 - 12.5	0.7	∿2.5	14	1.5	8	2	12
12.5- 35	1.0	∿7	17.5	5.0	15	7	25
35 - 130	1.5	∿ 26	30	20	50	25	100
130 - 230	1.9	∿ 46	38	35	90	45	175

> 230: Use percentage of sample adequate to run in the column with ID 1 cm or 1.5 cm

Materials

1. Solvents

All solvents used were high purity grade solvents (Burdick and Jackson "distilled in glass" grade). The chemicals were of A.R. grade.

2. Water

Trace organics were removed from double-distilled water by passing it through a column of Chromosorb 102, which was prewashed with dichloromethane.

3. Soxhlet Thimbles

Single thickness cellulose (Whatman) thimbles were shaken three times overnight with toluene:methanol 3:7 in glass jars on a shaker table.

4. Glassware

All glassware was cleaned with detergent, dipped in chromic-sulfuric acid solution, and rinsed successively with distilled water and methanol and dried at 110°C. Before use, the glassware was rinsed with dichloromethane as well as the solvent to be used in extraction. Syringes were sonicated three times in dichloromethane and then rinsed once with the same solvent.

5. Silica Gel

Silica gel was first sonicated with dichloromethane-methanol and then with hexane prior to activation.

6. Sodium Chloride

NaCl was heated overnight at 500°C.

7. Potassium Hydroxide

KOH was fued at 500°C for two hours in a nickel crucible.

8. Copper Granules

Copper granules were cleaned successively with 6N HCl, acetone and hexane.

Samples collected in 1975 were analyzed by Hewlett-Packard Model No. 5830A gas chromatography with FID detector. A glass SCOT column, 50m x 0.5mm, coated with OV-101 (SGE Scientific, Inc.) was used. The aliphatic fractions and aromatic fractions of Cook Inlet sediment samples studied in 1977 were analyzed by modified Varian 1400 and 1520C gas chromatography, respectively. They were equipped with a Grob injector and glass capillary columns (OV-101, J&W). The remainder of the samples in the program were analyzed by Hewlett-Packard Model No. 5840A gas chromatgraph equipped with 30m x 0.25 mm glass capillary column coated with OV-101 (J&W). Navarin Basin (1980) samples were analyzed in the same instrument, but with a fused silica capillary column (SP 2100, 25 m x 0.2 mm). Helium was used as a carrier gas. A detailed methodology concerning samples of a particular cruise is given in the annual reports (Kaplan _et al._, 1977, 1979, 1980; Brenner _et al._, 1978).

The integrated areas were fed into a PDP 11/10 computer and the concentrations of individual hydrocarbons on dry weight sediment basis were computed.

Gas chromatographic-mass spectrometric analyses (GC/MS) were carried out on a Finnigan model 4000 Quadruple Mass Spectrometer directly interfaced with a Finnigan Model 9610 gas chromatography. The GC was equipped with a glass capillary

(OV-101 J&W) for the analyses of aliphatic fractions. The aromatic fractions were analyzed using a SE 54 (J&W) glass capillary column. The GC/MS analyses of Navarin Basin samples were performed with a fused silica capillary column as described for gas chromatography. The mass spectrometric data were acquired and processed using a Finnigan Incos Model 2300 data system. About 25% of all the fractions separated by column chromatography (10-15% of the number of sediment samples studied in the program) were analyzed by GC/MS.

Data of all the samples were submitted on 044 format to the Data Center at Washington, D.C. Due to the complexity of distribution of numerous isomers, the identification of an aromatic component by GC/MS in one sediment sample cannot be extrapolated to a peak with the same Kovats index in another sample. It is not possible to run all the fractions (over 200) in GC/MS either. For the above reasons, concentrations of the aromatic hydrocarbon components were computed only for those samples run by GC/MS and reported on the coding sheets. The discussion on individual aromatic compounds is therefore restricted to GC/MS data only in this report.

RESULTS

Elemental analysis (total and organic carbon), complete gravimetric and gas chromatographic data have been submitted in earlier quarterly and annual reports for all the sediments analyzed in the program. We present here only a summary of selected organic geochemical data for each area studied in tables from 2 through 13. Data on polycyclic aromatic hydrocarbons presented in tables 11-13 refer to the resolved PAH compounds identified by GC/MS and quantitated by external standards. The total resolved PAH discussed in the text of this report refer to the sum of only those PAH compounds listed in the tables. Table 14 contains the comparative organic geochemical data from different areas in the Alaskan Shelf. Figures 1-8 show the station locations at different cruises. Gas chromatograms of hexane and hexane:benzene fractions of representative samples from various areas are presented in Figures 9 through 14. The relative distribution of extended di- and triterpenoids of sediments from a few stations are represented in figures 15-18 based upon the m/z 191 peak intensity from GC/MS analyses. Pertinent analytical results from sediments of different areas are summarized in Figure 19 for comparison. Appendix I shows the structures cited in the text. A detailed discussion on the organic geochemistry of Navarin Basin sediments is presented in this report since the samples were collected and analyzed after the submission of our last annual report in April, 1980.

Table 1. Areas of sediment sampling for heavy molecular weight hydrocarbon study from the Alaskan Shelf

Area	Date of Collection	Cruise	Sampler type	No. of samples analyzed
Southeastern Bering Sea	9/75	Discoverer	Steel Van Veen grab sampler	21
Gulf of Alaska	10/75			20
Beaufort Sea	8/76	USCGS Glacier	Aluminum Van Veen	11
Norton Sound	10/76	Sea Sounder	Modified Aluminum Van Veen sampler	18
	7/77			12[1]
	7/79	Discoverer		21
Kodiak Shelf	7/76	Sea Sounder	Van Veen sampler	15
Cook Inlet	6/76	Sea Sounder	Van Veen sampler	23
	11/77	Surveyor	Van Veen sampler	92
	4/78	Discoverer	Van Veen sampler	18
	8/78	Discoverer	Van Veen sampler	17
	5/79	Discoverer, Miss Vicki Ann (Charter boat)	Van Veen Sampler Shipek grab sampler, mud snapping, sampling device	14
Navarin Basin	4/80	USCGS Polar Star	Modified Van Veen, small Van Veen	28[3]

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[1] Four samples were collected from vibracores and box cores by Dr. K. Kvenvolden's group, USGS, California.

[2] Collected by Ms. J.W. Wiggs of University of Alaska.

[3] Collected by J. Haines of the University of Louisville, KY.

Table 2. Gravimetric and gas chromatographic data of Beaufort Sea sediment samples (1976 cruise)

Station Number*	Aliphatic Fraction[a] (µg/g)	Aromatic Fraction[a] (µg/g)	*n*-Alkanes (µg/g)[a]	Org. C (%)	$\frac{HC}{OC}\times 10^4$ [b]	$\frac{n\text{-Alkanes}}{OC}\times 10^4$ [c]	Pr/Ph	$\frac{Odd}{Even}$ [d]
1	14.31	9.42	2.99	0.89	26.7	3.41	1.60	3.37
2	24.88	15.49	1.44	0.74	54.6	2.03	1.32	4.29
3	41.02	18.7	3.36	0.91	65.6	3.69	1.82	1.78
4	36.30	14.11	3.12	0.63	80.0	4.43	2.04	3.37
5	28.43	13.99	3.21	0.83	51.1	3.91	2.11	3.58
6	19.87	12.56	4.63	1.01	32.1	4.91	1.82	3.57
7	12.83	8.46	2.09	0.79	27.0	2.88	2.55	3.25
8	16.46	12.65	4.17	0.39	74.6	10.88	2.50	3.83
9	23.73	9.40	3.73	0.68	48.7	5.53	1.73	3.53
10	34.53	14.59	5.08	0.63	78.0	8.17	1.89	3.91
11	22.44	12.15	1.84	0.51	67.8	3.67	1.67	5.00

* All are surface samples except 11 which is a bulk sample. Elementary sulfur was detected only in Sample 11.

a = Based on extracted dry sediment.

b = HC = total hydrocarbons, sum of aliphatic and aromatic fractions in µg/g dry sediment; OC = organic carbon

c = *n*-alkanes resolved by gas chromatography

d = odd/even = summed from C_{15} to C_{34}.

Pr = Pristane; Ph = Phytane

Table 3. Gravimetric and gas chromatographic data of Southeastern Bering Sea Sediment Samples

Station Number*	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	n-Alkanes (μg/g)[a]	Organic carbon (%)	$\frac{HC}{OC}$x10^4[b]	$\frac{n\text{-alkanes}}{OC}$x10^4[c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$[d]
8	5.7	2.8	0.56	0.23	36.9	2.4	2.70	2.99
12	3.4	1.4	0.33	0.14	34.3	2.3	3.32	1.76
17	13.0	5.2	1.09	0.76	23.9	1.4	3.97	3.43
19	7.4	4.5	2.57	0.39	30.5	6.6	5.81	3.17
24	6.1	5.4	0.66	0.33	34.8	2.0	3.39	2.96
28	8.7	4.1	2.93	0.59	21.7	5.0	10.20	4.09
35	180.1	60.8	n.r.	0.41	587.6	n.r.	n.r.	n.r.
37	5.8	4.0	0.76	0.41	23.9	1.8	1.76	3.28
38	4.9	10.6	1.64	0.66	23.5	2.5	5.18	4.41
40	1.9	2.6	0.61	0,32	14.1	1.9	3.37	3.41
41	1.4	0.5	0.41	0.37	5.1	1.1	n.d.	3.80
43	2.4	2.7	0.52	0.30	17.0	1.8	2.26	3.08
46	4.3	7.5	0.74	0.42	28.1	1.8	17.90	3.59
51	2.8	0.6	0.77	n.d.	25.4	n.d.	3.49	2.56
54	7.4	9.9	2.10	0.68	25.4	3.1	8.80	2.57
56	10.6	8.5	0.75	0.47	40.6	1.6	2.93	3.78
58	3.8	2.8	0.28	0.31	21.3	0.9	4.80	3.33
59	6.4	6.2	1.55	0.27	46.7	5.7	1.74	2.85
64	12.3	9.8	1.79	0.77	28.7	2.3	2.27	2.75
65	6.9	9.6	1.60	0.67	24.6	2.3	16.43	3.77
45B	3.9	4.9	0.78	0.76	11.6	1.0	3.78	1.96

*=Bulk samples of the upper 0-10 cm of surface sediment

n.r. = not resolved
n.d. = not determined

For explanation of the remainder of the symbols and abbreviations, see Table 2.

Table 4 . Gravimetric and gas chromatographic data of Norton Sound sediment samples

Station No.[s]	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	n-alkanes (μg/g)[a]	Organic carbon (%)	$\frac{HC}{OC} \times 10^4$[b]	$\frac{n\text{-alkanes} \times 10^4}{C}$[c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$[d]
1976								
47	9.6	7.5	3.28	0.93	13.4	3.7	2.00**	5.39
49	24.8	4.1	5.69	1.12	25.8	5.1	1.50**	6.06
70	2.2	6.2	0.01	0.31	27.1	0.1	8.00	1.65
88B	3.9	5.7	0.69	0.53	18.2	1.3	2.14	4.11
105	1.8	0.9	0.07	0.93	2.9	0.1	n.d.	11.21
125	0.1	2.4	0.69	1.18	2.6	1.3	2.00	4.02
131	9.0	2.9	7.18	0.96	27.3	6.3	n.d.	2.80
137	17.8	4.5	8.69	n.d.	n.d.	n.d.	3.00**	4.07
147	6.8	2.3	2.24	0.33	27.5	6.8	1.80**	2.85
154	16.3	4.2	5.45	0.99	20.7	5.5	3.60**	5.69
156	7.1	5.5	5.06	1.30	9.7	3.9	2.67**	5.57
162	2.3	2.3	0.45	0.92	5.0	0.5	2.00**	4.75
166s	1.1	0.8	0.16	1.16	1.6	0.1	4.00**	5.16
168S	3.2	2.2	1.48	1.10	4.9	1.4	3.50**	5.26
169S	2.6	4.0	0.95	0.33	20.1	2.9	3.60	4.47
170s	4.4	2.2	2.57	0.52	12.8	4.9	n.d.	5.80
172S	10.9	3.8	2.89	0.87	16.9	3.3	n.d.	4.70
174s	3.9	2.0	1.79	0.82	7.2	2.2	6.00**	4.50
1977								
34	0.8	0.7	0.09	0.12	12.4	0.8	2.0**	4.55
35	2.2	1.1	0.57	0.59	5.7	0.9	7.0**	5.15
39S	0.6	0.2	0.09	0.38	2.3	0.2	2.5**	5.35
41s	2.5	0.8	0.23	0.44	7.5	0.5	4.0**	4.78
42S	4.4	1.9	0.83	0.32	19.9	2.6	5.5**	4.78
43	1.0	1.7	0.38	0.60	4.5	0.6	6.5**	4.22
44	2.1	0.9	0.25	0.52	5.7	0.5	6.0**	3.21
48S	5.8	5.0	1.60	4.23	2.6	0.4	5.0**	6.37
14¶	5.4	1.3	1.22	0.28	23.8	4.4	3.1**	5.26
17¶	5.5	2.7	1.75	0.24	18,9	2.0	1.3**	5.12
17+	14.1	2.2	2.18	0.86	26.3	6.4	3.0**	5.67
17§	3.2	0.9	0.95	0.50	8.0	1.9	4.0**	5.34

Table 4 . Gravimetric and gas chromatographic data of Norton Sound sediment samples (continued)

Station No.	Aliphatic fraction (µg/g)	Aromatic fraction (µg/g)	n-Alkanes (µg/g)	Organic carbon (%)	$\frac{HC}{OC} \times 10^4$	$\frac{\text{n-alkanes}}{\text{Oc}}$	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$
1979								
1	4.7	3.3	3.54	0.72	11.1	4.9	0.75	3.37
1††	17.6	3.8	4.29	--	--	--	--	2.76
5	17.8	8.8	5,53	0.74	35.9	7.7	--	3.91
5§§	20.1	4.1	6.41	--	--	--	2.82	3.89
7	9.7	6.1	4.32	0.57	27.7	7.6	--	3.80
8	1.6	1.5	0.59	0.46	6.7	12.9	1.71	3.27
13	4.5	5.1	2.08	0.38	25.2	5.5	1.65	4.32
15	4.0	1.8	1.63	0.48	11.9	3.4	2.47	3.81
18	3.2	1.5	2.22	0.48	9.8	4.6	1.86	4.04
20	5.4	1.5	1.50	0.40	17.3	3.8	--	4.03
21	9.1	5.1	2.85	0,47	30.2	6.1	--	4.40
22	8.9	5.5	2.83	0.86	16.8	3.3	2.44	3.35
25	5.2	2.0	1.57	0.66	10.8	2.4	--	4.12
29A	2.8	1.0	1.38	0.41	9.3	3.4	1.50	4.33
29B	3.9	lost	1.34	0.54	--	2.5	--	3.56
33A	1.7	0.9	0.29	--	--	--	--	4.09
36	8.7	1.7	1.74	--	--	--	--	3.97
40	2.3	0.1	0.06	0.17	14.1	0.4	--	5.27
47A	1.4	1.1	0.44	--	--	--	--	4.29
49	2.5	3.0	0.61	--	--	--	8.88	4.18
50	1.7	1.9	0.25	0.28	12.9	0.9	--	3.87

Samples are 0-2 cm except B = bulk; S = surface; ¶ = 0-3 cm; † = vibracore, 0-3 cm; § = 160 cm vibracore, (USGS): †† = 15-25 cm; §§ = 82-90 cm; Samples 14-17 belong to a different program (USGS). ** Approximate values based upon peak heights. For explanation of remainder of symbols and abbreviations, see Table 2.

Table 5 . Gravimetric and gas chromatographic data of Navarin Basin sediment samples (1980 cruise)

Station Number*	Aliphatic Fraction (μg/g)[a]	Aromatic Fraction (μg/g)[a]	n-Alkanes (μg/g)[a]	Organic C (%)	$\frac{HC}{OC}$ x 10^4[b]	$\frac{\text{n-Alkanes}}{OC}$ x10^4[c]	$\frac{\text{Odd}}{\text{Even}}$[d]
2	8.13	2.24	0.27	0.49	21.2	0.57	3.99
3	1.37	1.74	0.32	0.89	3.5	0.37	4.88
4	1.93	2.49	0.30	0.36	12.3	0.84	4.88
5	2.25	2.93	0.42	0.43	12.0	1.00	4.77
6	4.86	3.75	0.52	0.59	14.6	0.89	4.75
7	7.16	9.18	1.45	1.04	15.7	1.40	4.85
8	15.38	7.31	1.93	--	--	--	4.88
9	11.51	4.78	1.52	0.90	18.1	1.70	4.74
10	4.82	8.21	1.63	1.08	12.1	1.52	4.84
12	18.02	8.67	1.28	0.96	27.8	1.34	4.10
13	1.83	2.83	0.52	0.68	6.9	0.77	4.27
14	8.94	11.93	1.98	1.20	17.4	1.65	4.10
15	8.33	6.81	1.98	1.18	12.8	1.68	3.55
16	21.83	7.20	1.60	1.02	28.5	1.58	3.75
17	6.01	10.65	1.30	1.15	14.5	1.14	4.26
18	47.50	4.97	1.60	1.18	44.5	1.36	3.72
19	7.55	9.17	1.37	0.98	17.1	1.41	4.00
20	34.66	10.40	1.83	--	--	--	4.15
21	12.32	16.50	2.63	1.07	26.9	2.46	4.38
22	8.03	9.25	1.39	1.08	16.0	1.29	4.07
23	8.68	5.58	1.46	0.85	16.8	1.73	4.6o
24	29.63	14.82	1.86	1.12	39.7	1.67	4.18
25	1.95	2.73	0.24	1.38	3.4	0.18	3.67
26	1.63	0.78	0.48	0.27	8.9	1.81	4.29
28	4.41	6.23	0.77	0.42	25.3	1.8s	4.45
30	4.04	1.14	0.20	0.19	27.3	1.07	3.55
32	7.56	2.13	0.28	0.20	48.5	1.41	4.42
33	7.07	1.36	0.42	0.32	26.3	1.31	4.08

---

*Samples 2-10 are from 0-2 cm taken with modified Van Veen grab sampler; 12-33 are predominantly surface, but taken with a small Van Veen sampler.

For explanation of remainder of symbols and abbreviations, see Table 2.

Table 6. Aliphatic Hydrocarbon Concentrations (rig/g) in 1980 Navarin Basin Sediment Samples

Station[†]	$\underline{n}$-C_{17}	Pristane	$\underline{n}$-C_{18}	$\underline{n}$-C_{19}	$\underline{n}$-C_{20}	$\underline{n}$-C_{21}	$\underline{n}$-C_{22}	$\underline{n}$-C_{23}	$\underline{n}$-C_{24}	$\underline{n}$-C_{25}
2					2	9	8	24	11	35
3		1	1	2	2	22	8	25	12	38
4				1	2	15	8	23	11	34
5	1	2	1	3	4	36	12	32	16	45
6	2	4	2	4	5	35	14	41	20	59
7	4	6	4	8	11	116	36	111	53	167
8		3	2	9	12	145	48	150	70	222
9	4	11	3	7	10	104	40	124	58	180
10	3	9	3	10	11	76	43	133	61	194
12				6	9	37	34	110	49	156
13	1		2	4	5	10	15	45	21	64
14			3	9	15	55	54	168	75	238
15	4		5	13	19	51	63	191	86	268
16				9	13	31	46	142	61	195
17	2		3	7	11	16	39	121	56	172
18				9	14	32	51	160	66	209
19			2	7	10	39	37	113	52	161
20				7	12	51	47	153	66	221
21			3	11	16	53	71	220	104	324
22	3	4	3	6	9	36	35	109	51	161
23	4	4	4	11	12	79	39	120	58	180
24				9	12	47	44	144	66	222
25		3		3	4	19	13	36	15	41
26			1	2	4	17	17	52	23	69
28	2		2	5	7	25	23	70	30	98
30	2		2	2	3	8	8	21	9	25
32					2	9	10	30	12	39
33				3	4	14	13	41	17	54

t = Samples 2-10 are from O-2 cm taken with the modified Van Veen grab sampler. 12-33 are predominantly surface but taken with a small Van Veen sampler. $\underline{n}$-C_{15} was detected only in samples 9 and 23 at the level of 2 rig/g; $\underline{n}$-C_{16} was detected only in samples 9, 23 and 30 at the level of 2 rig/g; Phytane was not detected in any of the samples.

Table 6. (Continued)

Station$^+$	n-C$_{26}$	n-C$_{27}$	n-C$_{28}$	n-C$_{29}$	n-C$_{30}$	n-C$_{31}$	n-C$_{32}$	n-C$_{33}$	n-C$_{34}$	Total n-Alkanes
2	11	61	8	44	14	40	2	11		279
3	13	66	10	50	5	55	4	16	1	328
4	12	60	10	55	5	50	3	15		304
5	15	79	11	70	7	67	5	22		428
6	20	106	15	82	8	79	5	26		525
7	56	291	41	226	22	211	14	71		1454
8	75	393	57	311	33	290	18	92	4	1931
9	61	318	45	240	25	219	13	65	3	1528
10	64	343	48	272	27	246	14	76	4	1637
12	51	270	35	214	54	179	9	59		1282
13	21	107	17	90	9	79	5	25		524
14	79	410	59	330	75	292	17	92	4	1985
15	90	466	79	431	50	395	25	125	5	1984
16	63	330	44	260	77	232	17	70		1607
17	57	286	40	217	29	183	11	56	3	1308
18	66	329	42	240	74	214	10	71		1603
19	55	282	42	230	55	206	12	65	3	1377
20	76	382	53	299	72	275	15	93		1838
21	113	563	84	437	51	408	26	130	6	2635
22	55	286	42	239	58	216	13	67	3	1398
23	63	316	48	255	29	239				1467
24	77	389	56	315	68	287	21	93		1865
25	12	49	6	26	13	18		4		248
26	21	103	13	74	7	62	4	18	1	489
28	31	168	22	127	17	106	6	33	1	776
30	8	38	5	28	6	26		8		204
32	13	62	8	43	8	38		9		282
33	17	87	11	63	15	58	3	18		420

Table 7. Gravimetric and gas chromatographic data of Western Gulf of Alaska sediment samples (1975 cruise)

Station Number *	Aliphatic fraction (μg/g)[a]	Aromatic fraction (μg/g)[a]	n-Alkanes (μg/g)[a]	Organic C (%)	$\frac{HC}{OC} \times 10^4$ [b]	$\frac{n\text{-Alkanes}}{OC} \times 10^4$ [c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$ [d]
101	1.1	0.4	0.06	0.18	8.3	0.3	1.81	1.28
102	2.2	0.9	0.16	0.18	17.2	0.9	1.38	1.03
103	3.2	4.0	0.17	0.53	13.6	0.3	5.00	1.61
104	17.8	5.6	1.48	0.39	60.0	3.8	1.04	1.31
105	3.8	6.7	0.34	0.76	13.8	0.5	5.48	1.13
119	14.3	5.8	0.85	0.74	27.2	1.2	4.56	1.24
120	12.5	6.5	1.27	0,13	146.2	9.7	6.86	2.52
121	13.2	13.5	2.00	0.18	148.3	11.1	6.04	2.23
124	11.9	6.4	1.0	0.92	19.9	1.1	4.52	1.97
133	2.0	1.3	0.30	0.35	9.4	0.9	3.54	2.02
134	4.3	15.3	0.97	1.09	17.9	0.9	6.17	2.41
137	1.7	1.6	0.28	0.34	9.7	0.8	1.86	1.68
160	1.5	0.5	0.20	0.31	6.4	0.6	3.94	2.00

* All are bulk samples of the upper 0-10 cm of surface sediment.

For explanation of the remainder of the symbols and abbreviations, see Table 2.

Table 9. Gravimetric and gas chromatographic data of Kodiak Shelf sediment samples (1976 cruise).

Station Number *	Aliphatic fraction (µg/g)[a]	Aromatic fraction (µg/g)[a]	n-Alkanes (µg/g)[a]	Organic C (%)	$\frac{HC}{OC} \times 10^{4}$ [b]	$\frac{\text{n-Alkanes}}{OC} \times 10^{4}$ [c]	$\frac{Pr}{Ph}$	$\frac{Odd}{Even}$ [d]
52	1.20	2.15	0.08	0.34	9.9	0.24	2.3	1.9
57	1.44	1.42	0.04	0.36	7.9	0.14	2.4	1.9
60	2.15	2.84	0.26	0.31	16.1	0.77	6.1	1.7
68	2.29	1.43	0.12	0.60	6.2	0.20	10.4	1.7
72	1.57	0.89	0.67	0.23	10,7	2.89	3.0**	3.8
75	2.06	0.36	0.03	0.33	7.3	0.08	12.2	0.8
80	0.51	0.47	0.01	0.35	2.8	0.03	6.2	2.1
80′	0.69	0.58	0.03	0.35	3.7	0.09	17.7	1.8
81	2.65	2.86	0.34	0.50	11.0	0.74	10.8	2.1
87	0.79	1.53	0.02	0.45	5.2	0.04	4.5**	2.6
92	5.13	6.64	0.84	1.17	10.1	0.71	6.4	1.3
93	1.87	2.27	0.27	1.01	4.1	0.27	2.8**	2.6
97	4.21	5.16	0.42	2.45	3.8	0.21	4.0	1.3
98	7.79	10.88	0.20	2.15	8.7	0.09	6,0	2.8
130	1.87	2.97	0.20	0.91	5.3	0.24	4.4	1.5

* Samples are 0-2 cm except 80′, which is 2-4 cm; elemental sulfur detected only in sample 92.

** Approximate values based upon measured peak heights.

For explanation of remainder of symbols and abbreviations, see Table 2.

Table 10 continued

UC100	150	0.99	0.75	0.05	1.9	2.6	0.2
UC200	150	1.24	1.35	0.10	1.9	8.3	0.3
UC300	101	4.55	5.16	1.11	2.9	5.3	1.6
CB8	---	13.08	7.24	1.38	4.6	1.6	1.5
CB8^R	---	9.43	7.68	1.66	4.8	2.0	1.8
Spring, 1979							
11	190	2.01	1.34	0.22	4.3	6.5	0.7
12	28	1.36,	2.13	0.42	5.6	3.5	4.6
13	200	1.11	5.65	0.10	2.4	n.d.	0.4
16A§	---	1.52	0.66	0.36	7.4	2.0	---
16B§	---	3.51	4.19	0.46	5.9	n.d.	---
17	45	3.66	4.20	1.47	3.8	3.5	3.9
18	180	0.43	3.04	0.04	1.7	n.d.	0.1
19	30	0.53	1.08	0.22	4.9	n.d.	1.5
22	35	1.99	0.28	<.01	n.d.	n.d.	---
23	35	0,54	0.87	<.01	n.d.	n.d.	n.d.
25	10	0.96	0.73	0.20	4.2	2.5	0.7
27	20	0.80	0.27	0.01	1.2	0.9	0.2
30	56	0.92	1.01	0.09	3.2	5.3	---
31	106	0.48	0.48	0.01	0.9	n.d.	0.1

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* For brevity, latitude and longitude are not given. Exact locations can be obtained from M.I.V. All samples are 0-2 cm except wherever mentioned. No elemental sulfur detected in any of these samples.

** Data of some samples from central Cook Inlet and Kachemak bay in these cruises omitted for brevity, but reported for samples collected from the same area in subsequent cruises.

R = replicate
† = 0-4 cm
§ = Bulk samples, collected by mud snapping sampling device
n.d. = not determined; too low to be calculated accurately
odd/even = summed from C_{15} to C_{33}

Table 12. Polycyclic aromatic hydrocarbons in sediment samples analyzed by GC/MS (rig/g)

	Southeastern Bering Sea		Norton Sound (1976)		Norton Sound (1977)		Norton Sound (1979)
	Station 59	Station 64	Station 131	Station 166	Station 35	Station 43	Station 25
O-Xylene	--	--	--	T	T	--	0.2
Isopropylbenzene	--	--	--	--	--	--	--
n-Propylbenzene	--	--	--	T	T	--	--
Indan	--	--	--	--	--	--	--
1,2,3,4-Tetramethylbenzene	--	--	--	T	--	--	--
Naphthalene	T	T	T	T	T	--	T
2-Methylnaphthalene	T	T	T	T	T	T	T
1-Methylnaphthalene	T	T	T	T	T	T	T
Biphenyl	--	--	T	T	T	T	--
2,6-Dimethylnaphthalene	--	--	T	T	--	--	--
Dimethylnaphthalenes[1]	--	--	T	T	--	--	0.1
Trimethylnaphthalenes	--	--	T	T	T	T	0.3
Fluorene	--	--	T	--	T	T	0.1
Dibenzothiophene	--	--	--	--	--	--	--
Phenanthrene	0.3	1.1	4.2[2]	0.2	1.9[2]	0.8[2]	0.4
Anthracene	--	--	--	--	T	T	--
Methylphenanthrenes	0.5	1.3	0.6	T	--	0*2	0.8
Fluoranthene	--	3.0	T	0.1	0.5	T	T
Pyrene	1.4	5.0	2.2[3]	0.1[3]	0.2	T	0.2
Benz(a)anthracene	--	--	--	--	T	--	--
Chrysene	1.2	0.9	3.0[2]	0.6	T	0.4	1.0
Benz(e)pyrene	--	T	T	T	--	--	T
Benz(a)pyrene	--	--	--	--	T	T	--
Perylene	T	T	9.8	T	T	1.3	9.4
Simonellite	--	--	--	See Pyrene	T	T	T
Cadalene	T	--	0.3	T	--	--	T
Retene	1.8	7.3	2.8[2]	--	T	3.1[2]	1.4

T = trace

[1] = Excludes 2,6-dimethylnaphthalene when identified

[2] = Coelutes with unknown compound

[3] = Coelutes with simonellite

Table 14. Comparative organic geochemical data from different areas in the Alaskan shelf

Area	% Org. C range	Total Hydrocarbons[1]	Range in rig/g			$\frac{\text{odd}}{\text{even}}$ Range	$\frac{Pr}{Ph}$ Range	UCM
			Resolved n-Alkanes[2]	Resolved PAH[2,3]	n-Alkane Maxima			
Beaufort Sea	0.4 -1.0	20,000-50,000	1,400-5,000	200-300	27 or 29	1.8-5.0	1.5-2.5	no
S.E. Bering Sea	0.1 - 0.8	1,900-22,000 (240,000)	300-2,900	3-20	27 or 29	1.8-4.0	2-18	no**
Norton Sound	0.1 - 1.3	1,900-29,000	10-5,400 (7,200; 8,700)	1-20	27	1.7-6.3 (11.0)	1-8	no
Navarin Basin	0.1 - 1.4	2,400-52,000	250-2,600	20-40	27	3.5-4.8	--*	no
Gulf of Alaska	0.1 - 1.1	1,500-26,000	60-2,000	100-200	22 and 27 or 29	1.0-2.5	1-7	yes**
Kodiak Shelf	0.2 - 1.2 (2.15;2.45)	900-18,000	10-800	6-100 (200)	27 or 29	0.8-2.8 (3.8)	2-18	no**
Cook Inlet	0.1 -1.4	900-39,000	< 10-3,600	10-300	27 or 29	0.9-5.9 (7.4)	1-12	no**

1 = Total hydrocarbons = sum of aliphatic and aromatic fractions from column chromatography.

2 = gas chromatographic data

3 = Sum of pAH identified by GC/MS and tabulated in tables 10-12. Inlet samples show UCM typical of weathered petroleum

* = Phytane below detection limits

** = Narrow UCM around C_{20}-C_{23} in all samples in Gulf of Alaska and in only a few samples in Kodiak Shelf and Cook Inlet. In Cook Inlet, two samples, and in southeastern 'Bering Sea, 1 sample, show UCM typical of weathered petroleum

(Values beyond the general range characteristic of a given area are quoted in parentheses).

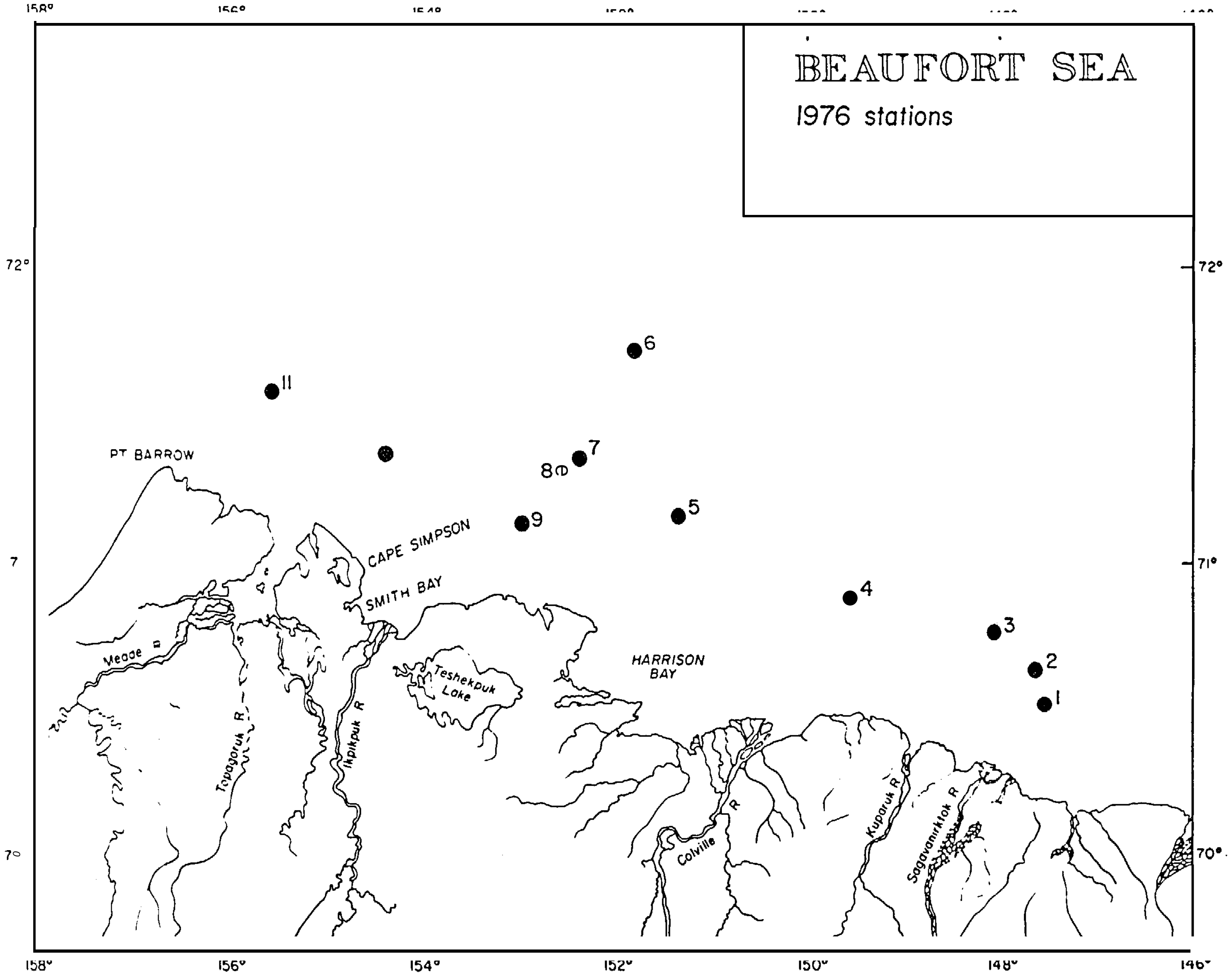

Figure 1: Sample locations in Beaufort Sea.

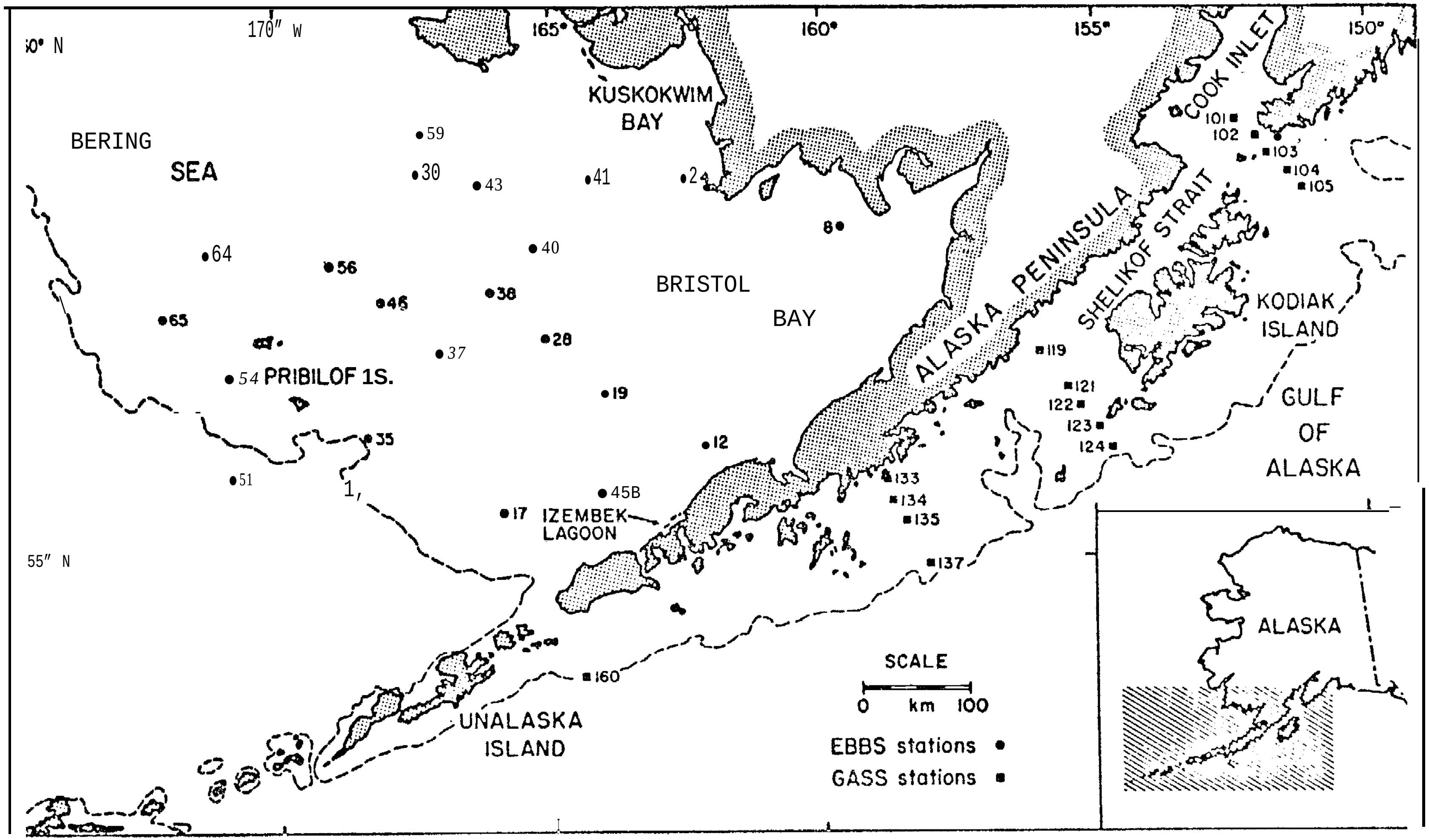

Figure 2: Sample locations in southeastern Bering Sea and western Gulf of Alaska.

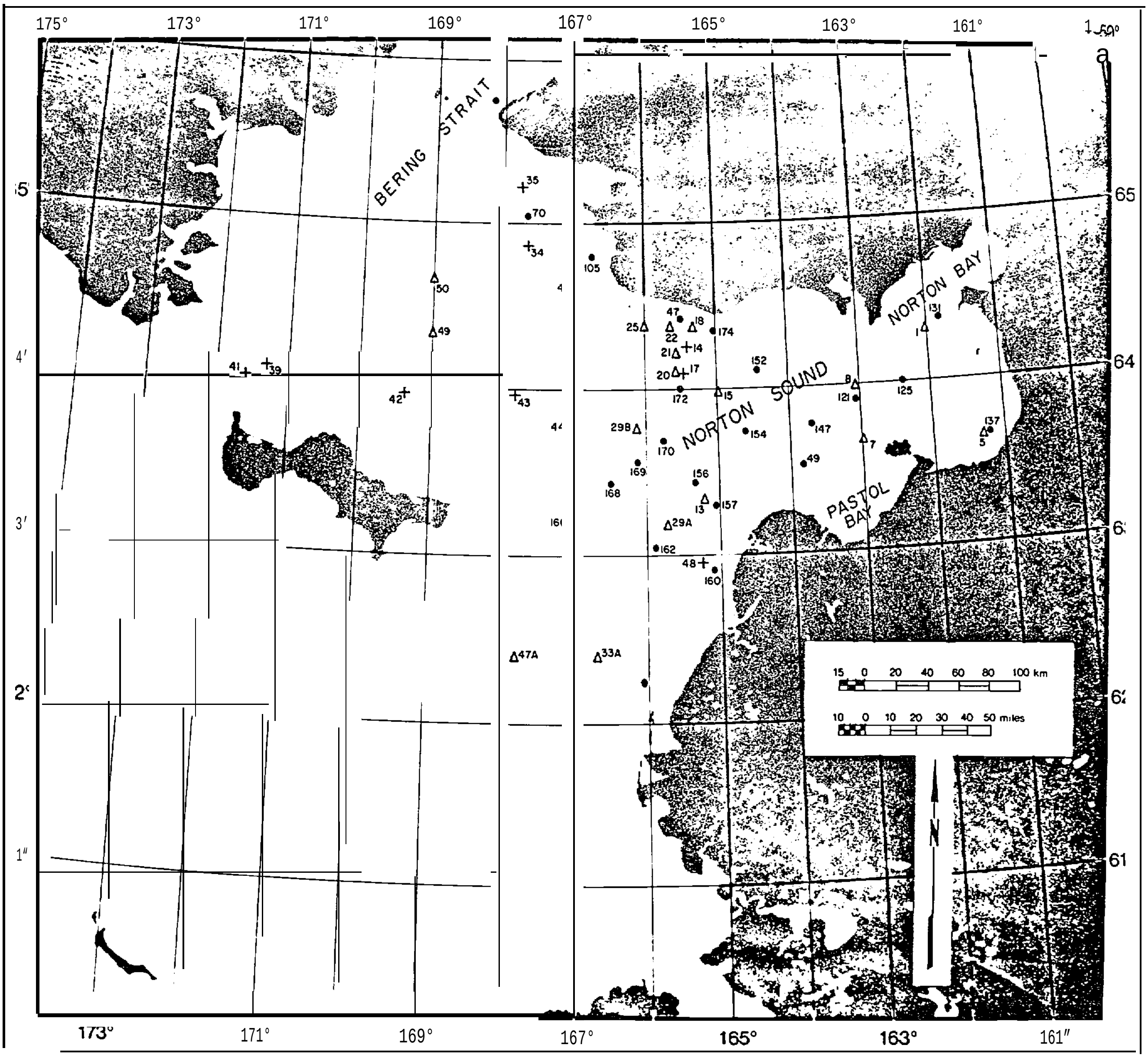

Figure 3: Sample locations in Norton Sound. . 1976 samples; + 1977 sample; A 1979 samples.

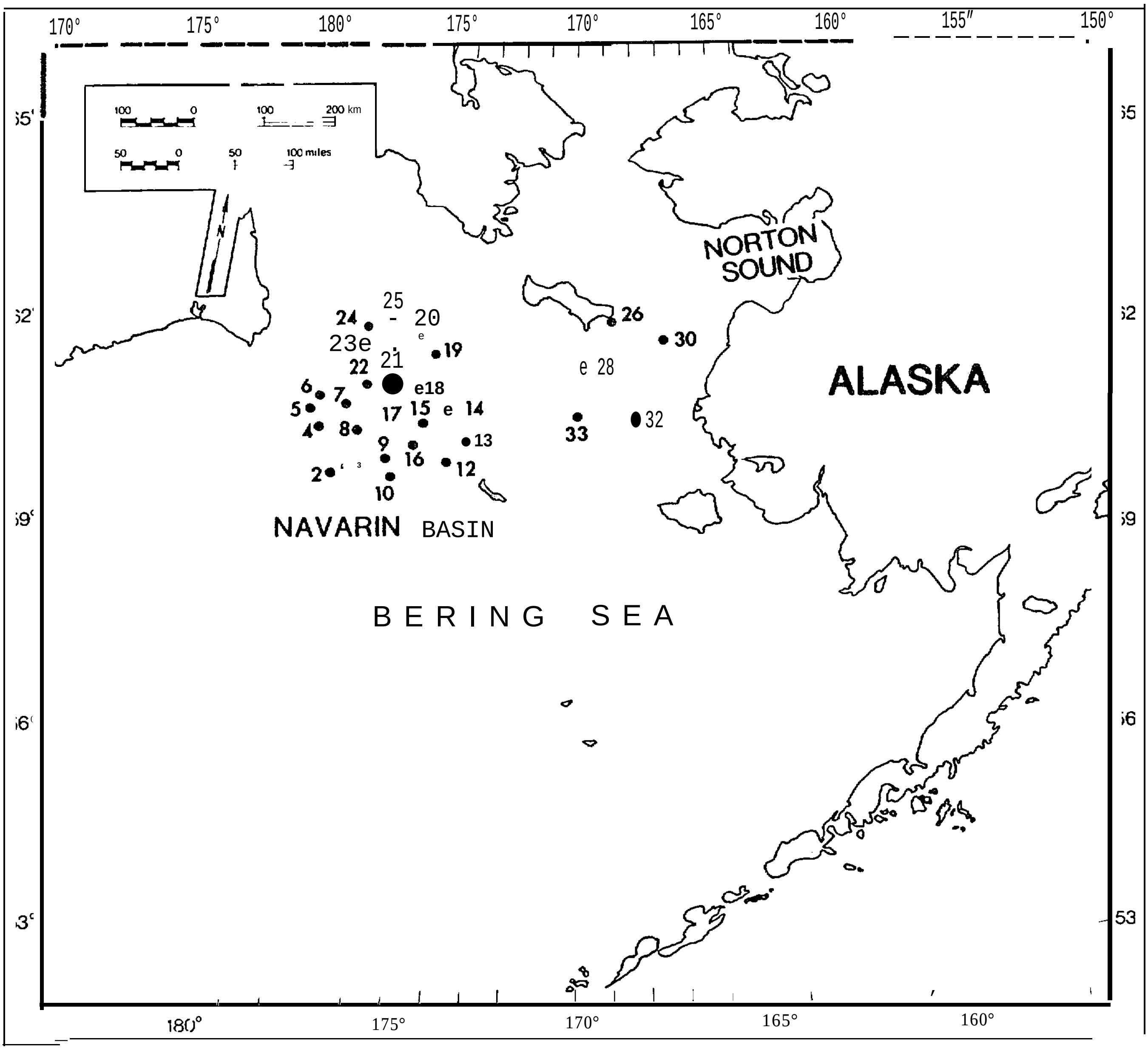

Figure 4: Sample locations in Navarin Basin.

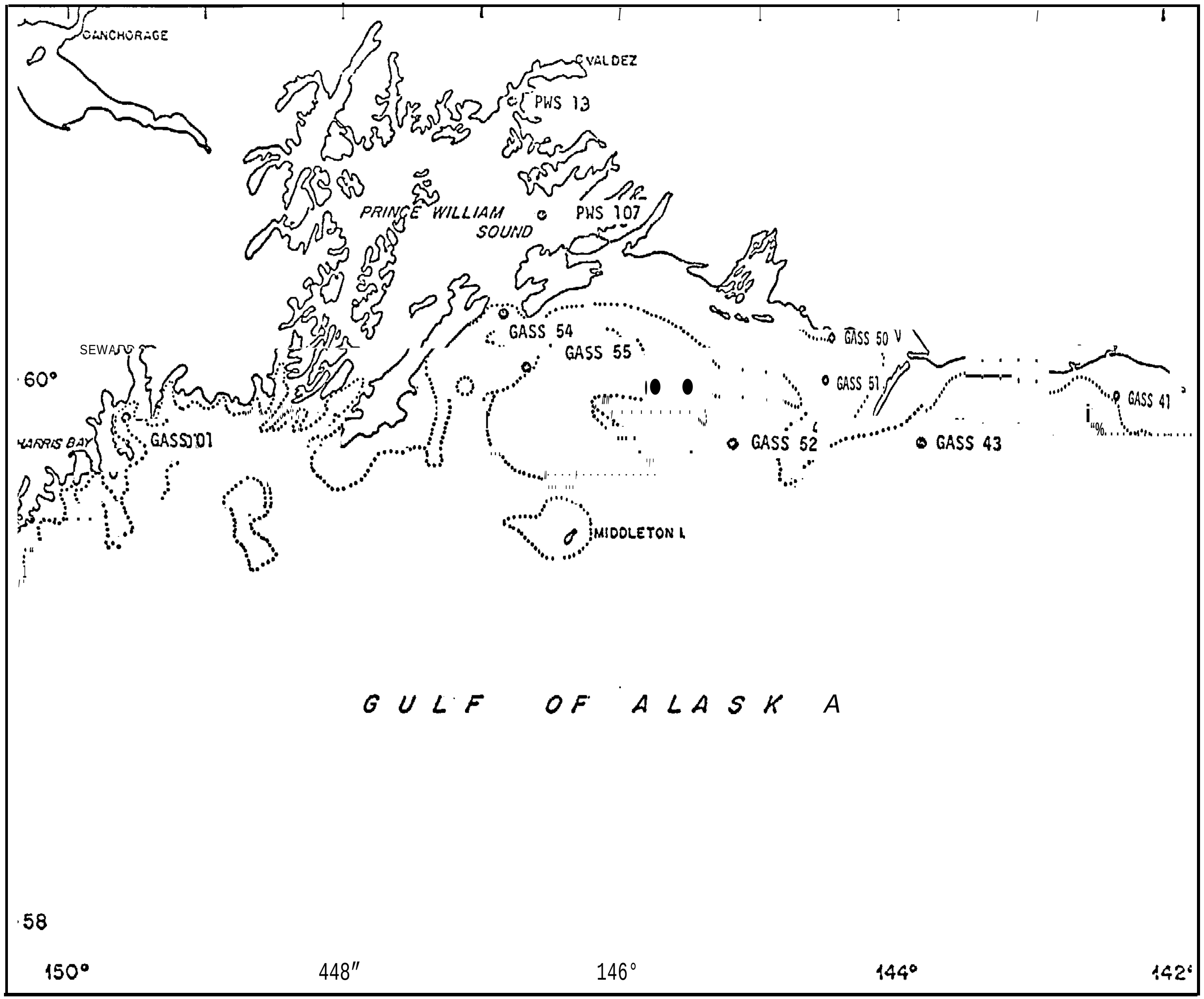

Figure 5: Sample locations in central and eastern Gulf of Alaska.

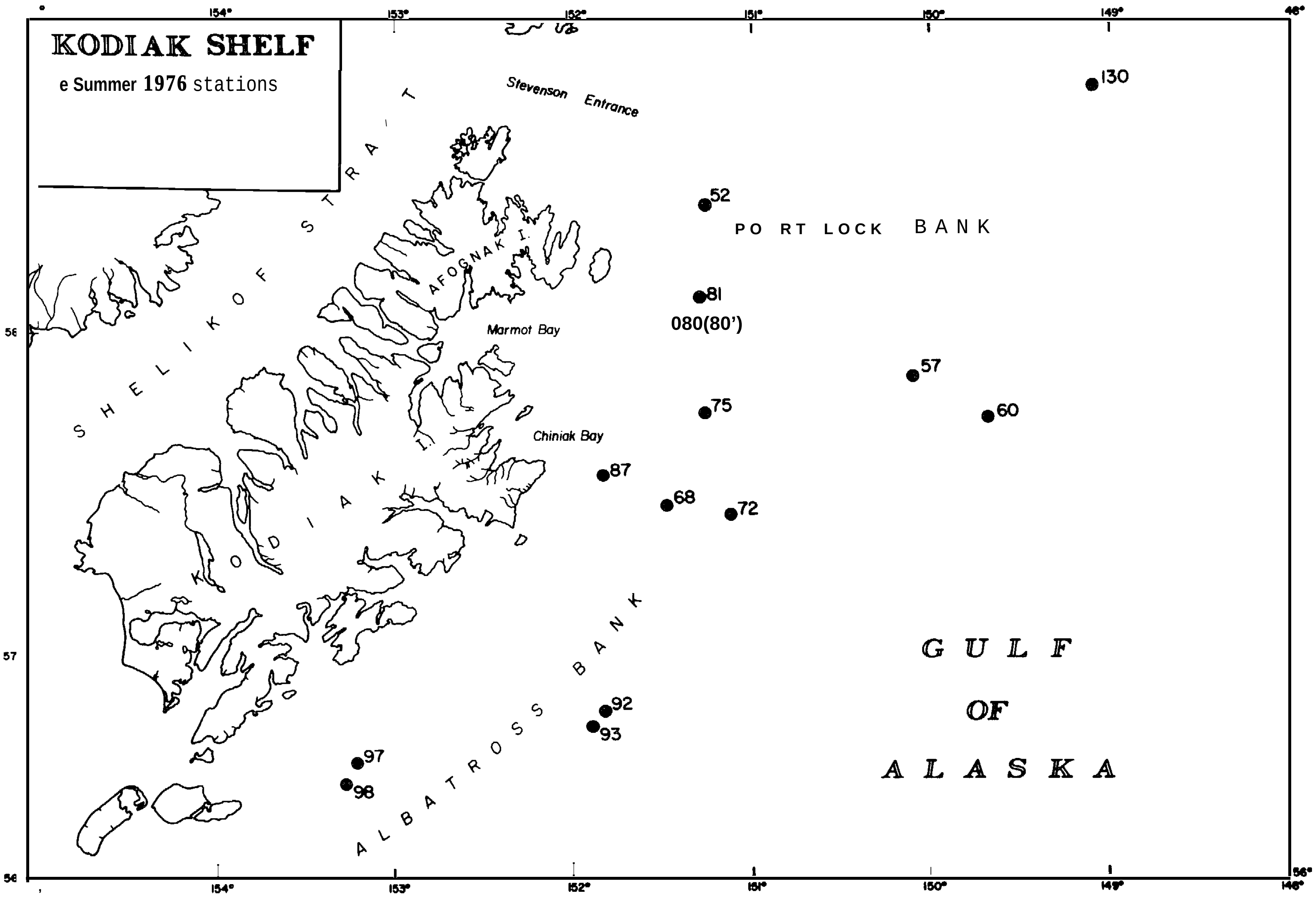

Figure 6: Sample locations in Kodiak Shelf.

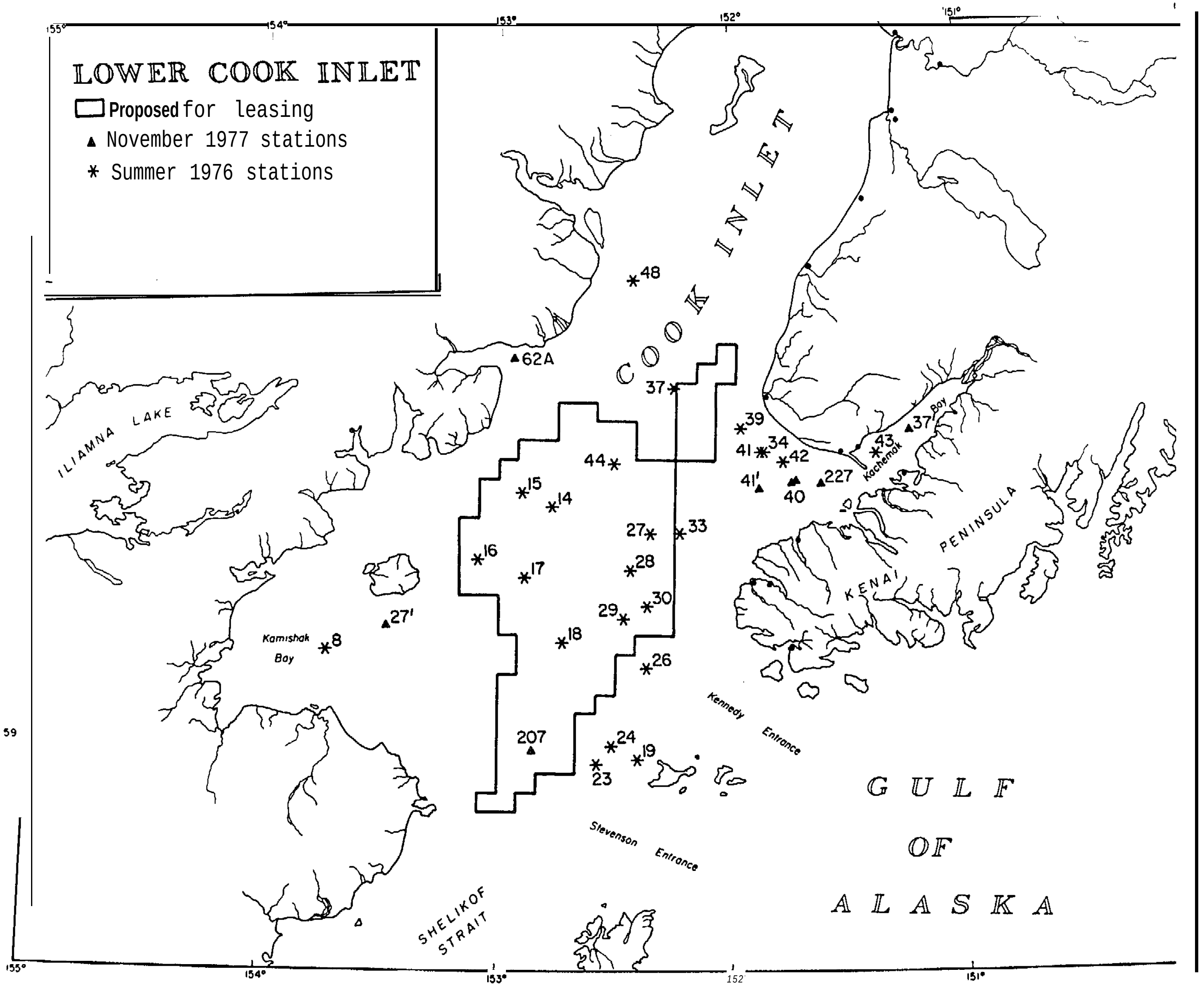

Figure 7: Sample locations in Cook Inlet; 1976 and 1977 cruises.

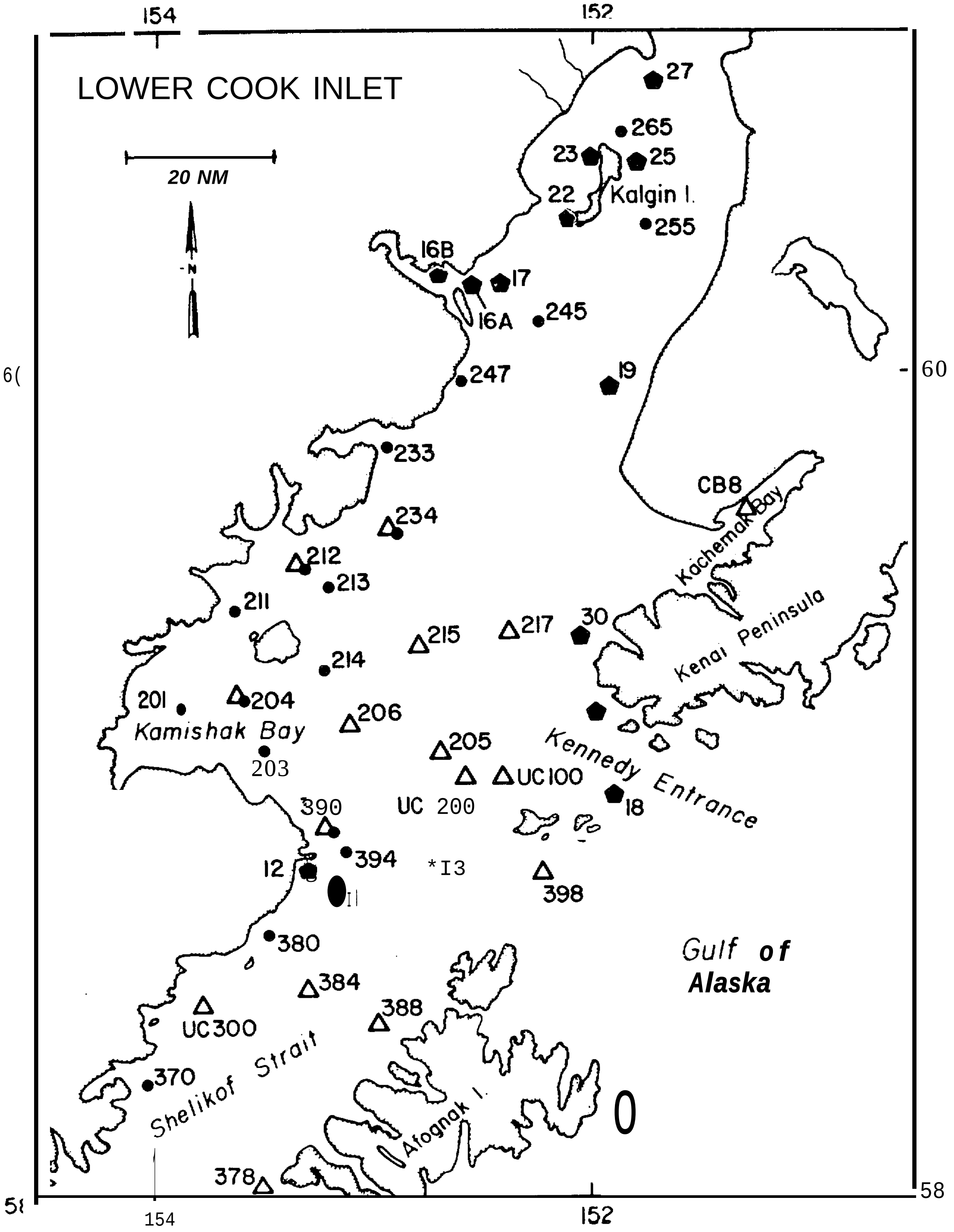

Figure 8: Sample locations in Cook Inlet. ● 1978 spring samples; △ 1978 summer samples; ⬟ 1979 spring samples.

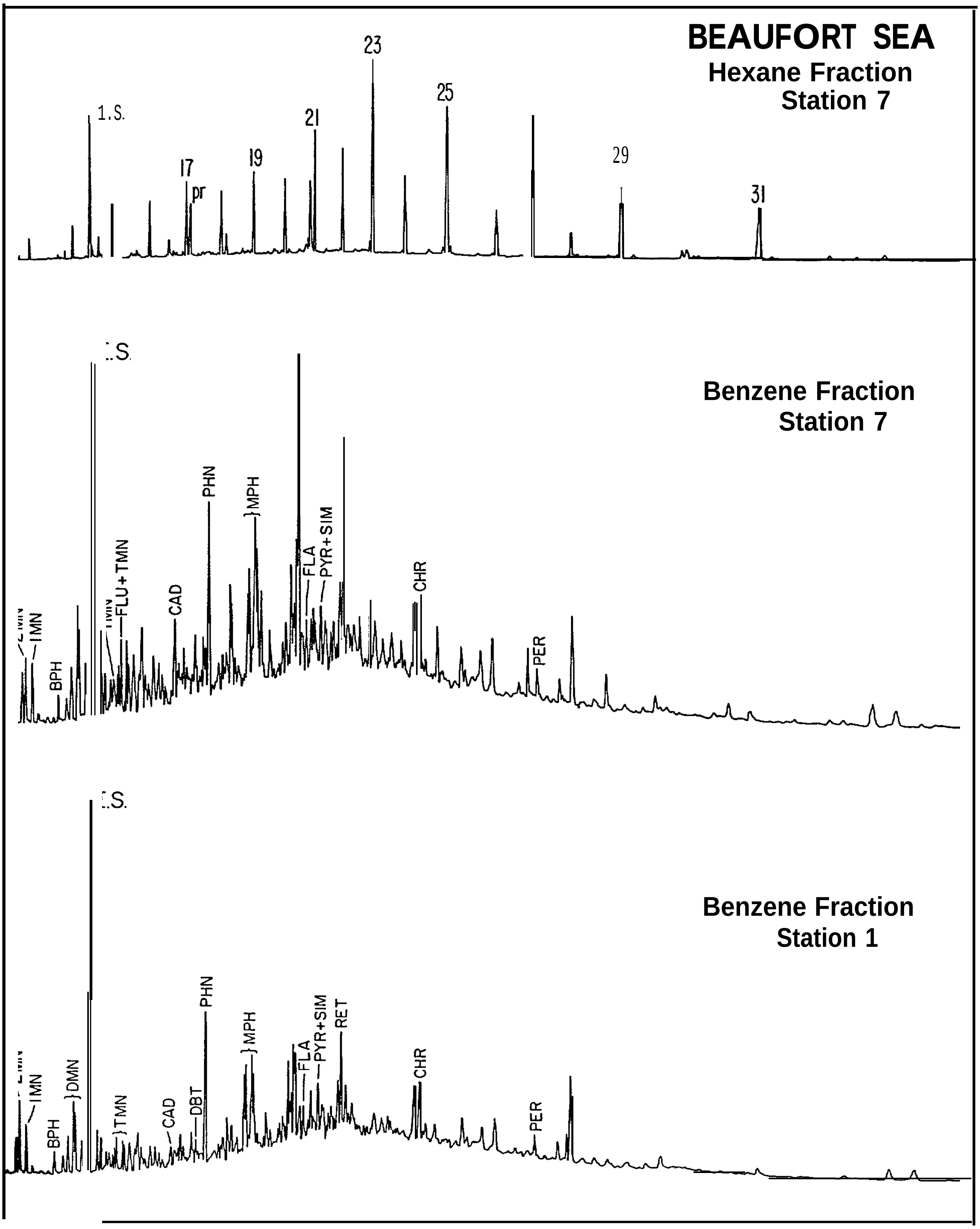

Figure 9: Gas chromatographic traces of hexane and benzene (hexane: benzene) fractions from Beaufort Sea sediments.

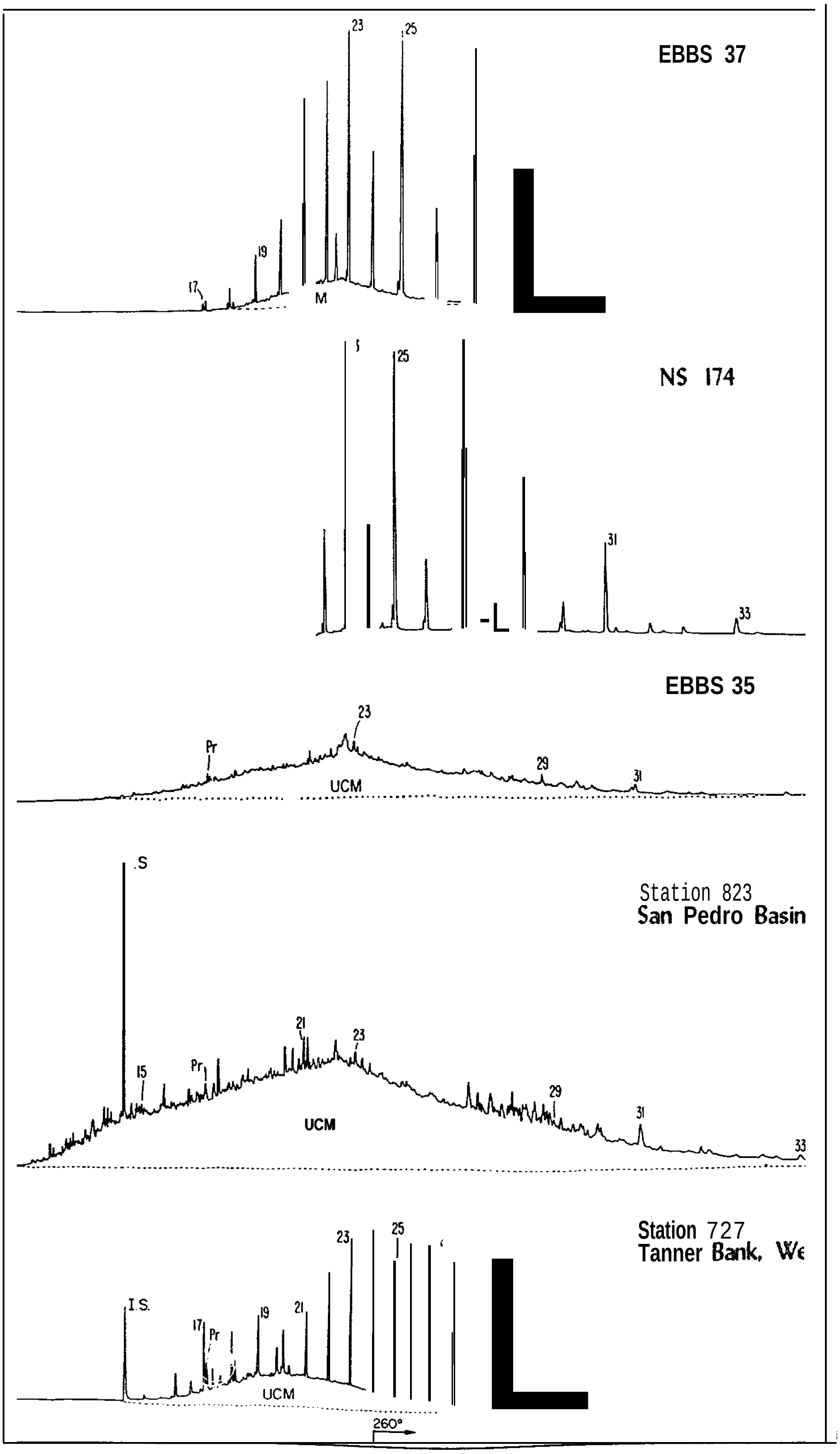

Figure 10: Gas chromatographic traces of hexane fractions from southeastern Bering Sea (EBBS), Norton Sound (NS) and Southern California Bight (San Pedro Basin and Tanner Bank) sediments.

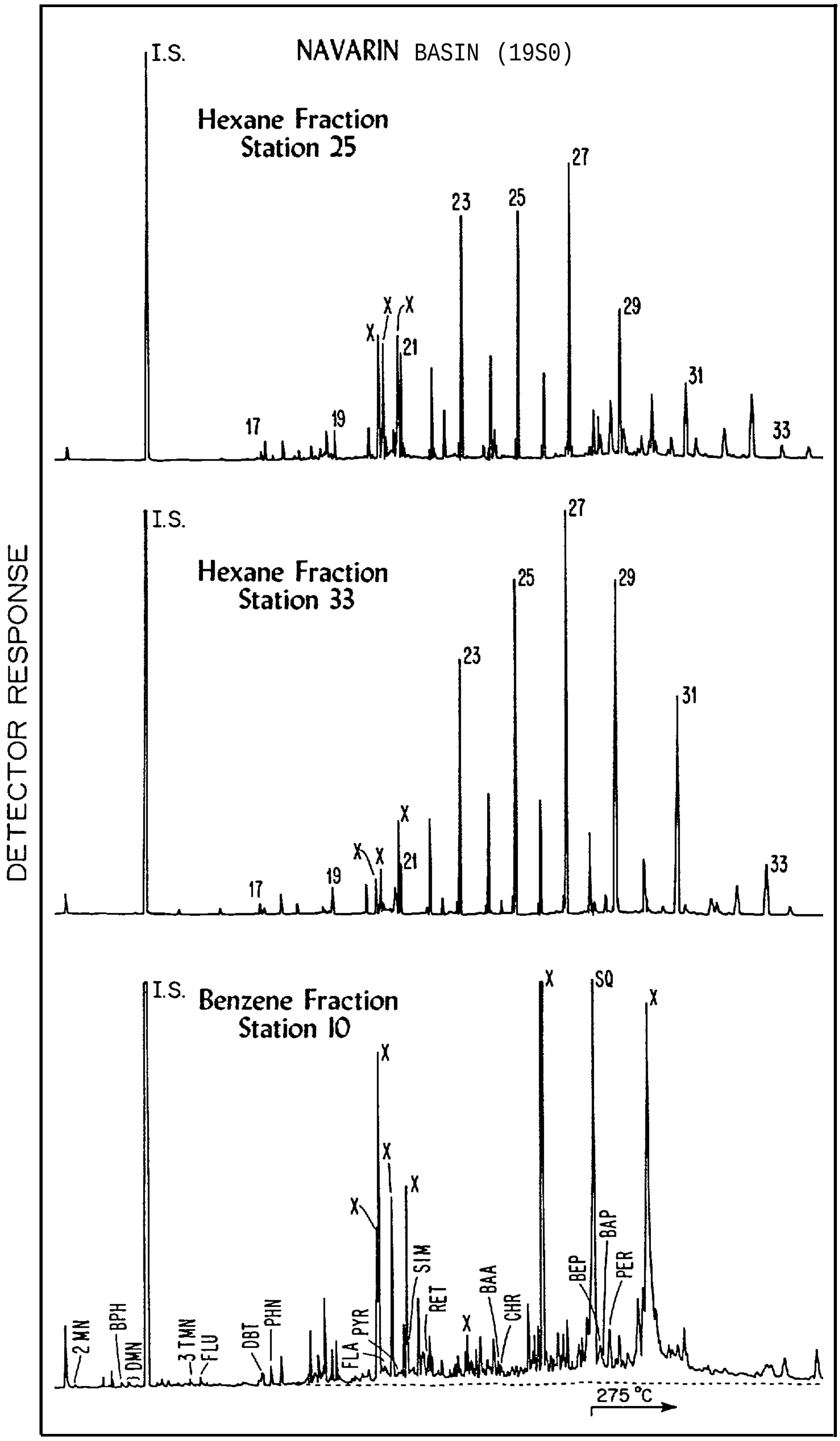

Figure 11: Gas chromatographic traces of hexane and benzene (hexane:benzene) fractions from Navarin Basin sediments.

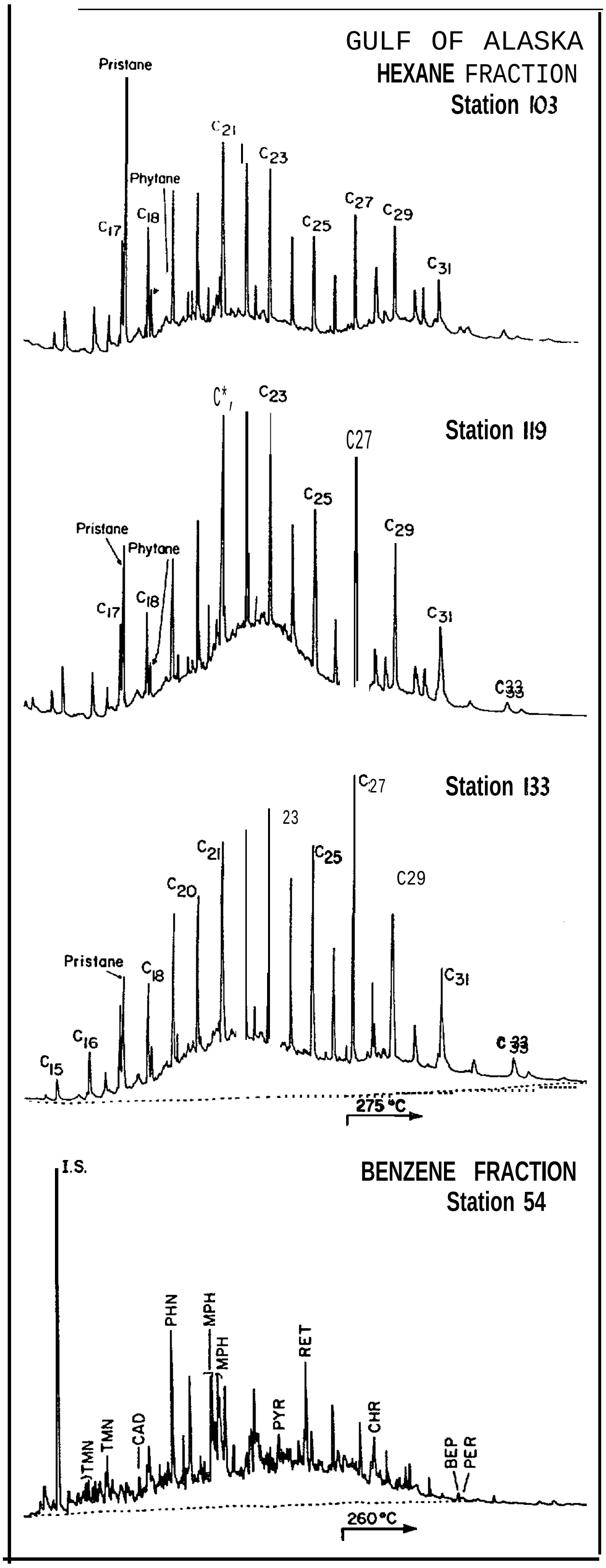

Figure 12: Gas chromatographic traces of hexane and benzene fractions from Gulf of Alaska sediments.

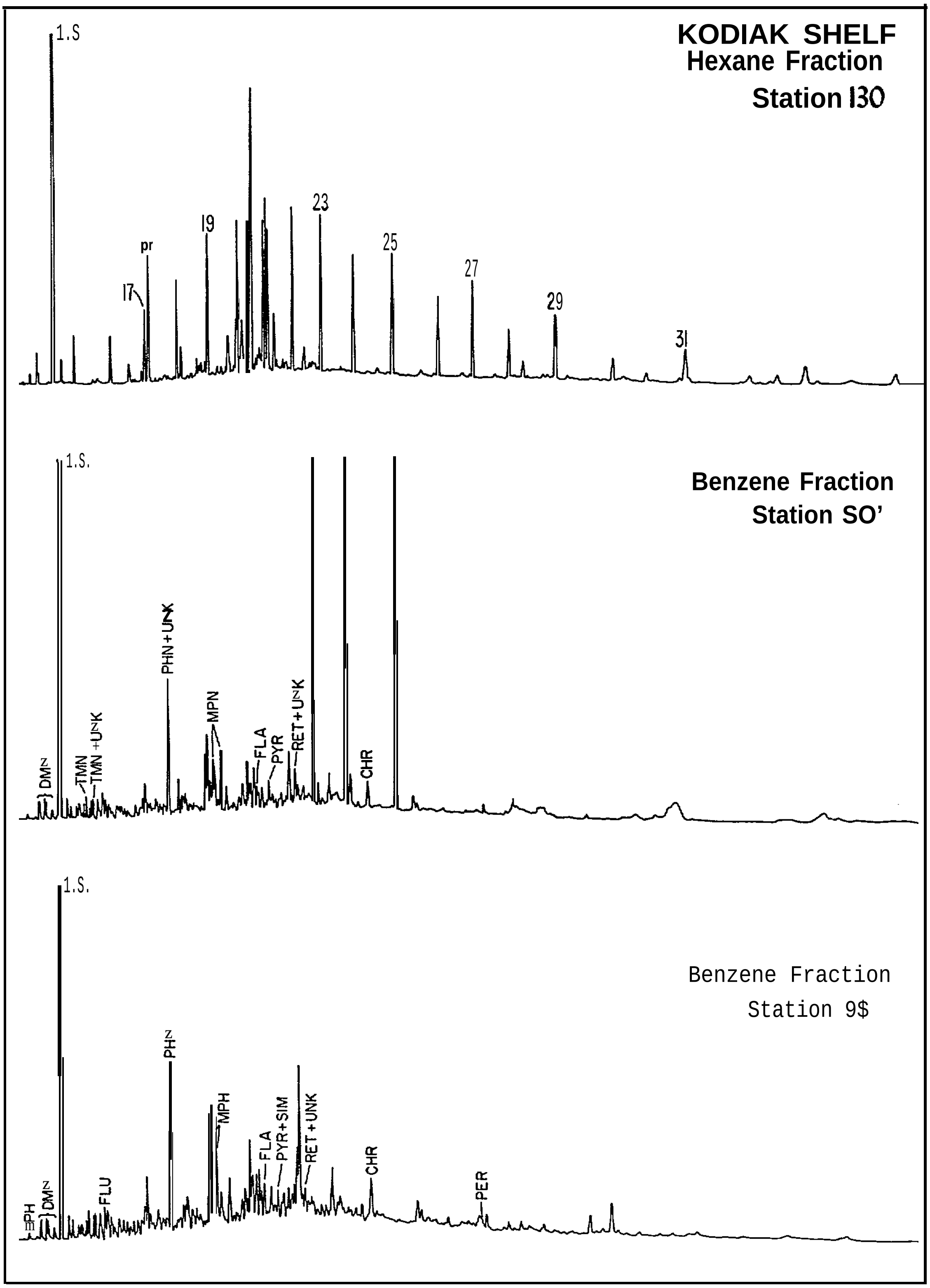

Figure 13: Gas chromatographic traces of hexane and benzene (hexane:benzene) fractions from Kodiak Shelf sediments.

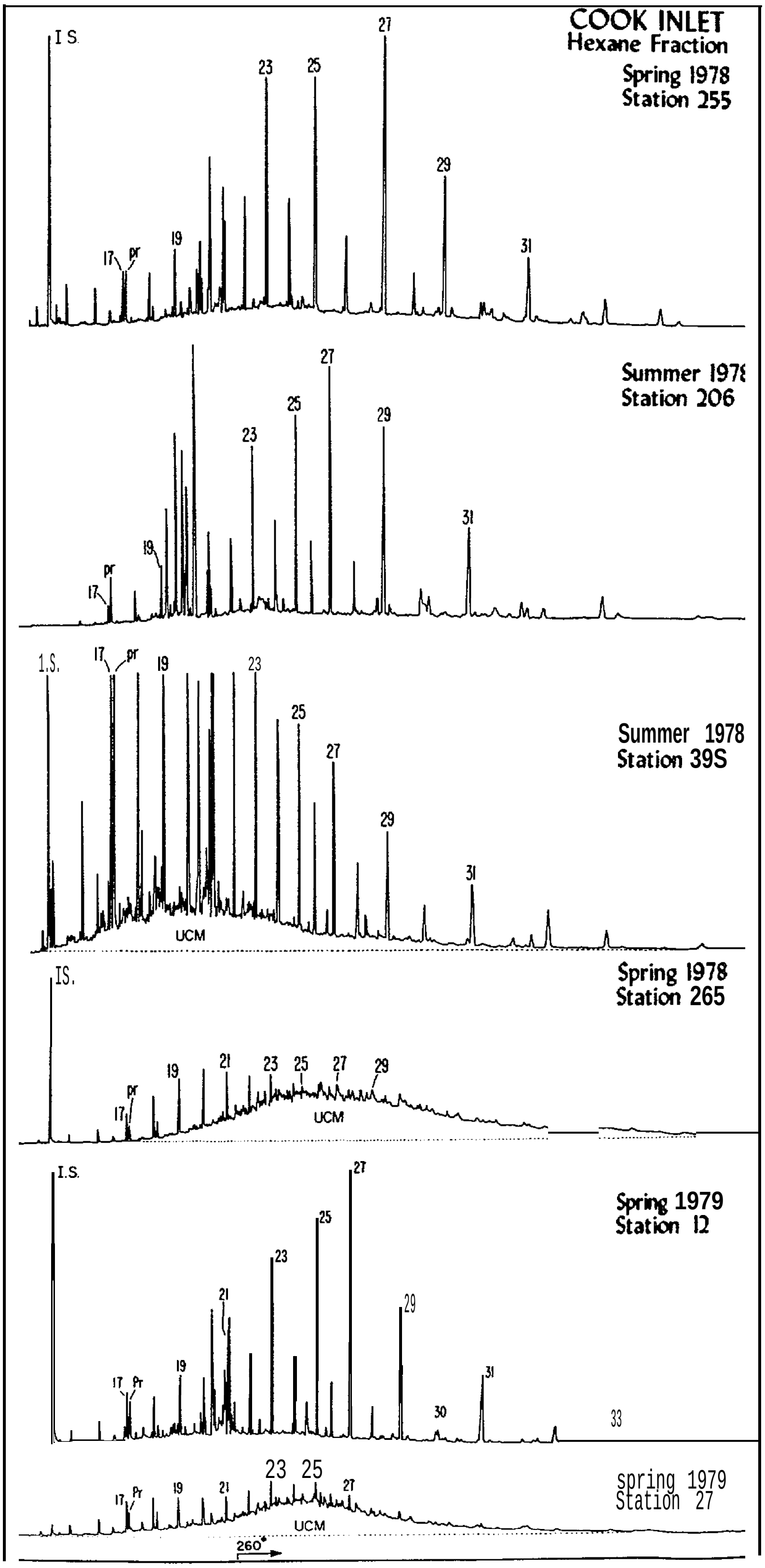

Figure 14: Gas chromatographic traces of hexane fractions from Cook Inlet sediments.

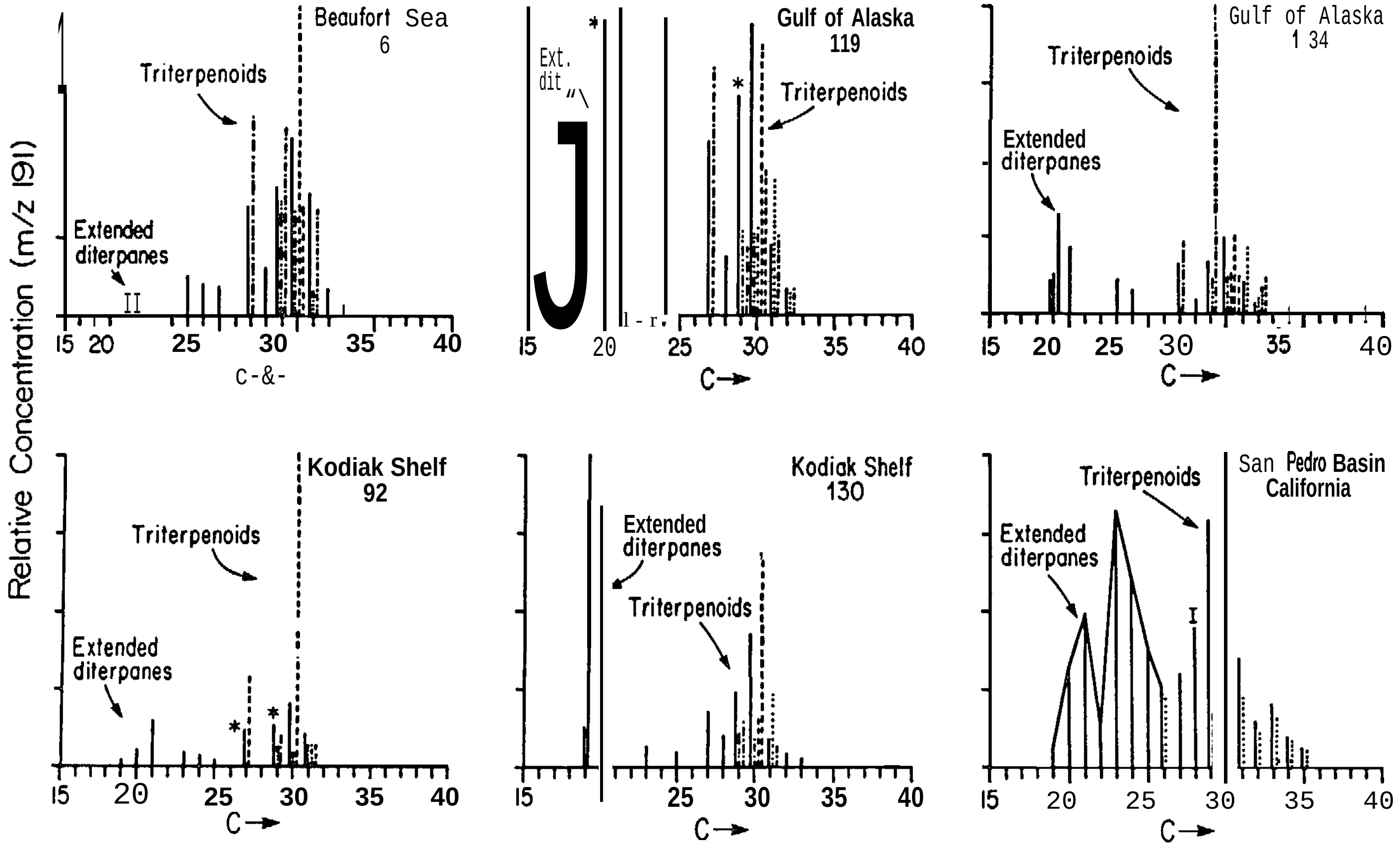

Figure 15: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. Beaufort Sea, Gulf of Alaska and Kodiak Shelf. 17α,21β (diasteromers at position 22 indicated by continuous and dotted lines ┬┬┬) ; —· —·— 17β,21β; —··· — 17β,21α; ----mono-enes; # coeluting with unknown.

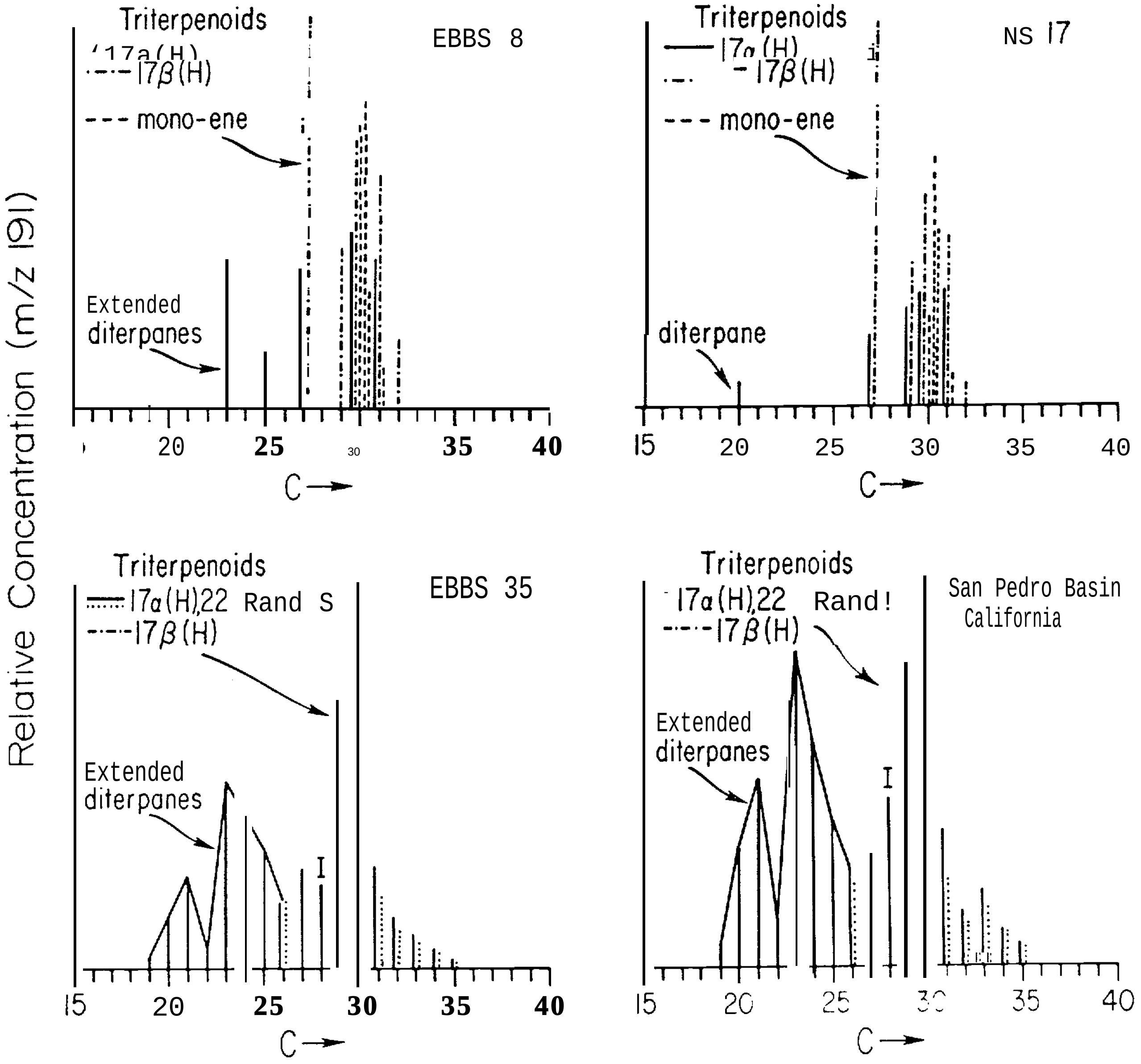

Figure 16. Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. EBBS = southeastern Bering Sea, NS = Norton Sound. For explanation of symbols, refer to Fig. 15.

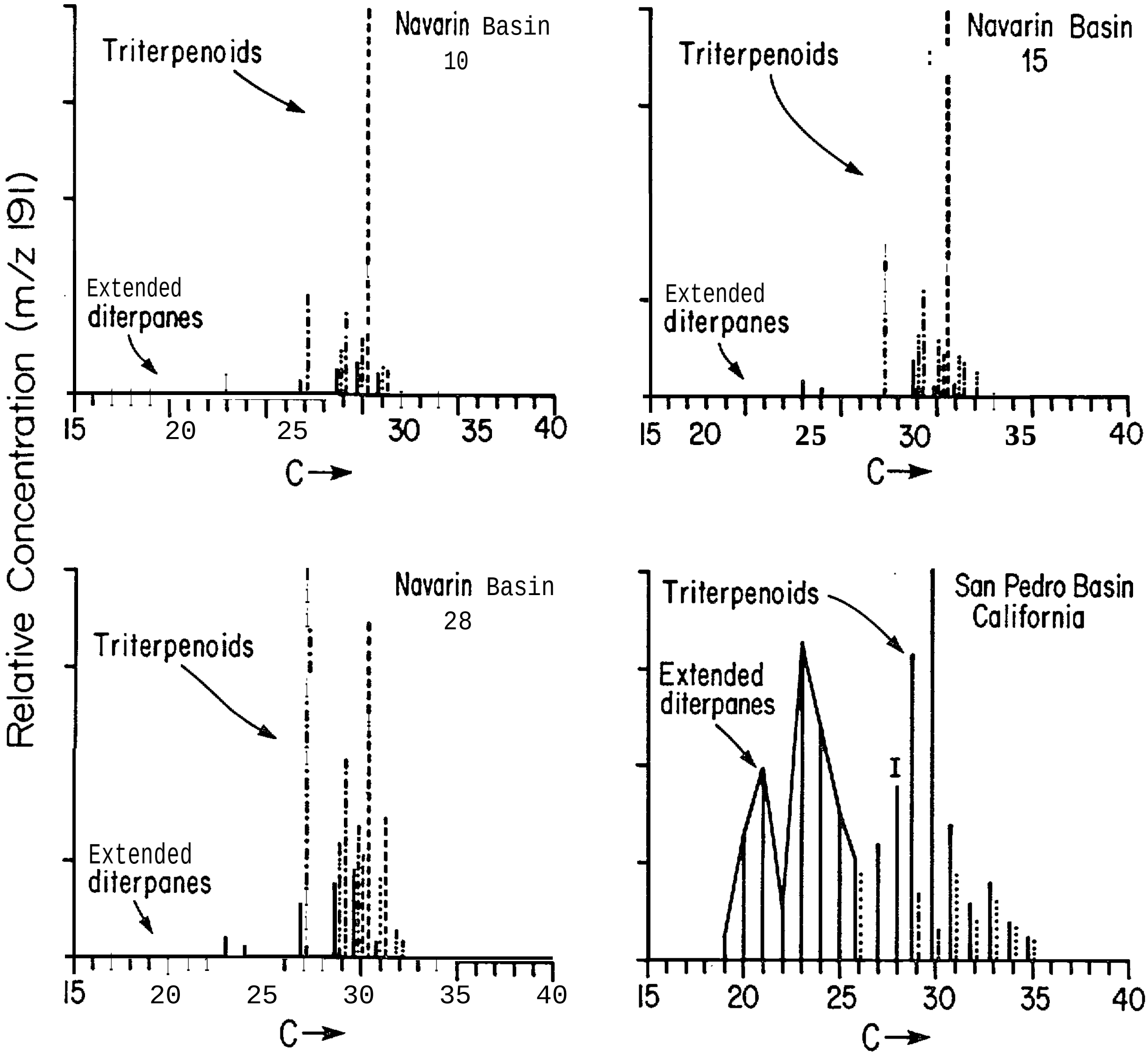

Figure 17: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. Navarin Basin. For explanation of symbols, refer to Fig. 15.

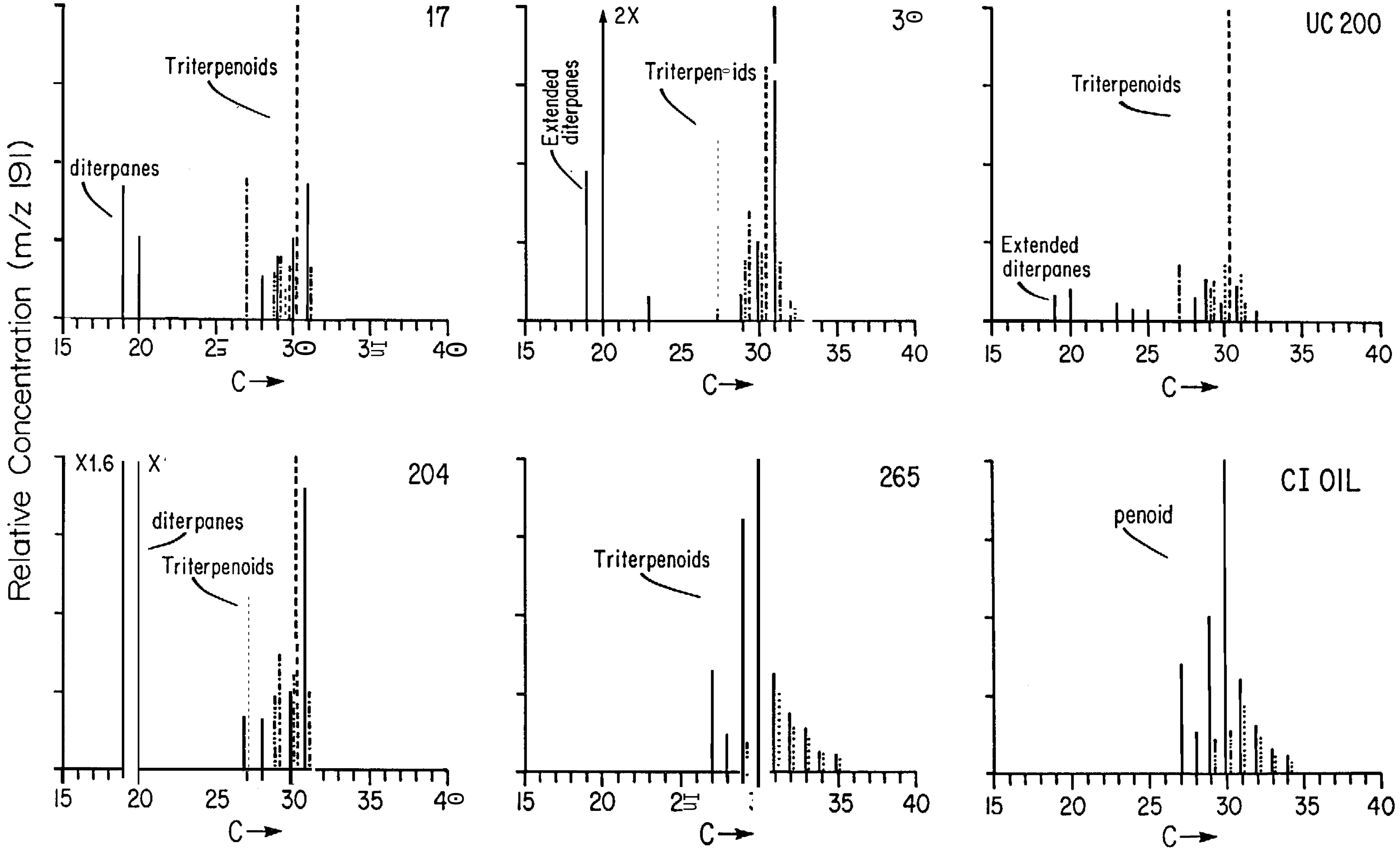

Figure 8: Relative distribution histograms of di- and triterpenoids based upon m/z 191 mass chromatograms. Lower Cook Inlet sediments and Cook Inlet oil. For explanation of symbols, refer to Fig. 15.

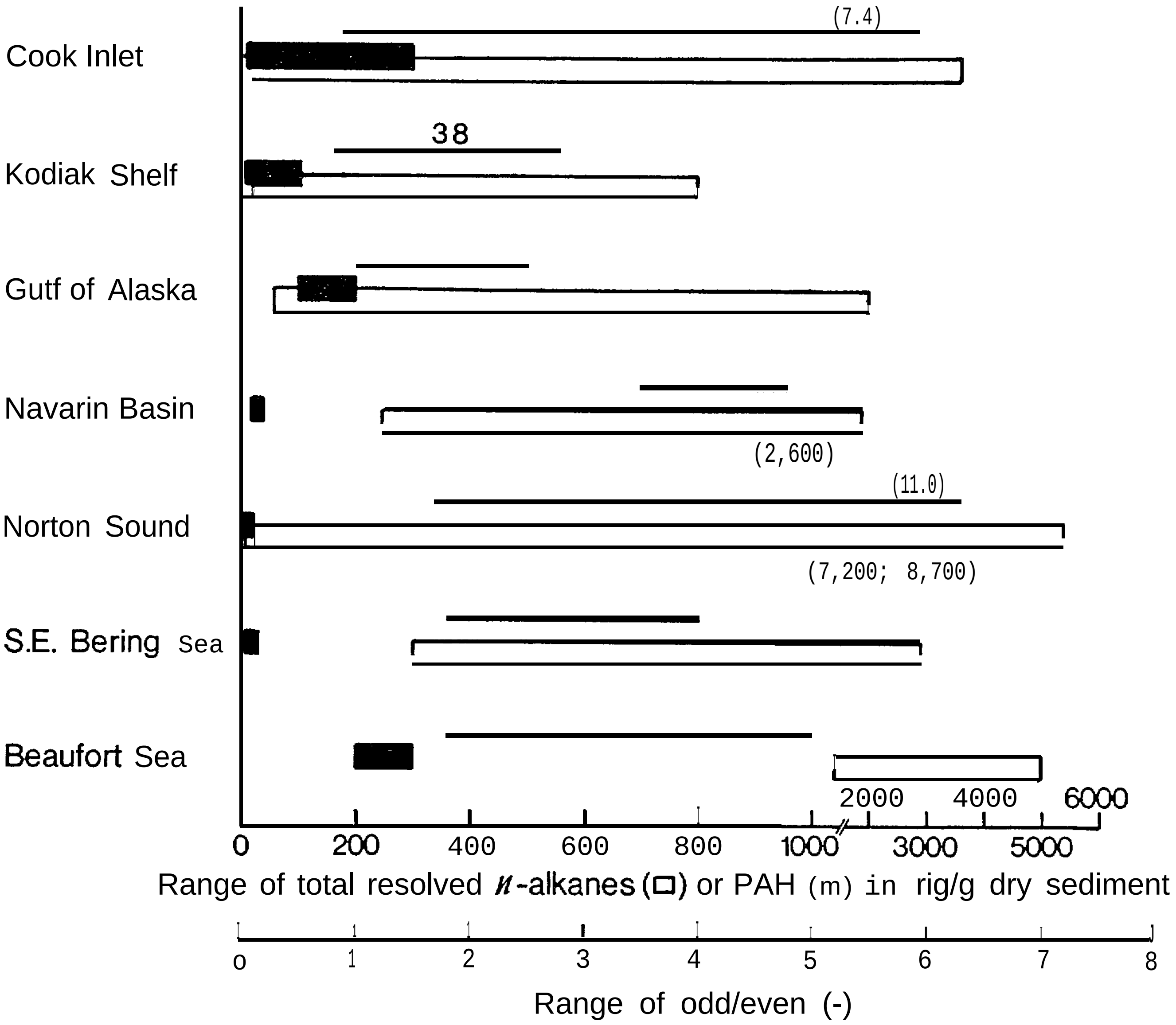

Figure 19: Selected organic geochemical data of sediments from different areas in the Alaskan outer continental shelf.

DISCUSSION

The vast latitudinal expanse of the Alaskan Shelf encompasses a variety of characteristic sedimentary and oceanographic regimes. Therefore, is was considered appropriate to discuss the organic geochemical data in the several regions of the Alaskan Shelf in terms of various geographic sections from north to south. The coastal region, including the shelf, is divided into the following areas: 1) Beaufort Sea, 2) Southeastern Bering Sea, 3) Norton Sound, 4) Navarin Basin, 5) Gulf of Alaska, 6) Kodiak Shelf and 7) Cook Inlet.

Beaufort Sea

Organic Carbon:

The organic carbon content ranges from 0.4 to 1.01 (Table 2) and is comparable to values reported for the continental shelf sediments (Naidu, 1978) from the Beaufort Sea collected in 1977. No clear trend in regional distribution is seen in the organic carbon contents. The values are typical of unpolluted geographical locations (Palacas et al., 1976).

Hydrocarbons:

The concentration ranges of total hydrocarbons and resolved n-alkanes, respectively, are 20,000-50,000 rig/g and 1,400-5,000 rig/g (Table 2) and these are less than the values reported for nearshore sediments (Shaw et al., 1978) and eastern Beaufort Sea sediments on the Canadian border (Wong et al., 1976). The n-alkanes maximize at C_{27} Or C_{29} and there is no measurable unresolved complex mixture (Fig. 9). The odd-even carbon preference data (Table 2) also indicate substantial input of terrigenous detritus in these sediments (Eglinton and Hamilton, 1963; Kolattakudy, and Walton, 1973). This is not surprising in view of the number of rivers along the shores of the study area, such as the

Meade, Ikpikpuk and Colville Rivers. Stations from 1 to 4 in particular receive the terrigenous input from Colville River, since clay mineral assemblages in the Barter Island are thought to originate in the Colville River (Naidu, 1978).

A marine biogenic origin for some of the organic matter is also indicated by the presence of pristane and heptadecane, which are derived from marine plankton. Phytane is also present in detectable quantities and Pr/Ph is generally between 1.5 to 2.5 (Table 2). The presence of phytane and Pr/Ph ratios around 1.0 in marine sediments are often inferred as indicating petroleum pollution (Speers and Whitehead, 1969; Zafiriou et al., 1972). However, several unpolluted sediment samples from the estuarine environment of the English Channel were found to have Pr/Ph ratios of almost unity and this was attributed to bacteria (Tissier and Oudin 1973). Bacterial may therefore account for the presence of some phytane in Beaufort Sea sediments. In short, the absence of unresolved complex mixture signal and the distribution pattern of major alkanes in the Beaufort Sea sediments can be attributed to recent biogenic-rich source with little or no anthropogenic input.

Small amounts of alkenes from C_{15} to C_{23} with one or two degrees of unsaturation have been detected by GC/MS analyses. These olefins could be of biogenic origin.

Several steranes, diterpanes (Structure I in Appendix I) and triterpenoids such as adiantane, hopane (III, $R=C_3H_7$), 22,29,30trisnorhopane (II, R=H) and a C_{31} methyltriterpane have been detected in sample 6 (Fig. 15). These triterpenoids and their extended homologs have probably been derived from recent biogenic activity (Simoneit, 1977) and not from petroleum (Dastillung and Albrecht, 1976). The absence of one of the two diastereomers at position 22 of the extended triterpanes also suggests the absence of petroleum input (Dastillung and Albrecht, 1976). These diastereomers are commonly found as 1:1 mixture in petroleum polluted sediments as in Southern California Bight (Simoneit and Kaplan, 1980; Venkatesan et al., 1980a).

The concentration of the resolved polynuclear aromatic hydrocarbons (PAH) is 200-300 rig/g (Table 12) in the sediments, and is generally comparable to the data reported by Wong and co-workers (1976) for sediments collected to the east of the present study area.

In the two samples, 1 and 7, analyzed by GC/MS, relatively large amounts of naphthalene, phenanthrene, pyrene, chrysene, etc. and their mono- and di-substituted alkyl homologs have been identified and the relative abundance decreases rapidly with further alkyl substitution (Figure 9, Table 12). This type of PAH distribution was previously found to result from mixed input from pyrolytic sources and possibly fossil fuel (Youngblood and Blumer, 1975). Similar observation on the nearshore sediment from Maguire Islands close to our station 1 has been reported by Shaw et al. (1979). Boreal forest fires are reported to be an insignificant source of PAH for the area (Wong et al., 1976). Lower latitude natural fires cannot be an important source of sedimentary PAH at those latitudes and hence such remote forest fires are also unlikely source in the distant Beaufort Sea environment (Laflamme and Hites, 1978). Long-distance transport from anthropogenic sources through atmospheric fallout could be an important source of the pyrolytic PAH in Beaufort Sea sediments (Shaw et al., 1979; Laflamme and Hites, 1978; Lunde and Bjorseth, 1977; Rahn et al., 1977). The other potential source of fossil PAH may be coal outcrops on the Meade River and the oil seep area near Smith Bay. The longshore bottom currents flowing westward (Pelletier, 1975) could carry eroded source materials discharged by the MacKenzie River into the area studied. MacKenzie River flows through regions with known fossil fuel deposits such as the Athabasca tar sands and Norman well oil seepage area. It is quite possible that unidentified offshore or onshore oil seeps also exist near the area of investigation.

Perylene is present at the same level as other PAH in these surface sediments (Station 1-10 rig/g; Station 7-40 rig/g; Table 11). Lower values have been reported ($\leq$ 7 rig/g) for Southeastern Beaufort Sea surface sediments by Wong *et al.* (1976). Perylene content is not anomalously high in the region as found in Namibian Shelf (Wakeham *et al.*, 1979) and the origin of perylene is uncertain. It could be from terrestrial (Bergmann *et al.*, 1964) or marine (Wakeham *et al.*, 1979) sources.

The presence of cadalene, retene and simonellite in these samples add support to the *n*-alkanes distribution for terrigenous input (Simoneit, 1977). Cadalene is thought to be derived from the diagenetic alteration of cadinene and other sesquiterpenes from higher plants. Simonellite (traces) and retene (the most abundant of the three) found in these sediments are the products of diagenesis of the diterpane, abietic acid occurring in higher plants, especially conifers. These compounds have been identified in the nearshore Beaufort Sea sediments (Shaw *et al.*, 1978) and the abundance of retene was attributed to the peat material which has not undergone sufficient diagenetic alteration to provide a full suite of fossil PAH.

Southeastern Bering Sea

Organic Carbon:

The organic carbon values are low (Table 3) considering the relatively high biological productivity of this continental shelf region (Simoneit, 1975), apparently as a result of a combination of oxic conditions at the sediment surface and a high-energy depositional environment (Sharma, 1974). The organic carbon content increases with decreasing mean grain size of the sediment (Bordovskiy, 1965; Sharma, 1974). Sediments in this region are reported to become progressively finer-grained from nearshore to the edge of the shelf (Sharma, 1974). The total hydrocarbon content of these sediments follows the same trend, with low concentrations of total hydrocarbons in coarse-grained sediments close to shore and higher concentrations in fine-grained sediments near the shelf edge (Table 3).

Hydrocarbons:

A detailed discussion of the distribution and dynamics of hydrocarbons in the eastern Bering Sea Shelf can be found in Venkatesan et al. (1980b). Only a brief summary of the study will be presented here.

The alkanes in sediments of the study area generally show a bimodal distribution typical of a mixture of allochthonous and autochthonous sources (Fig. 10; Table 3). In short, the absence of unresolved complex mixture and the distribution pattern of n-alkanes in most of the stations studied can be attributed to recent biogenic sources characteristic of unpolluted environments.

The only exception is sample 35, as presented in Fig. 10, whose gas chromatogram is characterized by a broad UCM in the entire elution range, with no measurable, resolved hydrocarbons. This pattern is typical of weathered petroleum contamination and is similar to the sediments from Southern California nearshore basins (Venkatesan et al., 1980a). The source of these hydrocarbons may be natural submarine seepage, although none have been reported in the southern Bering Sea shelf. However, faults in this area (Marlow et al., 1976) could allow leakage of petroleum from underlying reservoir rocks. The extensive fishing operations around this area make an anthropogenic origin for these hydrocarbons possible; it seems unlikely, however, since the chromatogram from station 37 (Fig. 10) and other samples from this area of intensive fishing do not show evidence of such petroleum contribution.

The anomalously high pristane content in some of the stations could be from the Calanus copepods found in this area (Motoda and Minoda, 1974) which contain high concentrations of pristane (Blumer et al., 1964) relative to other zooplankton genera.

In most of the stations, the triterpenoids appear to be derived mainly from bacteria or algae (DeRosa *et al*., 1971; Cardoso *et al*., 1976), and consist of 17β(H)-hop-22(29)-ene (diploptene, IV in Appendix I), hop-17,(21)-ene (V), 17 B(H) -22,29,30-trisnorphpane (II, R=H, 17β), and 176(H)-hopane (III, $R=C_3H_7$) and the series of extended 17β(H)-hopanes ranging from C_{31} to C_{33}, with only minor amounts of the 17α(H)-hopanes (III). These sediments contain predominantly C_{27}, C_{30}, and C_{31} ββ triterpanes (Fig. 16). Several C_{30} triterpenes with a double bond in addition to diploptene have also been detected. Most of the C29 triterpanes found are not hopanes and their identity has not yet been determined. The extended hopanes (> C_{31}) are present as single C-22 diastereomers. The presence of predominantly 17β(H) stereomers and of the triterpenes which are present in living organisms indicates that these compounds are of recent biogenic origin. The presence of only small quantifies of 17α(H) stereoisomers suggests that there is no input from petroleum components (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Venkatesan *et al*., 1980a). As a comparison, an example of recent sediment from San Pedro Basin Southern California Bight is given in Fig. 16, where the triterpanes are predominantly the 17α(H) homologs, and the extended hopanes (III) are present as one: one mixtures of the C-22 diasteromers (Venkatesan *et al.*, 1980a). There, the dominant homolog is 17a(H), 18a(H), 21β(H)-28,30-bisnorhopane ($C_{28}H_{48}$) which has been proposed to be a molecular marker of Southern California petroleum (Seifert *et al.*, 1978; Simoneit and Kaplan, 1980). Stations from the Eastern Bering Sea contain no C28 triterpenoid.

The only exception is station EBBS 35 (Fig. 16), which shows a triterpenoidal distribution very similar to petroleum-contaminated Southern California sediments. This is consistent with the observed *n*-alkane distribution pattern of this station, typical of weathered petroleum. This sample consists predominantly of $17\alpha(H)$ homologs and the extended hopanes are present as one:onemixtures of the C-22 diastereomers. The C_{28} bisnorhopane found in Southern California petroleum is also found in this sample, but is much less abundant than in Southern California Bight sediments (Venkatesan *et al.*, 1980a).

The resolved PAH compounds are at the level of 3-20 rig/g in the area, much less than those found in Beaufort Sea sediments. Concentrations of selected PAH compounds are presented in Table 12. In general, the parent PAH compounds are more abundant than their alkyl homologs, indicating pyrolytic origin (Youngblood and Blumer, 1975) possibly derived from forest fires or long distance transport through atmospheric fallout (Lund and Bjorseth, 1977; Rahn *et al.*, 1977).

The allochthonous lipids, the primary source of hydrocarbons in these surface sediments, are probably transported to the continental shelf by river discharge and erosion and redistribution of surface sediments. Correlation of the hydrocarbon distribution in the sediments of the eastern Bering Sea with the hydrocarbons extracted from eelgrass (*Zostera marina*) and sediments from within Izembek Lagoon indicates that the latter environment may not be a significant source of hydrocarbons in the outer shelf sediments. However, carbon isotopic analysis of humic and kerogenous substances from the lagoon and shelf sediments indicates that these biologically refractory organic materials may be transported to the shelf environment (Venkatesan *et al.*, 1980b).

The presence of relatively small amounts of autochthonous hydrocarbons in the sediments, in spite of the high biological productivity of the region suggests rapid and efficient recycling of marine lipids within the water column or at the sediment-water interface. Presence of higher concentrations of relatively labile hydrocarbons derived from the autochthonous sources, identified in only a few stations on the Bering Sea shelf, may be important in an assessment of the fate and effects of petroleum products introduced into this marine environment. Any petroleum contamination and deposition in those environments may last a long time.

Norton Sound

Organic Carbon:

Total organic carbon content (Table 4) ranges from 0.12 to 1.3% and is similar to Beaufort Sea, southeastern Bering Sea and other uncontaminated marine sedimentary regimes. Sediments in the open ocean have a slightly lower carbon content in general than those nearshore. Apparently, the organic carbon content in this region, unlike that of the southeastern Bering Sea sediments, is generally related to the distance from the presumed terrigenous source, the Yukon River.

Hydrocarbons:

The distribution and dynamics of hydrocarbons in Norton Sound sediments can be found in Venkatesan et al. (1980b) in greater detail. Only a brief review of our study in this area will be reported here.

The n-alkanes in these sediments are of biogenic origin, consisting of a mixed input from marine and terrestrial environments as seen from the gas chromatograms (Fig. 10) and the data on odd/even ratios, etc. in Table 4. The terrigenous input is apparently diluted with marine contribution gradually from nearshore (Stations 1, 5, 7, 49, 131, 137) to the open ocean (33Aand 47A; Fig. 3). Sediments from the Yukon prodelta are the richest in hydrocarbons. The northern part of Norton Sound seems to be impoverished in hydrocarbons, because there are no major rivers contributing to terrigenous silt.

Sediments from stations in Norton Sound, south of Nome (Stations 47, 172, 174, 14, 15, 16, 17, 18 and 22) suspected to be near petroleum gas seeps (Cline and Holmes, 1977) do not show n-alkane and triterpenoidal distributions characteristic of petroleum (Fig. 16 e.g., NS 17).

Polycyclic aromatic hydrocarbons in Norton Sound surficial sediments show pyrolytic origin (Table 12). A core analyzed from station 5 from surface down to 90 cm contains increasing amounts of phenanthrene, fluoranthene and benzo(e)-

pyrene, with depth. This trend emphasizes the importance of natural (forest) fires in the area, contributing to PAH in the preanthropogenic period. Perylene depth profile is not well defined, although it is the most abundant PAH in the core. However, a general decrease in the concentration of perylene is observed from nearshore to offshore sediments. This may lead us to conclude that perylene is derived from a terrigenous precursor although, in the absence of comparable data on depth profiles from a station in the open ocean (where terrestrial input is minimal), a marine precursor cannot be ruled out.

The di- and triterpenoids are of biogenic origin (Fig. 16). A detailed discussion of the triterpenoids in these sediments is presented by Kaplan et al (1 980) and Venkatesan et al. (1980 b).

Navarin Basin

Sample Collection:

In the cruise of the USCGC POLAR STAR in May, 1980 (Table 1) sediment samples, 2-25, were collected from Navarin Basin and samples 26-33 from around St. Lawrence Island and Cape Romanzof (Fig. 4). Surface (0-2 cm) samples, 2-11, were collected with a modified Van Veen sampler after which the sampler was lost in the Bering Sea. The rest of the samples are bulk samples, retrieved from a small Van Veen sampler.

Organic Carbon:

Organic carbon content (Table 5) of the sediments falls within the range from 0.1 to 1.4%, comparable to values observed in any other part of the Alaskan Shelf and is typical of unpolluted marine sediments (Palacas et al., 1976). These values are much lower than those observed in areas which have highly reducing conditions, such as Saanich Inlet and the Black Sea (Nissenbaum et al., 1971; Degens, 1971). No clear trend in regional distribution within the area is seen for the organic carbon contents.

Hydrocarbons:

The contents of the various resolved hydrocarbons are presented in Table 6. The total resolved *n*-alkane content ranges from 0.25 to 2.6 µg/g and is comparable to that found in Southeastern Bering Sea (Venkatesan *et al*., 1980b). Considering the remoteness of the area, the *n*-alkane contents of the sediments in this region is high, thus probably indicating greater contribution from marine productivity.

Representative gas chromatograms are presented in Fig. 4. The gas chromatograms exhibit flat baselines and a maximum at *n*-C_{27}. The odd/even ratios are similar to those observed in Norton Sound falling within a narrow range from 3.5 to 4.8, indicative of substantial terrigenous influx. This is contrary to what is expected from the geography of the region where allochthonous input from rivers and lagoons should be minimal. This is also surprising in view of our observation in the Norton Sound region (Venkatesan *et al*., 1980b) where the terrigenous detritus appeared to be diluted by open ocean sedimentation. However, the data suggests that at least part of the terrigenous detritus is transported to this Basin from the Yukon River delta in Norton Sound. Probably smaller waves with shorter periods generated by northeasterly winds move southward in the direction of Navarin Basin (Larsen *et al*., 1980); or, sediment could possibly be transported from the southern Bering Sea where major wave trains originate and move northward into Navarin Basin and Norton Sound.

Pristane is present in a few samples and in very low amounts (1-11 rig/g). Phytane if present is below the detection limits, again indicating that the environment is "clean", free of petroleum hydrocarbons.

In short, the absence of unresolved complex mixture signals and the distribution pattern of major alkanes in the Navarin Basin sediments can be attributed entirely to recent biogenic input.

The sediments in this basin contain much larger amounts of olefins eluting around Kovats indices 2100, 2600, 2800 and 3000, than the *n*-alkanes and aromatic compounds compared to any other area in the Alaskan shelf. The most dominant olefins around 2100 may be the same alkenes found in other parts of the Alaskan Seas (Kaplan *et al.*, 1979; 1980). The other olefins occurring in the gas chromatograms of the aromatic fractions are next in order of abundance (at least 80% of that eluting around Kovats index 2100). In most of the samples analyzed (23 out of 28) olefins at Kovats index $\sim$ 2600, $\sim$ 2800 and $\sim$ 3000 are the dominant compounds in the polynuclear aromatic hydrocarbons fraction. The distribution pattern of these three major olefins in the sediments from Navarin Basin is unique to this area in the entire Alaskan Shelf studied so far. A few sediments in other parts of Alaska contain moderate amounts of squalene, an olefin eluting around Kovats index 2800. The olefin eluting around KI 2600 is a C_{25} tetraene similar to the one reported by Barrick and Hedges (1981) from Puget Sound sediments. Yet as far as we know the olefin eluting around Kovats index 3030 has not been reported in the literature. This is a $C_{30}H_{50}$ compound which is prominent in all the samples. The mass spectra indicates that it is a fused bicyclic tetraene with the two fused rings at one end of the molecule. The identity of the compound needs to be confirmed by hydrogenation. This could be an intermediate product between squalene and a triterpenoid. The abundance of these polyolefins indicate input from phytoplankton or zooplankton.

Trace amounts of diterpanes ranging from C_{19} to C_{24} have been identified by GC/MS (Fig. 17). These are probably derived from resinous higher plants (Simoneit 1977). Diterpenes also occur in small amounts.

In most of the stations, the triterpenoids appear to be derived mainly from bacteria or algae (DeRosa *et al.*, 1971; Cardoso *et al.*, 1976) and consist of 17β(H)-hop-22(29)-ene (diploptene, IV) as the most predominant component (Fig. 17).

The other predominant homologs are the C_{27} triterpenoid, 17β(H)-22,29,30-trisnorhopane (II, R=H) and C_{30} and C_{31}, 17β(H),21β(H)-hopanes (II). The C_{29} moretane (17β(H),21α(H) and iso-hop-13(18)-ene are present in moderate amounts in most of the stations. The presence of minor quantities of 17α(H) stereomers and the presence or predominance of only one C-22 diastereomer (in hopanes $\geq C_{31}$) suggest the absence of input from petroleum components (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Venkatesan et al., 1980a)

The resolved polycyclic aromatic hydrocarbons (PAH, 20-40 rig/g, Table 11) in sediments from this area are comparable to those found in Norton Sound and southeastern Bering Sea and an order of magnitude less than in Beaufort Sea sediments (Table 11). The presence of phenanthrene, methylphenanthrenes, pyrene and floroanthene indicates pyrolytic sources rather than input from crude oil shales (Coleman et al., 1973; Youngblood and Blumer, 1975).

Perylene is present in large amounts (6-12 rig/g) compared to other PAHs in the samples. It has to be noted, however, that in Norton Sound, samples of perylene content appeared to decrease progressively from nearshore to offshore sediments suggestive of a terrigenous precursor for perylene (Venkatesan et al., 1980b) in the area. The data in the Navarin Basin lends support to this argument. Note that substantial terrigenous influx has been indicated earlier by higher odd/even ratios in Navarin Basin.

Cadalene and simonellite occur only in traces whereas retene is found in measurable amounts (Table 11). These diterpenoids are molecular markers derived from terrigenous resinous plants again, suggesting the allochthonous input into the Basin.

By virtue of its location, Navarin Basin should be expected to be impoverished in terrestrial material. Yet our data do indicate substantial terrigenous hydrocarbons in the sediments. The hydrocarbon and n-alkane contents, and odd/even ratios are in the same range as observed for Norton Sound and southeastern

Bering Sea. This would suggest that the latter two areas contribute terrestrial matter to Navarin Basin by wave action and sediment transport. Consequently any oil spillage arising from future petroleum development in Norton Sound or southeastern Bering Sea would be expected to affect the benthic ecosystem in Navarin Basin as well. Hydrocarbon levels should therefore be monitored in Navarin Basin also in the event of exploration and drilling in the other two areas.

Gulf of Alaska

Organic Carbon:

The organic carbon content (Table 7 and 8) varies from 0.1 to 1.1% and is similar to that observed in southeastern Bering Sea and Norton Sound sediments. This low amount is characteristic of unpolluted environments. No clear trend of organic carbon content with grain size or distance from the shore is evident.

Hydrocarbons:

Total hydrocarbons and resolved n-alkanes are comparable to those found in southeastern Bering Sea (Tables 7 and 8). The alkanes range in length from n-C_{15} to n-C_{33}, and have a bimodal distribution with maxima at either n-C_{22} and/or n-C_{27} or C_{29}. An odd carbon predominance exists in the C_{25} to C_{33} region, while no such predominance exists in the C_{22} region. Therefore, the resultant odd/even ratio from C_{15} to C_{33} falls in the range 1 - 2.5 (Tables 7 and 8). Associated with the cluster of n-alkanes maximizing at n-C_{22} is a narrow unresolved complex mixture as illustrated in the chromatograms in Figure 12. The nonselective distribution of n-alkanes maximizing around n-C_{22} and the associated unresolved complex mixture could be derived from bacterial decomposition of algal material (Johnson and Calder, 1973; Cranwell, 1976) rather than from petroleum. The lack of petroleum residues in these sediments is consistent with the absence of oil-utilizing microorganisms in this area (Atlas, 1976). The alkanes from n-C_{25} to n-C_{33} with odd carbon preference are characteristic of terrigenous higher plants whose contribution is probably not enough to dilute the autochthonous contribution from microbial activity. In contrast to the predominance of allochthonous hydrocarbons in the southeastern Bering Sea, much wider range in the relative proportion of marine and terrestrial hydrocarbons is encountered in the Gulf of Alaska sediments. This is consistent with the textural distribution of sediments which varies considerably, regionally as well as locally, in the Gulf (Sharma, 1979), while a gradation in the sediment grain size is evident in the eastern Bering Sea from nearshore to offshore.

The di- and triterpenoids are of biogenic origin with the predominance of 17β(H),21β(H)-hopanes and also several di- and triterpenes (Figure 15). The 17α(H),21β(H)-hopane (C_{30}) is present at relatively higher levels in station 119 than encountered in other Alaskan areas. Yet, the lack of a homologous series of extended triterpanes and the absence of both the diasteromers at position 22 with 1:1 ratios would indicate the absence of petroleum in the sediments.

Resolved PAH compounds in this region is an order of magnitude greater than those found in Bering Sea or Norton Sound, but comparable to that in Beaufort Sea (Table 11). Since microbial activity appears to be dominant in this area, it is possible that by unknown mechanisms, the marine bacterial population could accumulate (Hase and Hites, 1976) or contribute to the PAH content, in addition to long distance atmospheric transport of pyrolytic PAH. Methyl phenanthrenes and phenanthrene are the dominant PAH and pyrene is present in moderate amount whereas fluoranthene is found only in traces. Fluoranthene to pyrene ratio is much less than that found in other Alaskan areas or in the Recent sediments from other parts of the world (LaFlamme and Hites, 1978). This type of distribution leads us to conclude that pyrolytic PAH have less significant contribution to the area than probably bacterial synthesis or bioaccumulation of specific PAHs. However, a more detailed study is necessary before any meaningful conclusion is drawn regarding the sources of PAHs. Terrigenous input is indicated by the presence of retene, cadalene and simonellite as is evident from the <u>n</u>-alkane distribution.

The presence of relatively labile polyolefins in sediments, eluting around *n*-C_{21} may indicate relatively less oxidizing depositional environments as discussed previously on the southeastern Bering Sea sediments. The sediments at station 121 and 134 have high organic carbon (1.1%) and clay contents compared to other Gulf of Alaska and Southeastern Bering Sea sediments, suggesting a sedimentary regime favorable to the accumulation of organic material. Sediments which apparently accumulate and preserve labile lipids should be considered areas of continental shelf that would be most affected by petroleum introduced into the marine environment.

Kodiak Shelf:

Organic Carbon:

Organic carbon content (Table 9) is within the range 0.2 - 1.2% and comparable to values typical of unpolluted marine sediments and similar to those found in eastern Bering Sea and Gulf of Alaska. Stations 97 and 98 have the highest percent organic carbon (2.15; 2.45%, Table 9) and these stations contain sediments of clayey silts. Two other stations having organic carbon $\geq$ 1.0% (92 and 93%, Table 9) are in the region reported to contain clayey silty sand, while in the rest of the stations studied, mainly sandy gravel or gravelly sand prevail (Sharma, 1979). This would explain the low organic carbon content observed in most of the sediment samples.

Hydrocarbons:

The total resolved *n*-alkanes range from 20 to 800 rig/g (Table 9). Distinct trends in hydrocarbon distribution were not noticed, although the highest hydrocarbon levels and organic carbon contents were found at the southernmost stations, 92, 97 and 98. In general, excluding these three stations, Kodiak area sediments have the least lipid and *n*-alkane content of all the sites investigated. The resolved *n*-alkanes (10-420 rig/g) are less by an order of magnitude compared to those of Beaufort Sea sediments and about 2-5 times less than in any other Alaskan area studied.

A representative gas chromatogram is given in Figure 13. Most of them have a maximum at n-C_{27}, except a few which maximize at n-C_{29}. The odd/even ratios are generally between 0.8 and 2.8 and are conspicuously lower than in the other sites, indicating that terrigenous input is substantially reduced in this area (Table 9). Unlike the other regions which may receive allochthonous material from rivers and intertidal marshes, transport of allochthonous material to the area around Kodiak Shelf is expected to be minimal because of the steep rugged topography of the Alaskan Peninsula which borders the shelf on one side and the Pacific water and the Gulf of Alaska on the other side. This region lacks large rivers and barrier island marshes. However, allochtonous organic material may be transported to this area from Cook Inlet, although the major sediment transport is reported to be through Shelikof Strait into the western Gulf of Alaska (Sharma, 1979).

A very narrow unresolved complex mixture signal localized around n-C_{21} to n-C_{23} could be attributed to the bacterial decomposition (Johnson and Calder, 1973; Cranwell, 1976) of algal material rather than a petroleum source. It is more likely that sediments in the west and south, rather than east of Kodiak Shelf would be contaminated with petroleum where hydrocarbons from natural seeps in Cape Douglas or from the oil and gas production in upper Cook Inlet would be expected to be transported by surface currents and deposited.

The abundance of polyolefins in the sediments indicate input from phytoplankton or zooplankton and similar polyolefins have been detected in continental shelf sediments from the Gulf of Mexico (Gearing et al., 1976) and the Atlantic Coast (Barrington et al., 1977). Kodiak area is known for high biological productivity and is important for commercial and sport fisheries. It is therefore not surprising to see relatively more input of marine organic matter into sediments around this area.

Several diterpanes, diterpenes, triterpanes and their extended homologs characteristic of biogenic origin have been detected in the two samples (stations 92 and 130) analyzed by GC/MS, similar to the other areas studied. The two diastereomers (S and R) at position 22 of the C_{31} and C_{32} triterpanes have been detected in both the samples and the diastereomer eluting earlier is present only in trace amounts mixed with a C_{30} triterpene (Figure 15).

The concentrations of resolved aromatic hydrocarbons are in the range of 6-100 rig/g except in station 98 (200 rig/g) which has the highest aromatic content of all the stations in the area (table 11, Fig. 13). Station 80 represented in the figure shows typical distribution pattern of aromatic compounds in the area (not considering the three major peaks which will be discussed later). Samples 80 and 98 contain phenanthrene, methyl phenanthrenes, naphthalene, fluoranthene, pyrene, chrysene and their methylated homologs (Table 11). Benzo(E)pyrene, pyrelene and coronene were detected in both the samples, whereas benzo(A)pyrene is present only in station 98. In station 80, the three major peaks are 2-butoxy-2-oxoethylbutylphthalate, bis(2-hexyl-ethyladipate) and dioctylphthalate, respectively, the sources for which are unknown. No other station in this area appears to contain these compounds, as evident from the gas chromatographic profiles. Procedure blank did not contain these compounds. The PAH content in Kodiak area sediments is comparable to that in Gulf of Alaska. Since the *n*-alkanes profile indicates substantial marine input, it is likely that marine bacteria contribute to the PAH budget in these sediments probably by bioaccumulation (Hase and Hites, 1976) in addition to pyrolytic input.

Traces of simonellite, cadalene and retene are present but are usually less abundant than those found in Norton Sound, southeastern Bering Sea, Gulf of Alaska or Navarin Basin. This indicates much less terrigenous input in this region.

Sediments in a few stations having high organic carbon and clay contents relative to other stations in this region imply a favorable sedimentary regime for the accumulation of organic material. This region where sediments apparently accumulate and preserve especially labile lipids such as alkenes derived from the autochthonous sources, may be important in the assessment of the fate and effects of petroleum into the marine environment. Any petroleum deposition in those environments may have a long residence time.

Cook Inlet

Organic Carbon:

The total organic carbon contents vary from 0.06 to 1.57% and are characteristic of unpolluted, relatively coarse marine sediments (Table 10). The Kachemak Bay and Shelikof Strait regions contain relatively fine-grained sediments and higher organic carbon content (> 1%) than the sandy gravel or gravel (Sharma, 1979) found in the northern and central regions of Cook Inlet, including Kamishak Bay. This might indicate enhanced hydrocarbon accumulation in the two former regions. The higher values observed in Kachemak Bay are also from the very high primary productivity persisting over several months in this area. Phytoplankton productivity and standig stocks of chlorophyll *a*, found to be highest in Kachemak Bay, decrease steadily to low values in the middle of the inlet (Larrance *et al.*, 1977). Part of the organic matter that is produced in the Kachemak Bay region probably settles to the sea floor and gets buried within the sediments. However, the remaining fraction of the organic matter produced in Kachemak Bay may eventually be deposited in Shelikof Strait via the net water circulation to the north in the eastern shore and to the southwest along the western shore into Shelikof Strait (Muench *et al.*, 1978; Hein *et al.*, 1979). This would contribute to the higher organic carbon content in the Shelikof Strait area.

Hydrocarbons:

Replicate samples collected from a total of six stations on different cruises had similar gravimetric and gas chromatographic data (Table 10) within the limits of experimental error, indicating the homogeneity of samples 'retrieved and reliability of the experimental method employed. The analyses of samples from stations 204, 212, and 390 in both spring and summer (1978) also gave similar gravimetric and gas chromatographic results (Table 10), indicating that there might be no apparent seasonal variation in the hydrocarbon input to the sediments (Kaplan et al., 1979). These findings may be related to the study of Roubal and Atlas (1978) who observed no significant differences between counts of hydrocarbon utilizers in summer-fall and winter-spring samples from lower Cook Inlet despite the higher concentrations of suspended matter found in spring (Feely et al., 1978). Thus, the data for all the samples are discussed in this report emphasizing the geographical distribution of hydrocarbons in the sediments rather than the seasonal variation.

The lipid, total hydrocarbon, alkane, and resolved n-alkane contents follow the same trend as organic carbon. They are generally high in and around Kachemak Bay (stations 37', 43 and 227; Figures 7 and 8, Table 10) and low in the central and upper parts (except stations 27, 255 and 265) of lower Cook Inlet. Stations near Shelikof Strait are next to Kachemak Bay in the order of abundance of lipids and alkanes, whereas the western part (Kamishak Bay) is moderately enriched with lipids. A detailed discussion of the hydrocarbons distribution in the area can be found in the annual report by Kaplan et al. (1980).

The n-alkanes in sediments of the study area generally show a bimodal distribution of biogenic origin, typical of mixed marine and terrestrial hydrocarbons (Fig. 14). An odd-carbon predominance of n-alkanes characteristic of terrigenous plants is evident in most stations (Table 10), suggesting the influence of major rivers in the area. The n-fatty acids (unbound) present in these samples are also typical of a mixed marine and terrestrial input.

A few stations in Shelikof Strait and near Barren Islands (UC100, UC200, UC300, 378, 394 and 398; e.g., Fig. 14) show moderately large unresolved complex mixtures in the gas chromatograms of their aliphatic fractions. The GC/MS data (Fig. 18) of these samples rule out the presence of oil input. This type of distribution could be attributed to bacterial decomposition of algal material (Johnson and Calder, 1973; Cranwell 1976)

Exceptions are stations 265 and 27 north of Kalgin Island, which show distributions of n-alkanes and triterpenoids, characteristic of oil pollution (Fig. 14 and 18). The triterpenoidal distribution of sediments from Station 265 is similar to that in Cook Inlet oil (samples obtained from J. Payne, SAI, California) as illustrated in Fig. 18. In both the sediment and oil, the diterpanes occur as mixtures and therefore, are not represented in the histogram. Oil production activities in upper Cook Inlet may be the contaminating source in Station 27 and 265. However, the possibility of a local seep around Kalgin Island with similar triterpenoidal distribution cannot be ruled out.

The following are other data which corroborate our results on HMWHC from station 265: The source of anomalously high concentrations of ethane and propane observed in upper Cook Inlet has been attributed to chronic petroleum seeps and/or fossil fuel development in the area (Cline et al., 1979). The petroleum hydrocarbon pollution apparent at stations 265 and 266 (northeast of 265, sediment not collected for HMWHC analysis) has also been inferred from microbiological studies. The effect of crude oil on the uptake of glucose and glutamic acid in the water samples were minimal in the stations taken nearest to the existing drilling platforms north of Kalgin Island (stations 265 and 266), indicating that the populations in this area have been exposed to crude oil and thus are resistant to its acute effects (Griffiths and Morita, 1979).

A complex mixture of PAH compounds was identified by GC/MS in all the sediments (Table 13). The relative distribution of parent homologs and their alkylated derivatives is characteristic of pyrolytic (natural and/or anthropogenic) sources.

Perylene is found in the samples from trace amounts to 50 rig/g. Like any other aliphatic or aromatic compound, perylene is also found at higher concentrations in Kachemak Bay (CB9-51 rig/g) and Shelikof Strait (388, UC300) than in Kamishak Bay or the central part of Cook Inlet (203, 233, Table 13). Origin of perylene in these sediments is most probably terrestrial (Bergmann *et al*., 1964; Aizenshtat, 1973). GC/MS analysis of sediments from deep cores at different stations would give more information about the origin and precursors of perylene.

The Kalgin Island area is probably the most important commerical fishing region for salmon (Stern, 1976) and halibut. Our data indicate that the sediments from this region have been contaminated with petroleum possibly from the production activities in upper Cook Inlet. This could lead to detrimental effects on the ecosystem in this region. Oil released chronically at low levels may not be deleterious since the pollutants appear to get diluted and dispersed within a short distance from the source, owing to the dynamics of water circulation in the area. But any major spill, tank or pipeline blowout may release hydrocarbons in considerable amounts such that they would be dispersed and redeposited eventually in Shelikof Strait. In that event, marine life around Shelikof Strait will be the most affected. Indeed, studies of Feely *et al*., (1979) show that little sedimentation occurs in the central basin of lower Cook Inlet and that the embayments along the coasts of lower Cook Inlet and Shelikof Strait may be receiving most of the fine particulate discharged from the coastal rivers of upper Cook Inlet. Further, suspended particles from Cook Inlet have been shown to be efficient scavengers of crude oil (Feely *et al*., 1978). Thus, any modern sediment deposited in Shelikof Strait should reflect major changes in upper Cook Inlet or in Kachemak Bay. Future environmental monitoring studies should therefore be concentrated around Kalgin Island and Shelikof Strait.

CONCLUSIONS

Organic Carbon

The organic carbon content ranges generally from 0.1 to 1.4% in the sediments from Alaskan Continental Shelf (Table 14) and these values are typical of unpolluted marine sediments. Sediments in the open ocean have a slightly lower carbon content than those from nearshore e.g., in Norton Sound and Cook Inlet. In southeastern Bering Sea, however, the sediments are progressively finer-grained from nearshore to the edge of the shelf and the organic carbon content increases gradually from nearshore to the shelf edge. In short, the organic carbon content in the Alaskan sediment is related to the distance from the terrigenous source of detrital minerals.

Hydrocarbons

The alkanes in sediments of the Alaskan outer continental shelf generally show a bimodal distribution (Table 14) of biogenic origin, typical of a mixture of marine autochthonous and terrestrial allochthonous hydrocarbons with few abiotic and no detectable anthropogenic components. This is indicated by greater than unity of odd/even values and by the dominance of odd chain length n-alkanes of C_{23} to C_{31} carbon atoms. These n-alkanes are derived from higher plants (Maxwell, 1971) as a result of inputs from terrigenous detritus (Simoneit, 1977). Marine origin is indicated by the dominance of heptadecane and pristane in some samples (Sargent et al., 1976). Pristane particularly in the Bering Sea region could be contributed by Calanus copepods (Motoda and Minoda, 1974). Phytane when present in moderate amounts can be thought to be produced biosynthetically (Maxwell et al., 1971) by bacteria (Tissot and Oudin, 1973), rather than from petroleum (Zafiriou et al., 1972). In short, the absence of unresolved complex mixture signal and the distribution patterns of major alkanes in the Alaskan Seas are characteristic of a pristine environment. A narrow unresolved complex mixture signal localized around n-C_{21} to n-C_{23} in all the Gulf of Alaska and a few of Kodiak Shelf and Cook Inlet sediment samples, has been observed. This could be attributed to the bacterial decomposition (Johnson and Calder, 1973; Cranwell, 1976) of algal material rather than a petroleum source.

The molecular markers such as diterpenoids, 17β(H),21β(H) and olefinic triterpenoids and extended 17β(H),21β(H)-hopanes also reflect biogenic origin of the lipids in most of the sediment samples.

Exceptions are stations 27 and 265, north of Kalgin Island, in lower Cook Inlet, which show a typical weathered petroleum distribution of n-alkanes. The triterpenoidal residue consists predominantly of 17α-hopanes and R and S diastereomers at position 22 in nearly 1:1 abundance which are characteristic of petroleum contamination. This material could probably be derived from petroleum production and transport in upper Cook Inlet.

The n-alkane and triterpenoidal distribution in Station 35 from southeastern Bering Sea also reflect a weathered petroleum input.

Some of the stations near Norton Sound, south of Nome, suspected to be near natural gas seeps do not show n-alkane and triterpenoidal distributions characteristic of petroleum.

A complex mixture of PAH compounds is identified by GC/MS in all the sediments. The relative distribution of parent homologs and their alkylated derivatives is characteristic of pyrolytic (natural and/or anthropogenic) sources. Station 1 in Beaufort Sea possibly shows fossil PaH input to some extent. Perylene 1,12 benzoperylene and coronene whose origin is still debatable have been detected in all sediment extracts. A gradual decrease in the concentration of perylene with distance from the presumed terrigenous source is noted in Norton Sound sediment samples. Also, in our extensive investigation of surface sediments from the entire Alaskan Seas, we found that Kodiak Shelf sediments contain only trace amounts of perylene, although other PAH compounds are relatively more abundant in these samples. Kodiak Shelf is noted for is high biological productivity where marine hydrocarbons predominate over terrestrial hydrocarbon components. Navarin Basin sediments which show substantial terrestrial input, also contain relatively higher perylene content (Table 11), although little terrigenous influx would be expected from its geographical location in the offshore area as discussed earlier. Thus, our data indicate that it is most likely the terrigenous precursor which contributes to the generation of perylene in Alaska, rather than a marine precursor as suggested by Wakeham _e_t _a_l. (1979) from their study of perylene in two Nambian Shelf sediment cores in the offshore area of southwest Africa, where terrestrial input is minimal. They found perylene content to increase with depth of the sediment core. We have analyzed a core from station 5 in Norton Sound (nearshore, where terrestrial input is considerable) from O-2 cm to 90 cm at 5-10 cm intervals. Perylene is the most abundant PAH compound throughout the core (to be published). There are fluctuations in the perylene depth profile in this core and it is not clear whether there is a significant increase in its concentration as a function of depth. Fluctuations in the quantity of precursor input may be the reason for this type of depth concentration profile. However, we do not have data on the depth profile of perylene concentration from an offshore Alaskan area where terrestrial input is negligible. Therefore, marine precursor for perylene cannot be ruled out, either. Analyses of a sediment core from Kodiak Shelf (terrigenous source minimal) would be helpful in confirming whether perylene in Alaskan sediments is derived from a terrestrial or marine origin.

High molecular weight hydrocarbon data of surface sediments from different regions of the Alaskan shelf indicate that the entire Alaskan area is uniformly "clean" free of petroleum contaminants except in a few isolated cases. Table 14 shows that the organic carbon content in these sediments is $\leq$ 1.5%, characteristic of pristine environment. Unresolved complex mixture is present in a very few samples and the total hydrocarbon contents in the sediments vary from 0.9 to 50 µg/g. These values are low; petroleum hydrocarbon levels of uncontaminated coastal sediments elsewhere are usually below 70µg/g (Clark and MacLeod 1977). However, there are differences in the hydrocarbon contents in the various areas of the Alaskan shelf. Beaufort Sea sediments have the highest hydrocarbon budget, whereas Kodiak Shelf sediments have the lowest. Resolved n-alkanes follow the same trend (Fig. 19), but PAH compounds do not exhibit the same pattern and the Gulf of Alaska and Kodiak Shelf sediments are rich in PAH biologically-produced, as well as those produced by pyrolytic combustion. Even though the PAH content in the above two areas is as high as that observed in Beaufort Sea sediments, the pyrolytic and biogenic imprint predominates in the former areas while a mixed pyrolytic and fossil PAH profile is reflected in the latter (Tables 11-13).

Terrigenous influx is indicated by the maxima at C_{27} or C_{29} in all the sediments (Table 14). The odd/even ratios in Fig. 19 illustrate that the terrestrial input varies from region to region in the Alaskan outer continental shelf. Of all the areas investigated, Norton Sound and Cook Inlet receive the maximum plant wax contribution whereas Gulf of Alaska and Kodiak Shelf, the least. Beaufort Sea, Navarin Basin and southeastern Bering Sea are second in the order of plant wax content. Allochthonous hydrocarbons are to be expected in Beaufort Sea, Cook Inlet, Norton Sound and Bering Sea from their geographical location. It is rather surprising to notice relatively higher terrigenous lipids in Navarin Basin. Terrestrial lipids are probably transported to this area from southeastern Bering Sea and/or Yukon Prodelta in Norton Sound. In short, Navarin Basin could be a sink for terrigenous lipids. This implies that any petroleum contaminant from production activities in Norton Sound or southeastern Bering Sea could affect Navarin Basin equally or more than the other two areas.

In the lower Cook Inlet area, the lipid, hydrocarbons and organic carbon contents are generally high in and around Kachemak Bay and stations in Shelikof Strait are next in the order of the abundance of organic matter. Central and upper parts of the inlet have the least. It appears that organic matter produced in Kachemak and Kamishak Bays may be deposited in the Shelikof Strait, an hypothesis which is consistent with the postulated net circulation pattern of the water and suspended matter (Muench et al., 1978; Feely et al., 1979). This observation suggests that petroleum hydrocarbons released in considerable amounts resulting from any major spill, tank or pipeline blow out in upper Cook Inlet would be dispersed and redeposited eventually in Shelikof Strait. Further, suspended particles from Cook Inlet are known to be efficient scavengers of crude oil (Feely et al., 1978). Future environmental monitoring studies should therefore be focussed on Kalgin Island (where petroleum hydrocarbons have been identified) and Shelikof Strait.

The major sediment transport from Cook Inlet is through Shelikof Strait into Western Gulf of Alaska (Sharma, 1975). Petroleum hydrocarbons could therefore be traced in the sediments of Gulf of Alaska in the event of major oil release from upper or lower Cook Inlet in the future. Eastern Kodiak Shelf would probably be less affected except in a few southernmost stations. Sediments in these stations have higher clay and organic carbon contents and imply favorable regime for the accumulation of organic material.

Relatively labile polyolefins are present in large amounts in a few stations in southeastern Bering Sea, Gulf of Alaska, in all the stations in Kodiak Shelf and Navarin Basin. This may indicate relatively less oxidizing depositional environment. Such areas of the continental shelf where sediments apparently accumulate and preserve labile lipids would be most affected by petroleum introduced into the marine environment.

Thus our organic geochemical study is able to point out areas of sedimentation which would be more affected by petroleum pollution. Future environmental monitoring studies should be focussed on these sensitive areas whenever exploration or oil drilling operations are carried out in the vicinity.

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PUBLICATIONS AND PRESENTATIONS

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Venkatesan, M.I., M. Sandstrom, S. Brenner, E. Ruth, J. Bonilla, I.R. Kaplan and W.E. Reed (1980). Organic geochemistry of surficial sediments from the Eastern Bering Sea. In: *The Eastern Bering Sea Shelf: Oceanography and Resources*, (D.W. Hood and J.A. Calder, Eds.), Vol. 1, OMPA/DOC, USA; 3$3%409.

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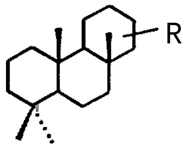
Venkatesan, M.I., S. Brenner, E. Ruth, J. Bonilla and I.R. Kaplan (1980). Organic geochemistry of surficial sediments from lower Cook Inlet, Alaska. To be submitted to *Chemical Geology*.

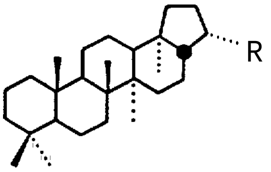
Venkatesan, M.I. *et al.* (1980). Distribution and dynamics of hydrocarbons in different areas of Alaskan outer continental shelf: A comparative study and its implications. In preparation.

APPENDIX I

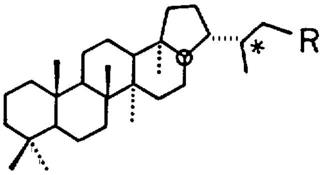
STRUCTURES CITED IN THE TEXT



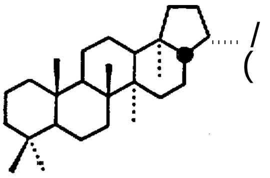
I. extended diterpanes, C_nH_{2n-4}
R= C_2H_5-$C_{12}H_{25}$



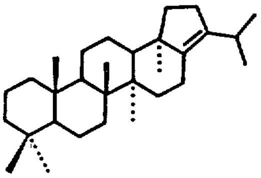
II. 17β (H),
21β(H)-hopanes, C_nH_{2n-8}
R=H,C_2H_5,C_3H_7



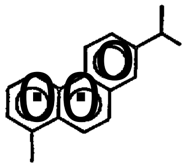
111. extended 17α (H),
21β (H)- hopanes, C_nH_{2n-8}
R= CH_3-C_5H_{11}



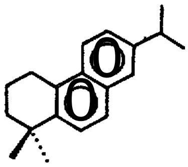
IV. diploptene, $C_{30}H_{50}$



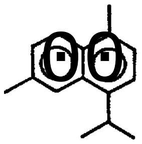
V. hop-17 (21) -ene, $C_{30}H_{50}$



VI. retene, $C_{18}H_{18}$



VII. simonellite, $C_{19}H_{24}$



VIII. cadalene, $C_{15}H_{18}$