AN ABSTRACT OF THE THESIS OF

Sarah E. Walinsky for the degree of Honors Baccalaureate of Science in Environmental Science and the degree of Honors Baccalaureate of Liberal Arts in Philosophy presented on May 22, 2007. Title: Distribution and Origin of Organic Matter Preserved in Modern Surface Sediments throughout Coastal SE Alaska

Abstract approved: _____
Fred Prahl

Twenty seven modern (top 1-2cm) sediment samples from multicores retrieved from throughout coastal SE Alaska were analyzed for their organic matter content and the source composition. Total organic carbon (TOC) as well as biogenic silica (bioSi), and calcium carbonate ($CaCO_3$) content were analyzed to evaluate the organic matter content and its context with respect to total sediment mass. Terrestrial and marine contribution to TOC content was assessed from interpretation of the spatial distribution of elemental (C/N), stable isotopic ($\delta^{13}C$, $\delta^{15}N$) and a variety of lipid biomarker measurements. Results showed that TOC was highly enriched in the region of the study area south of 58^{o}N off the coast of the Queen Charlotte and Baranof Islands. TOC was highly correlated with bioSi content ($r = +0.98$), indicating that the majority of the TOC originates from diatom production in this area. C/N, $\delta^{13}C$ and $\delta^{15}N$ results indicated higher terrestrial contribution to TOC deposited north of 58°N and higher marine contribution to the south. Lipid biomarkers of marine origin, such as long chain (C_{37-39}) alkenones and highly branched isoprenoid (HBI) C_{25} and C_{30} hydrocarbons, were most enriched in the sediments south of 58°N, consistent with results from bulk analyses. However, brassicasterol and dinosterol, two sterols indicative of diatoms and dinoflagellates, respectively, displayed no recognizable spatial pattern. Concentrations for homologous series of long chain (>C_{20}) n-alkanes, n-alcohols and n-acids of terrestrial

origin were distributed in a pattern largely counter to that of the bulk analyses. Long chain n-alkane signatures isolated from northern sediments were not typical of higher plants but rather displayed a lack of odd carbon number predominance. Those in southern sediments were typical of higher plants and accompanied by a major relative amount of the pentacyclic triterpene, 17β(H),21β(H)-hop-22(29)-ene (diploptene). These biomarker observations suggest that the terrestrial component of TOC deposited in sediments north of 58^{o}N is fossil organic matter associated with glacial outwash of major rivers in that area, while that in sediments depositing to the south is derived from more modern soil erosion processes.

Key Words: Gulf of Alaska, total organic carbon, stable isotopes, lipid biomarkers, sediments, terrestrial, marine

Distribution and Origin of Organic Matter Preserved in Modern Surface Sediments throughout Coastal SE Alaska

By

Sarah E. Walinsky

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I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My Signature below authorizes release of my project to any reader upon request.

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Sarah Elizabeth Walinsky, Author

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Introduction

Biogeochemical cycling of organic carbon plays an important role in controlling atmospheric oxygen (pO_2) and carbon dioxide (pCO_2) levels (BERNER, 1982). Burial of organic matter in marine sediments provides a source for pO_2 and a sink for pCO_2. Thus, defining patterns of organic carbon burial in marine sedimentary environments, and, determining the processes responsible for setting these patterns are key to unraveling how human activities influence climate change.

The organic matter preserved in ocean sediments represents an unknown blend of terrestrial and marine source inputs, an issue particularly relevant along coastal margins. Terrestrial sources include erosion of relatively fresh (litter from higher plant) and degraded (humous in soils, kerogen in minerals) materials while marine sources include 'export' production from phytoplankton in surface waters and bacterial biomass responsible for degrading both terrestrial and marine materials. The relative proportion of the different contributions and the absolute amount of organic matter deposited and ultimately buried depends on the sedimentary setting.

Continental margins are a dominant area for organic carbon burial, accounting for >80% of the estimated ~130×10^{12} g buried each year throughout the ocean (HEDGES and KEIL, 1995). Niggemann et al. (2007) focused on two parts of the Chilean coastal upwelling region: an arid hinterland with low clastic sediment inputs ~23°S off Antofagasta and a humid hinterland with high sediment loading ~36°S off Concepción. They found that such climatic differences can have significant bearing on the organic matter content, composition, and turnover of underlying coastal sediments independent of water column productivity and vertical particle flux.

Along the northern Gulf of Mexico shelf, Gordon and Goni (2003) looked at the heterogeneity of terrestrial contributions to the sediments. They found more vascular plant debris deposition close to the mouth of the Atchafalaya River, while the terrestrial material deposited farther out on the shelf was representative of soil-derived organic matter. Their work indicated that reliable quantification of terrestrial contribution to organic matter in this marine shelf environment must be done using a three-end-member mixing model.

A similar study to our own was conducted in the eastern South Atlantic around the mouth of the Congo River (SCHEFUβ et al., 2004). This study looked at the lipid biomarker and bulk organic geochemical characteristics of the sediments to identify the sources, transport pathways, and preservation processes of the organic matter in this area. This study was used as a precursor for investigating paleoenvironmental changes throughout the SE Atlantic. They found the highest marine organic matter content along the coast, especially in the upwelling portion of their study region. They also examined an area highly influenced by the Congo River where a large amount of terrigenous organic matter was introduced. Lipid biomarker analysis showed a large amount of marine production resulted from nutrient rich river water entering the marine system from of the Congo River plume and eastern Angola Basin during the summer. The marine production was also enriched via upwelling during the winter in this study site (SCHEFUβ et al., 2004). Most of the terrestrial biomarker signatures were a result of river inputs from the Congo River or from trade winds.

Studies similar to our study of the SE Alaskan continental margin have been done throughout much of the world's continental margins. However, most of them have been

conducted along temperate and tropical margins as was the case in the examples cited above. Very little study of arctic and subarctic continental margins has been done.

In this respect, our study of SE Alaska in the subarctic Pacific is relatively novel. By performing geochemical analysis of modern sediments recently cored in this region, we can draw comparisons other continental margins. Furthermore, from knowledge obtained through analysis of these modern sediments, we can facilitate our efforts to understand how climate-related, environmental change has affected the inputs and distribution of organic matter throughout this region of the subarctic Pacific.

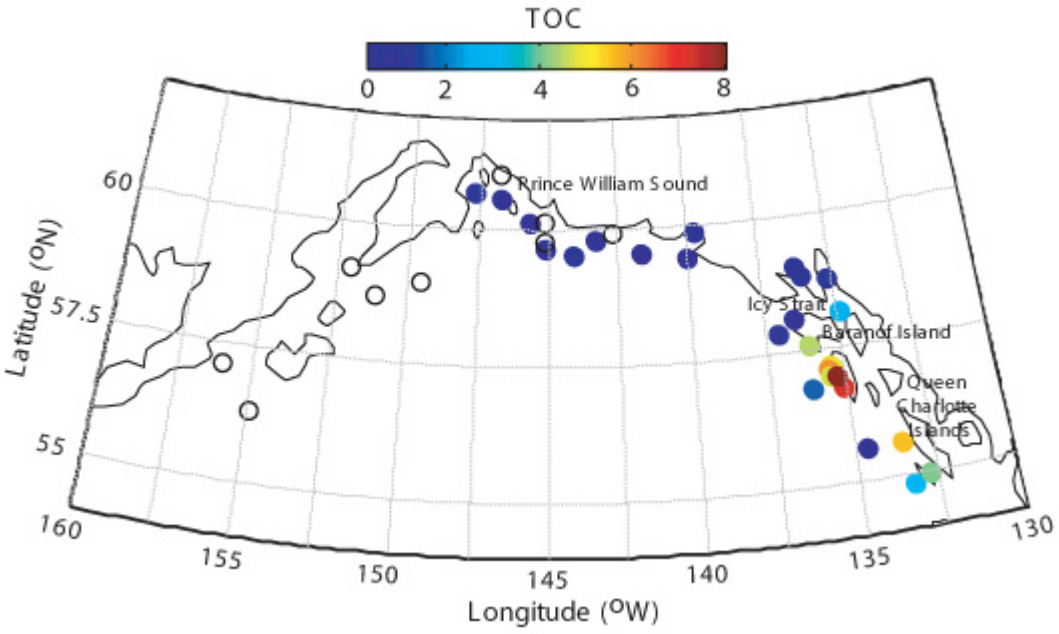

Figure 1. Each of the cores used within this site survey are represented in the colored circles above. The total organic carbon (TOC) percent concentration for each of the 27 cores analyzed in this site survey are represented by the color of the circle, based on the legend above. The unfilled circles represent sites studied by Peters et al. (PETERS et al., 1978) (see data in Fig. 3).

This paper presents data obtained by various geochemical analyses of surface intervals (0-2cm) from 27 multicores collected throughout coastal SE Alaska (Figure 1). Results include measurements of: total organic carbon (TOC) and biogenic silica (bioSi)

content, elemental (C/N) and isotopic ($\delta^{13}C$, $\delta^{15}N$) composition of organic matter, and lipid biomarker composition derived from both marine and terrestrial sources. We view this information collectively to obtain coherent answers to two basic questions about the quantity and quality of organic matter accumulating in surface sediments of coastal SE Alaska:

1. How variable is the organic matter content of sediments depositing today throughout this study region?
2. What is the blend of terrestrial to marine organic matter preserved in these sediments and how much does it change spatially?

Methods

Description of Study Area. The region of the Gulf of Alaska that was cored in this study is comprised of a range of oceanographic settings. Coring was preformed throughout coastal and inland waters of SE Alaska from 55°N to 61°N. In the region north of Icy Strait situated at ~58°N and extending to Prince William Sound, there is a large amount of river borne, erosional input of minerals and associated organic materials derived from extensively glaciated, highly mountainous landscape. Satellite imagery for this area shows quite dramatically the large plumes of sedimentary input from these glaciated sites (see website link?). Moving west, there are a few samples further out on the continental shelf. The other samples east of 140°W are all tucked in the islands and inlets within the Glacier Bay, Juneau, and Sitka Sound area. These are influenced by diminishing extent of glaciation, especially those samples south of 58°N along the coastal margin of Baranof Island and the Queen Charlotte Islands. These sites are also

influenced by river and stream inputs from drainage of landscape where modern soils are developing.

Sediment Collection. Twenty-seven multicores were collected in the summer of 2004 on a cruise off coastal SE Alaska aboard the RV Maurice Ewing. Further details about the core sites (latitude, longitude, water depth) are given in Table 1. Upon recovery of the cores at sea, each of the eight obtained by a single deployment of the mulitcorer was stored vertically and transported under refrigeration (4°C) for archival in the Oregon State University Core Repository (http://corelab-www.coas.oregonstate.edu/). At OSU, each core was split lengthwise and each half stored horizontally in D-tubes under refrigeration until sampling. All samples for this study were 1 cm thick depth intervals taken at or from as near as possible to the top of each core (Table 1). Sample intervals not depicted as 0-1 cm in the description reflect settling that occurred during vertical storage of the core. Reported values are indexed to the top of the core liner. True core depths for these samples are given by the interval shown in parentheses.

Each sediment sample was freeze-dried and homogenized by shaking or, if necessary, gentle grinding with a spatula. A variety of organic geochemical analyses were then performed on sub-samples of this homogenized material.

Elemental and Isotopic Analyses of Carbon and Nitrogen. Total carbon (TC), total organic carbon (TOC) and total nitrogen (TN) content of each sediment was determined. TC values were obtained by analysis of untreated sediment. Briefly, subsamples (~10mg) were weighed into tin boats using a Cahn C-31 microbalance, and then carefully compressed using forceps into compact balls for analysis using a Carlo Erba NA-1500 elemental analyzer. Details of instrumental setup are given elsewhere (VERARDO et al.,

Table 1. Results from bulk elemental and stable isotopic analysis of surface sediment deposited at 27 sites in SE Alaskan study area.

Site	Description	Lat	Lon	Depth	Interval	TOC	bioSi	$CaCO_3$	Lithic	C/N	$\delta^{13}C$	$\delta^{15}N$
				cm	cm	wt%	wt%	wt%	wt%	molar	‰	‰
North												
JUN2	Lisianski Inlet	58.12	136.48	260	3-4 (0-1)	0.53±0.05	4.0	4.4±0.3	91	7.9±0.3	-21.3±0.3	5.9±0.8
JUN3	Lynn Canal	58.14	134.92	608	6-7 (2-3)	2.39±0.05	15.3	5.9±0.4	74	9.6±0.1	-20.4±0.1	6.1±0.1
JUN4	Upper Lynn Canal	58.80	135.19	263	4-5 (0-1)	0.84±0.12	6.1	2.6±0.7	90	10.0±1.8	-20.7±1.3	4.9±0.6
GOA13	Lower Muir Inlet	58.90	136.09	306	2-3	0.29±0.00	1.2	8.4±0.2	90	9.9±0.1	-21.4±0.2	4.6±0.2
GOA14	Upper Muir Inlet	59.06	136.25	265	5-6 (2-3)	0.30±0.03	1.9	10.2±0.06	87	11.5±0.4	-20.4±1.2	2.9±0.1
GOA7	Malispina Shelf	59.39	140.00	192	2-3	0.61±0.15	0.9	7.0±0.35	91	11.4±2.6	-22.2±0.7	4.4±1.0
KB1	Khitrov Basin	59.53	144.13	686	2-3	0.82±0.12	2.5	2.2±1.02	94	10.6±1.4	-22.8±0.2	3.9±1.2
MS1	Malispina Shelf	59.55	141.69	148	2-3	0.51±0.07	0.8	2.5±0.11	96	12.7±1.5	-23.1±0.6	3.1±0.5
GOA4	Kayak Trough	59.65	145.15	194	2-4	0.40	1.1	2.4	96	12.7	-24.4	2.5
GOA6	Bering Trough	59.82	143.26	176	2-3	0.43±0.01	0.2	2.2±0.04	97	11.3±0.1	-24.5±0.0	3.7±0.2
GOA10	Yakutat Bay	59.89	139.68	253	2-3	0.64±0.01	3.3	3.9	92	7.7±0.1	-22.4±0.1	5.5±0.1
GOA3	Copper River Delta	60.15	145.66	125	0-1	0.56±0.02	2.1	3.5±0.41	93	12.2±0.8	-23.4±0.4	3.7±0.8
GOA2	Lower Prince William Sound	60.56	146.77	401	2-3	0.38	0.1	5.2	94	10.1	-24.0	4.2
GOA1	Upper Prince William Sound	60.66	147.71	744	2-3	0.78±0.12	3.9	1.4±0.35	93	10.8±2.2	-21.7±1.2	4.2±1.1
South												
BAR3	Deep Inlet	56.96	135.27	89	22-23 (0-1)	8.0±0.01	32.5	3.8±0.41	48	10.9±0.1	-21.4±0.5	6.5±0.5
BAR1	Crawfish Inlet	56.77	135.14	106	7-8 (2-3)	7.2	33.1	4.7	48	9.8	-20.7	6.7
BAR7	Nakwasina Inlet	57.18	135.41	119	0-1	5.2±0.06	29.1	2.5±1.0	58	9.8±0.1	-21.3±0.3	6.7±0.2
BAR8	Katlian Bay	57.16	135.36	151	2-3 (0-1)	4.7±0.06	17.2	1.0±0.04	73	11.1±0.2	-21.8±0.1	7.0±0.1
BAR4	Sitka Sound	57.10	135.53	178	6-7 (2-3)	5.9	28.3	7.1	53	9.6	-20.4	7.0
JUN1	Slocum Arm	57.59	136.08	178	3-4 (0-1)	4.3±0.65	13.5	39.9±3.7	38	8.1±0.9	-21.4±0.4	6.7±0.4
POW2	Trough West of Dall Island	54.82	133.28	193	0-1	3.0	13.3	6.7	74	9.2	-20.5	7.0
POW4	Gulf of Esquibel	55.60	133.49	200	0-1	5.5±0.04	25.4	9.9±0.26	54	9.0±0.0	-20.4±0.1	7.2±0.1
BAR9	Outer Sitka Sound	57.01	135.49	205	4-5 (2-3)	4.6±1.27	23.9	17.5±7.5	49	8.0±1.7	-21.2±0.1	5.8±0.5
POW5	Sumner Trough	55.59	134.68	268	0-1	0.62±0.10	0.6	10.4±1.1	88	9.2±0.8	-21.9±1.9	4.7±0.3
POW1	Cordova Bay	54.97	132.74	400	2-3	3.9±0.27	17.9	5.8±3.5	68	9.9±0.2	-21.0±0.7	6.7±0.3
GOA12	Cross Sound	57.87	137.08	430	2-3	0.96±0.16	4.7	5.3±1.1	88	10.2±2.0	-24.3±7.2	4.9±0.8
BAR5	Sitka Slope	56.79	136.15	1820	0-1	1.4	4.2	2.8	90	10.0	-21.3	6.1

1990). In order to best calibrate this instrument, standards (cysteine - $C_3H_7NO_2S$ and acetanilide - C_8H_9NO) were handled and analyzed similarly in quantities (0.05 to ~1.0 mg) that yielded responses bracketing the carbon and nitrogen signal of the samples.

TOC and TN content were assessed from analysis of sub-samples pre-treated by the vapor acidification method of Hedges and Stern (1984). Acid pre-treatment was done to remove inorganic carbon. Briefly, sub-samples were weighed into silver boats, the amount (~10-20mg) depending upon the sample and the open boats were carefully transferred to a Teflon block. Each was wetted by addition of deionized water (100 μL) and the block was subsequently placed into a glass desiccator containing a small beaker of concentrated HCl. The desiccator was sealed for a minimum of 16 hrs, but usually 24 hrs. Afterward, the block was removed and placed in an oven (60°C) for a minimum of 6 hours, but typically overnight, to completely dry the samples. Each silver boat was then carefully compressed with forceps into a compact ball using an additional tin boat to assure complete sample containment. These were then analyzed using a Carlo Erba NA-1500 elemental analyzer interfaced to a Delta XL plus isotope ratio mass spectrometer (FRY et al., 1992) rather than a thermal conductivity detector. This method of detection allowed not only quantification of TOC and TN content, but also measurement of the stable isotopic composition of both. All such stable isotopic data is reported in standard $\delta^{13}C$ and $\delta^{15}N$ notation using PeeDee Belemnite (PDB) and atmospheric nitrogen gas as the reference.

The total inorganic carbon (TIC) content of each sediment sample was calculated from the difference between TC and TOC measurements. Assuming all TIC occurs as calcium carbonate ($CaCO_3$), the $CaCO_3$ content of each sample was assessed from TIC

content using the multiplication factor 8.3 (100/12). Values for the molar ratio of total organic carbon to total nitrogen (C/N) were also calculated using the assessed TOC and TN content. Typical precisions for each analysis are indicated by the tabulated standard deviations.

Biogenic Silica Analysis. Sub-samples of each sediment were analyzed for biogenic silica content using a slight modification of the method described by Mortlock and Froelich (1989). All analyses were performed by Andrea Krumhardt and Bruce Finney (University of Alaska, Fairbanks). All values are reported as 'bioSi', a parameter which is defined as 2.4 times the weight percentage Si content of the sample. Briefly, this method leaches biogenic silica from sedimentary materials using a dilute sodium carbonate solution and the resultant Si concentration is measured by a standard spectroscopic method (STRICKLAND and PARSONS, 1972).

Isolation and Analysis of Lipid Biomarkers. A sub-sample of each sediment was analyzed for a variety of marine and terrestrial biomarkers contained within four different lipid compound classes (hydrocarbons, ketones, alcohols and acids). Freeze-dried material (~2 g) was extracted (10 ml, 5x) with a 3:1 methylene chloride in methanol solution using an automated solvent extractor (Dionex ASE 200). Immediately after extraction, each sample solution was spiked with a known amount of the following recovery standards: 3-methytricosane (aiC_{24}), nonadeca-10-one, 5α-androstanol and 18-methyleicosanoic acid. These four compounds were added to act as yield tracers for all biomarkers quantified gas chromatographically in the hydrocarbon, ketone, alcohol, and acid fractions, respectively.

The solution (50 mL) was then partitioned into hexane (10mL, 3x) after an addition of deionized water (10 mL). Combined hexane fractions were then washed against a 50% saturated NaCl solution and subsequently dried over anhydrous Na_2SO_4 overnight. The hexane was evaporated to ~1 mL using a Zymark Turbovap and then to dryness under a gentle stream of pre-purified N_2. The resultant total extractable lipid (TEL) residue from each sample was saponified by refluxing (1 hr) in a 1N ethanolic KOH solution and separated by solvent partitioning into a neutral and acidic fraction (CHRISTIE, 2003).

Each neutral fraction was separated into a hydrocarbon, ketone and alcohol fraction compound class by means of column chromatography on silica gel. Details of this aspect of the analytical procedure are described elsewhere (PRAHL and PINTO, 1987). The hydrocarbon fraction was quantitatively analyzed directly by capillary gas chromatography with flame ionization detection (GC-FID) Long-chain alkenones (BRASSELL, 1993) contained in the ketone fractions were isolated by means of urea adduction (CHRISTIE, 2003), a technique yielding very clean fractions (XU et al., 2001) that lend themselves to direct quantitative analysis by GC-FID . The alcohol fraction was silylated using bis-trimethylsilyltrifluoracetamide (BSTFA, Sigma-Aldrich) and then analyzed quantitatively by GC-FID. Acidic fractions were first methylated using 14% BF_3 in MeOH (Sigma-Aldrich) (CHRISTIE, 2003), then silylated using BSTFA and subsequently analyzed quantitatively by GC-FID.

All GC-FID quantitation was done by an internal standard method using hexamethylbenzene (HMB), 3-methylheneicosane (aiC_{22}), and hexatriacontane (nC_{36}) as internal standards to facilitate assurance of reliable instrument performance. All reported

concentrations have been corrected for standard recovery efficiency which averaged 75% for hydrocarbons (aiC_{24}), 70% for ketones (nonadecan-10-one), 163% for alcohols (5α-androstanol) and 105% for acids (18-methyleicosanoic acid). Many, but not all samples were analyzed in duplicate to evaluate reproducibility for the complete analytical workup procedure. Typical precisions for each analysis are indicated by the tabulated standard deviations.

A gas chromatograph equipped with flame ionization detection (FID) was employed for all analyses. Except for ketone fractions containing alkenones, all chromatographic separations were accomplished using an HP-5 fused silica column (30m x 0.32mm i.d. with 0.25um film thickness), a constant head pressure of hydrogen carrier gas (~10 psig) and temperature programming (100-300^{o}C at 5^{o}C/min). Alkenones were separated and quantified using a VF-1 fused silica column (60m x 0.32mm i.d. column, 0.25um film thickness), a constant flow of hydrogen carrier gas (1.5mL/min) and temperature programming similar to above. An HP5971 benchtop GC mass spectrometer equipped with a an HP-5 fused silica column similar to that described above and temperature program but with helium rather than hydrogen as the carrier gas was employed to confirm all biomarker identifies by comparison of electron impact spectra either with those obtained by direct analysis of authentic standards or published in the literature.

Results and Discussion

Spatial Distribution for Organic Matter. TOC content of sediments varied widely (0.3 to 8% by weight) throughout the study region (Table 1). A map of the complete data set (Fig. 1) shows spatial variability in TOC content is not random, however.

Sediments depositing south of ~58oN are much more enriched in TOC than those depositing to the north (4.2 ± 2.3% versus 0.7 ± 0.3%). Closer examination of this map reveals that sediments depositing south of ~58oN, near the coasts of the Queen Charlotte Islands and Baranof Island are, in fact, more enriched in TOC than those depositing farther offshore.

Given this geographic trend for TOC content, tabulated data for all organic geochemical measurements have been arranged in two groups to facilitate description and interpretation. The two groups are: 1) those north and 2) south of Icy Strait located at ~58^{o}N (Fig. 1). Notably, the first five (Jun2, 3, 4, GOA13, 14) of the fourteen sites comprising the northern group are situated within the inland waters of SE Alaska (Fig. 1). The other nine northern sites are on the continental margin adjacent to the open waters of the Gulf of Alaska. Also, three (POW1, BAR5, GOA12) of the thirteen sites comprising the southern group lie beneath waters deeper than 400m on the continental slope. The other ten sites lie beneath much shallower waters situated in close proximity to the outer coasts of Baranof Island and the Queen Charlotte Islands.

Biogenic silica (bioSi) content also varied widely (~1 to 33% by weight) throughout the study region. A scatter plot (Fig. 2a) shows the variation in bioSi content is highly correlated with that observed for TOC ($r^2 = 0.95$). This observation provides evidence that the geographic pattern for TOC content in these sediments is shaped by diatom productivity, particularly those sediments depositing along the coasts of Baranof Island and the Queen Charlotte Islands.

Literature shows that the quantitative relationship observed between bioSi and TOC in our SE Alaskan study region (bioSi = 4.6 x TOC – 0.003) is much like that found in

other continental margins, e.g. Long Island Sound, Walvis Bay, Northern Carolina slope and the Gulf of California (DEMASTER, 2002). Figure 2a puts this point into a clear quantitative perspective.

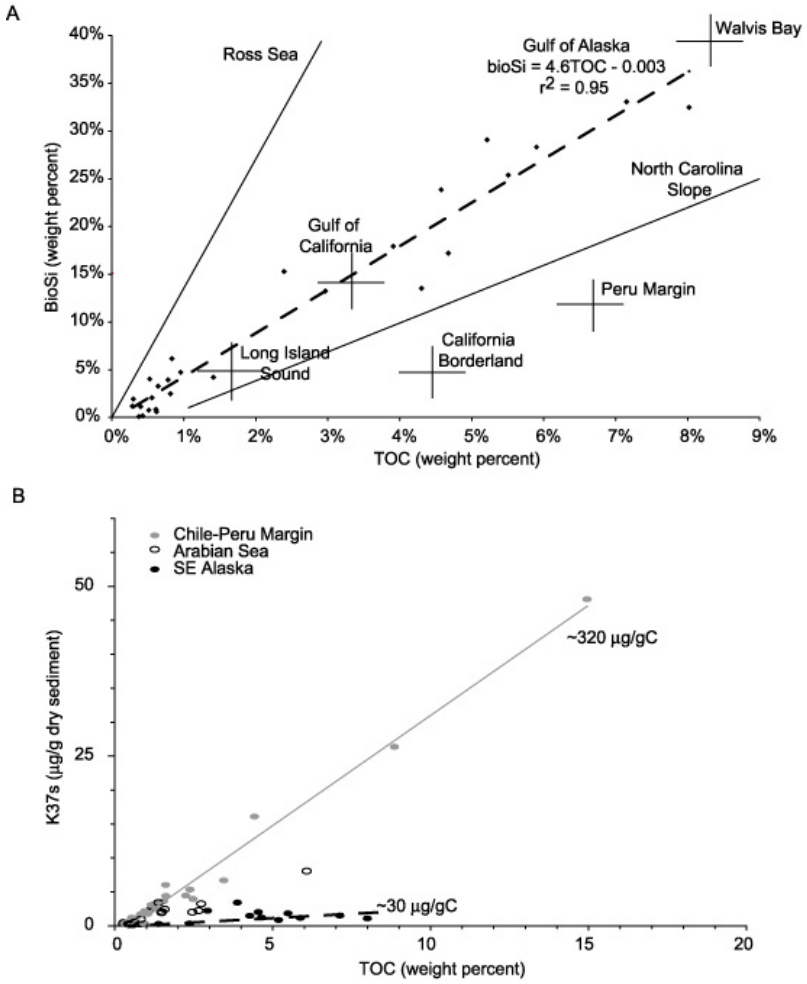

Figure 2. Scatter plots for A) bioSi and B) K37s alkenones vs. TOC. In A), results from analysis of sediments in our study region are represented by blue symbols. All other data in this scatter plot was obtained from Figure 2 in DeMaster (2002). In B), the red trend line and circles represent data obtained from our study region. The black circles and trend line represent results from sediment analysis in the Chile-Peru Margin (PRAHL et al., 2006) and the unfilled circles represent results obtained from sediment analysis in the Arabian Sea (Prahl and Dymond, unpublished JGOFS data).

$CaCO_3$ content was measurable in sediments throughout our study region but, in the vast majority of cases, at quite low levels (Table 1). With the exception of two sites (JUN1: ~40% and BAR9: ~18%), values were uniformly low, averaging 4.9 (± 2.8%). In the complete sample set, the combined weight percentage for organic matter (estimated by 2 x TOC), bioSi, and $CaCO_3$ comprised only a small amount of the total sediment weight. The accounted proportion of total sediment mass averaged 36% and 9% in the

southern and northern region, respectively. This finding indicates that most of the sediment mass, regardless of collection site, derives from eroded crustal minerals off the land. Nonetheless, this inferred 'lithic' component is much less in sediments from the southern region (64%) than the northern region (91%), due to the input of biogenic silica from diatom productivity in overlying surface waters.

In summary, the organic matter content of sediments depositing today throughout our study region was found to be quite variable spatially, but the geographic pattern of variability was far from random. Given this knowledge, results from bulk elemental and stable isotopic analyses as well as from marine and terrestrial biomarker analyses will now be discussed. The aim is to define the relative contribution of marine to terrestrial source of organic matter in these sediments, and in particular, to determine whether or not this blend varies spatially in any systematic way.

Bulk Elemental and Stable Isotopic Assessments of Organic Matter Source. Measurements of the molar ratio for total organic carbon to total nitrogen content (C/N) and stable isotopic composition of TOC ($\delta^{13}C$) and total nitrogen ($\delta^{15}N$) were made in each of the sediment samples. This data set provides first-order insight to the origin of organic matter accumulating in these sediments and the extent of variability in its marine-to-terrestrial blend throughout the overall study region.

C/N values ranged from 7.7 to 12.7 with values measured in sediments depositing north of Icy Strait, on average, higher (10.6 ± 1.5) than those depositing to the south (9.6 ± 0.9). If the five inland water sites assigned to the northern group (JUN2, 3, 4 and GOA13, 14) are excluded in this comparison, the contrast is even more pronounced (11.0 ± 1.5 versus 9.7 ± 1.0). On this basis, the blend of organic matter contained in sediments

throughout our study region would appear to be non-uniform. The observed pattern fits the interpretation that sediments depositing north of Icy Strait contain a greater proportion of nitrogen-depleted terrestrial organic matter relative to nitrogen-enriched marine organic matter (KEIL et al., 1994) than those depositing to the south.

This interpretation is nicely complemented by $\delta^{13}C$ and $\delta^{15}N$ data for these samples. $\delta^{13}C$ values ranged from -24.5 to -20.4‰ in the entire dataset. The average value measured in sediments from the northern group (-22.3 ± 1.4‰) is more ^{13}C-depleted than that measured in those from the south (-21.4 ± 1.0‰). This spatial contrast is even more conspicuous if the five inland sites assigned arbitrarily to the northern group are excluded (-23.2 ± 1.0 versus 21.4 ± 1.0‰). $\delta^{13}C$ values laying in the range of -19 to -22‰ are often cited as bracketing the composition for the pure marine signature preserved in sediments (e.g., HEDGES and MANN, 1979) while a value of approximately -26‰ is considered indicative of pure terrestrial organic matter (e.g., FRY and SHERR, 1984). Thus, based on traditional interpretation of our $\delta^{13}C$ data for TOC, sediments now depositing in our study region to the north of Icy Strait show a greater terrestrial influence relative to marine organic carbon content than those depositing to the south. However, there is one possible, noteworthy wrinkle in this interpretation. Phytoplankton growing in colder waters can, for physiological reasons, display more ^{13}C-depleted values than those growing in warmer waters (e.g., PANCOST and PAGANI, 2006 and references therein}. Reference to the World Ocean Atlas using the Ocean Data View interface (http://odv.awi-bremerhaven.de/) reveals that, for any given season, there is no major difference in sea-surface temperature throughout our study region. So, it would seem that this wrinkle poses no significant concern.

$\delta^{15}N$ data obtained from analysis of total nitrogen (TN) in our set of sediment samples correlate in a strong, positive way ($r = 0.646$) with the $\delta^{13}C$ results (Figure 3). TN contained in sediments depositing north of Icy Strait (4.2 ± 1.0‰) is more ^{15}N-depleted than that in sediments to the south, a compositional contrast that is strengthened if the five inland water sites from the northern group are excluded (3.9 ± 0.9‰ versus 6.3 ± 0.8‰). Once again, this observation fits the interpretation that organic matter contained in the northern sediments is more enriched in terrestrial organic matter while that in the southern region is more enriched in marine organic matter (e.g. SCHUBERT and CALVERT, 2001); (PETERS et al., 1978).

Our data set for $\delta^{13}C$ and $\delta^{15}N$ is displayed in Fig. 3 as a scatter plot. Simple Model I regression analysis (LAWS, 1997) of this data yields the following linear equation: $\delta^{15}N = 0.71 \times \delta^{13}C + 20.7$ ($r^2 = 0.61$). This relationship is broadly similar what Peters et al. (1978) documented from analysis of sediment collected at locations in the vicinity of our study region (some but not all overlapping) as well as elsewhere (e.g. California borderlands). The scatter plot for our data set is annotated with assumed values of $\delta^{13}C$ and $\delta^{15}N$ for pure marine (-20‰, +6-7‰) and terrestrial (-26‰, 0‰) organic material (e.g. PETERSON and FRY, 1987). Given these assumed values are reasonable depictions of endmember compositions, all sediments from our study region appear to contain a dominant component of marine organic matter. And, judging from the lay of data for sediments depositing today south (filled diamonds) and north (open diamonds) of Icy Strait, organic matter in the former sediments appears to be almost exclusively marine-derived while that in the latter is still predominantly marine-derived but could contain a 30-40% component that is terrestrial-derived.

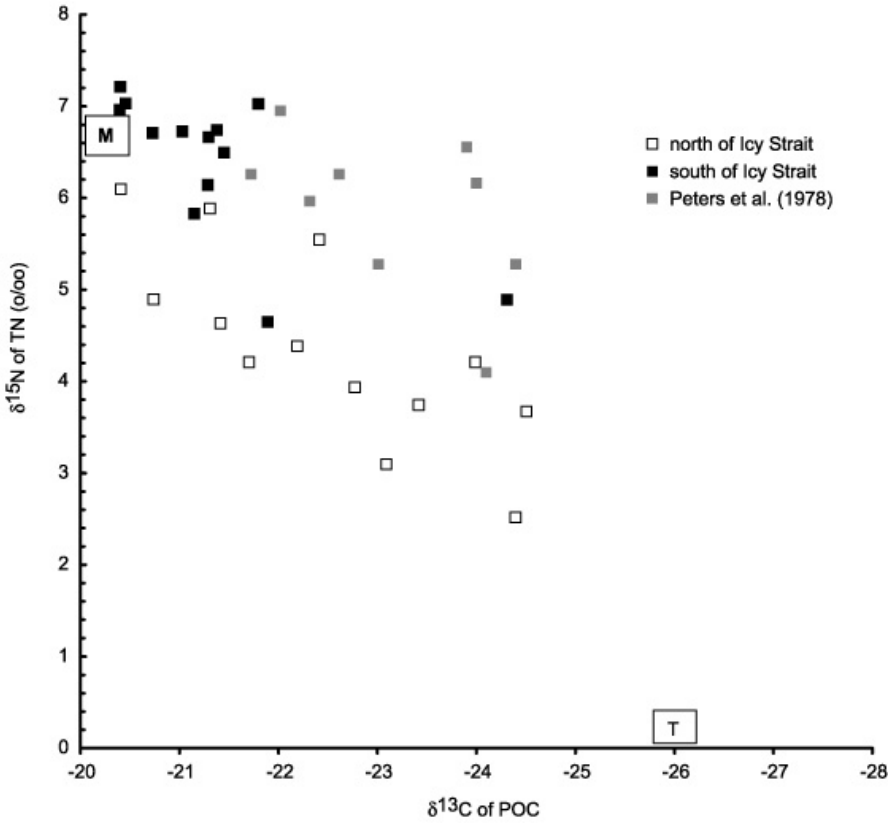

Figure 3. Large squares are data for samples from this study. Filled symbols represent sediments depositing south of 58°N while open symbols represent those depositing north of 58°N. The M and T squares indicate putative endmember compositions for pure marine and terrestrial organic matter, respectively. The small grey squares are data from Peters et al. (PETERS et al., 1978). Only four of the nine sites overlap with this study, the other five are for sediments collected along the western side of the Gulf of Alaska.

In summary, results from bulk elemental (C/N) and isotopic ($\delta^{13}C$, $\delta^{15}N$) analyses are completely consistent with the interpretation that sediments depositing on the SE Alaskan continental margin north of Icy Strait are more enriched in terrestrial (or depleted in marine) organic matter than those depositing to the south. In order to more fully support develop this environmental interpretation, findings from our quantitative analysis of marine and terrestrial biomarkers in these sediments will now be brought into perspective.

Biomarker Assessments of Organic Matter Composition and Spatial Variability. Lipid biomarkers of both marine and terrestrial origin were measurable in sediment throughout our study region. Marine indicators include hydrocarbons, ketones and sterols derived from specific phytoplankton taxa (diatoms, dinoflagellates, haptophytes,

see (VOLKMAN et al., 1998), as well as fatty acids from phytoplankton more generically (CHUECAS and RILEY, 1969). Terrestrial indicators include homologous series of n-alkyl lipids derived from the epicuticular wax of higher plants (KOLATTUKUDY, 1976).

Figure 4 shows 'representative' gas chromatographic compositions of a) hydrocarbon, b) alcohol and c) acid fractions isolated from these sediments. Each chromatogram has been annotated to identify the types of quantitative lipid biomarker information that was obtained by means of GC-FID analysis.

Marine Hydrocarbon Biomarkers. Highly branched isoprenoid (HBI) hydrocarbons containing twenty-five (C_{25}) and thirty (C_{30}) carbon atoms and multiple sites of unsaturation (alkenes) (VOLKMAN et al., 1994) were observed in sediments throughout our study area. This molecular signal was strongest in sediments depositing south of Icy Strait, particularly in some of the biogenic Si-rich sites examined along the outer coastline of the Queen Charlotte Islands and Baranof Island (Fig. 1).

A representative GC 'fingerprint' of the HBI25 and HBI30 mixture in the biogenic silica-rich sediments is shown in Fig. 5 (see inset). Quantitative data for HBI25 and HBI30 was assembled (Table 2) by summing the concentrations of GC peaks identified in this figure. A scatter plot showing the total organic carbon-normalized concentration (/gC) of HBI25 and HBI30 in the biogenic silica-enriched southern sediments was quite strongly correlated. At these sites, the C_{30} components occurred ~10 times more abundantly than the C_{25} components. In sediments where this biomarker signal was detected at much lower concentrations, the relative quantity of HBI30 to HBI25 was much closer to unity.

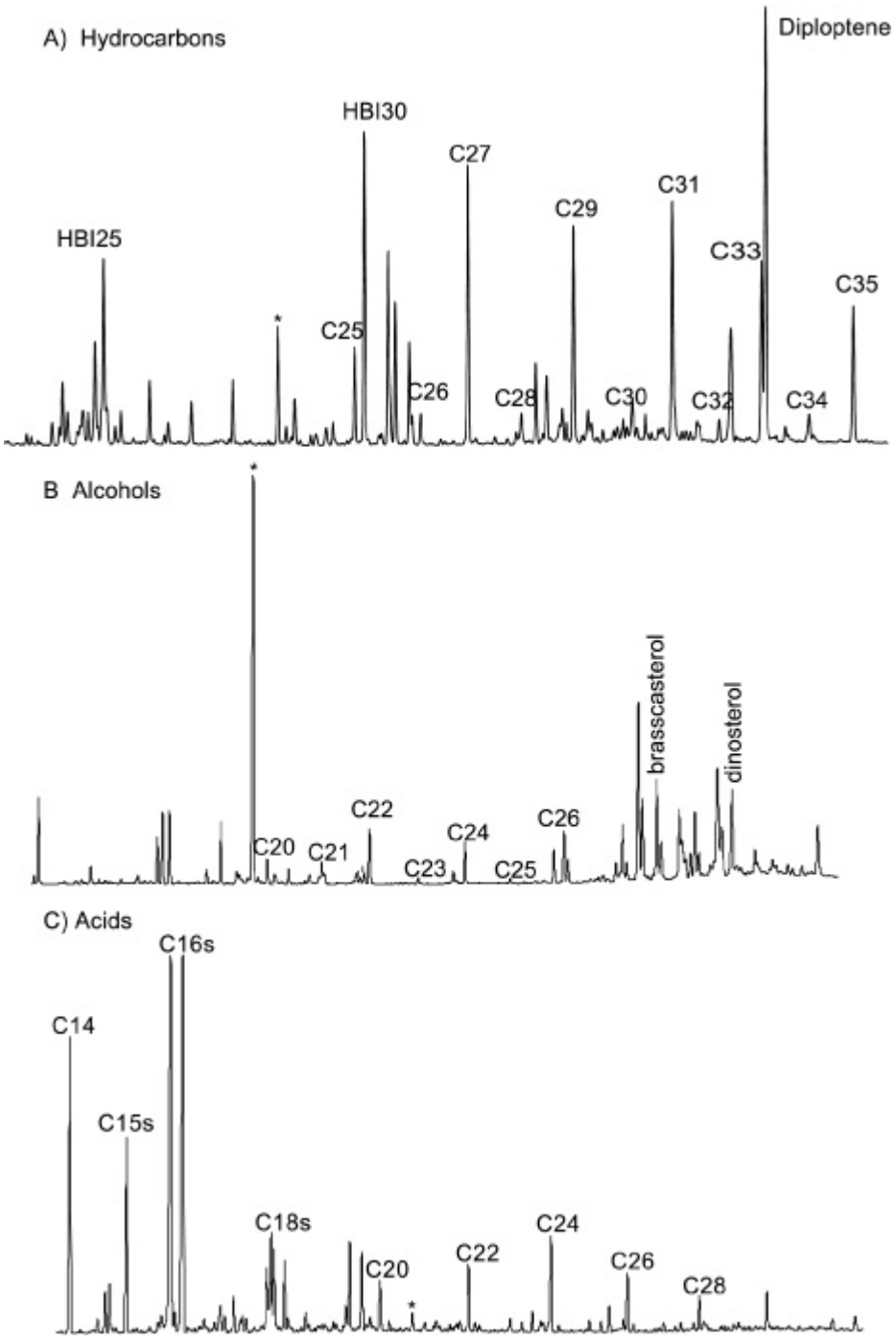

Figure 4. Representative gas chromatograph traces for a) alkane b) sterol/alcohol and c) fatty acid alcohols are shown. The long chain terrestrial biomarkers are indicated by the carbon numbers displayed.

Table 2. Results from gas chromatographic analysis of phytoplankton biomarkers contained in hydrocarbon (HBI25, HBI30), alcohol (brassicasterol, dinosterol), ketone (K37s) and acid ($\Sigma FA_{14\text{-}18}$, ΣFA_{15}) fractions isolated from 27 SE Alaskan surface sediments (see Figure 1 and Table 1 for more information).

	HBI25	HBI30	Brassicasterol	Dinosterol	K37s	$\Sigma FA_{14\text{-}18}$	ΣFA_{15}
Site	μg/gC	μg/gC	μg/gC	μg/gC	μg/gC	μg/gC	μg/gC
North							
JUN2	6.0	15	3	43	106	6700	850
JUN3	0	0.0	15	7	10	2320	420
JUN4	0	3.7	37	50	0	3770	740
GOA13	0	8.1	57	38	0	4670	580
GOA14	0	2.0±2.9	51±48	23±3	0	4610±410	570±200
GOA7	0.6	11.7	32	34	4	1760	220
KB1	1.1±0.5	2.3±0.5	36±18	25±21	15±11	2120±900	330±200
MS1	0.7	12.5	53	29	7	2200	270
GOA4	2.7±2.9	16±0.7	55±26	33±12	0	2680	280
GOA6	0.4	8.8	73	27	32	1240	75
GOA10	1.7±2.4	3.7±5.2	40±29	41±17	15±14	2440±350	310±90
GOA3	0.4±0.6	6.1±1.3	13±5	17±3	0	3310	420
GOA2	0	3.0	46	38	0	3190	320
GOA1	0.9	8.4	15	19	0	2790	380
South							
BAR3	6.4	26	40	62	12	5580	760
BAR1	9.1±3.1	35±10	86±43	75±48	20±5	2430	420
BAR7	7.4	44	32	35	15	4160	1000
BAR8	1.2	20	20	36	24	820	200
BAR4	34	370	212	271	18	3100	570
JUN1	13	93	43	30	32	1620	280
POW2	6.7	23	38	49	72	1300	320
POW4	2.4	3.1	14	17	32	1850	360
BAR9	1.8	1.4	33	34	42	1510	260
POW5	0	0.3±0.4	42±13	26±6	74±72	1730±680	230±31
POW1	2.4	1.9	48	43	85	1430	340
GOA12	3.0	3.7	80	29	23	6059	270
BAR5	0.3±0.4	0.8	49±28	50±2	13	960±170	98±3

Finding C_{25} and C_{30} HBI enriched in the biogenic silica-rich deposits is of interest because these alkenes originate from diatoms. According to current literature, these compounds are in fact only biosynthesized by four genera of diatoms: *Rhizosolenia, Haslea, Navicula,* and *Pleurosigma* (SCHEFUβ et al., 2004). Early work of Volkman et al. (1994) suggested that compositional details about HBI distributions could be further

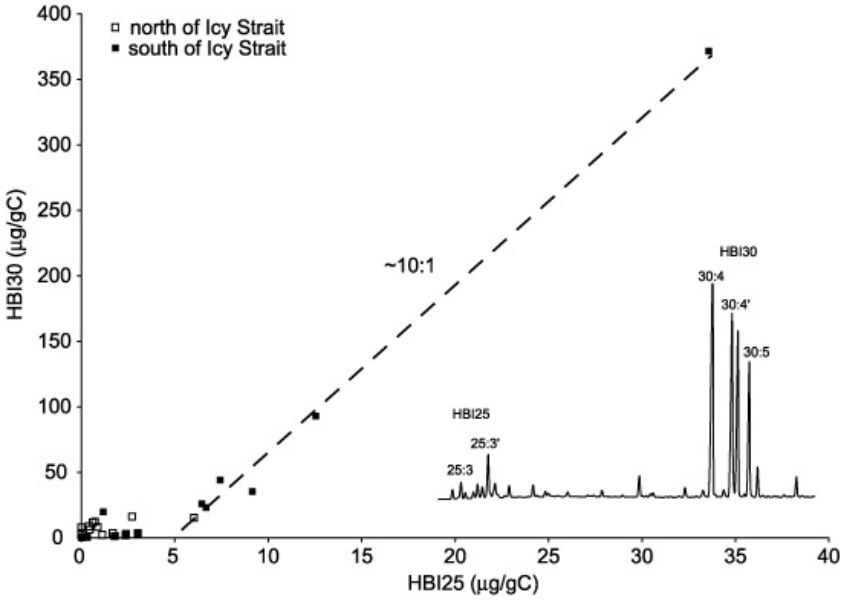

Figure 5. Scatter plot of C_{30} HBI versus C_{25} HBI with the north and south values demarked by blue and red dots, respectively. The sites with bioSi enrichment have a ~10:1 ratio shown by the regression line. A representative gas chromatograph trace with the HBI peaks shown by the stars is inlaid on the scatter plot.

diagnostic of a particular diatom source. Batch cultures of a *Haslea* species contained only HBI25 while that of a *Rhizosolenia* species contained only HBI30. On this basis, HBI25 and HBI30 have been dubbed haslenes and rhizenes, respectively (ROWLAND et al., 2001). However, further investigation of Rhizosolenid algae has shown that the HBI structure is not quite taxonomically distinctive (e.g. ROWLAND et al., 2001).

Nonetheless, high enrichment of diatom-derived HBI in sediments from south of Icy Strait supports conclusions about organic matter composition that was drawn from the bulk elemental and stable isotopic data set. But, this reinforcement is not so convincing when spatial patterns for concentrations of other marine phytoplankton biomarker are examined.

Marine Sterol Biomarkers. Chromatograms of alcohol fractions from most sites contained relatively complex sterol mixures (Fig. 4b). Two components are particularly distinctive in the case of all sterol mixtures: 24-methylcholesta-5,22-dienol (brassicasterol) and 4,23,24-trimethylcholesta-22-enol (dinosterol). These compounds

are commonly equated with organic matter contribution from marine diatoms and dinoflagellates, respectively (VOLKMAN, 1986).

Although brassicasterol is often used as a biomarker for diatoms, it is also present in many haptophyte algae (VOLKMAN, 1986). Assuming diatoms are the predominant source of brassicasterol in our study region, this compound, unlike the case for HBI, was not found to be highly enriched in sediments from the southern region. Excluding data from one seemingly anomalous site (BAR4), its concentration (Table 2) in sediments from the southern and northern region of the study area was on average indistinguishable (44 ± 21 μg/gC versus 38 ± 20 μg/gC).

Dinosterol was also detectable throughout the study region (Table 2). Again, excluding results from BAR4, dinosterol concentrations were on average the same in sediments from the southern and northern region (40 ±16 μg/g C versus 30 ±12 μg/gC). So, the marine contribution to TOC would appear, from the perspective of sterol biomarkers, relatively uniform throughout the study region.

Alkenone Biomarkers. Ketone fractions in sediment from the southern region all contained long-chain (C_{37} to C_{39}), unsaturated methyl and ethyl ketones as distinctive, often dominant components. These compounds, known collectively as alkenones, are now well-recognized biomarkers of specific haptophyte algae, most notably the coccolithophorid *E. huxleyi* (BRASSELL, 1993). C_{37} components comprised ~50% of the total alkenone signal. The concentration of the total C37 compounds (K37s, Table 2) in sediments from the southern region averaged 36 ± 25μg/gC.

Alkenones were also detectable in sediments from the northern region but only in about half of the core sites. And concentrations at these sites were generally lower than

those in sediments from the southern region. This finding implies marine organic matter is more enriched in sediments from the southern region, a pattern which corroborates the interpretation advanced about for bulk elemental and stable isotopic data.

A scatter plot of our data for K37s versus TOC (Fig. 2b) shows that alkenone-producing phytoplankton are a more minor contributor to the TOC signal preserved in sediments from coastal SE Alaska than is the case along the continental margin off Chile-Peru (PRAHL et al., 2006) and in the Arabian Sea (Prahl and Dymond, unpublished JGOFS data). The explanation for this observation is either because alkenone producers are a more minor contributor to the marine component of TOC in these sediments or TOC in sediments throughout our study area, even in the southern region, contain a much greater terrestrial organic matter contribution than is the case for the Chile-Peru margin or the Arabian Sea.

Fatty Acid Indicators of Marine Phytoplankton. A series of even carbon numbered, short chain (C_{14}, C_{16}, C_{18}), saturated and mono-unsaturated fatty acids was measured in sediments throughout our study area (Fig. 4c). Such series are are common constituents of marine phytoplankton generally (e.g. CHUECAS and RILEY, 1969). But, marine phytoplankton are not the exclusive source of such series. Short chain fatty acids with these characteristics could also be introduced by allochthonous input of soil organic matter (e.g., ZOU et al., 2006) or even by autochthonous bacterial biomass (e.g., (GOOSENS et al., 1986) that actively affects degradation of both marine and terrestrial forms of organic matter in these sediments.

The combined concentration of total saturated and mono-unsaturated nC_{14}, C_{16} and C_{18} fatty acids ($\Sigma FA_{14\text{-}18}$) was quantified in each sample (Table 2). As observed for the

two marine phytoplankton-specific sterols, brassicasterol and dinosterol, $\Sigma FA_{14\text{-}18}$ values were not obviously different in sediments from the southern relative to the northern region, as might be expected. If anything, the average value in the north was in fact somewhat higher than that in the south (2150±1020 μg/gC versus 1690±1520 μg/gC).

Fatty Acid Indicator of Bacterial Contribution. Odd carbon number, normal and branched fatty acids were also measured in all samples. C_{15} compounds provide the most conspicuous examples (Fig. 4c). Such fatty acids are recognized biomarkers of bacteria such a *Desulfvibrio* spp, heterotrophs that grow anaerobically using sulfate as a terminal electron acceptor (ATLAS and BARTHA, 1981). The combined concentration of total C_{15} fatty acids (ΣFA_{15}, Table 2) covaried with that of $\Sigma FA_{14\text{-}18}$ ($r = 0.63$). Consequently, the concentration for these bacterial indicators also displayed effectively no discernable spatial trend, averaging 410 ± 210 μg/gC and 390 ± 250 μg/gC in the northern and southern regions, respectively.

In summary, the data set for marine lipid biomarkers produce a somewhat conflicting impression about spatial variations in the relative marine to terrestrial blend of organic matter preserved in sediments throughout this study region. Data for diatom-derived HBI and haptophyte-derived alkenones generally support the interpretation based on the bulk elemental and isotopic data that the blend is not uniform with sediments depositing on the continental margin north of Icy Strait, where there is a larger component of terrestrial organic matter than those depositing to the south. However, a cursory read of data for the diatom and dinoflagellate-derived sterols and the generic phytoplankton-derived fatty acids imply there is little or no discernable spatial variation in the marine to terrestrial blend of organic matter.

Spatial Distribution for Terrestrial Indicators. To gain one final perspective on the best answer to our second question about the blend of organic matter contained in these sediments and how it varies spatially, we examined quantitative data for terrestrial biomarkers. As illustrated in Fig. 4, hydrocarbon (a), alcohol (b) and acid (c) fractions isolated from sediments throughout our study area contained strong signals for homologous series of long chain ($>C_{20}$) n-alkyl compounds with strong carbon number preference. The observed odd-carbon number predominant $C_{25\text{-}35}$ n-alkane series and even-carbon number predominant $C_{20\text{-}30}$ n-alkanol and n-alkanoic acid series are characteristic of the epicuticular wax from higher plants (KOLATTUKUDY, 1976). Clearly, terrestrial organic matter makes some contribution to the TOC content of sediments throughout our study area.

The combined concentration of even carbon number, long chain (C_{20} to C_{28}) fatty acids (Fig. 4c) varied by a factor of 4 in the complete data set ($\Sigma FA_{20\text{-}28}$, Table 3). However, unlike the case for bulk properties of organic matter (C/N, $\delta^{13}C$, $\delta^{15}N$) or the marine biomarkers (HBI and alkenones), the variability displayed no discernable spatial trend with average concentration approximately equal in the northern and southern regions (486 ± 166 μg/gC versus 538 ± 206 μg/gC).

The combined concentration of even carbon numbered, long chain (C_{20} to C_{26}) fatty alcohols (Fig. 4b) did display a spatial pattern ($\Sigma FAlc_{20\text{-}26}$, Table 3). However, highest values were measured in sediments from the southern region (average: 140 ± 61 ug/gC), not the northern region (87 ± 54 ug/gC) where bulk elemental and isotopic analyses suggest the terrestrial contribution to TOC is greatest. Finally, combined concentrations for odd carbon numbered, long chain ($C_{25\text{-}35}$), n-alkanes ($\Sigma C_{25\text{-}35}$. Table 3) displayed the

expected pattern with a higher average value in the northern (105 ± 46 μg/gC) relative to the southern (59 ± 30 μg/gC) region.

Table 3. Results from gas chromatographic analysis of terrestrial biomarkers contained in acid (ΣFA_{20-28}), alcohol ($\Sigma FAlc_{20-26}$) and hydrocarbon (ΣC_{25-35}, CPI_{25-35}, $Dipl/\Sigma C_{25-35}$) fractions isolated from 27 SE Alaskan surface sediments (see Figure 1 and Table 1 for more information).

Site	ΣFA_{20-28} μg/gC	$\Sigma FAlc_{20-26}$ μg/gC	ΣC_{25-35} μg/gC	CPI_{25-35}	$Dipl/\Sigma C_{25-35}$
North					
JUN2	770	88	91	3.4	0.12
JUN3	440	21	31	5.8	0.18
JUN4	500	120	74	4.2	0.085
GOA13	760	230	140	2.9	0.040
GOA14	570±24	100±34	120±16	2.9±0.5	0.01±0.01
GOA7	340	39	120	1.4	0.019
KB1	340±23	44	52	1.5±0.0	0.02±0.02
MS1	360	50	120	1.6	0.027
GOA4	430	88±58	210±3	1.4±0.2	0.01±0.01
GOA6	330	100	63	1.2	0.072
GOA10	370±100	67±16	96±14	1.5±0.0	0.065±0.02
GOA3	440	55±14	120	1.9±0.0	0.045±0.01
GOA2	770	150	150	2.3	0.000
GOA1	390	62	82	1.8	0.094
South					
BAR3	1080	160	99	7.6	0.20
BAR1	460	220±95	100±1	9.4±0.6	0.11±0.03
BAR7	750	110	96	6.4	0.14
BAR8	660	160	93	7.7	0.14
BAR4	630	850	63	6.7	0.20
JUN1	500	99	61	4.4	0.20
POW2	410	140	42	3.2	0.15
POW4	510	110	43	5.4	0.18
BAR9	380	110	20	5.5	0.18
POW5	330±33	65±17	28±1	1.9±0.2	0.15±0.01
POW1	520	110	49	3.5	0.22
GOA12	420	120	29	3.1	0.19
BAR5	330±52	290±41	39±5	2.8±0.4	0.083±0.02

Closer inspection of the GC traces for hydrocarbon mixtures contained in sediments from the northern region, particularly all sites on the continental margin adjacent to the Gulf of Alaska, yielded an important observation. The putative signal for the vascular plantwax-derived n-alkane series in these sediments lacked the diagnostic strong odd-to-

even carbon predominance characteristic of that such a terrestrial source. Tabulated values for CPI_{25-35}, an index that gauges the odd-to-even predominance in a given homologous series of n-alkanes (BRAY and EVANS, 1961) show this point nicely. CPI_{25-35} values for all sediments in the southern region and three of the five sites in the inland water section of the northern region (JUN2, 3, 4) are high (5.2 ± 2.1), as expected for a predominant vascular plantwax source. The average CPI_{25-35} value measured in northern sediments from the continental margin (and the two inland sites from Glacier Bay – GOA13, 14) is much lower (1.9± 0.6) and approaches the value of 1 indicative of n-alkane contribution from some type of 'fossil' source (BRAY and EVANS, 1961).

A possible explanation for this finding is that the organic matter deposited in these northern sediments, which are presumed to contain a 30-40% terrigenous contribution to TOC (Fig. 3), reflects an input of fossil organic matter (kerogen) within lithic materials introduced erosionally by the major glacial outwash of rivers in this region of SE Alaskan continental margin. Although sediments from the southern region, also receive riverborne, erosional contributions from the land, the organic matter characteristic of such input in the south is in the form of humus associated with more modern soils and not 'rock flour' from recent glacial outwash.

Regardless how the source of the apparent fossil signature is explained, once recognized, it is apparent that sediments in the southern region of our study area actually contain the highest plantwax n-alkanes concentrations. Hence, the spatial pattern for the both plantwax n-alkane and n-alcohol concentrations in our study region are not counter but rather consistent with one another. Nonetheless, the distributional pattern for all

available higher plantwax lipid data yields an interpretation clearly at odds with that advanced for the bulk elemental and isotopic data sets.

Hydrocarbon fractions isolated from all sediments in the southern region of our study area contained the pentacyclic triterpene, 17β(H),21β(H)-hop-22(29)-ene (diploptene, see PRAHL et al., 1992) as a significant component (Fig. 4a). Diploptene was not such a conspicuous component of hydrocarbon fractions isolated from sediments in the northern region, however. Values for the ratio of diploptene to long chain n-alkane concentration ($D/\Sigma C_{25\text{-}35}$, Table 3) average 0.16 ± 0.04 in the southern region whereas those in the northern region average 0.06 ± 0.05, clearly demonstrating this distributional pattern.

A study of diploptene in sediments from the coastal margin of Washington State showed that erosional input of soil-derived organic matter could account for the presence of this biomarker (PRAHL et al., 1992). In the case of the Washington coastal margin, eroded soils are primarily contemporary. It was suggested, based on interpretation of results from compound specific $\delta^{13}C$ analysis, that diploptene, derived from the bacterial microflora active in these soils (RIES-KAUTT and ALBRECHT, 1989), provides a stable 'biomarker' of this contemporary, allochthonous input. Although such isotopic measurements have yet to be made on the diploptene in our coastal SE Alaskan sediments, we now suggest an erosional input of relatively contemporary soil organic matter is the source of both this triterpene and the higher plantwax signal detected in SE Alaskan sediments depositing to the south of Icy Strait.

Conclusions

Throughout this paper, we have been working to answer two key questions about organic matter deposited in sediment throughout coastal SE Alaska. The first question is to

determine the variability of the organic matter content in these contemporary sediments. It was found that organic carbon was fairly variable throughout this region; however, there was a strong pattern to the variability. In the southern region of our sampling site, around the outer coastlines of Baranof Island and the Queen Charlotte Islands, the TOC content was found to be greatet.

The next guiding question was to determine the ratio of terrestrial to marine organic matter preserved in these sediments and how it changes spatially. It was found that the bulk elemental and isotopic analyses produced a pattern of higher concentration of terrestrial markers north of 58°N in comparison to a more marine signature in the southern region. The marine and terrestrial biomarkers did not consistently paint the same picture that the bulk elemental and isotopic composition produced, however. Concentrations (/gC) for C_{25} and C_{30} HBI of diatom origin and K37 alkenones of haptophyte origin were highest in the southern region as expected. However, the fatty acid indicators of marine phytoplankton and bacterial contributions as well as the marine sterol biomarkers showed no clear spatial variability.

The higher plantwax assessment of organic matter source, using long chain ($>C_{20}$) n-alkane, n-alcohol and n-acid signatures, displayed either no clear spatial variability or a pattern completely opposite to expectation. Closer inspection of the n-alkane signatures contained in most sediments from north of 58°N showed they were not predominantly of higher plantwax origin. Many showed low CPI values (Table 2) which indicated that they were most likely fossil-derived. Taking this finding into consideration, n-alkane data would suggest sediments deposting south of 58°N contain the a greater contribution of terrestrial organic matter originating from a higher plant source. This discrepancy with

the bulk assessment is perhaps best explained if the region north and south of Icy Strait at ~58^{o}N receive different types of terrestrial input. Perhaps this is a modern soil erosion versus fossil story. If so radiocarbon dating could provide appropriate insight. The terrestrial organic matter input in the north may be depositing in higher amounts, but this deposition is a result of a fossil organic component intimately associated with eroded minerals from recent glacial outwash. However, the terrestrial organic matter depositing south of 58°N is in smaller relative amounts and derived from erosion of organic matter associated with contemporary soils.

The results of this study now provide us with an idea of what sediments throughout region of coastal SE Alaska look like in the current climate regime. This information can now be used in the context of downcore analyses to investigate how conditions have changed in the past. Downcore changes can be used to look at such processes as how glaciers have moved in response to Holocene climate change and how human factors such as deforestation may have impacted regional patterns of erosion over the past century.

References

Atlas R. M. and Bartha R. (1981) *Microbial Ecology - Fundamentals and Applications*. Addison-Wesley Publishing Company.

Berner R. A. (1982) Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *American Journal of Science* **282**, 451-473.

Brassell S. C. (1993) Applications of biomarkers for delineating marine paleoclimatic fluctuations during the Pleistocene. In *Organic Geochemistry: Principles and Applications* (ed. M. H. Engel and S. A. Macko), pp. 699-738. Plenum Press.

Bray E. E. and Evans E. D. (1961) Distributions of *n*-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* **36**, 1185-1203.

Christie W. W. (2003) *Lipid Analysis: Isolation, Separation, Identification and Structural Analysis of Lipids (Third Edition)*. The Oily Press.

Chuecas L. and Riley J. P. (1969) Component fatty acids of the total lipids of some marine phytoplankton. *Journal of the Marine Biological Association of the United Kingdom* **49**(1), 97-116.

DeMaster D. J. (2002) The accumulation and cycling of biogenic silica in the Southern Ocean: revisiting the marine silica budget. *Deep-sea Research II* **49**, 3155-3167.

Fry B., Brand W., Tholke K., and Garritt R. (1992) Automated analysis system for coupled $\delta^{13}C$ and $\delta^{15}N$ measurements. *Analytical Chemistry* **64**, 288-291.

Fry B. and Sherr E. B. (1984) $\delta^{13}C$ measurements as indicators of carbon flow in marine and freshwater ecosystems. *Contributions in Marine Science* **27**, 13-47.

Goosens J., Rijpstra W. I. C., Duren R. R., deLeeuw J. W., and Schenck P. A. (1986) Bacterial contribution to sedimentary organic matter; a comparative study of lipid moieties in bacteria and Recent sediments. *Organic Geochemistry* **10**, 683-696.

Gordon E. S. and Goni M. A. (2003) Sources and distribution of terrigenous organic matter delived by the Atchafalaya River to sediments in the northern Gulf of Mexico. *Geochimica et Cosmochimica Acta* **67**(13), 2359-2375.

Hedges J. I. and Keil R. G. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry* **49**, 81-115.

Hedges J. I. and Mann D. C. (1979) The lignin geochemistry of marine sediments from the southern Washington coast. *Geochimica et Cosmochimica Acta* **43**, 1809-1818.

Keil R. G., Tsamakis E., Fuh C. B., Giddings J. C., and Hedges J. I. (1994) Mineralogical and textural controls on the organic composition of coastal marine sediments: hydrodynamic separation using SPLITT-fractionation. *Geochimica et Cosmochimica Acta* **58**(2), 879-893.

Kolattukudy P. E. (1976) *Chemistry and Biochemistry of Natural Waxes*. Elsevier.

Laws E. A. (1997) *Mathematical Methods for Oceanographers*. John Wiley & Sons.

Mortlock R. and Froelich P. (1989) A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep Sea Research* **36**(9), 1415-1426.

Niggemann J., Ferdelman T. G., Lomstein B. A., Kallmeyer J., and Schubert C. J. (2007) How depositional conditions control input, composition, and degradation of organic matter in sediments from the Cilean coastal upwelling region. *Geochimica et Cosmochimica Acta* **71**, 1513-1527.

Pancost R. D. and Pagani M. (2006) *Controls on the carbon isotopic compositions of lipids in marine environments*. Springer-Verlag.

Peters K. E., Sweeney R. E., and Kaplan I. R. (1978) Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnology and Oceanography* **23**, 598-604.

Peterson B. J. and Fry B. (1987) Stable isotopes in ecosystem studies. *Annual Reviews in Ecological Systems* **18**, 293-320.

Prahl F. G., Hayes J. M., and Xie T.-M. (1992) Diploptene: an indicator of terrigenous organic carbon in Washington coastal sediments. *Limnology and Oceanography* **37**, 1290-1300.

Prahl F. G., Mix A. C., and Sparrow M. A. (2006) Alkenone paleothermometry: lessons from marine sediment records off western South America. *Geochimica et Cosmochimica Acta* **70**, 101-117.

Prahl F. G. and Pinto L. A. (1987) A geochemical study of long-chain *n*-aldehydes in Washington coastal sediments. *Geochimica et Cosmochimica Acta* **51**, 1573-1582.

Ries-Kautt M. and Albrecht P. (1989) Hopane-derived triterpenoids in soils. *Chemical Geology* **76**, 143-151.

Rowland S. J., Allard W. G., Belt S. T., Masse G., Robert J.-M., Blackburn S., Frampton D., Revill A. T., and Volkman J. K. (2001) Factors influencing the distributions of polyunsaturated terpenoids in the diatom, *Rhizoselenia setigera*. *Phytochemistry* **58**, 717-728.

Schefuβ E., Versteegh G. J. M., Jansen J. H. F., and Sinninghe Damste J. S. (2004) Lipid biomarkers as major source and preservation indicators in SE Atlantic surface sediments. *Deep Sea Research I* **51**, 1199-1228.

Schubert C. J. and Calvert S. E. (2001) Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. *Deep Sea Research I* **48**, 789-810.

Strickland J. D. H. and Parsons T. R. (1972) *A Practical Handbook of Seawater Analysis*. Fisheries Research Board of Canada.

Verardo D. J., Froelich P. N., and McIntyre A. (1990) Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 analyzer. *Deep-sea Research I* **37**, 157-165.

Volkman J. K. (1986) A review of sterol markers for marine and terrigenous organic matter. *Organic Geochemistry* **9**(2), 83-99.

Volkman J. K., Barrett S. M., Blackburn S. I., Mansour M. P., Sikes E. L., and Gelin F. (1998) Microalgal biomarkers: a review of recent research developments. *Organic Geochemistry* **29**, 1163-1179.

Volkman J. K., Barrett S. M., and Dunstan G. A. (1994) C_{25} and C_{30} highly branched isoprenoid alkenes in laboratory cultures of two marine diatoms. *Organic Geochemistry* **21**(4), 407-413.

Xu L., Reddy C. M., Farrington J. W., Frysinger G. S., Gaines R. B., Johnson C. G., Nelson R. K., and Eglinton T. I. (2001) Identification of a novel alkenone in Black Sea sediments. *Organic Geochemistry* **32**, 633-645.

Zou L., Sun M.-Y., and Guo L. (2006) Temporal variations of organic carbon inputs into the upper Yukon River: Evidence from fatty acids and their stable carbon isotopic compositions in dissolved, colloidal, and particulate phases. *Organic Geochemistry* **37**(8), 944-956.