Relationships between carbon isotopic composition and mode of binding of natural organic matter in selected marine sediments

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Abstract

We have investigated the relationships between radiocarbon (^{14}C) and stable carbon (^{13}C) isotopic composition and the different modes of binding of organic matter (OM) present in surficial sediments from near-shore and continental margin sites that vary in terms of input and depositional conditions. To improve our understanding of the entire OM pool, isotopic analysis of sedimentary sub-fractions, as opposed to individual compounds, was performed. This was achieved by sequentially treating sediments by solvent extraction to examine unbound compounds, followed by saponification to cleave ester linked moieties. Isotopic analysis was then performed on the bulk sediment and resulting residues. The molecular composition of the extracts was examined using gas chromatography/mass spectrometry (GC/MS), and the relative contributions of terrestrial and marine biomarkers were assessed. Radiocarbon abundances ($\Delta^{14}C$) of the bulk sediment reflect a mixture of modern, pre-aged and fossil carbon. Offsets in $\Delta^{14}C$ between the bulk sediment and sediment residues demonstrate varying associations of these carbon pools. For the majority of sites, a negative offset between extracted (EX-

RES) and saponified (SA-RES) sediment residues results from the removal of relatively ^{14}C-rich material during saponification. Saponification extracts (SAEs) are mainly composed of short chain (*n*-C_{12} to *n*-C_{24}) alkanoic acids with an even/odd dominance indicating a predominantly marine algal or microbial source. This provides evidence for the protection of labile marine carbon by chemical binding. This study aims to bridge the gap between molecular level and bulk OM analyses in marine sediments.

Keywords

Radiocarbon; stable carbon; marine; sediments; biomarker

1. Introduction

Approximately 90% of organic carbon (OC) buried globally in the ocean is sequestered in shelf and slope sediments (Hedges and Keil, 1995 and references therein). This OC is comprised of a complex mixture of autochthonous and allochthonous material of different ages stemming from a variety of sources. For example, continental margin sediments can contain significant quantities of both modern and "pre-aged" OC (Eglinton et al., 1997; Blair et al., 2003; Goñi et al., 2005). Potential sources of "pre-aged" carbon may arise from remobilization of soil carbon (e.g. Masiello and Druffel 2001), weathering of sedimentary rocks (e.g. Drenzek et al., 2007) and resuspension and redistribution of marine OM (Mollenhauer et al., 2005). To assess relative contributions of marine, terrestrial, pre-aged and fossil OC to marine sediment, abundances and distributions of molecular markers such as hydrocarbons, *n*-alkanoic acids and alkanols are typically examined (e.g. Meyers and Ishiwatari, 1993). Carbon isotopic compositions of OM such as stable carbon ($\delta^{13}C$) can also be used as indicators of both source and carbon flow (Fry and Sherr, 1984; Prahl et al., 1994),

while natural abundance radiocarbon measurements ($\Delta^{14}C$) can also serve as sensitive tracers of OM inputs (e.g. Eglinton et al., 1997).

As well as understanding the composition of OC pools, physical associations and chemical binding between OC and bulk macromolecular organic matter (MOM) is important. These associations have the potential to influence the overall fate of OC in the marine environment (Farrington and Quinn, 1971; Lee et al., 1977; Zegouagh et al., 1996). For example, "free" compounds that are not covalently bound with MOM may be more easily degraded than those that are "bound" and covalently linked by an ester, ether or C-C bond. Compounds defined as "free" are those that are solvent extractable, whereas those released only by harsher chemical treatment, are considered "non-extractable", or "bound" to the insoluble organic or inorganic matrix. It is important to note that not all "non-extractable" compounds are covalently bound to MOM; some may be physically entrapped in MOM or mineral matrices (Knicker and Hatcher, 1997 and references therein) and only released when the matrices themselves are altered by chemical treatment. Conversely, the extractability of a compound does not necessarily imply that it is susceptible to degradation. For example, organic compounds sorbed to mineral surfaces may be readily extractable, but physically protected from degradation (Keil and Hedges, 1993). Nevertheless these different associations likely exert strong controls on the preservation of labile organic compounds (Wakeham, 1999), as well as their residence times in different carbon reservoirs. Binding to MOM may, for example, slow the delivery of a terrestrially derived organic compound to the ocean through association with relatively immobile particulate phases (e.g. soil).

To enhance understanding of the sources and overall fate of OC in the oceans, it is clear that both the composition and mode of binding of OM that accumulates in

marine sediments must be determined. The majority of OM source assignments for marine sediments to date, however, are based on biomarkers (e.g. Volkman et al., 1998 and references therein), which are easily extractable, but represent only a tiny fraction of the OC pool in sediments and so lack quantitative significance. Conversely, bulk compositional characteristics such as C/N ratio, $\delta^{13}C$ composition (e.g. Jasper and Gagosian, 1990) and $\Delta^{14}C$ measurements are insufficiently sensitive to demonstrate and resolve multiple sources. These approaches have been expanded upon through examination of $\Delta^{14}C$ and $\delta^{13}C$ signatures of different organic compound classes of sedimentary OM and sinking particulate OM (e.g. Wang and Druffel 2001; Hwang et al., 2005 and references therein). By fractionating the total OM pool into total lipid, total hydrolysable amino acids (THAA), total carbohydrates (TCHO) and remaining acid insoluble residue, much has been learned about the different sources and cycling of OM preserved in sediments. These fractionation methods have also been applied to examine OC cycling in soils (Trumbore et al., 1989) with particular focus on the size, age, variability and turnover of refractory soil OM (Falloon and Smith, 2000 and references therein). The various modes of chemical binding, physical association and structural conformation of the different pools of OM in marine sediments have not, however, been well characterized at a molecular level. This study attempts to provide a link between these bulk, compound class and biomarker analyses by coupling the composition of different extractable OC pools to the isotopic composition of bulk residues remaining after sequential chemical treatment. By evaluating the relationship between isotopic abundance of different sedimentary OM pools and their predominant biomarker composition in the context of source and mode of binding, we aim to enhance our knowledge of the entire OM pool in marine sediments. The sites in the investigation

vary in terms of depositional environment, with different extents of OC derived from marine, terrestrial, ancient and petrogenic carbon sources. To some degree, they can be considered end member environments that provide a framework from which predictions about sediments containing more complex mixtures of inputs can be made.

2. Experimental

2.1 Study area and samples

Locations, dates, depths and other details of the sites are listed in Table 1. The samples are from coastal and continental margin settings, which have previously been subjected to molecular isotopic studies. Organic-rich marine sediments were collected from the shelf under the upwelling system of the Peru Margin (PM) where sediment accumulation rates are high (up to 1 cm yr^{-1}; Parkes et al., 1993), as well as Guaymas basin (GB), a hydrothermal system with active petroleum production in the sub-surface (Simoneit et al., 1992). Open shelf and river dominated sediments were collected from the Washington Margin (WM), and include a site from the inner shelf (Station 1), near the mouth of the Columbia River, and the upper slope depocenter (Station 4). Sediments were also collected from the Eel River Margin (ERM) which has a narrower shelf than WM and is subject to more episodic delivery of sediment (Nittrouer 1978; Prahl et al., 1994). High sedimentation rates (0.2-0.4 cm yr^{-1}) are observed at ERM along the shelf (Sommerfield and Nittrouer, 1999), and sediments reflect mixtures of carbon derived from kerogen and modern terrestrial and marine sources (Blair et al., 2004). River-dominated sediments were also collected from the Mackenzie shelf (MS) and Beaufort slope (BS) in the Canadian Arctic, where significant inputs of pre-aged OC have been reported to be co-deposited with significant OC from vascular plants and marine algae (MacDonald et al., 1988; 1992; 1998; Goñi et al., 2005; Drenzek et al., 2007).

2.2 Sequential lipid extraction

Sediments were air-dried and homogenized with a mortar and pestle before passing through a 1mm sieve. Two to twenty grams of each sample were sequentially treated as previously described (White et al., 2005). Briefly, the sediments were extracted with dichloromethane (DCM) and methanol (MeOH) (9:1) using pressurized fluid extraction (100ºC, 1000 psi). The resulting total lipid extracts (TLEs) were reduced in volume by rotary evaporation and percolated through a copper column plugged with combusted glass wool to remove elemental sulfur and any entrained particulate matter. The solvent extraction step was not performed for GB, MS and BS samples because they had been extracted as part of prior investigations (Pearson et al., 2005; Drenzek et al., 2007). Aliquots of the TLE from these sediments were reserved for GC/MS analysis. Solvent-extracted sediments were refluxed at 70ºC for 2 h with 0.5 N KOH in MeOH (100 mL) and water (20 mL). After cooling, the reaction mixture was separated by centrifugation (1500 rpm), the supernatant removed and the remaining sediment rinsed with MeOH, followed by DCM and then hexane. These extracts were combined with the supernatant in a separatory funnel. The alkaline extract (supernatant) was back-extracted with hexane (3 x 50 mL) to obtain a neutral fraction before acidification with 4N HCl to pH 2 and extraction with DCM (3 x 50 mL) to obtain an acidic fraction. Both fractions were reduced in volume by rotary evaporation and dried by passing through a small glass pipette column of anhydrous Na_2SO_4 plugged with glass wool (this also served to remove any particles from the extracts).

2.3 Bulk sediment analysis

Aliquots of dried unextracted sediment (TOC), as well as solvent-extracted (EX-RES) and saponified sediment residues (SA-RES) were acidified to remove inorganic

carbon and analyzed for organic carbon content as described in White et al. (2005). Stable carbon isotope ratio ($\delta^{13}C$) and radiocarbon abundance ($\Delta^{14}C$) were measured on purified carbon dioxide (CO_2) after combustion of the samples in the presence of cupric oxide (CuO). Stable carbon isotopic compositions were determined using isotope ratio mass spectrometry (irMS) and ^{14}C content using accelerator mass spectrometry (AMS) at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (WHOI) after conversion of the CO_2 to graphite (McNichol et al., 1994). All ^{14}C measurements are expressed as $\Delta^{14}C$ values, which is the ‰ deviation from the international standard for ^{14}C dating, Standard Reference Material 4990B "Oxalic Acid". Precision for $\delta^{13}C$ and $\Delta^{14}C$ measurements are ~0.1 and 2-5‰, respectively. The results were reported as $\Delta^{14}C = [f_m e^{(1950-x)\lambda}-1] \times 1000$ (Stuiver and Polach, 1977), where λ=1/8267 (y^{-1}), f_m= fraction modern ^{14}C (corrected for isotopic fractionation using $\delta^{13}C$), and x is the year of collection (see Table 1). This corrects for decay of ^{14}C since time of collection to time of measurement. Isotopic and elemental analysis of the TOC from GB, MS and BS had previously been performed (see Table 2) and was not repeated here.

2.4 Gas chromatography-mass spectrometry (GC/MS)

Aliquots of TLEs and saponified neutral and acidic extracts were spiked with an internal standard (*n*-C_{36} alkane, 4 μg), prior to derivatization with bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in pyridine. For compound identification, electron ionization (EI) spectra were acquired with an Agilent 6890 series gas chromatograph interfaced to an Agilent 5973 mass selective detector (MSD). A post column split to a flame ionization detector allowed quantification of compounds of interest relative to the internal standard. Compounds were separated on a J&W DB-5MS

column (60 m x 0.32 mm i.d, 0.25 μm film thickness) with He carrier gas at a constant flow of 1 ml min^{-1}. The initial oven temperature was 40°C (1 min hold) and was ramped at 20°C min^{-1} to 130°C and then at 2°C min^{-1} to 320°C (30 min hold). Spectra were acquired between *m/z* 40-650 at a scan rate of 1 cycle s^{-1}. Short chain (*n*-C_{12} to *n*-C_{22}) and long chain (*n*-C_{24} to *n*-C_{34}) alkanoic compounds were identified from mass spectral and GC retention characteristics. The flame ionization detector response was calibrated regularly by injection of *n*-alkane, *n*-alkanoic acid and *n*-alkanol standards.

3. Results

3.1 General trends in carbon isotope composition of surface sediments

There is considerable range in the $\Delta^{14}C$ values of the bulk untreated sediment prior to solvent extraction (TOC) for the sites. The $\Delta^{14}C$ values, ranging from -737 to -68‰ (Table 2, Fig. 1), likely reflect varying mixtures of modern, pre-aged and fossil OM of marine and terrestrial origin. The sediments from PM, GB and WM (St. 1 and 4) display $\Delta^{14}C$ values that compare well with those obtained for other core top sediments (e.g., McNichol et al., 1994; Wang et al., 1996; Eglinton et al., 1997; Masiello and Druffel, 2003; Hwang et al., 2005; Komada et al., 2005) whereas sediments from ERM, MS and BS are all significantly depleted ($\Delta^{14}C$ ~ -750 to -300‰; Fig. 1), likely due to significant contributions of fossil OC. This fossil carbon is derived from kerogen from bedrock in the case of ERM sediments (Blair et al., 2004) and pre-aged soil material and bitumen or kerogen for MS and BS sediments (Goñi et al., 2005; Drenzek et al., 2007).

The $\delta^{13}C$ values of the bulk TOC range from -26.0 to -20.6 ‰ (Table 2, Fig. 1). In general, the organic-rich marine sediments from PM and GB and sediments from St. 4, located on the upper slope of the Washington Margin are the most rich in ^{13}C (-22.1 to -20.6‰), reflecting significant contributions of marine carbon. Sediments from WM

St. 1, ERM, MS and BS are, however, more depleted (-25.9 to -24‰), indicating the presence of more C_3 vascular plant-derived carbon (Fry and Sherr, 1984; Prahl et al., 1994) and/or fossil carbon (kerogen; Drenzek et al., 2007).

3.2 General trends in biomarkers released from sequential treatments

Representative chromatograms for the TLE, saponification extract (SAE) acidic fraction and neutral fraction from ERM are illustrated (Fig. 2). These chromatograms indicate the dominance of *n*-alkanoic compounds and sterols in the GC-amenable portion of the extracts. Note the presence of methylated *n*-alkanoic acids in the SAE acidic fraction that arise from methylation of a small portion of the total *n*-alkanoic acids during the saponification procedure. These were included in the quantification of *n*-alkanoic acids.

The summary of the data from all TLE chromatograms (Figs. 3a and 4) provides insights into the composition and source of material removed by solvent extraction. For each TLE, varying proportions of short (*n*-C_{12} to *n*-C_{22}) and long (*n*-C_{24} to *n*-C_{34}) chain alkanoic acids and alkanols with even/odd predominance reflect inputs from marine and terrestrial sources, respectively. There are also significant contributions from *n*-alkanes, which are predominantly odd numbered in the TLE from PM, WM St. 1 and WM St. 4 (carbon preference index, CPI, 6.1 to 10.4; Fig. 4) and hence plant wax derived (Collister et al., 1994). In samples where they contribute < 5% to the *n*-alkanoic portion, the even numbered *n*-alkane concentrations are below detection limit. The predominance of odd numbered *n*-alkanes is not observed for the TLE from ERM, MS and BS (CPI 1.6 to 2.7; Fig. 4), indicative of a thermally-mature fossil carbon source (Brassell and Eglinton, 1980). All TLEs also contain C_{27}-C_{29} sterols (e.g. Fig 2a), but

these are not discussed further as their source assignment is generally more equivocal (Volkman, 2005).

The major difference between the biomarker composition of the TLE and SAE is the absence of long chain (*n*-C_{24} to *n*-C_{34}) alkanols and *n*-alkanes in the SAE, which is typical for all the sediments except ERM (Figs. 3 and 4). The GC-amenable fractions of the SAEs are dominated by short chain alkanoic acids (*n*-C_{12} to *n*-C_{22}; Fig. 2b and 3b) with a strong even/odd predominance (Fig. 5), indicating a marine algal or bacterial source. This dominance, however, is not observed in GB where they contribute ~20% and there is a significant (~80%) contribution of polycyclic aromatic hydrocarbons (PAHs), including naphthalenes, phenanthrenes and their alkylated derivatives, fluoranthene, anthracene and fluorene (shown as "other" in Fig. 3b). These PAHs are nonextractable, but unlikely to be covalently bonded to the OM as they are not functionalized. Instead, they may be encapsulated in the sedimentary matrix, possibly via close association with OM or mineral grains. All SAE neutral fractions also contain C_{27}-C_{29} sterols (e.g. Fig. 2c) that are likely esterified to MOM, but these are not discussed as mentioned previously.

To determine the significance of the contributions of different biomarkers in the TLE and SAE, the proportion of TOC that is solvent extractable and saponifiable, and the quantity of this material that is quantified by GC, was assessed (Table 3). To calculate the % TOC that was extractable, portions of the extracts were weighed and converted to carbon equivalents, considering contributions from hydrogen and oxygen (the biogenic compounds examined comprise ~ 80% carbon and this value was taken as the average). This value was then divided by the organic carbon content of the bulk unextracted sediment (TOC, Table 3). While only selected GC-amenable compounds

were characterized, representing a limitation of the study, it also serves to highlight the strength of the isotopic approach since differences in isotopic composition between sediments and residues yields information about non-GC amenable carbon pools. Furthermore, examination of $\Delta^{14}C$ shifts between bulk residues and the $\Delta^{14}C$ of the resulting extracts that lead to these shifts has been performed, and these values are consistent with one another (White et al., 2005). In the context of the biomarkers in the "free" (TLE) and "bound" (SAE) pools, the isotopic abundances of sediments and their residues are discussed below in more detail.

4. Discussion

To assess the relationship between carbon isotopic composition of the bulk sediments and resulting residues, the difference in isotope abundances ($\Delta^{14}C$ and $\delta^{13}C$) of the residues (EX-RES represented by gray circles; SA-RES represented by open circles) from the bulk TOC (black filled circle at the origin) are shown for each of the samples been grouped by depositional environment (Fig. 6a-c). Arrows indicate significant offsets between the residues as a result of the chemical treatment.

The isotopic composition of the TOC for organic-rich marine sediment from PM does not show any significant offset in $\Delta^{14}C$ between bulk sediment and sediment residue and only slight (~0.3‰) enrichment in $\delta^{13}C$ from the bulk TOC to the SA-RES. This is demonstrated by the close proximity of the EX-RES and SA-RES in both $\Delta^{14}C$ and $\delta^{13}C$ space around the origin. The coherence in isotopic values indicates that the OC removed by the sequential treatment is isotopically similar to that in the original bulk sediment as well as that remaining in the residue. Biomarkers in the TLE and SAE at this site display similar relative distributions, apart from the absence of long chain (*n*-C_{24} to *n*-C_{34}) alkanols and *n*-alkanes in the SAE, as previously described. Similarity in

the composition of the different pools of OM in PM sediments has previously been observed through analysis of organically-bound phosphorus, which also showed little variance between sequentially chemically treated sediments (Laarkamp, 2000). The homogeneity of the sediments is likely due to the fact that the organic-rich sediments of PM are almost exclusively derived from a marine source.

In contrast to PM, the sediment and residues from GB become successively more ^{14}C-rich as the sequential treatment is performed (Fig. 6a). The TOC is the most depleted (-197‰) followed by the EX-RES (-184‰) and the SA-RES (-163‰). Guaymas Basin is an unusual environment in which hydrothermal petroleum is produced in deeper sediments as a result of magmatic heating and subsequently migrates upwards. The change in richness of ^{14}C in residues results from the removal of relatively ^{14}C depleted material at each step. Solvent-extractable *n*-alkanoic acids isolated from the microbial mat of *Beggiotoa,* exhibit depleted $\Delta^{14}C$ values (-418‰ to -227‰) that are similar to that of hydrothermal petroleum, indicating the consumption of pre-aged carbon by the bacterial community (Pearson et al., 2005). For this study, we examined the sediment underlying the microbial mat and the results are consistent with Pearson et al. (2005), and show that solvent extraction removes compounds relatively depleted in ^{14}C. Notably, the TLE in this study is comprised predominantly of short chain *n*-alkanoic acids (~90%, Fig. 3a). The SAE, as previously described, consists primarily of PAHs (~80%; Fig. 3b), which represent a component of the ^{14}C-depleted hydrothermal petroleum, thereby explaining the remaining ^{14}C-rich residue. The sediments and residues also become successively enriched in ^{13}C as the sequential treatment is performed (Fig. 6a). We attribute this trend to the removal of fossil carbon, which is typically more depleted (Reddy et al., 2002) than that from marine and

terrestrial sources. The latter would derive predominantly from C_4 vegetation from the surrounding arid landscape of NW Mexico and the Baja Peninsula.

Significant offsets in $\Delta^{14}C$ are observed between TOC and EX-RES of surface sediments from the river-influenced WM St. 1 and ERM (Fig. 6b). These offsets, however, have different trajectories. In the case of WM St.1, the $\Delta^{14}C$ EX-RES is somewhat lower than that of the TOC, indicating a weak association and facile removal of more recently synthesized (^{14}C-rich) material by solvent extraction. This interpretation is supported by the molecular composition of the TLE (Fig. 3a), which has significant contributions from long chain (*n*-C_{24} to *n*-C_{34}) alkanols (~20%) and alkanoic acids (~5%) with an even/odd predominance, as well as long chain (*n*-C_{23} to *n*-C_{31}) alkanes (~15%) with an odd/even predominance (CPI 10.4; Fig. 4). These biomarkers are characteristic of vascular plant biomass and are particularly abundant at WM St. 1 on the inner shelf proximal to the Columbia River mouth. Absolute abundances of *n*-alkanes on the WM continental shelf average 165 μg g^{-1} C (Prahl et al., 1994). Radiocarbon analysis of individual terrestrial biomarkers in surface sediment from a nearby site determined that they are younger than the TOC (Eglinton, unpublished results), supporting these bulk level interpretations. No significant offset in $\Delta^{14}C$ between TOC and EX-RES (Table 2) is observed for WM St. 4, which is further offshore than St. 1 (upper continental slope). This is likely due to a decrease in the contribution of terrestrial plant material, which while less obvious from the TLE biomarker distribution (Fig. 3a), is consistent with prior studies that report a decrease in the carbon-normalized abundances of plant wax n-alkanes with increasing distance offshore from the WM (Prahl et al., 1994). No significant offset in $\delta^{13}C$ between TOC and EX-RES (Table 2, Fig. 6b) for either WM St. 1 or 4 is observed. This is to be

expected for St. 4 where an offset in $\Delta^{14}C$ was also not observed. The absence of a change in $\delta^{13}C$ at St. 1, however, suggests that even though significant ^{14}C-rich terrestrial biomass has been removed, the remaining EX-RES is still predominantly of terrestrial origin, most likely derived from C_3 vegetation due to its $\delta^{13}C$ value of -25.3‰ (Prahl et al., 1994). The $\delta^{13}C$ of the SA-RES is, however, more depleted (-26.2‰) indicating the removal of more ^{13}C-enriched material of marine origin (Prahl et al., 1994).

In sharp contrast to WM St. 1, the radiocarbon content of EX-RES from ERM 0-2cm is considerably more ^{14}C-rich (by ~100‰) than the TOC (Fig. 6b). Analysis of the *n*-alkanes, which comprise ~20% of the GC-quantified TLE (Fig. 3a), reveals a low CPI (1.6; Fig. 4), betraying the presence of petrogenic hydrocarbons associated with the supply of OM from erosion of ancient sedimentary rocks on the adjacent continent (Blair et al., 2004). Large quantities of unaltered bedrock containing predominantly Type III kerogen and plant debris-rich surface soil are delivered from the continent as a result of episodic flood events. As a consequence, widespread and rapid (0.2-0.4 cm yr^{-1}) accumulation of sediment occurs over the shelf (Sommerfield and Nittrouer, 1999). The sediments examined are from the middle of the flood depocenter on the shelf. The results imply that the fossil OC in these sediments resides predominantly in the extractable (unbound) form, i.e. not as kerogen, and that the sedimentary rock from which the OC is derived is thermally mature and has released most of its hydrocarbons. Extractable lipids depleted in $\Delta^{14}C$ relative to the bulk sediment are also observed in surface sediments from the Black Sea (Eglinton et al., 1997) and work by Hwang et al. (2005) consistently demonstrates extractable lipids that are depleted in both $\Delta^{14}C$ and $\delta^{13}C$ relative to bulk sediment. The $\delta^{13}C$ of the ERM sample, however becomes

successively more depleted as the sequential treatment proceeds. This indicates that the remaining residue is likely comprised of refractory aliphatic biopolymers synthesized from lipids that are typically depleted relative to the bulk biomass. This has previously been observed in salt marsh sediments (White et al., 2005).

Surface sediments and residues from MS and BS exhibit the most negative $\Delta^{14}C$ values (-823 to -725‰; Table 2). For both samples, the TOC is the most ^{14}C-rich and the SA-RES the most depleted, implying that ^{14}C-rich OC is removed as the sequential treatment progresses. This overall trend is supported by previous work in the NE Pacific where more labile, and hence extractable, OM pools consisting of amino acids and carbohydrates were found to be ^{14}C-rich relative to the refractory OM pools (Wang and Druffel, 2001). The TLEs in the MS and BS sites are dominated by short chain *n*-alkanoic acids (Fig. 3a), which have been shown to have modern ^{14}C values (Drenzek et al., 2007). In MS sediments they are predominantly of short chain (*n*-C_{14} to *n*-C_{22}) length and constitute 83% of the TLE, whereas in BS sediments they comprise a mixture of short (*n*-C_{14} to *n*-C_{22}) and long (*n*-C_{24} to *n*-C_{28}) chain lengths, constituting 24 and 31% of the TLE respectively. Both samples also have contributions from short (*n*-C_{18} to *n*-C_{22}) and long (*n*-C_{24} to *n*-C_{28}) chain *n*-alkanols and varying contributions from *n*-alkanes (5 and 25% for MS and BS respectively) with OEP of 1.9 and 2.7 respectively. These have previously been shown to be derived from a mixture of higher plant leaf waxes and erosion of sedimentary rocks in the drainage basin (Yunker et al., 1993; Drenzek et al., 2007). The $\delta^{13}C$ value of the TOC for MS is more depleted than BS (-26.0 and -23.8‰ respectively; Table 2) and does not change by more than 0.1-0.2‰ throughout the sequential chemical treatment. The more ^{13}C-enriched BS sample,

1 does, however, become more depleted throughout the chemical treatment (Table 2)
2 indicating removal of more ^{13}C-enriched material, likely of marine origin.

3 The most significant offset in $\Delta^{14}C$ for MS and BS, however, is observed (~ -
4 70‰) between EX-RES and SA-RES (Fig. 6c), likely due to the SAE being composed
5 predominantly (~90-100%) of fresh marine biomarkers such as short chain (*n*-C_{12} to *n*-
6 C_{22}) *n*-alkanoic acids (as in Zegouagh et al., 1996) and *n*-alkanols (Fig. 3b) that are rich
7 in ^{14}C. These observations are also seen for other depositional environments in this
8 study, including WM St. 4 and ERM, and are supported by analysis of Ross Sea
9 sediments by Ohkouchi et al. (2003), in which $\Delta^{14}C$ values for ester-bound short chain
10 alkanoic acids were found to be relatively uniform and higher relative to bulk sediment.
11 The higher values likely reflect the incorporation of bomb ^{14}C-containing dissolved
12 inorganic carbon (DIC) into the biomarker pool. These observations provide strong
13 evidence for the protection of labile marine carbon via chemical binding to the
14 sedimentary matrix. Free *n*-alkanoic acids are especially susceptible to degradation if
15 they are short chain and unsaturated (Sun and Wakeham, 1994; Zegouagh et al., 1996)
16 and, while they can also derive from bacterial communities responsible for this
17 degradation, these would most likely be present in the TLE (as intact phospholipids) as
18 opposed to the SAE. Long chain *n*-alkanoic acids from higher plants are, however, more
19 resistant to degradation, most likely due to a protective matrix association (Zegouagh et
20 al., 1996).

21 The remaining non-hydrolyzable portion of the TOC (SA-RES) for MS and BS
22 is extremely depleted in ^{14}C (-823 to -819‰). These values are consistent with $\Delta^{14}C$
23 compositions of liberated *n*-hydrocarbons upon pyrolysis of the insoluble, non-
24 extractable OM from BS (Drenzek et al., 2007). The latter are thought to be derived

from kerogen and/or vascular plant cutan (the residual, predominantly aliphatic macromolecular material that remains after solvent extraction and acid hydrolysis; Nip et al., 1986), which is pre-aged on the continent prior to delivery to the Beaufort Sea.

5. Conclusions

Variations in $\Delta^{14}C$, $\delta^{13}C$ and molecular composition of different OM fractions from sediments are evident at a variety of sites characterized by depositional setting. The major observations are summarized as follows:

• No significant offsets in $\Delta^{14}C$ (and $\delta^{13}C$ to a lesser extent) are observed between sediments and their respective residues in regions subject to predominantly marine inputs, such as those underlying the Peru upwelling region.

• For some depositional systems, solvent extraction may leave behind a more ^{14}C-depleted residue, as a result of the removal of ^{14}C-rich terrestrial material in the case of inner shelf sediments of the Washington margin. This negative offset in $\Delta^{14}C$ diminishes further offshore (WM St. 4) on the slope, where terrestrial inputs are less significant.

• For some depositional settings, solvent extraction results in a more ^{14}C-rich residue as a result of the removal of ^{14}C-depleted soluble materials such as hydrothermal petroleum (GB), or petrogenic hydrocarbons (ERM).

• In some cases (WM St. 4, ERM, MS and BS) saponification results in a more ^{14}C-depleted residue due to hydrolytic liberation of ^{14}C-rich material of predominantly marine origin. This finding provides evidence for the protection of labile marine carbon via chemical binding.

• Conversely, saponification may also lead to a more ^{14}C-rich residue when fossil organic carbon is removed by this treatment, as observed for the GB.

• Environments where $\Delta^{14}C$ values of sediment residues become successively more depleted with each chemical treatment (as in the case of MS and BS), reflect the presence and persistence of non-hydrolyzable, and thus presumably highly refractory, pre-aged or fossil carbon.

The approach adopted in this study complements previous bulk OM as well as biomarker studies, and serves to bridge the information gap on the sources and compositions of non-GC amenable components that comprise the majority of OM in marine sediments.

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Table 1
Location, collection date, water depth, sediment depth, and core type for samples

Location		Date Collected	Water depth (m)	Sediment Depth (cm)	Core Type
Peru Margin (PM)					
S. America	11˚59.8'S, 77˚47.4'W	1992	309	0-2	BC [a]
Guaymas Basin (GB)					
Gulf of California	27˚00.0'N, 111˚24.3'W	1998	2015	0-1	PC [b]
Washington Margin (WM)					
USA, Station 1	46˚20.0'N, 124˚18.1'W	2001	84	0-2	BC [a]
Station 4	46˚49.0'N, 125˚00.5'W		644	0-1	MC [c]
Eel River Margin (ERM)					
USA, Station 1	40˚49.9'N, 124˚19.1'W	2001	70	0-2	BC [a]
Mackenzie Shelf (MS)					
Arctic, Station 5	70˚01.7'N, 133˚43.3'W	1987	25	0-2	GS [d]
Beaufort Slope (BS)					
Arctic, Station 144	71˚43.3'N, 141˚40.0'E	1991	1650	4-5	BC [a]

[a] Box core.
[b] Push core.
[c] Multi core.
[d] Grab sampler.

Table 2
Organic carbon (%), stable carbon and radiocarbon abundances [a] for bulk samples and respective residues

Sample	% OC TOC [b]	% OC EX-RES [c]	% OC SA-RES [d]	$\delta^{13}C$ (‰) TOC [b]	$\delta^{13}C$ (‰) EX-RES [c]	$\delta^{13}C$ (‰) SA-RES [d]	$\Delta^{14}C$ (‰) TOC [b]	$\Delta^{14}C$ (‰) EX-RES [c]	$\Delta^{14}C$ (‰) SA.-RES [d]
Peru Margin (0-2 cm)	13.22	16.34	11.93	-20.6	-20.5	-20.3	-68.0	-72.2	-72.5
Guaymas Basin (0-1 cm)	nm [e]	3.35	2.14	-21.6 [f]	-21.0	-20.9	-197 [f]	-184	-163
Washington Margin, Station 1 (0-2 cm)	1.59	1.20	1.31	-25.4	-25.3	-26.2	-114	-140	-125
Washington Margin, Station 4 (0-1 cm)	2.34	2.52	1.92	-22.2	-22.1	-22.1	-159	-154	-178
Eel River Margin, Station 1 (0-2 cm)	0.81	0.79	0.70	-25.2	-25.6	-26.1	-320	-216	-231
Mackenzie Shelf, Station 5 (0-2 cm)	1.56 [g]	1.48	1.34	-26.0 [g]	-25.9	-25.8	-737 [g]	-748	-819
Beaufort Slope, Station 144 (4-5 cm)	1.11 [g]	1.21	0.99	-23.8 [g]	-24.0	-24.4	-725 [g]	-749	-823

[a] All $\Delta^{14}C$ values corrected for ^{14}C decay since time of collection to time of measurement (see text); [b] For untreated sediment prior to solvent extraction; [c] Extracted sediment residue; [d] Saponified sediment residue; [e] Not measured; [f] Reported by Pearson et al. (2005); [g] Reported by Drenzek et al. (2007).

Table 3
Extractable, saponifiable and non-hydrolyzable organic carbon (%) and extract (%) quantified by GC

Sample	Extractable TOC % [a]	GC-quantified (% extract) [b]	Saponifiable TOC % [a]	GC-quantified (% SAE) [b]	% TOC non-hydrolyzable [c]
Peru Margin (0-2 cm)	24	1	7	9	69
Guaymas Basin (0-1 cm)	nm [d]	nm [d]	39	10	nm [d]
Washington Margin, Station 1 (0-2 cm)	19	24	1	13	80
Washington Margin, Station 4 (0-1 cm)	21	7	44	4	35
Eel River Margin, Station 1 (0-2 cm)	48	22	9	13	43
Mackenzie Shelf, Station 5 (0-2 cm)	nm [d]	nm [d]	34	1	nm [d]
Beaufort Slope, Station 144 (4-5 cm)	nm [d]	nm [d]	45	6	nm [d]

[a] Calculated by weighing a portion of the dried total lipid extract (TLE) or saponification extract (SAE) and converting to carbon equivalents (see text); [b] % TLE and SAE quantified by GC calculated by dividing quantity of compounds identified by weight of TLE and SAE; [c] % by weight not extractable or saponifiable; [d] Not measured.

FIGURE CAPTIONS

Figure 1. $\Delta^{14}C$ and $\delta^{13}C$ values for unextracted sediment residues (TOC).

Figure 2.Gas chromatograms of a) total lipid extract (TLE), b) saponification extract (SAE) acidic fraction and c) saponification extract (SAE) neutral fraction from Eel River Margin (ERM). Biomarkers *n*-alkanoic acids, *n*-alkanols, *n*-alkanes and sterols are labeled with "▲", "■", "●" and "♦" respectively. Cx above the peaks refers to the total number of carbon atoms and "m" signifies that the compound is methylated.. Number after the colon refers to the number of double bonds. The internal standard hexatriacontane is designated by "*is*", external contaminants with "*e*" and unidentified compounds that are a significant contribution of the extract with "*".

Figure 3. Relative contribution of *n*-alkanoic acids, *n*-alkanols and *n*-alkanes for sediments to a) the total lipid extract (TLE) and b) saponification extract (SAE).

Figure 4. Percent contribution to compound class for individual *n*-alkanoic acids, *n*-alkanols and *n*-alkanes in the total lipid extract (TLE); * represents unsaturated counterpart of previous *n*-alkanoic acid. Values superimposed on histogram bars represent those off scale. Odd/even predominance (OEP) for *n*-alkanes is indicated. NDP = not detected present.

Figure 5. Percent contribution to compound class for individual *n*-alkanoic acids and *n*-alkanols in saponification extract (SAE) for sediments; * represents unsaturated counterpart of the previous *n*-alkanoic acid. NDP = not detected present.

Figure 6. Difference in $\delta^{13}C$ value of extracted residue (EX-RES; filled gray symbols) and saponified residue (SA-RES; open symbols) subtracted from $\delta^{13}C$ value of bulk sediment (TOC; filled black symbol) expressed as $\Delta\delta^{13}C$ ‰ vs. differences in $\Delta^{14}C$ of the EX-RES and SA-RES subtracted from the TOC expressed as $\Delta\Delta^{14}C$ ‰ for a) organic rich sediments, b) open shelf and river dominated sediments, and c) Arctic sediments. Error bars represent 0.1‰ for $\delta^{13}C$ values and 10‰ for $\Delta^{14}C$.

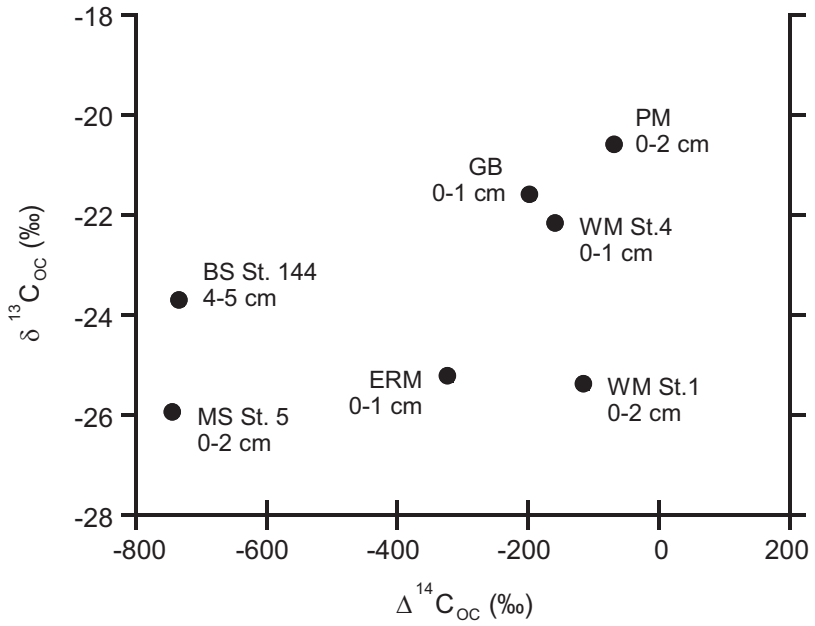
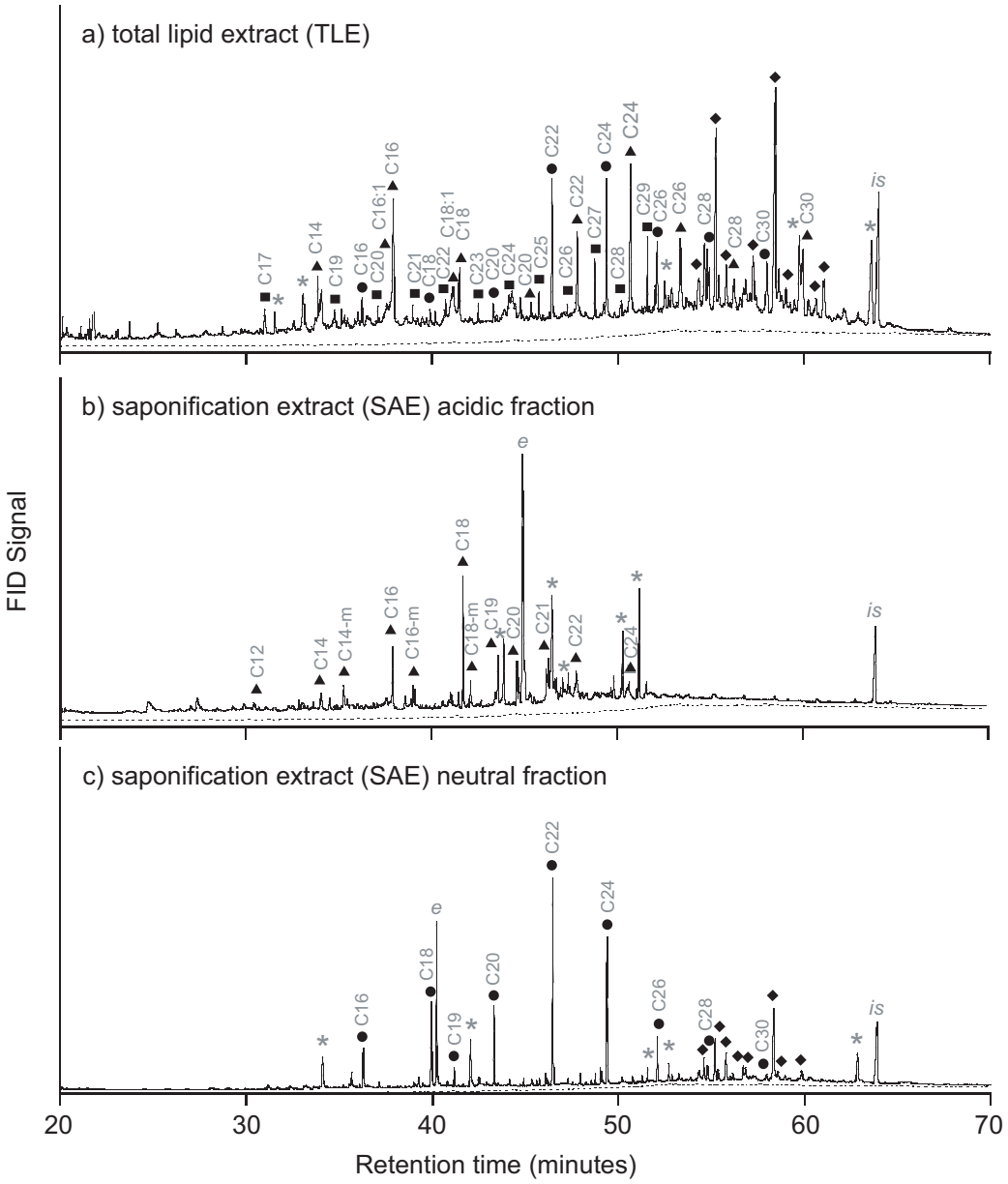

-18
-20
-22
-24
-26
-28
-800
-600
-400
-200
0
200
δ 13C OC (‰)
Δ 14C OC (‰)
PM
0-2 cm
GB
0-1 cm
WM St.4
0-1 cm
BS St. 144
4-5 cm
ERM
0-1 cm
WM St.1
0-2 cm
MS St. 5
0-2 cm

Figure 1.


a) total lipid extract (TLE)
b) saponification extract (SAE) acidic fraction
c) saponification extract (SAE) neutral fraction
FID Signal
Retention time (minutes)
20
30
40
50
60
70
C12
C14
C14-m
C16
C16-m
C18
C18-m
C19
C20
C21
C22
C24
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C28
C30
e
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Figure 2.

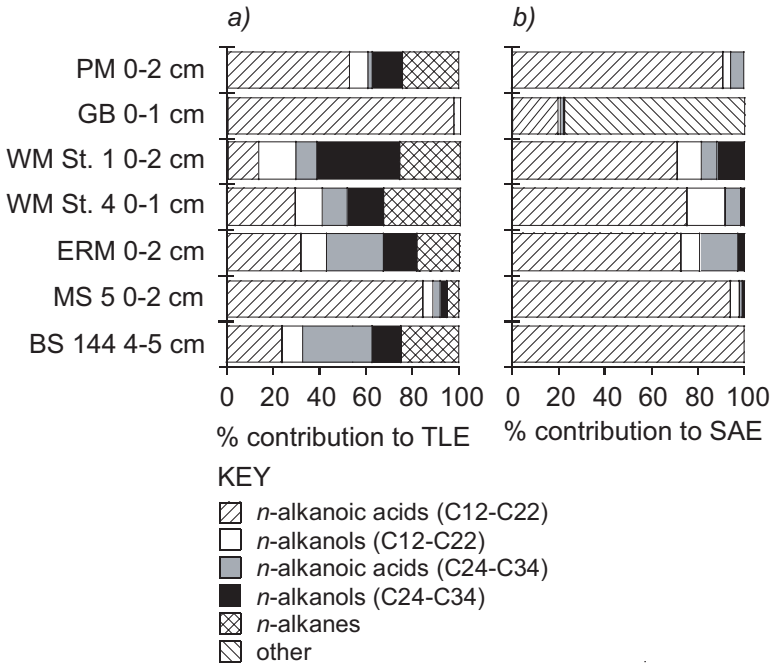
a)
b)
PM 0-2 cm
GB 0-1 cm
WM St. 1 0-2 cm
WM St. 4 0-1 cm
ERM 0-2 cm
MS 5 0-2 cm
BS 144 4-5 cm
0 20 40 60 80 100
% contribution to TLE
0 20 40 60 80 100
% contribution to SAE
KEY
n-alkanoic acids (C12-C22)
n-alkanols (C12-C22)
n-alkanoic acids (C24-C34)
n-alkanols (C24-C34)
n-alkanes
other

Figure 3.

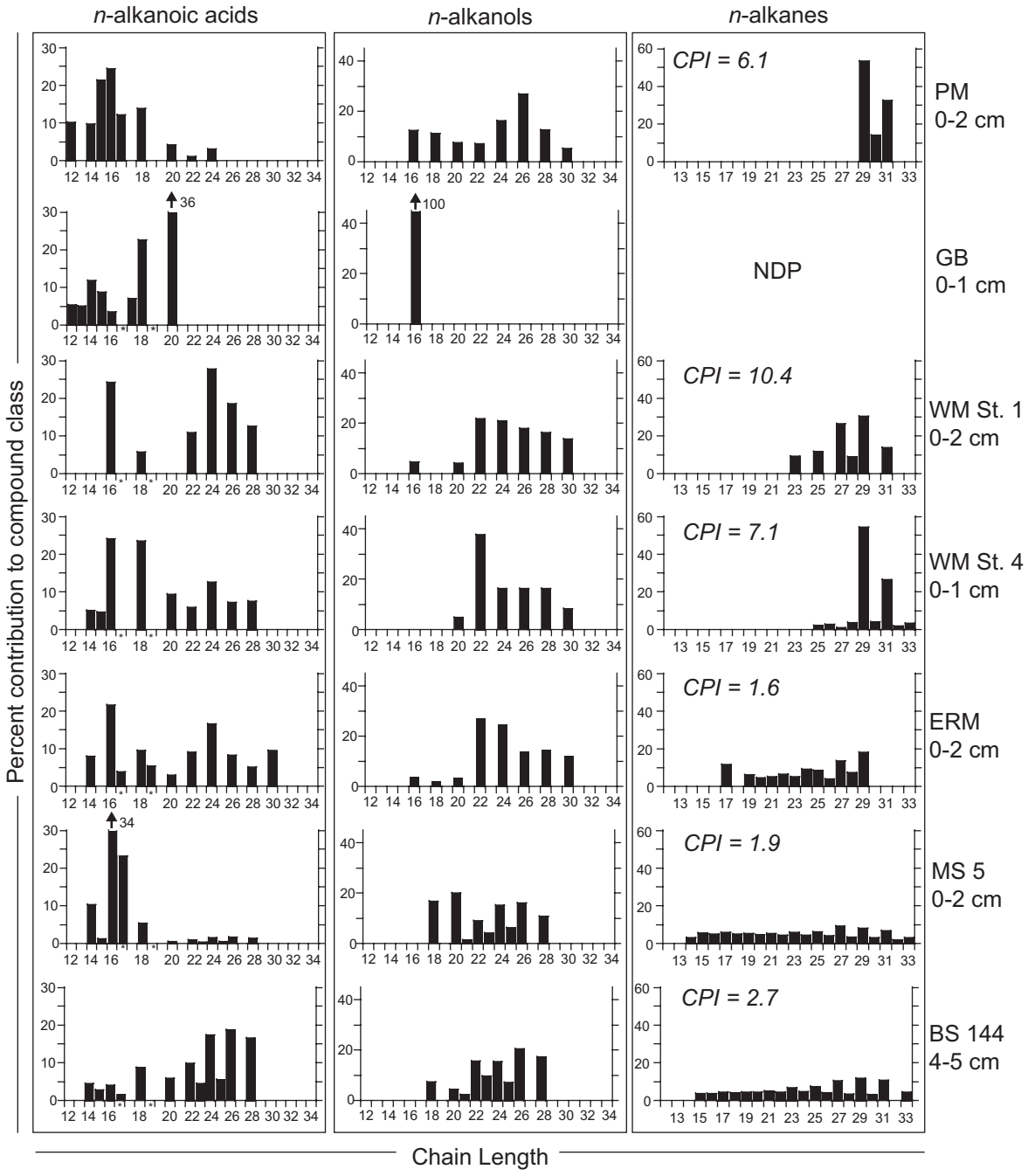
n-alkanoic acids
n-alkanols
n-alkanes
Percent contribution to compound class
Chain Length
CPI = 6.1
PM
0-2 cm
36
100
NDP
GB
0-1 cm
CPI = 10.4
WM St. 1
0-2 cm
CPI = 7.1
WM St. 4
0-1 cm
CPI = 1.6
ERM
0-2 cm
34
CPI = 1.9
MS 5
0-2 cm
CPI = 2.7
BS 144
4-5 cm

Figure 4.

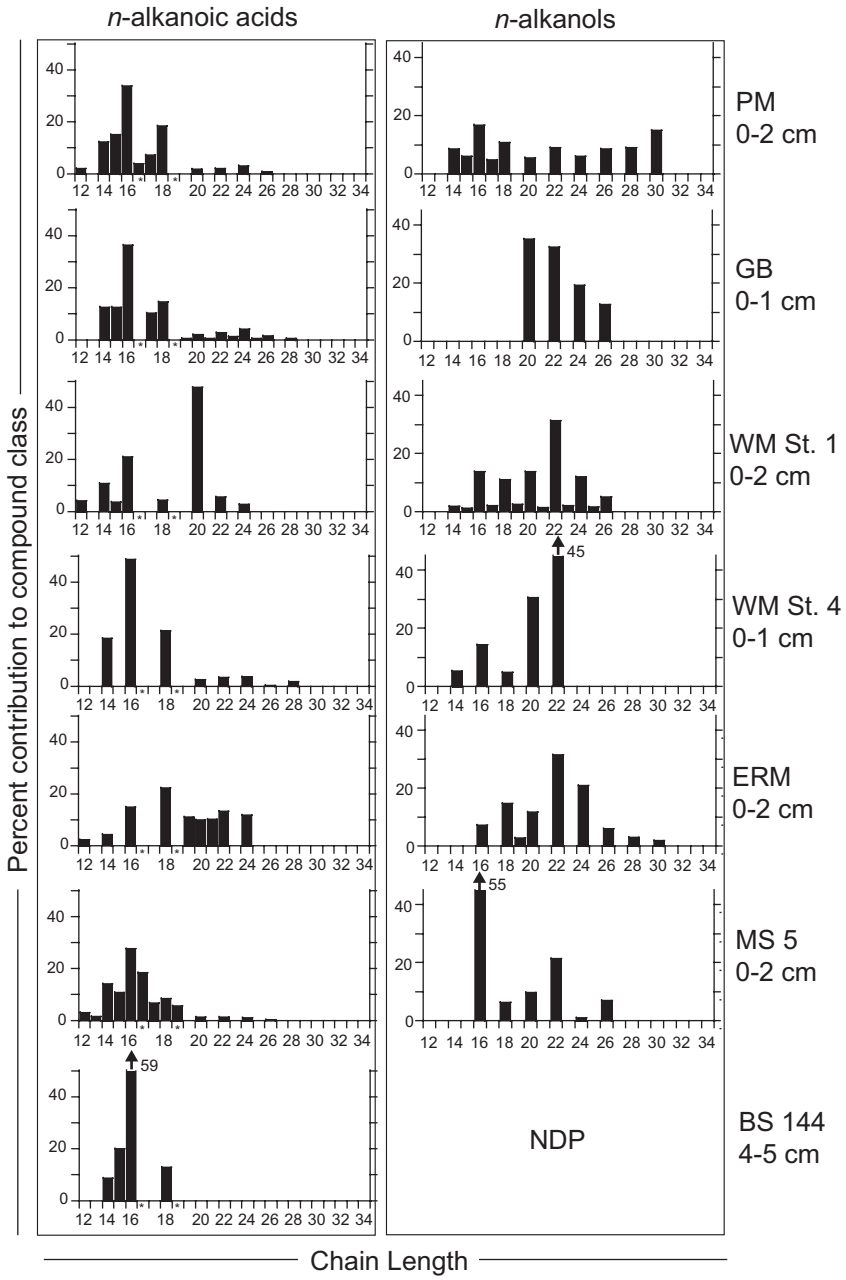
n-alkanoic acids
n-alkanols
Percent contribution to compound class
Chain Length
PM
0-2 cm
GB
0-1 cm
WM St. 1
0-2 cm
WM St. 4
0-1 cm
ERM
0-2 cm
MS 5
0-2 cm
BS 144
4-5 cm
NDP
45
55
59

Figure 5.

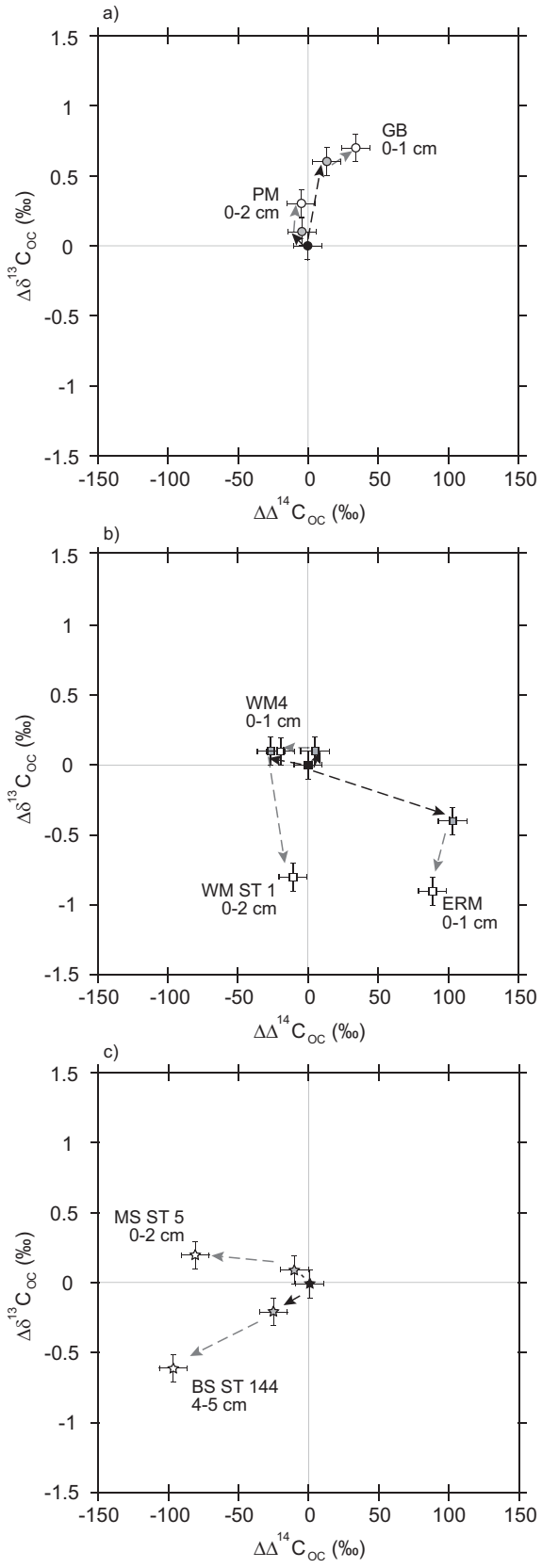
a)
GB
0-1 cm
PM
0-2 cm
b)
WM4
0-1 cm
WM ST 1
0-2 cm
ERM
0-1 cm
c)
MS ST 5
0-2 cm
BS ST 144
4-5 cm
$\Delta\delta^{13}C_{OC}$ (‰)
$\Delta\Delta^{14}C_{OC}$ (‰)

Figure 6.