

Sources and transport of terrestrial organic matter in Vancouver Island fjords and the Vancouver–Washington Margin: A multiproxy approach using $\delta^{13}\text{C}_{\text{org}}$, lignin phenols, and the ether lipid BIT index

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Abstract

The Branched and Isoprenoid Tetraether (BIT) index (a ratio of marine and terrestrial glycerol dialkyl glycerol tetraether [GDGT] membrane lipids) was recently introduced as a proxy for the fraction of fluvially derived organic carbon (OC) buried in marine sediments. We investigate the source and distribution of terrestrial OC in marine sediments in a large spatial data set that encompasses the Washington–Vancouver Island Margin, Vancouver Island fjords, and Puget Sound with the goal of comparing the BIT index to other traditional measures of terrestrial OC ($\delta^{13}\text{C}$ of OC [$\delta^{13}\text{C}_{\text{org}}$] and lignin phenols). $\delta^{13}\text{C}_{\text{org}}$ values and lignin concentrations indicate that the fjords are a significant trap for undegraded, wood-derived terrestrial material, with surface sediments containing up to 76% terrestrial OC. These proxies also show significant terrestrial OC contributions to margin sediments (up to 54%), with most likely an angiosperm source from the Columbia River. In contrast to $\delta^{13}\text{C}_{\text{org}}$ values and lignin concentrations, BIT index values indicate extremely low terrestrial carbon throughout the study area (BIT index values range from 0 to 0.28) and are uncorrelated with the other proxies. Though the BIT index did not correlate with other proxies, margin GDGT concentrations varied offshore similarly to other terrestrially derived OC and are well-correlated with other proxies. We suggest that the BIT index is best interpreted as a proxy for soil- or peat-derived OC. The majority of terrestrially derived OC delivered to sediment in this area has a lignin-rich, nonsoil source. The disparity between the BIT index and other proxies implies that the BIT index significantly underestimates terrestrial relative to marine OC input to sediments in areas in which riverine OC input is not soil or peat derived.

Burial of organic carbon (OC) on continental margins is estimated to account for the majority of the total carbon burial in the ocean and is a significant sink for terrestrial OC (Hedges and Keil 1995). Understanding the sources and fate of this terrestrial OC in marine sediments is thus of importance in understanding global biogeochemical cycles. In this study, we use two traditional proxies for terrestrial OC input to sediments—the $\delta^{13}\text{C}$ of bulk sedimentary OC ($\delta^{13}\text{C}_{\text{org}}$) and the concentration of lignin phenols—to examine the sources and quantity of terrestrial OC in sediments throughout the Washington–Vancouver Island Margin, Vancouver Island fjords, and Puget Sound. We compare these results to those obtained using a recently introduced proxy for terrestrial OC in marine sediments, the Branched and Isoprenoid Tetraether (BIT) index

(Hopmans et al. 2004), to evaluate this proxy in a new location.

The Columbia River is the dominant source of terrestrial OC to the Washington Margin and Cascadia Basin. Transport of the Columbia River plume brings fluvially derived material northward, toward the Olympic Peninsula and Vancouver Island (Sternberg 1986; Ridge and Carson 1987). Previous work in this region used $\delta^{13}\text{C}_{\text{org}}$, carbon:nitrogen (C:N) ratios, lignin phenols, and *n*-alkanes to demonstrate that terrestrial OC contributed between 15% and 60% of the total OC in margin sediments (Prahel et al. 1994).

The coast of Vancouver Island is indented by a series of temperate fjords. Terrestrial carbon enters fjords from rivers at the head of each fjord, as well as from non-point source debris inputs from the sides of the fjords. Temperate fjords are thought to potentially trap significant amounts of carbon as a result of the high input of refractory (terrestrial) OC. Nuwer and Keil (2005) demonstrated the importance of fjords in storing terrestrial OC, estimating that fjord sediments may be responsible for trapping at least 12% of the total OC buried in continental margins over the last 100,000 years. Analysis of $\delta^{13}\text{C}_{\text{org}}$ and C:N ratios of fjord sediments demonstrated that the fjord sediments can contain up to ~85% terrestrial OC (Nuwer and Keil 2005).

The BIT index is a new tool for evaluating terrestrial carbon input, and it differs from previous proxies for terrestrial OC in that it employs a peat- and soil-derived microbial biomarker (Hopmans et al. 2004). The BIT index is the ratio of two distinct kinds of microbial ether-linked membrane lipids, one archaeal and one bacterial (Fig. 1).

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Crenarchaeol (Fig. 1, IV), an isoprenoidal glycerol dialkyl glycerol tetraether (GDGT) membrane lipid, is found in the domain archaea and was initially proposed to be an exclusive biomarker for nonthermophilic marine group 1 crenarchaeota (Schouten et al. 2000; Sinninghe Damsté et al. 2002). Although ubiquitous in marine environments, crenarchaeol was later shown to be widespread in terrestrial environments as well, including soils (Leininger et al. 2006), peats (Herfort et al. 2006; Weijers et al. 2006a,b), lakes (Schouten et al. 2000; Powers et al. 2004), and hot springs (Pearson et al. 2004; Zhang et al. 2006; Schouten et al. 2007) and has now been identified in an isolated ammonia-oxidizing thermophile from Yellowstone National Park, *Nitrosocaldus yellowstonii* (de la Torre et al. in press). The terrestrial lipids used in the BIT index are branched, nonisoprenoidal, ether-linked membrane lipids (Fig. 1, I–III), suggested to derive from anaerobic soil- and peat-dwelling bacteria (Hopmans et al. 2004; Weijers et al. 2006b). The BIT index is the ratio of the chromatographic peak areas of the terrestrially derived branched lipids (I–III) to the terrestrial lipids and crenarchaeol combined (I–IV), thus:

$$BIT\ index = (I + II + III) / (I + II + III + IV) \quad (1)$$

The index was first proposed to range from 0 to 1, with 0 representing a completely marine sample and 1 a completely terrestrial sample. However, recent studies demonstrating the presence of terrestrial crenarchaeol indicate regional variability in lipid abundance and indicate that the BIT index is better interpreted as a range of 0–0.1 for marine-dominated samples and a range of 0.8–1 for terrestrially dominated samples (Herfort et al. 2006; Weijers et al. 2006a). Previous work has shown that the BIT index has low values in open ocean sediments and some coastal areas, midrange values in some coastal areas and some lakes, and values near 1 in peats (Hopmans et al. 2004). BIT index estimates of terrestrial input near the Congo River mouth and the North Sea agree well with those estimated using $\delta^{13}C_{org}$ (Hopmans et al. 2004; Herfort et al. 2006). BIT index values, $\delta^{13}C_{org}$, and *n*-alkane concentrations from the Gulf of Lions showed similar patterns of terrestrial OC abundance (Kim et al. 2006).

Studies employing the BIT index are few, and there are several assumptions inherent in this index that have not been fully validated. While complications arising from terrestrially sourced crenarchaeol are now recognized, other issues may also complicate interpretation of the BIT index in different environments (i.e., Herfort et al. 2006; Kim et al. 2006; Weijers et al. 2006a). For example, crenarchaeol is used in the index as a proxy for marine carbon sources. However, so far no study has verified a direct relationship between sedimentary crenarchaeol and marine productivity or OC storage in sediments. Likewise, it was assumed that the concentrations of branched lipids in the sediment are directly proportional to the total input of fluvial terrestrial OC into the marine environment (Hopmans et al. 2004). This would require that the production, deposition, transport, and burial of branched lipids was proportional to that of the majority of terrestrial OC. Finally, despite a lack of empirical evidence, it is assumed

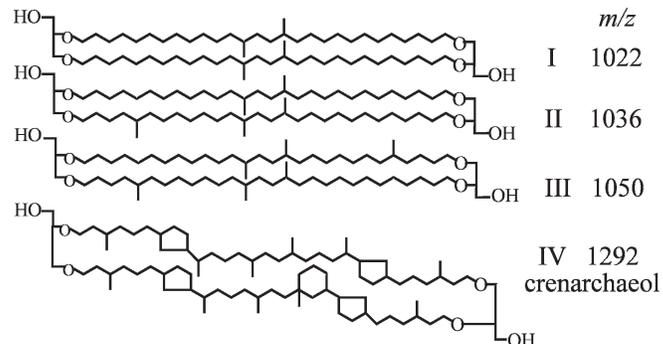


Fig. 1. Structures of the four glycerol dialkyl glycerol tetraether (GDGT) lipids used in the BIT index. I–III, Branched, nonisoprenoidal, bacterial lipids; IV, crenarchaeol.

that because of the structural similarities between the lipids, both kinds of lipids degrade at the same rate.

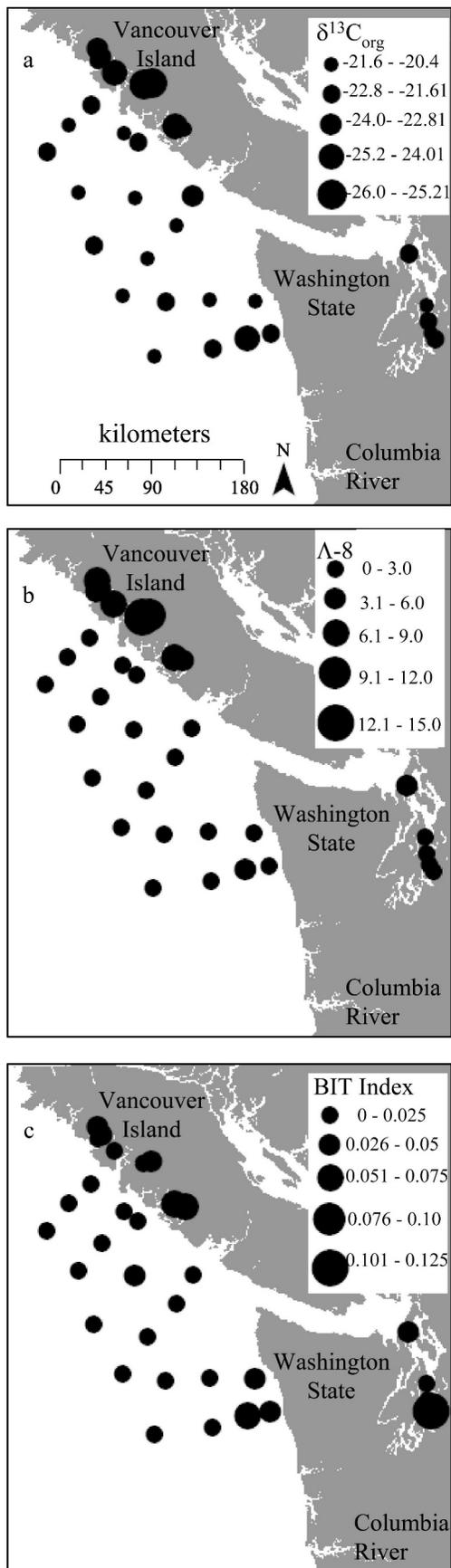
Given that most studies so far have been conducted in peat- or soil-rich environments, it is unknown how representative the terrestrial branched lipids are of total terrestrial OC in a peat- or soil-poor environment. The current study area provides a good opportunity to test this index in a system in which traditional proxies have previously proved effective in describing terrestrial OC.

Methods

Sample collection—Surface sediments were analyzed from the Washington–Vancouver Island Margin, two Vancouver Island fjords, and Puget Sound. Margin sediment was obtained using a multicorer during a summer 2004 cruise aboard the RV *Wecoma*. All cores were sliced into 0.5–2-cm sections immediately after sampling, and the 2–3-cm interval was used for lipid, lignin, and bulk geochemical analyses. Vancouver Island fjord and Puget Sound sediments were collected using a Van Veen grab (approximately the top 20 cm) during a cruise aboard the RV *Clifford A. Barnes* in the summer of 2005 (Vancouver Island) and the aboard the RV *Thomas G. Thompson* in spring 2006 (Puget Sound). Terrestrial samples, including beach, soils, river bar, and higher plant material, were collected by hand in 2005 from the head of Bedwell and Tofino Fjords, three Olympic Peninsula sites: the mouth of the Quillayute River, the Hoh Rainforest (inland), and the Hoh River (inland), as well as three Seattle beaches: Alki Beach, Discovery Park, and Shilshole. All samples were stored frozen and freeze-dried prior to analysis.

Elemental and $\delta^{13}C_{org}$ analysis—Weight percent OC and nitrogen and the $\delta^{13}C$ of homogenized, acidified samples were obtained in triplicate using a Finnigan Delta XL continuous-flow isotope ratio mass spectrometer interfaced with a Carlo Erba NC 2500. Errors were $\pm 0.1\%$ for elemental analyses and $\pm 0.6\%$ for stable isotope analyses.

Lignin analysis—Analyses of lignin phenols were performed via gas chromatography (GC) following alkaline CuO oxidation of bulk sediment (Hedges and Ertel 1982), following the procedure outlined by Goni and Montgom-



ery (2000). Bulk sediment was oxidized in an alkaline CuO solution, under N₂ pressure, using a microwave digestion apparatus. Recovery standards (1.15 mmol L⁻¹ trans-cinnamic acid and 0.344 mmol L⁻¹ ethyl vanillin) were added, and the solutions were acidified to a pH of 1 using concentrated HCl. The aqueous phase was extracted using ethyl acetate and then dried over Na₂SO₄ and the solvent evaporated under N₂. Samples were redissolved in pyridine and then analyzed via GC, scanning in constant pressure mode at 65.6 kPa (but otherwise using the same procedure as outlined in Goni and Montgomery [2000]), and detected using a flame ionization detector. Error on triplicate analyses was $\pm 9\%$.

GDGT analysis—Procedures for lipid analyses were adapted from Hopmans et al. (2000, 2004). Freeze-dried samples were ultrasonically extracted three times with methanol, three times with dichloromethane (DCM):methanol (1:1), and three times with DCM, and the extracts were combined. The dried total extract was dissolved in hexane:isopropanol (IPA) (99:1) and in some cases was filtered with a 0.45- μ m syringe filter. Lipids were analyzed using liquid chromatography–mass spectrometry (LC-MS) on a Hewlett Packard 1100 series LC-MS using a Prevail Cyano column (2.1 \times 150 mm, 3 μ m; Alltech) and a gradient elution modified from Hopmans et al. (2004). Samples were injected (10–50 μ L) at a flow rate of 0.2 mL min⁻¹ and eluted with 99% hexane:IPA for 5 min, followed by a gradient to 1.8% IPA in 50 min. Solvent was held for 10 min in 10% IPA and was then allowed to re-equilibrate in 99% hexane:IPA over a period of 20 min. Lipids were detected using atmospheric pressure-positive ion chemical ionization mass spectrometry of the eluent on an Agilent Ion Trap Mass Spectrometer, with the following specifications: nebulizer pressure: 413.7 kPa; drying gas pressure: 48.3 kPa; scanning 700–1,450 m/z. BIT index values were calculated using integrated LC-MS peak areas of extracted ion chromatograms for each compound. The error on calculated BIT index values for samples extracted in triplicate was $\pm 6\%$. As a result of the lack of a quantitative standard, absolute concentrations are not available for the lipids. However, replicate analyses demonstrated the precision of relative concentrations. The relative concentration of each GDGT was calculated by normalizing each peak area to the largest peak area for that compound in the data set. Linearity of the detector response was confirmed using a dilution series that included the range of sample concentrations.

Results

Bulk OC and $\delta^{13}C_{org}$ —Margin sediments ranged from 0.11% to 3.2% OC, fjord sediment from 2.4% to 5.8% OC,

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Fig. 2. Spatial distributions of (a) $\delta^{13}C_{org}$ (‰), (b) $\Lambda-8$ (mg lignin 100 mg OC⁻¹), and (c) BIT index values for margin, Vancouver Island fjord, and Puget Sound samples.

Table 1. Terrestrial end-member data for Vancouver Island (VI) and Olympic Peninsula (OP) samples.*

Sample	BIT index value	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\Lambda-8$ (mg 100 mg OC ⁻¹)	Ad: Al _v
VI surface soil	0.54	-26.7	3.84	0.43
VI soil, 10-cm depth	0.74	-25.5	2.42	1.28
VI bedwell inlet sand	0.99	-25.5	1.64	0.40
VI leaf litter	nd	—	—	—
OP QRB No. 1	0.87	-27.1	1.95	0.84
OP QRB No. 2	1.0	-27.7	0.67	0.30
OP HRB No. 1	1.0	-26.8	2.80	0.07
OP HRB No. 2	nd	-25.7	1.12	0.55
OP HRF OD	nd	—	2.97	0.55
OP HRF, 10-cm depth	1	-26.7	3.95	0.69

* BIT, Branched and Isoprenoid Tetraether (index); OC, organic carbon; OD, organic detritus; QRB, Quillayute River Bar; HRB, Hoh River Bar; HRF, Hoh Rain Forest (inland); Ad: Al_v, vanillic acid: vanillin ratio; nd, no lipids detected. Samples for which data are not available are indicated by a dash (—). All data are from surface samples, unless otherwise noted.

and Puget Sound sediments from 0.12% to 2.2% OC. C:N values showed little variability on the margin, averaging 9.0 ± 1.0 . The fjords had highly variable C:N ratios, ranging from 9.3 to 54.0, with an average of 18.8 ± 13.9 . Puget Sound C:N ratios ranged from 7.5 to 17.0, with an average of 10.2 ± 2.9 .

$\delta^{13}\text{C}_{\text{org}}$ values ranged from -21.2‰ to -25.6‰, with the most depleted values occurring in Nootka Inlet, the northernmost Vancouver Island fjord (Fig. 2a). Estimates of the percent terrestrial OC in these sediments can be made using a simple mixing model, in which the marine end member is -21‰ and the terrestrial end member is -27‰. The marine end member is estimated from the $\delta^{13}\text{C}_{\text{org}}$ versus $\Lambda-8$ relationship (Fig. 3) and the terrestrial end member from terrestrial samples analyzed for this study (Table 1). While the true values of these end members depend on the exact sources of OC to the sediments, these values are in agreement with those of past work (Keil et al. 1994). Using this mixing model, terrestrial OC on the margin and Puget Sound averaged $13\% \pm 5\%$ and $18\% \pm 11\%$, respectively. The fjord average is significantly higher ($p < 0.05$), at $43\% \pm 7\%$ terrestrial OC, with a maximum value of 76% in Nootka Inlet (Fig. 4a). These results are similar to those of previous studies (Prahl et al. 1994; Nuwer and Keil 2005). The marine end member in particular may be disputed, as previous work indicates that phytoplankton in the water column are enriched relative to phytoplankton that have settled to the sediment and may have $\delta^{13}\text{C}_{\text{org}}$ values of -17‰ to -19‰ (Hedges et al. 1999; Nuwer and Keil 2005). Using an enriched marine end member of -18‰ would increase estimates of the % terrestrial OC, resulting in a maximum value of 86% terrestrial OC in Nootka Inlet and a doubling of calculated % terrestrial OC throughout much of the study area.

Lignin phenols—Lignin phenols were detected in sediments from all stations analyzed. The concentration of eight common lignin phenols normalized to OC concentration, $\Lambda-8$, ranged from 0.054 to 10.853 mg lignin 100 mg OC⁻¹ throughout the study site. The concentration of eight lignin phenols normalized to gram of sediment, $\Sigma-8$, ranged from 1.2×10^{-5} to 0.052 g lignin g dry weight⁻¹. Both had maximum values in the fjords, specifically Nootka Inlet (Figs. 2b, 4b). Prahl et al. (1994) reported

similar lignin values for the Cascadia Basin and the Washington Margin. There is a negative correlation between $\Lambda-8$ and $\delta^{13}\text{C}_{\text{org}}$ ($R^2 = 0.6696$, $p \leq 0.05$), indicating that more lignin phenols can be found in more ¹³C-depleted samples (Fig. 3).

BIT index values—The BIT index values throughout the study area were extremely low (Figs. 2c, 4c). Sediment values ranged from 0 to 0.28, with an average of 0.021 ± 0.003 on the margin, 0.05 ± 0.02 in the fjords, and 0.02 ± 0.03 in Puget Sound. The fjord values are significantly higher than the margin values ($p < 0.05$). However, there is no offshore trend on the margin. Also, there is no correlation between BIT index values and % terrestrial OC calculated from lignin concentrations (Fig. 5a) or $\delta^{13}\text{C}_{\text{org}}$ values (Fig. 5b) throughout the study area. While relative concentrations of branched lipids in the fjords also did not correlate to % terrestrial OC calculated using other proxies, there was a correlation between the margin concentrations and $\Lambda-8$ ($R^2 = 0.8487$, $p \leq 0.05$; Fig. 5c) and $\delta^{13}\text{C}_{\text{org}}$ ($R^2 = 0.4573$, $p \leq 0.05$; Fig. 5d). BIT index values of terrestrial end members varied from 0 to 1, depending on the location and type of the sample, with considerable patchiness among samples from the same site (Table 1; Fig. 5b). GDGTs were undetectable in dead leaves and plants lying on, but not incorporated into, the soil. Several soil and river bar samples had significant amounts of crenarchaeol, yielding midrange BIT index values (0.54–0.82). However, other soil and river bar samples contained little or no crenarchaeol and had the expected terrestrial BIT index value of 1, or close to 1.

Discussion

Sources of terrestrial OC in surface sediments indicated by lignin phenols—Studies of $\delta^{13}\text{C}_{\text{org}}$ and lignin phenols have yielded insights into the contribution of terrestrial OC to sediments of the Washington Margin and, to a lesser extent, the Vancouver Island fjords (i.e., Prahl et al. 1994; Keil et al. 1998; Nuwer and Keil 2005). Here we present both margin and fjord data for the first time in a single study, allowing for a cohesive picture of the quantity and source of terrestrial OC in these regions, and we compare these data to data from the newly introduced BIT index.

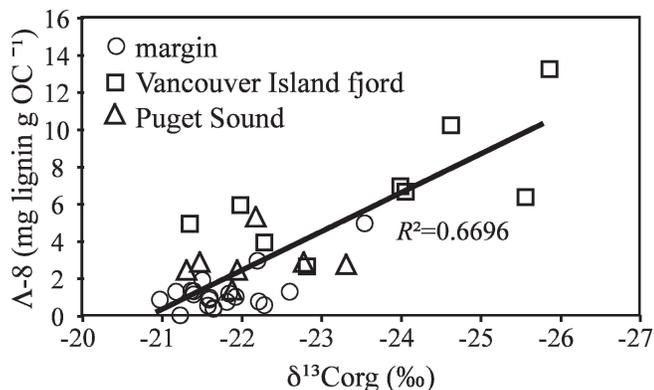


Fig. 3. Correlation between $\Sigma-8$ (mg lignin g dry weight⁻¹) versus $\delta^{13}C_{org}$ for all margin, Vancouver Island fjord, and Puget Sound samples.

Both the $\delta^{13}C_{org}$ values and lignin phenol abundances measured here confirm that the Vancouver Island fjords and Puget Sound are effectively trapping terrestrial OC and have a higher proportion of terrestrial OC relative to the margin (Figs. 2, 4). If the majority of the terrestrial OC is being trapped in fjords, and thus fails to be transported to the margin, then the margin most likely has a major point source at the Columbia River. This is analogous to what has previously been shown for mineral delivery (i.e., Sternberg 1986). If that is the case, we would expect that fjord lignin phenols would reflect Vancouver Island plant life, while lignin phenols on the margin would reflect sources from the Columbia River.

Plots of the lignin phenols—syringyl to vanillyl phenols (S:V) versus cinnamyl to vanillyl phenols (C:V)—indicate that fjord and margin sediments have different terrestrial carbon sources (Fig. 6). The fjords exhibit a woody gymnosperm source, characteristic of the Vancouver Island pine forests. The margin appears to have a predominately nonwoody angiosperm source (Fig. 6), similar to the grassland sources of terrestrial OC to the Columbia River (Hedges et al. 1984). Changes in S:V may also indicate changes in degradation, as studies have shown a correlation between S:V and increased diagenesis of amino acids (Keil et al. 1998; Hedges et al. 1999; Nuwer and Keil unpubl. data). Degradation would drive (S:V):(C:V) closer to the origin (0,0). However, diagenesis of lignin phenols either in soils or in the marine environment cannot account for the observed S:V values (*see later discussion*). These source assignments are consistent with previous work for these fjords, Lake Washington, and the margin.

$\Lambda-8$ is substantially elevated in the fjords relative to the margin (Fig. 2b). This implies that the fjords are trapping wood-sourced lignin, which has a much higher lignin content than the plant average. Delivery of wood-sourced lignin to fjords is consistent with the environment of Vancouver Island, a soil-poor region that currently has an abundance of large woody debris from logging (Jakob 2000). The retreat of the Cordilleran Ice Sheet during the last deglaciation removed sand and gravel from much of the island, depositing it in lowlands. Today the island is

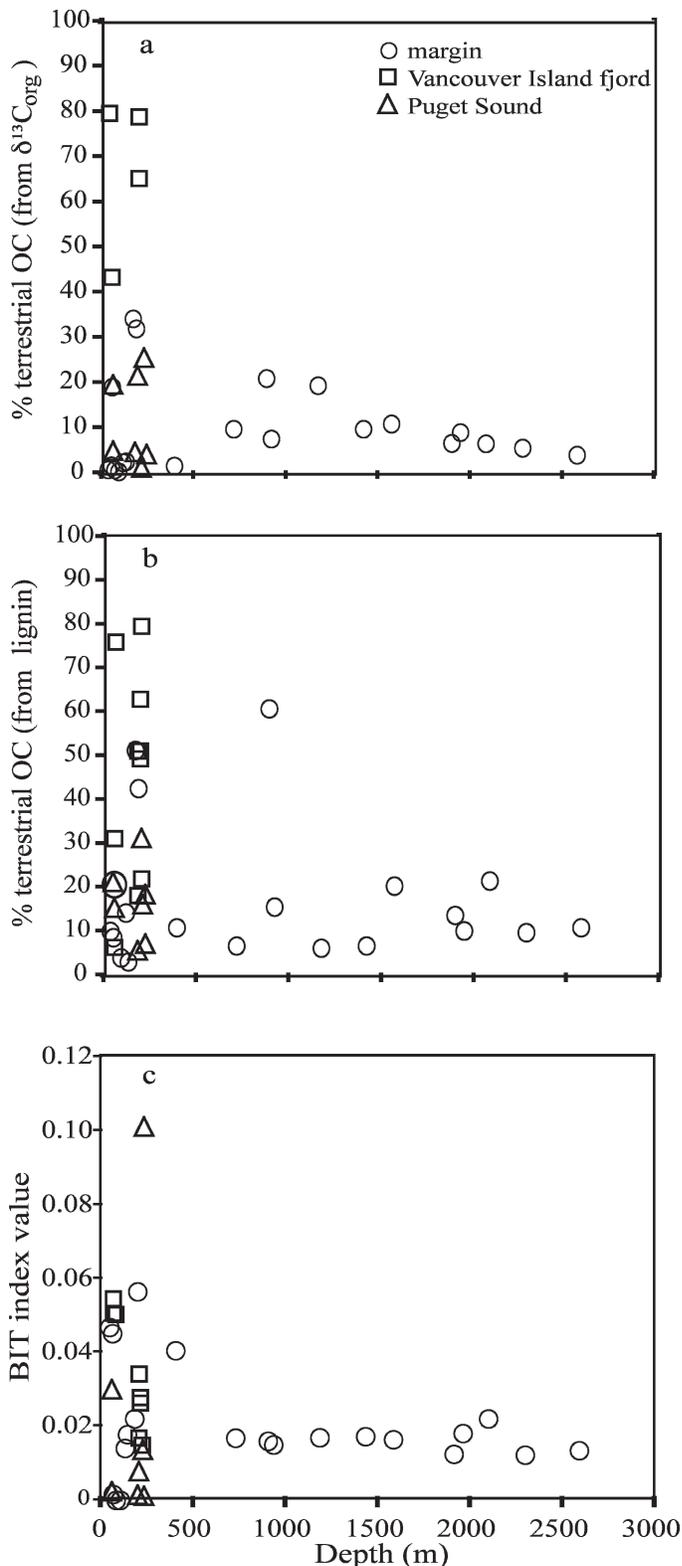


Fig. 4. Values for (a) % terrestrial OC calculated from $\delta^{13}C_{org}$, (b) % terrestrial OC calculated from lignin, and (c) BIT index values, plotted versus station depth (m) for margin, Vancouver Island fjord, and Puget Sound samples.

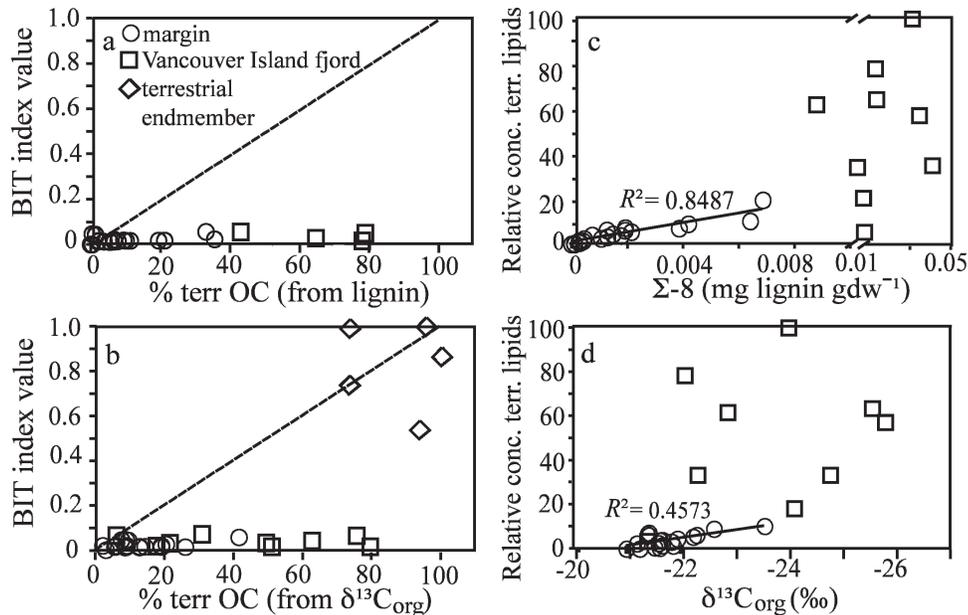


Fig. 5. BIT index values plotted versus (a) % terrestrial OC calculated from lignin and (b) % terrestrial OC calculated from $\delta^{13}\text{C}_{\text{org}}$, showing no correlation between BIT index values and other proxies. Relative concentrations of branched lipids (g dry weight^{-1}) plotted versus (c) $\Sigma\text{-8}$ ($\text{mg lignin g dry weight}^{-1}$) and (d) $\delta^{13}\text{C}_{\text{org}}$, with linear regressions for margin samples shown. Dashed line shows theoretical relationship between BIT index values and % terrestrial OC.

characterized by mountainous forests that lack well-developed soil (McCull et al. 2005). Thus, even prior to the onset of heavy logging, it is likely that undegraded woody debris, not soil, would still have been a dominant source of terrestrial OC to the fjords. Unlike these fjord stations, nearshore margin stations are likely dominantly influenced by Columbia River terrestrial OC and have lignin phenol compositions typical of averaged plant material, containing a substantial amount of soft-tissue plant matter in addition to the woody debris.

Comparison of proxies for terrestrial OC in fjord sediments—BIT index values of sediments throughout the study area indicate that there is a very low proportion of terrestrially derived GDGTs relative to crenarchaeol. If the terrestrial GDGTs are proportional to the total terrestrial OC contribution to the sediments, this indicates that the terrestrial OC contribution is very low throughout the study area. However, previous work (i.e., Prahl et al. 1994; Nuwer and Keil 2005) and the stable isotope and lignin phenol data presented in this study indicate otherwise (Fig. 4a,b). While all proxies imply a higher terrestrial OC contribution in the fjords than either on the margin or in Puget Sound, the magnitude and spatial distribution of this contribution vary to such an extent between the BIT index and the other two proxies that there is no statistically significant correlation between them (Fig. 5a,b). The BIT index fails to identify terrestrial OC, even at stations that have very depleted $\delta^{13}\text{C}_{\text{org}}$ signatures and the highest concentrations of lignin phenols. Interestingly, the $\delta^{13}\text{C}_{\text{org}}$ and $\Lambda\text{-8}$ do correlate with each other (Fig. 3). The low BIT index values are especially misleading in the fjords, where the majority of the OC can be terrestrially derived.

The varying sources of lignin and GDGTs can explain inconsistencies between the proxies. The branched GDGTs used in the BIT index have been detected exclusively in peat, soil, and other microbially processed, terrestrially derived material (Hopmans et al. 2004; Herfort et al. 2006; Weijers et al. 2006a, 2007). In this study, bacterial GDGTs were present in all soils and most riverbeds analyzed, but they were not detected in non-soil-incorporated plant debris (Table 1). Terrestrially derived bacterial GDGTs in sediments would appear to be indicative of soil-derived terrestrial OC and not of other, fresher, vascular plant debris. Lignin phenols can be present either as undegraded vascular plant debris or incorporated into soils. The high lignin concentrations concurrent with low BIT index values imply that the majority of the lignin may not have been heavily processed through soil.

A plot of N:C ratios versus $\delta^{13}\text{C}_{\text{org}}$ values supports the hypothesis that nonsoil vascular plant debris is the dominant source of terrestrial OC to the sediment (Fig. 7). OC in the sediment can be partitioned using elemental composition and $\delta^{13}\text{C}_{\text{org}}$ values as a result of the disparate end members for soil, vascular plant, and marine plankton (Hedges and Mann 1979; Ertel and Hedges 1985; Keil et al. 1994). Marine plankton tends to be enriched in ^{13}C relative to all terrestrial carbon and to have high N:C ratios. Mineral-bound, or soil-derived, organic matter tends to have more depleted $\delta^{13}\text{C}_{\text{org}}$ values, but it has similarly high N:C ratios, while vascular plant debris $\delta^{13}\text{C}_{\text{org}}$ values are depleted and have a significantly lower N:C ratio. The majority of the margin N:C and $\delta^{13}\text{C}_{\text{org}}$ values fall in or near the marine planktonic end member, indicating very low contributions of any terrestrial OC (Fig. 7). Fjord values vary from a marine planktonic to

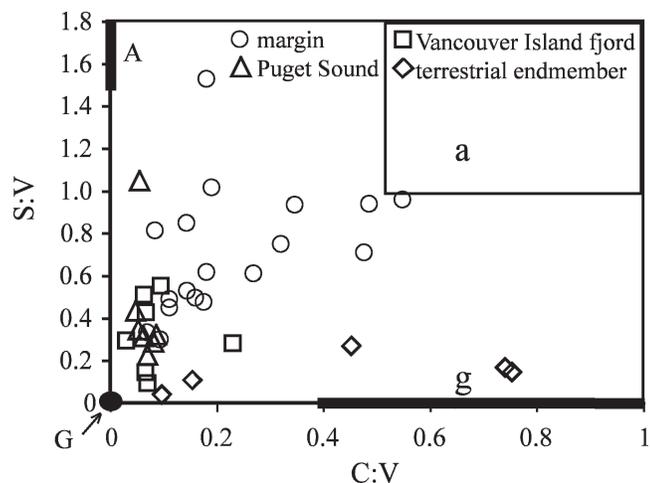


Fig. 6. Plot of syringic:vanillic acid (S:V) versus cinnamic:vanillic acid (C:V) for margin, Vancouver Island fjord, Puget Sound stations, and terrestrial samples. End members in rectangles are characteristic of angiosperm wood (A), gymnosperm wood (G), angiosperm soft tissue (a), and gymnosperm soft tissue (g).

vascular plant debris signature, but they show little apparent influence of soil carbon (Fig. 7).

If the majority of the lignin phenols in fjord sediments are indeed coming from vascular plant debris instead of soil, the distribution of lignin phenols present should be indicative of a fresh, nondegraded source. Ratios of various lignin phenols are useful in determining the degree of lignin degradation (Hedges and Ertel 1982). Since the aldehyde form of a lignin degrades to the acid form under oxic conditions, the ratio of vanillic acid to vanillin ($Ad:Al_v$) can be used as a measure of degradation. 3,5-Dihydroxybenzoic acid has recently been indicated as a proxy for soil carbon (Houel et al. 2006; Dickens et al. 2007). Both these ratios are low in fjord sediment (Fig. 8), indicating that the lignin is relatively fresh or non-soil derived. This is in agreement with a nonsoil, vascular plant source for the majority of the terrestrial OC in the fjords.

Possible causes of low BIT index values—The BIT index values reported here are consistently lower than those seen in other areas (i.e., Herfort et al. 2006; Kim et al. 2006), making it apparent that local conditions are an important factor to consider when employing the BIT index. What is it about this region that causes the BIT index to be so low? Although a lack of soil is likely to be the primary cause of low BIT index values in this region, other factors can contribute to low BIT index values in this and other regions. For example, a significant source of terrestrial crenarchaeol to the sediments would lower BIT index values. Several soil samples in our study had BIT index values less than 1 as a result of the presence of terrestrial crenarchaeol, which might partially account for the low BIT index values seen throughout the region. However, the lowest BIT index value observed on land, in a sample that contained lipids of interest, was 0.54, over an order of magnitude larger than the average fjord value, and 27 times larger than the average

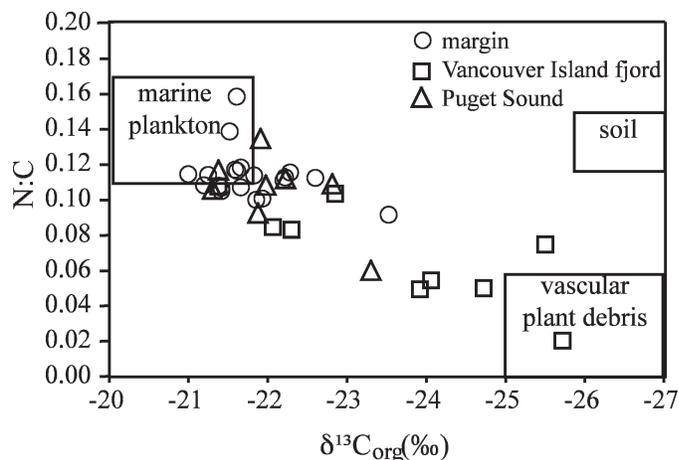


Fig. 7. Ratios of organic nitrogen to carbon (N:C) versus $\delta^{13}C_{org}$ (‰) for margin, Vancouver Island fjord, and Puget Sound stations. Source assignments are for soil, vascular plant debris, and marine planktonic end members.

margin value. This implies that, assuming similar delivery and burial of all terrestrially derived lipids, at least 90% of the crenarchaeol in the fjords and 96% of the crenarchaeol in the margin is of marine origin. Terrestrial crenarchaeol would not appear to be capable of significantly affecting the observed BIT index values.

Setting aside the influence of terrestrial crenarchaeol, low BIT index values can be obtained by having either a large amount of marine crenarchaeol or a very small amount of terrestrial GDGTs deposited in the sediment. If the amount of crenarchaeol is greater in this area compared with other regions, it may overwhelm terrestrial GDGTs. Previously, analysis of several Southern North Sea sediments indicated that low BIT index values were due to high crenarchaeol concentrations, despite relatively high concentrations of terrestrial GDGTs (Herfort et al. 2006). The Vancouver Island fjords are indeed extremely productive, with high chlorophyll concentrations in the surface water year-round (Keil unpubl. data). It is possible that crenarchaeol concentrations would be high in proportion to this high productivity, as some crenarchaeota appear to live chemoautotrophically off of NH_4 (Könneke et al. 2005), which is produced during organic matter decomposition. Efficient export of this crenarchaeol in the shallow water column of the fjords would decrease the BIT index. It is not known if the abundance of crenarchaeota is correlated with primary productivity in these fjords. However, given the depleted $\delta^{13}C_{org}$ and the high lignin concentrations, it is unlikely that marine carbon dominates sedimentary OC in areas like the fjords. Thus, high crenarchaeol concentrations are not a likely cause of the low BIT index values observed here.

It remains that the BIT index underestimates terrestrial carbon inputs in our study area because the relative proportion of branched bacterial lipids being deposited in the sediment must be low, a circumstance attributed above to low soil input to this region. The dominance of fresh, vascular plant debris over soil carbon makes sense in the context of the study area. This area is geologically distinct from other

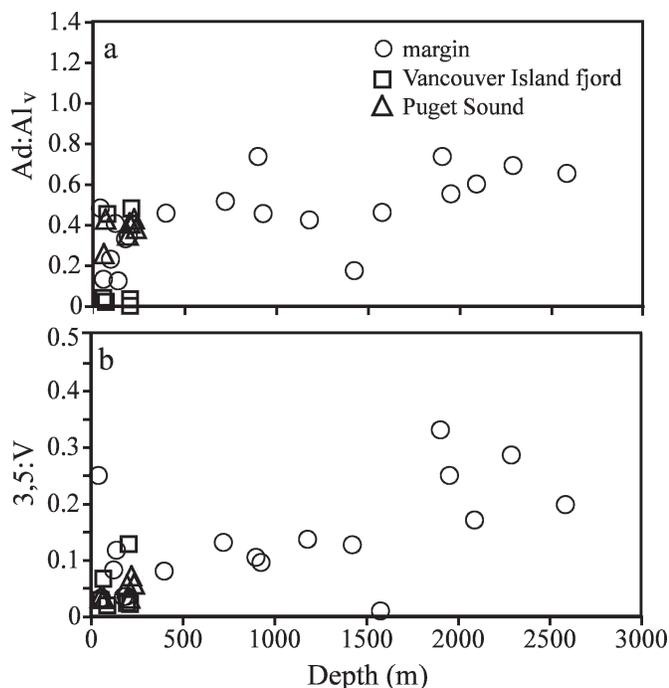


Fig. 8. Ratios of (a) vanillic acid to vanillin (Ad:Al_v) and (b) 3,5-dihydroxybenzoic acid to vanillin (3,5:V) versus station depth (m) for margin, Vancouver Island fjord, and Puget Sound stations.

regions studied using the BIT index, as it is characterized by a low proportion of sedimentary rock and a paucity of well-developed soil (McCull et al. 2005). In addition, Vancouver Island has been the site of a large amount of logging, which could lead to terrestrial OC being transported as fresh woody debris into the fjords without ever being incorporated into a soil (Jakob 2000). Thus, the BIT index consistently underestimates the terrestrial OC contribution and poorly represents the sources of OC to sediments in this area.

Offshore trends in terrestrial OC on the margin—Lignin phenols from the margin and Puget Sound sediments were more degraded than in fjords and exhibited an offshore increase in degradation state (Fig. 8). Two possible mechanisms could be responsible for the increase in the lignin degradation state offshore. One possibility is that the compounds are degraded in situ during offshore transport. Alternatively, given that the source of terrestrial OC to the margin is different than to the fjords, the degradation of lignin could have occurred pretransport, and the more highly degraded compounds could be preferentially transported offshore on fine particles. This would occur because the soil-derived, more-degraded fraction is associated preferentially with the fine fraction (Keil et al. 1998). While it is impossible to determine the dominant mechanism in this area from these data, it is possible to assess whether the increase in degradation state could be attributed to the increasing dominance of soil-derived lignin offshore.

If soil-derived OC does become more influential offshore, it might be concluded that BIT index values should likewise increase offshore; however, they do not (Fig. 4c). However, since the BIT index is a ratio of

terrestrial and marine lipids, and because there is no production of terrestrially derived lipids offshore, only crenarchaeol, the BIT index value should not increase, but rather should decrease or remain constant offshore. In addition, recent work indicates that terrestrial GDGTs are distributed over all density fractions of the sediment but are most abundant on the same density fraction as crenarchaeol (<1.6 g cm⁻³) (Walsh and Ingalls unpubl. data). It is expected that compounds in the same density fraction will be transported similarly; thus, it is unlikely that terrestrial GDGTs would be preferentially accumulated offshore over marine crenarchaeol, and the BIT index is constrained to constant or diminishing values during offshore transport.

While the BIT index shows no correlation with either $\delta^{13}\text{C}_{\text{org}}$ values or the concentration of lignin phenols, there is a strong offshore correlation ($R^2 = 0.8487$, $p < 0.05$) between the concentration of terrestrial lipids and the concentration of lignin phenol and a lesser, but still significant, correlation ($R^2 = 0.4573$, $p < 0.05$) between the concentration of terrestrial lipids and $\delta^{13}\text{C}_{\text{org}}$ values (Fig. 5c,d). Concentrations of both lignin phenols and terrestrial lipids are highest in sediments underlying ~300 m of water and decrease offshore (Fig. 9c–f). $\delta^{13}\text{C}_{\text{org}}$ values follow a similar trend, with the most depleted values occurring at ~300-m water depth (Fig. 9b). This indicates that while the BIT index is uncorrelated with the other proxies in the data set presented here, the terrestrial lipids themselves are behaving similarly to other compounds of terrestrial origin.

If terrestrial lipids are transported similarly to other terrestrial material, why is there no correlation between the BIT index and the other proxies? To state this question another way, why is the BIT index so invariable throughout the margin? Though, as discussed above, it is impossible that the majority of the crenarchaeol has a terrestrial source, crenarchaeol concentrations vary offshore similarly to the terrestrially derived compounds, with the highest crenarchaeol concentrations found in sediments at ~300-m water depth (Fig. 9g,h). Since the BIT index is a ratio and the concentration of crenarchaeol is so much larger than the concentrations of the branched lipids, dividing one concentration by the other results in a very small near-constant value throughout the study area. The decrease in crenarchaeol per gram of OC offshore indicates that crenarchaeol is not proportional to the amount of total OC buried at these stations nor the amount of marine carbon buried (Fig. 9a,h). The assumption inherent in the BIT index, that crenarchaeol is proportional to marine carbon storage, is obviously not valid on the margin. It is possible that the higher nearshore crenarchaeol concentrations are due to the availability of NH_4 from upwelling and increased productivity nearshore, resulting in more abundant or efficiently exported crenarchaeol. While the cause of this offshore trend is not known, this regional variability in the crenarchaeol concentrations, which so closely mimics the terrestrial lipid concentrations, causes BIT index values to be extremely uniform throughout the margin.

In conclusion, the proxies used in this study indicate that terrestrially derived OC can be the dominant source of carbon in the Vancouver Island fjords and is an important component of the sediments throughout much of the

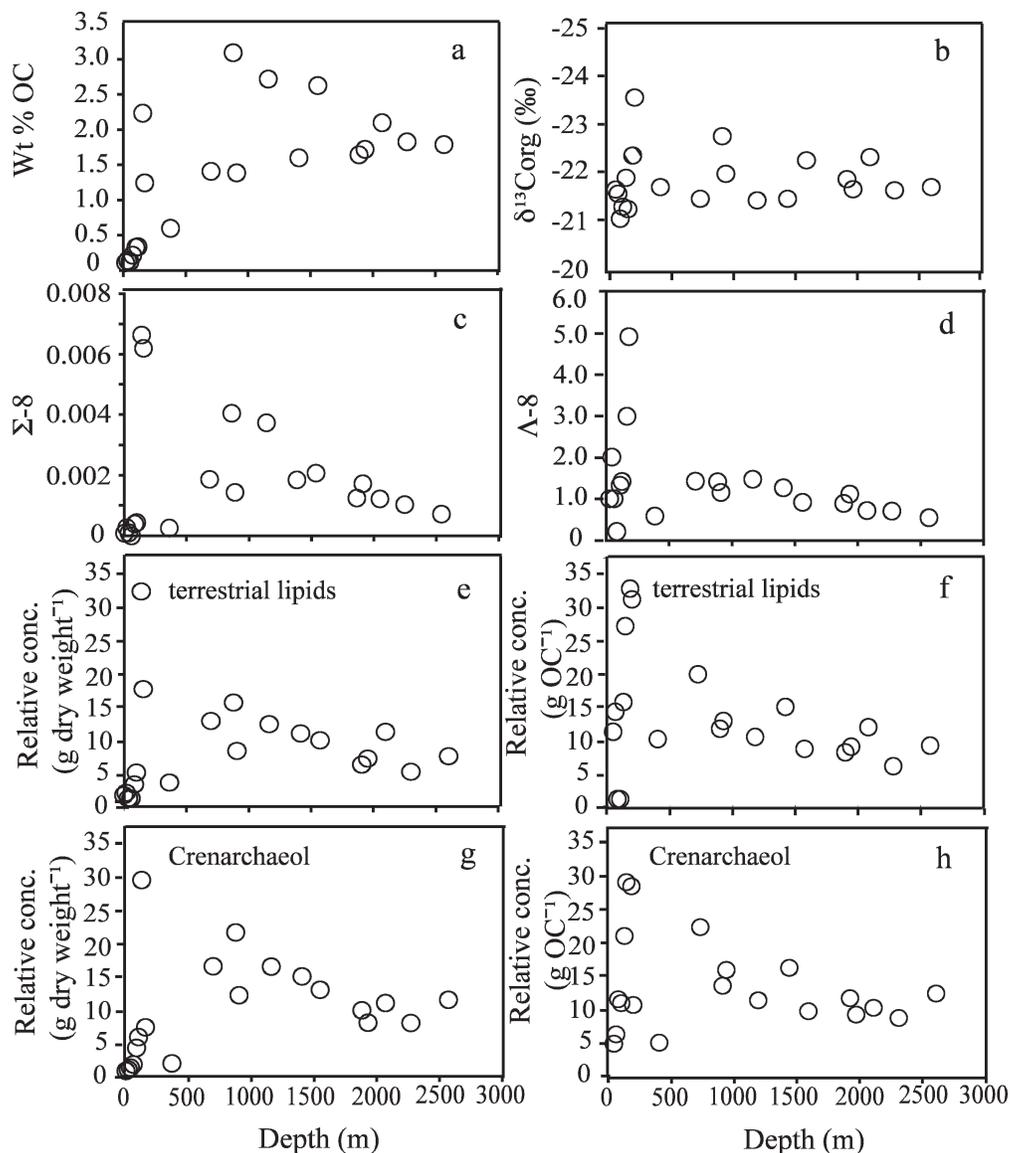


Fig. 9. Margin values for (a) weight %OC, (b) $\delta^{13}C_{org}$, (c) $\Sigma-8$ (mg lignin g dry weight⁻¹), (d) $\Lambda-8$ (mg lignin 100 mg OC⁻¹), (e) relative terrestrial lipid concentration (g dry weight⁻¹), (f) relative terrestrial lipid concentration (g OC⁻¹), (g) relative crenarchaeol concentration (g dry weight⁻¹), and (h) relative crenarchaeol concentration (g OC⁻¹), all plotted versus station depth (m).

Washington–Vancouver Island Margin and Puget Sound. Given the low input of soil-derived bacterial lipid biomarkers to this area and the freshness of the lignin phenols in fjord sediments, this study indicates that much of the terrestrial OC trapped in fjord sediments is composed primarily of undegraded, wood-derived material. However, terrestrial OC on the margin likely has a Columbia River–derived angiosperm source.

While diverse components of terrestrial OC, such as bacterial lipids or lignin phenols, appear to be similarly transported offshore, the quantities of these components are vastly different and in varying stages of degradation. Thus, exclusively examining only one group of biomarkers, or extrapolating total terrestrial OC contribution from a possibly nonrepresentative biomarker, could be misleading.

This work indicates that the BIT index is not a valid proxy for terrestrial OC in this soil- and peat-poor region. Researchers are cautioned to take into consideration the appropriateness of the BIT index before using it in a study area in which there is a lack of peat, well-developed soil, or sedimentary rock, such as in active margins. More work is needed to fully understand the relationships between the proxies and how we can use them to quantify and identify sources of terrestrial OC in marine sediments.

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