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Compound-specific radiocarbon dating of the varved Holocene sedimentary record of Saanich Inlet, Canada

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[1] The radiocarbon contents of various biomarkers extracted from the varve-counted sediments of Saanich Inlet, Canada, were determined to assess their applicability for dating purposes. Calibrated ages obtained from the marine planktonic archaeal biomarker crenarchaeol compared favorably with varve-count ages. The same conclusion could be drawn for a more general archaeal biomarker (GDGT-0), although this biomarker proved to be less reliable due to its less-specific origin. The results also lend support to earlier indications that marine crenarchaeota use dissolved inorganic carbon (DIC) as their carbon source. The average reservoir age offset ΔR of 430 years, determined using the crenarchaeol radiocarbon ages, varied by ±110 years. This may be caused by natural variations in ocean-atmosphere mixing or upwelling at the NE Pacific coast but variability may also be due to an inconsistency in the marine calibration curve when used at sites with high reservoir ages. *INDEX TERMS:* 1055 Geochemistry: Organic geochemistry; 4267 Oceanography: General: Paleoceanography; 4802 Oceanography: Biological and Chemical: Anoxic environments; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4860 Oceanography: Biological and Chemical: Radioactivity and radioisotopes; *KEYWORDS:* compound-specific radiocarbon dating, crenarchaeol, reservoir age, NE Pacific, Saanich Inlet

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1. Introduction

[2] Radiocarbon analysis has been used since the 1950s for dating purposes, but it is only since the development of accelerated mass spectrometry (AMS) in the 1980s that sample size requirements have been reduced to the extent that compound-specific radiocarbon analysis (CSRA) has become possible [*Eglinton et al.*, 1996]. Radiocarbon analysis of specific sedimentary organic compounds of known origin (so-called "biomarkers") can in theory be used as an alternative dating method for organic carbon-rich sediments. Dating based on total organic matter is often not possible since this is a complex mixture derived from a multitude of sources varying in radiocarbon age [*Eglinton et al.*, 1997; *Pearson et al.*, 2001]. CSRA may be of particular utility for samples where other dating methods are impractical or to supplement dates on "traditional" materials (e.g., organic macrofossils or carbonate), in order to increase precision or resolution [*Eglinton et al.*, 1997]. To date, CSRA has almost exclusively been used to address carbon source related questions, by investigating the spread in radiocarbon age between different sedimentary components [*Pearson et al.*, 2001; *Petsch et al.*, 2001; *Ohkouchi et al.*, 2002] in a manner that is comparable to radiocarbon analysis of fractions from the total organic carbon [e.g., *Druffel et al.*, 1996; *Megens et al.*, 1998; *Wang et al.*, 1998; *Trumbore*, 2000; *Raymond and Bauer*, 2001b]. Recently, *Ohkouchi et al.* [2003] showed that CSRA might be used for improving the sediment chronology of Antarctic margin sediments.

[3] Here we further evaluate the potential of CSRA as a dating tool for marine sediments by comparing the radiocarbon ages of different biomarkers produced in the marine environment with independently determined ages for sediment deposited over the later Holocene. For this purpose, varve-dated sediments from Saanich Inlet (Figure 1), recovered during leg 169S of the Ocean Drilling Program (ODP) in 1996 [*Bornhold et al.*, 1998] were used. This site was chosen because of its high sedimentation rates and its relatively high organic carbon content, and for its well-constrained sediment ages. In addition to the ODP samples, very recent Saanich Inlet sediments deposited before and after aboveground nuclear weapons testing, recovered by freeze coring, were also examined. The increase in atmospheric ^{14}C resulting from these activities (the so-called "bomb-spike") provides an effective tracer to follow surface-ocean derived biomarkers [*Pearson et al.*, 2000]. In addition to a correspondence with surface ocean DIC, the validity of compound-specific radiocarbon dating requires that the biomarkers are deposited coeval with the rest of the sediment. For instance, *Ohkouchi et al.* [2002] found that lateral transport of fine-grained particles greatly affected the

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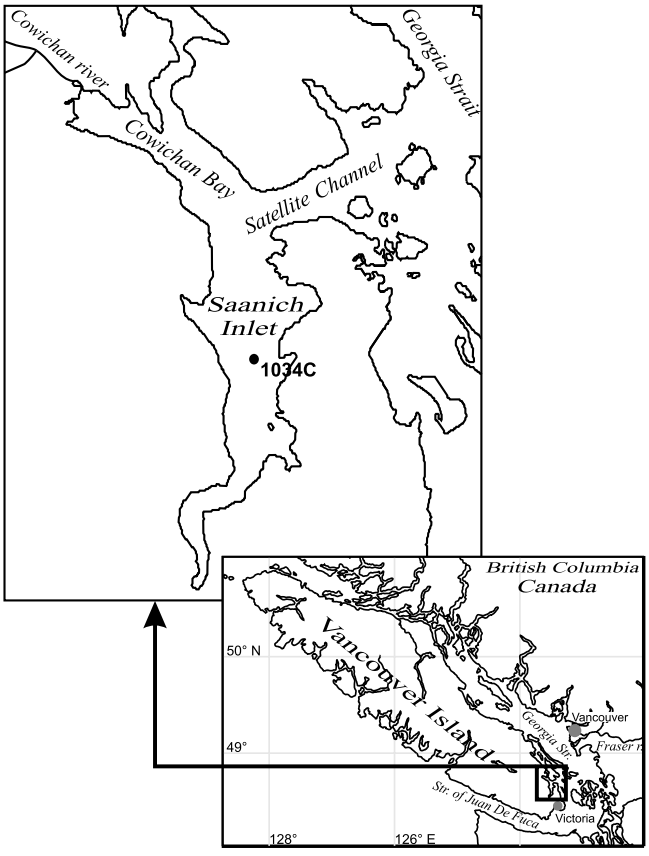

Figure 1. Map of the southern Georgia Strait showing Saanich Inlet and the location of ODP hole 1034.

radiocarbon ages of haptophyte-derived alkenones, when compared with the ages obtained from planktonic foraminifera that were not displaced after their initial sedimentation. In Saanich Inlet, resuspension of the benthic layer occurs to a small extent, while some lateral transport of sill sediment toward the basin is also observed [*Sancetta and Calvert*, 1988], occurring mainly near the fjord mouth during deep water renewals. However, because of the high accumulation rates and the local scale of these processes, it can be assumed that such effects will not significantly influence biomarker ages.

[4] To fully evaluate the potential of biomarker ^{14}C dating, the calibration from conventional radiocarbon age to calendar years must also be considered. Calibration of atmospheric CO_2 derived samples is fairly straightforward [*Stuiver et al.*, 1998b]. However, for marine derived samples the reservoir age, i.e., the greater age of dissolved inorganic carbon (DIC) compared to atmospheric CO_2, needs to be taken into account. The marine calibration curve of *Stuiver et al.* [1998a] is based upon the atmospheric calibration curve, but incorporates a global average reservoir age through time $R_g(t)$ of around 400 ^{14}C years. A complicating factor is that the reservoir age varies worldwide between 200 and 1300 ^{14}C years [*Stuiver et al.*, 1998b, and references therein], due to ocean circulation patterns and zlocal upwelling and mixing. Therefore a site specific reservoir age offset ΔR needs to be known in order to obtain accurate calibrated ages. In this study, the obtained biomarker radiocarbon ages could be directly compared with sediment calendar ages, as well as with previously measured regional reservoir ages, thus providing the opportunity to evaluate the potential reservoir age variations of Saanich Inlet through time. Regional or local reservoir ages may not always have varied parallel with the global changes [e.g., *Siani et al.*, 2001], especially at coastal sites with varying fresh water input and upwelling [e.g., *Ingram and Southon*, 1996]. Improving the spatial resolution of independently determined reservoir ages will contribute to the development and/or accuracy of regional calibration curves. Furthermore, paleoceanographic studies may also benefit from robust records of regional or local reservoir age variations, as they might reveal past climatic or oceanographic changes.

2. Setting

[5] The sediment samples used for this research were taken from ODP core 1034C, leg 169S, in Saanich Inlet, British Columbia, Canada (Figure 1). This is a fjord at the southeast coast of Vancouver Island with a maximum depth of 237 m. The deeper part of the basin is isolated from the strait of Georgia by a two-fold sill with depths of 65 and 75 m in the Satellite channel. The near-surface circulation pattern in Saanich Inlet is highly variable, and affects only the waters above sill depth. Surface water is largely derived from the Strait of Georgia, influenced by fresh water from the Fraser River, that has its highest discharge in summer, and by fresh water from the Cowichan River, which has its highest discharge during winter and spring. This causes the salinity of the surface water to vary between 25 and 29 psu, while below sill depth a salinity of ~31 psu prevails. The resulting strong pycnocline causes the deeper part of the basin to be isolated [*Anderson and Devol*, 1973; *Takahashi et al.*, 1977]. Together with a relatively high primary production and subsequent heterotrophic degradation, this isolated setting supports the development of anoxia, which is prevalent below 120 m water depth throughout most of the year, and is virtually permanent below 200 m [*Richards*, 1965; *Bornhold et al.*, 1998]. "Bolus shaped" deep water renewals occur annually between August and October to a depth of 100 m, and on average every other year to a depth of 200 m, depending on the density of the introduced water [*Anderson and Devol*, 1973]. This water comes from Juan de Fuca Strait and is a mixture of warm, well mixed and oxygenated surface water and relatively cold and saline deep water from upwelling at the Pacific coast. During bottom water renewal, the present anoxic water mass is displaced upward, with relatively minor mixing along the interface between the two water masses [*Bornhold et al.*, 1998, and references herein].

[6] *Gucluer and Gross* [1964] estimated that 65% (wt.) of Saanich Inlet sediment is clay- and silt-sized terrigenous material, mainly introduced by the Fraser and Cowichan river. The remaining 35% is of biogenic, mainly silicious phytoplanktonic origin. Part of this planktonic material is produced outside the fjord, mainly in the Satellite Channel [*Hobson and McQuoid*, 2001]. The terrigenous material

Table 1. Origin and Age of the Sediment Subsamples Used in This Study

Core Section	Composite Core Depth, m	Section Depth, cm	Sediment Age
Freeze core	–	0–52	1984–1998 AD
Freeze core	–	116–141	1932–1950 AD
1034C 1H-5	6.02–7.45	0–78; 103–150	568–465 BP
1034C 2H-3	10.9–12.1	0–124	1111–977 BP
1034C 2H-4		0–150	1273–1125 BP
1034C 3H-6	26.8–28.3	0–10; 30–150	2707–2533 BP
1034C 4H-4	34.0–35.1	0–109	3600–3500 BP
1034C 5H-4	43.6–44.3	0–69	4940–4840 BP

causes a dark color in winter, which in summer turns to a lighter color by a sequence of successive diatom blooms. Because of the virtually permanent anoxic bottom water conditions, benthic fauna are absent and the seasonal record of deposition is preserved as fine laminae, resulting in a rhythmical varved sequence spanning approximately the last 6000 years [*Bornhold et al.*, 1998]. Because the varved sequence is virtually complete, the age of the cored sediments can be determined with an annual resolution. *Nederbragt and Thurow* [2001] compiled composite varve records from parallel cores from two locations in the fjord by correlation of massive beds and characteristic features in the varve pattern. This approach reduced the error introduced by missing varves. The obtained floating varve-count age scale was calibrated with published radiocarbon dates obtained from wood remains.

3. Materials and Methods

3.1. Sediment and Water Samples

[7] Sediment subsamples from different depths (Table 1) were obtained from advanced hydraulic piston (APC) cores taken in 1996 at Hole 1034C of Ocean Drilling Project leg 169S, Saanich Inlet, Canada [*Bornhold et al.*, 1998] (Figure 1). The calendar ages of the subsamples were determined using the varve-based age model of *Nederbragt and Thurow* [2001]. In addition to the ODP samples, a 150 cm-long freeze core was taken from the upper sediment of Saanich Inlet in 1998. Dating was performed by a combination of ^{210}Pb dating and varve counting. A prebomb (1932–1950 AD) and a postbomb (1984–1998 AD) sample were selected for analysis.

[8] In order to obtain DIC-^{14}C values of the water column, four water samples were taken with Niskin bottles from respectively 40, 105, 140 and 200 m depth at the center of the Inlet from the R/V *Clifford A. Barnes* in early August 2003.

3.2. Extraction

[9] Sediment samples were freeze dried before lipid extraction, resulting in 100–150 g dry sediment. Part of this sediment was reserved for TOC analysis. Extraction was done using an Automated Solvent Extractor (Dionex Corp., Sunnyvale, CA, USA), using a dichloromethane-methanol (DCM-MeOH, 9:1 v/v) mixture, deployed over three static cycles of 5 min of 100°C and 1000 psi. The extracts dissolved in DCM, were washed with double distilled water in a separatory funnel to remove salt and subsequently dried over small columns filled with Na_2SO_4. Solvent was removed by rotary evaporation followed by evaporation under a stream of nitrogen.

3.3. Isolation of Compounds

[10] The extracts were separated into two fractions by column chromatography over activated Al_2O_3 with *n*-hexane (hydrocarbon fractions) and DCM-MeOH (1:1 v/v; polar fractions) as eluents. Hexane was removed from the hydrocarbon fractions by rotary evaporation and the residues were subsequently dissolved in a solution of urea in methanol, and evaporated to dryness under a stream of nitrogen. The resulting urea crystals were rinsed with *n*-hexane to remove nonlinear hydrocarbons before the crystals were dissolved in double distilled water to liberate straight-chain *n*-alkanes. The latter were recovered by extraction of the water phase with hexane. The recovered fractions contained almost exclusively a series of *n*-alkanes. The C_{27}, C_{29} and C_{31}*n*-alkanes were isolated from these fractions by preparative capillary gas chromatography (PCGC) using a low-bleed fused silica capillary column (25 m × 0.32 mm) coated with CP Sil 5 (film thickness 0.52 μm) mounted on a Hewlett-Packard 6890 gas chromatograph in conjunction with a Gerstel preparative fraction collector, similar to that described by *Eglinton et al.* [1996].

[11] From the polar fractions the glycerol dialkyl glycerol tetraethers (GDGTs) crenarchaeol and GDGT-0, and the Δ^5 sterols, 4-methyl sterols and chlorophyll-derived phytol were isolated using the procedure described by *Smittenberg et al.* [2002]. In short, repeated semipreparative normal phase HPLC was performed to isolate the selected biomarkers from sediment extracts, while flow injection analysis-mass spectrometry (FIA-MS) was used for rapid analysis of collected fractions to evaluate the separation procedure. Phytol was released from chlorophyll moieties during a saponification step using 1 M aqueous KOH in MeOH. After isolation, the fractions containing 4-methyl sterols were eluted over a column filled with precombusted silicalite (PQ Zeolites, Netherlands) with ethyl acetate, a method similar as described by *West et al.* [1990], to remove *n*-alkanols. A faint green color persisted in most sterol fractions after isolation, probably caused by chlorophyll moieties of similar polarity. These were removed by performing base hydrolysis of the fractions in 3 mL 0.5 M KOH in methanol at 100°C for 2 hours in reaction tubes. The sterols were recovered by adding an equal amount of pure water, and rinsing the water-methanol phase three times with hexane-DCM (9:1 v/v). After evaporation of the solvents, the fractions were taken up in DCM and dried over a small column filled with Na_2SO_4. In contrast to the other sediment intervals, from the sediment interval corresponding to 1273–1125 BP only a GDGT-0 fraction was isolated. This fraction was subjected to ether bond cleavage using the method described by *Hoefs et al.* [1997], resulting in a fraction containing C_{40} biphytanes. Four GDGT fractions were split in two or three subfractions to assess reproducibility.

3.4. Gas Chromatography and Gas Chromatography-Mass Spectrometry

[12] To evaluate the composition of the lipid extracts and of isolated fractions, gas chromatography (GC) and gas

chromatography-mass spectrometry (GC-MS) was performed on aliquots of the extracts. GC was performed using a Fisons 8000 series instrument equipped with an on-column injector and a flame ionization detector (FID). A fused silica capillary column (25 m $\times$ 0.32 mm) coated with CP Sil 5 (film thickness 0.12 μm) was used with helium as carrier gas. Known amounts of deuterated ante-iso C_{22}-alkane standard were added to the aliquots for quantification. The fractions were subsequently dissolved in pyridine together with bis(trimethylsilyl)trifluoroacetamide (BSTFA) and this mixture was heated (60°C; 20 min) to convert alcohols into their corresponding trimethylsilyl ethers. The derivatized fractions were dissolved in ethyl acetate and injected at 70°C. The oven was programmed to 130°C at 20°C/min and then at 4°C/min to 320°C at which it was held for 10 min. Quantification of eluted compounds was performed by comparing their integrated peak areas with that of the added standard.

[13] GC-MS was performed using a Hewlett-Packard 5890 gas chromatograph interfaced to a VG Autospec Ultima mass spectrometer operated at 70 eV with a mass range of m/z 50–800 and a cycle time of 1.7 s (resolution 1000). Gas chromatography was performed as described above. Compounds were identified by comparison of mass spectra and retention times with those reported in literature.

3.5. High-Performance Liquid Chromatography-Mass Spectrometry

[14] Aliquots of polar fractions (see below) were made suitable for injection on an HPLC system following the method as described by *Hopmans et al.* [2000]. High-performance liquid chromatography-mass spectrometry (HPLC-MS) was performed on a Hewlett-Packard (Palo Alto, CA, USA) 1100 series HPLC equipped with an autoinjector and Chemstation chromatography manager software, coupled to an HP 1100 MSD mass spectrometer using atmospheric pressure chemical ionization (APCI-MS), operated in positive ion mode. Compounds were identified by comparison of mass spectra and retention times with those reported in literature. Quantification was performed by integration of peaks in the summed mass chromatograms of $[M + H]^+$ and $[M + H]^+ + 1$ ions and comparison with a standard curve obtained using a dilution series of a known amount of a GDGT-0 standard, as described by *Smittenberg et al.* [2002].

3.6. Stable Carbon Isotopic Analysis

[15] Compound specific stable carbon isotopic compositions of the cholesterol standard and of the *n*-alkane, the Δ^5 sterol, the 4-methyl sterol and phytol fractions were measured. Analyses were performed on a Delta-C or a Delta-plus XL irm-GC/MS-system, both in principal similar to the Delta-S system as described previously by *Merritt et al.* [1995]. The carbon isotopic compositions of derivitized compounds (phytol and sterols) were corrected for added carbon molecules by using bis(trimethylsilyl)trifluoroacetamide (BSTFA) with a known carbon isotopic value. Values reported were determined by two or three replicate analyses, and the results were averaged to obtain a mean value and to evaluate the measurement error. Values are reported in standard delta notation relative to the VPDB standard, with a standard error of 0.3‰. In most cases, the δ^{13}C values of 5% aliquots of the CO_2 produced upon combustion during preparation for radiocarbon analysis (see below), were determined on a VG PRISM mass spectrometer.

3.7. Radiocarbon Analysis

[16] Freeze-dried and homogenized sediments containing approximately 1 mg total organic carbon (TOC) were prepared for radiocarbon analysis by a warm acid treatment (10% HCl, 60°C, 3 hrs) to remove carbonates. They were subsequently rinsed with distilled water until neutral and filtered on precombusted (850°C, 8 hours) quartz filters, dried overnight (60°C) and transferred into precombusted quartz tubes for AMS sample preparation. Furthermore, leaf remains and a seed were recovered from two sediment samples. These terrestrial macrofossils were also prepared for radiocarbon analysis by an acid-base-acid treatment to remove humic and fulvic acids, following standard procedures.

[17] Preparation for ^{14}C AMS analysis of isolated fractions was done following the procedure described by *Eglinton et al.* [1996] and *Pearson et al.* [1998]. In short, after isolation the biomarkers were dissolved in a minimal volume of DCM and eluted over a precombusted (480°C, 8 hours) small column filled with silica to remove any column bleed material. The fractions were collected into precombusted (850°C, 8 hours) quartz tubes and dried under a stream of nitrogen. After the addition of (also precombusted) CuO(s) as the oxidizing agent, the tubes were vacuum sealed and combusted (900°C, 5 hours) to yield CO_2. Of all fractions, except the *n*-alkane fractions, 5% aliquots were used for δ^{13}C analysis. The remaining CO_2 was reduced to graphite with Co(s) as a catalyst. The sediments for TOC analysis, and the terrestrial macrofossils were also put in precombusted quartz tubes and treated in the same way as the biomarker fractions, except that also 1 mg of Ag(s) was added to the quartz tubes, and that Fe(s) was used as a catalyst for graphitization. DIC from water samples was prepared using standard procedures. Radiocarbon analysis was performed on the obtained graphite targets at the National Ocean Sciences AMS facility (NOSAMS) at Woods Hole (MA, USA).

3.8. Reporting and Calibration of Radiocarbon Ages

[18] Radiocarbon contents of all lipids were corrected for 0.1 μmol carbon with a fraction modern of 0.25, which is assumed to have been added during the combustion process, based on prior work [*Pearson et al.*, 1998]. The corrected radiocarbon contents are reported as fraction modern (f_m). f_m is also known as A_{SN}/A_{ON} [*Stuiver and Polach*, 1977], or as $^{14}C_N$ [*Mook and Van der Plicht*, 1999] and represents the ^{14}C activity of a fraction compared to the activity of a "modern" international standard, both corrected for carbon isotopic fractionation using their respective δ^{13}C values. Furthermore, conventional radiocarbon ages are reported, i.e., the ages calculated from measured radiocarbon contents using the traditional Libby half-life of radiocarbon [*Stuiver and Polach*, 1977]. The radiocarbon contents are also reported as initial, or age corrected, Δ^{14}C values. This follows the convention of many studies in cases where the actual (calendar) age of a radiocarbon dated sample is

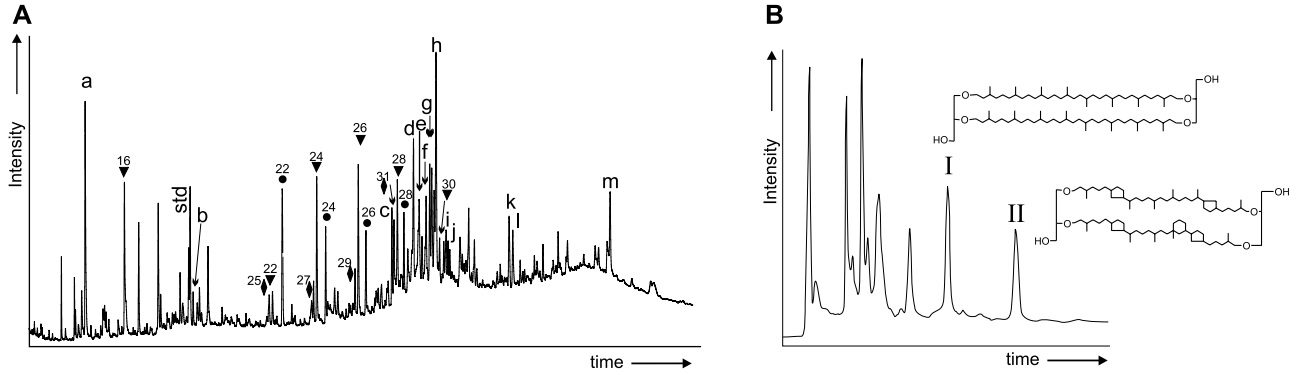

Figure 2. (a) Typical gas chromatogram of a total lipid extract of Saanich Inlet sediment. Diamonds, *n*-alkanes; triangles, *n*-alkanoic acids; circles, *n*-alcohols. Numbers refer to the number of carbon atoms. Lowercase letters a-m refer to loliolide, phytol, cholest-5-ene-3β-ol (''cholesterol''), 24-methyl-cholest-5-ene-3β-ol, 24-ethyl-cholest-22-ene-3β-ol, 24-ethyl-cholestadiene-3β-ol, 24-ethyl-cholest-5-ene-3β-ol and 24-ethyl-cholest-3β-ol (''sitosterol'' and ''sitostanol''), 4,23,24-trimethyl-5α(H)-cholest-22-ene-3β-ol (''dinosterol''), isomers of 4-methyl, 24-ethyl-5α(H)-cholest-3β-ol (''dinostanol''), 17β,21β(H) C_{32} hopanoic acid, 17β,21β(H) C_{32} hopanol, and tricyclic biphytanediol, respectively. Here std is internal standard. (b) Total ion current obtained by HPLC-APCI-MS, mass range *m*/*z* 200–1450, of a polar fraction of a representative Saanich Inlet sediment extract. I: GDGT-0 II: Crenarchaeol. The early eluting peaks are mainly chlorophyll derivatives.

known [*Stuiver and Polach*, 1977]. In the literature, initial $\Delta^{14}C$ may also be encountered as Δ, or as $^{14}\delta^{i}_{N}$ [*Mook and Van der Plicht*, 1999].

$$\text{initial } \Delta^{14}C = \left(f_m \times e^{(\lambda \times \text{yrBP})} - 1\right) \times 1000\,‰$$

λ is the decay constant (1/8267 years^{-1}) of ^{14}C, and yrBP the year of deposition, i.e., the sediment age in calendar year BP, which is the age scale used in age model of Saanich Inlet [*Nederbragt and Thurow*, 2001]. These values express the radiocarbon contents corrected for decay between deposition and the year of measurement, and thus reflect the initial radiocarbon content at the time of sedimentation. This can be useful for the determination of the carbon source or sources of the various biomarkers, as they can be compared with historic atmospheric and oceanic radiocarbon concentrations.

[19] Radiocarbon ages were calibrated using the atmospheric calibration curve of *Stuiver et al.* [1998a] implementing a moving average over the sedimentary year span. In the same way, marine-derived biomarker ages were calibrated using the marine calibration curve, applying a regional reservoir age offset (ΔR) of 401 years, in accordance with the reservoir age of 801 years previously determined for Saanich inlet [*Bornhold et al.*, 1998].

4. Results

[20] Gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography-mass spectrometry (HPLC-MS) of the lipid extracts of the various sediment samples revealed very similar biomarker compositions throughout the investigated core samples. Representative chromatograms are shown in Figure 2. Table 2 lists the recovered amounts and $\delta^{13}C$ values of the biomarkers used for this study, as well as the radiocarbon contents of the bulk and biomarker fractions. The radiocarbon contents of the >300 μg split fractions were the same within the measurement error of 0.05 f_m (Table 2). However, small splits indicated that some machine induced isotopic fractionation occurred toward higher f_m values when samples <100 μg are concerned. This confirms the conclusion of *McNichol et al.* [2001] that great care should be taken in the analysis of very small samples, and that errors will be relatively large. Because most fractions are, however, larger than 100 μg (Table 2), and because the effect seems to be relatively small (<0.03 f_m), this uncertainty associated with small samples is considered not to significantly influence the interpretation of the results.

[21] The conventional radiocarbon ages and the calculated initial $\Delta^{14}C$ values are given in Table 3. This table also presents the DIC radiocarbon contents of the water samples from various depths that were taken in 2003. Tables 4a and 4b lists the biomarker ages as calibrated with the atmospheric calibration curve, and for marine-derived biomarkers also the calibrated ages obtained with the marine calibration.

5. Discussion

5.1. Biomarkers Isolated for Radiocarbon Analysis

5.1.1. Selection Criteria

[22] The main goal of our research was to determine whether the ^{14}C content of specific biomarkers could be used for sediment dating. To this end these biomarkers have to meet several criteria. First, they need to be present in sufficient amounts in the sediment to be able to isolate them in quantities large enough for AMS (i.e., >30 μg C [*Pearson et al.*, 1998], but preferably >300 μg C). Therefore only the

Table 2. Amounts, Stable and Radiocarbon Isotopic Compositions of Sedimentary Total Organic Carbon (TOC), Terrestrial Macrofossils, and Isolated Biomarkers Originating From Differently Aged Sediment Layers[a]

Sediment Age	TOC	Terrestrial Macrofossils	*n*-Alkanes	Crenarchaeol	GDGT-0	Δ5 Sterols	4-Methyl Sterols	Phytol
				Amount, μg				
1984–1998 AD	1242		32	204	211	152	166	335
1932–1950 AD	1117	668	77	569	587	186	212	268
568–465 BP	919		115	317	510	430	373	99
				418	383			
				58[b]	89[b]			
1111–977 BP	966	395	140	425	630	284	359	392
1273–1125 BP					358[c]			
					361[c]			
					99[b,c]			
2707–2533 BP	949		146	498	666	385	124	179
				554				
3600–3500 BP	737			550		100	78	157
4940–4840 BP	796		52	372	431		110	68
				$\delta^{13}C$, ‰				
1984–1998 AD	−22.3		−31.4	−21.6	−22.1	−22.3	−23.7	−20.0
1932–1950 AD	−22.1	−28.2	−31.4	−21.5	−21.6	−22.1	−22.6	−21.7
568–465 BP	−21.6		−31.7	−21.8	−21.6	−21.5	−21.8	−22.0
				−21.6	−21.3			
				−21.3[S]	−21.6[b]			
1111–977 BP	−22.0	−27.6	−32.1	−21.3	−21.2	−23.2	−22.0	−20.5
1273–1125 BP					−22.3[c]			
					−22.8[c]			
					−21.0[b,c]			
2707–2533 BP	−22.0		−31.6	−21.4	−21.7	−22.3	−23.0	−20.8
				−21.4				
3600–3500 BP	−22.1		−31.6			−22.8	−24.8	−20.1
4940–4840 BP	−22.3		−31.2	−21.3	−21.8		−24.1	−18.8
				^{14}C, f_m				
1984–1998 AD	0.898		0.546	1.059	1.045	1.026	0.957	1.005
1932–1950 AD	0.825	0.987	0.544	1.935	0.910	0.916	0.879	0.921
568–465 BP	0.780		0.590	0.829	0.826	0.789	0.859	0.836
				0.840	0.823			
				0.868[b]	0.843[b]			
1111–977 BP	0.670	0.864	0.507	0.788	0.659	0.714	0.770	0.776
1273–1125 BP					0.772[c]			
					0.763[c]			
					0.796[b,c]			
2707–2533 BP	0.584		0.459	0.657	0.658	0.657	0.695	0.658
				0.649				
3600–3500 BP	0.533			0.607		0.668	0.672	0.638
4940–4840 BP	0.456		0.380	0.536	0.549		0.648	0.620

[a]Phytol, chlorophyll derived phytol. Amounts are determined after combustion to CO_2 by nanometry, with an error of 5 μg. $\delta^{13}C$ values are expressed relative to VPDB, with an error of 0.3‰ for all samples, except *n*-alkanes which have an error of 0.5‰. The error of the fraction modern radiocarbon (F_m) is 0.005 or less. Multiple values are fractions split before combustion.

[b]Small split replicate.

[c]Measured on corresponding biphytanes.

most abundant biomarkers present in the Saanich Inlet sediments were considered. Second, the carbon source used by the organisms producing the biomarker needs to be known in order to determine which calibration curve should be applied for conversion to calendar ages. Ideally, biomarkers derived from organisms using atmospheric CO_2 as their carbon source, i.e., of terrestrial origin, should be used because then age calibration can be performed without reservoir age corrections and associated uncertainties. However, a third criterion is that biomarkers should be incorporated in the sediment shortly after production. Biomarkers with a terrestrial origin may be retained in the soil carbon pool for a substantial period of time before they are transported to the sediment [*Raymond and Bauer*, 2001a], and thus have to be disqualified. Biomarkers produced in the marine environment reflecting the ^{14}C content of a DIC pool that has been reasonably stable through time meet all criteria mentioned above. In that respect they are similar to calcareous macrofossils or planktonic foraminifera, particles that are often used for radiocarbon dating of marine sediments. Planktonic biomarkers can thus be considered as their molecular equivalents. Not all marine biomarkers are, however, suitable for ^{14}C dating. Biomarkers that are (partly) produced by heterotrophic organisms using DOC and POC as their carbon source, must be disqualified because some of this carbon substrate can be of substantial age due to its refractory nature [*Williams and Druffel*, 1987; *Raymond and Bauer*, 2001b]. A final consideration is the

Table 3. Initial Radiocarbon Contents and Conventional Radiocarbon Ages of Sedimentary Total Organic Carbon (TOC), Terrestrial Macrofossils, and Isolated Biomarkers Originating From Differently Aged Sediment Layers[a]

Sediment Age[b]	TOC	Terrestrial Macrofossils	*n*-Alkanes	Crenarchaeol	GDGT-0	Δ5 Sterols	4-Methyl Sterols	Phytol	Atmospheric CO_2 $\Delta^{14}C$	Marine DIC $\Delta^{14}C$-49‰[c]
					Initial $\Delta^{14}C$, ‰					
1984–1998 AD	−107 ± 4		−446 ± 9	+54 ± 9	+40 ± 8	+21 ± 7	−48 ± 9	−0 ± 9	+150	see 2003 data
1932–1950 AD	−174 ± 4	−12 ± 3	−455 ± 5		−89 ± 6	−84 ± 7	−120 ± 9	−79 ± 9	−20	−104
568–465 BP	−170 ± 3		−372 ± 5	−118 ± 6	−121 ± 3	−158 ± 3	−86 ± 4	−111 ± 3	+3	−99
				−106 ± 4	−124 ± 3					
				−76 ± 9[d]	−102 ± 8[d]					
1111–977 BP	−240 ± 3	−20 ± 4	−425 ± 5	−106 ± 5	−232 ± 3	−191 ± 5	−126 ± 4	−119 ± 7	−17	−108
1273–1125 BP					−106 ± 3[e]					
					−116 ± 3[e]					
					−73 ± 8[d,e]					
2707–2533 BP	−200 ± 3		−370 ± 4	−98 ± 3	−96 ± 3	−100 ± 3	−47 ± 6	−97 ± 5	+8	−84
				−109 ± 3						
3600–3500 BP	−182 ± 3			−68 ± 3		+26 ± 6	+32 ± 7	−21 ± 6	+16	−74
4940–4840 BP	−177 ± 2		−314 ± 6	−32 ± 4	−7 ± 3		+169 ± 5	+121 ± 7	+50	−42
					^{14}C *Age, years BP*					
1984–1998 AD	870 ± 35		4710 ± 130	modern	modern	modern	350 ± 75	35 ± 70	modern	modern
1932–1950 AD	1540 ± 35	110 ± 30	4890 ± 75		760 ± 50	710 ± 65	1030 ± 85	660 ± 75	170	870
568–465 BP	1990 ± 30		4240 ± 70	1510 ± 55	1540 ± 30	1900 ± 35	1230 ± 40	1450 ± 30	480	1310
				1400 ± 40	1570 ± 35					
				1130 ± 90[d]	370 ± 80[d]					
1111–977 BP	3220 ± 35	1180 ± 40	5460 ± 80	1910 ± 45	3130 ± 40	2710 ± 55	2100 ± 40	2030 ± 75	1150	1900
1273–1125 BP					2060 ± 45[e]					
					150 ± 40[e]					
					1770 ± 75[d,e]					
2707–2533 BP	4320 ± 45		6250 ± 80	3370 ± 40	3350 ± 40	3380 ± 35	2920 ± 65	3360 ± 40	2480	3230
				3470 ± 35						
3600–3500 BP	5060 ± 45			4010 ± 40		3250 ± 70	3200 ± 80	3620 ± 75	3320	4050
4940–4840 BP	6310 ± 40		7880 ± 120	5020 ± 60	4810 ± 50		3490 ± 65	3830 ± 90	4360	5090
DIC water depth, m		40	105	140	200					
$\Delta^{14}C$, ‰		−6.4 ± 4.0	−4.7 ± 3.7	22.3 ± 3.4	38.5 ± 3.9					
$\delta^{13}C$, ‰		−0.52	−1.29	−1.61	−1.93					

[a]Furthermore are the radiocarbon contents and $\delta^{13}C$ values of DIC presented, as measured on water samples taken in 2003 from different depths. Atmospheric and marine radiocarbon contents and ages are values of the calibration curve published by *Stuiver et al.* [1998a] or *Levin et al.* [1997], averaged over the sediment age span. See text for the use of a reservoir age offset ΔR of 401 years. Initial $\Delta^{14}C$ values are age corrected radiocarbon contents based on the sediment ages, calculated as discussed in the text. Multiple values are from fractions split before combustion. Phytol, chlorophyll-derived phytol.

[b]Sediment ages are in calendar years.

[c]Here −49‰ is equivalent with a ΔR of 401 ± 25 years.

[d]Small split replicate.

[e]Measured on corresponding biphytanes.

spatial context of the samples. *Ohkouchi et al.* [2002] showed that alkenones isolated from sediments of the Bermuda rise were up to 7000 years older than planktonic foraminifera from the same sediment depth, pointing to lateral transport of the alkenones with fine-grained sediments. However, as pointed out in the introduction, the marine part of the sediment and co-occurring marine biomarkers in Saanich Inlet are anticipated to be of local and contemporary origin. Thus the Saanich Inlet sediment extracts were screened for potential biomarkers that would likely match the above mentioned criteria, which is discussed below.

5.1.2. Δ^5 Sterols

[23] *Pearson et al.* [2000] showed that the entire compound class of sterols could serve as an excellent proxy for the ^{14}C content of ocean surface water DIC. In the open ocean, DIC-assimilating phytoplankton can be assumed to be practically the only sterol source. However, terrestrial higher plants also produce sterols [*Volkman*, 1986], and in coastal areas this may compromise their possible applicability for sediment dating. The generally most dominant sterol class in recent sediments are the Δ^5 sterols. This is also the case in the Saanich Inlet (Figure 2), with concentrations of the most abundant Δ^5 sterol, 24-methyl-cholest-5-ene-3β-ol, ranging between 2 and 8 μg/g sediment, and with decreasing concentrations with increasing age. The overall $\delta^{13}C$ values of the Δ^5 sterols are −22 ± 1‰ (Table 2), which suggests an almost exclusively marine source for the Δ^5 sterols [*Pancost et al.*, 1997; *Schouten et al.*, 2000a]. Indeed, Saanich Inlet is known to be highly productive [*Timothy and Soon*, 2001], and the sedimentary organic carbon to be of a predominantly marine origin [*McQuoid*, 2001]. Furthermore, sterols produced on land are generally for a large part degraded, transformed or bound before reaching any (marine) sediment [*Cranwell*, 1981]. For these reasons, the Δ^5 sterols as group were considered to be a good candidate for compound-specific radiocarbon dating.

5.1.3. 4-Methyl Sterols

[24] A second major sterol group are the 4-methyl sterols, which are predominantly produced by dinoflagellates [*Boon et al.*, 1979; *Mansour et al.*, 1999], a widely distributed

algal group. The most common 4-methyl sterol, dinosterol, was present in concentrations of 4–9 μg/g sediment in the Saanich Inlet (Figure 2). Dinoflagellates are often autotrophic, but heterotrophy is also very common, while mixotrophy is sometimes also observed [*Hoek et al.*, 1995]. However, the carbon isotopic composition of the different dinoflagellate groups will not be very different from each other, as the carbon isotopic composition of heterotrophs generally reflect that of their diet [*Grice et al.*, 1998], which is mainly of a phytoplanktonic origin [*Hoek et al.*, 1995]. Indeed, the δ^{13}C values of the 4-methyl sterol fraction are −22‰ to −24‰, similar to the Δ^5 sterols (Table 2), also pointing to a marine origin. Therefore 4-methyl sterols are expected to show the same radiocarbon contents as Δ^5 sterols. Possibly, they may be superior to the Δ^5 sterols for compound-specific radiocarbon dating of sediments, because higher terrestrial plants do not produce 4-methyl sterols.

5.1.4. Chlorophyll-Derived Phytol

[25] Phytol is the side-chain of most common chlorophylls, and can be regarded as an almost exclusively phytoplankton derived biomarker [*Sun et al.*, 1998, and references herein] for the same reasons as the Δ^5 sterols. Free phytol concentrations were lower than 1 μg/g sediment (Figure 2). However, saponification of the extracts using aqueous 1 M KOH/MeOH resulted in much larger quantities, up to 30 μg/g sediment. The δ^{13}C values of phytol are −20 ± 1‰ (Table 2). This points toward the same marine planktonic origin as the sterol fractions, as biosynthetic effects generally cause the δ^{13}C value of phytol to be 2–4‰ higher than the sterols of the same algal species [*Schouten et al.*, 1998b]. Therefore chlorophyll-derived phytol was also selected for compound-specific radiocarbon dating.

5.1.5. Glycerol Dialkyl Glycerol Tetraethers

[26] The glycerol dialkyl glycerol tetraethers (GDGTs) crenarchaeol and GDGT-0 (see Figure 2 for chemical structures) occur ubiquitously in marine sediments [*Schouten et al.*, 2000b; *Sinninghe Damsté et al.*, 2002a, 2002b]. Although primarily produced by cosmopolitan pelagic *Crenarchaeota*, crenarchaeol has also been detected in some lacustrine [*Schouten et al.*, 2000b] and terrestrial environments (unpublished results). GDGT-0 is produced by a suite of archaea, occurring virtually everywhere on Earth [*Schouten et al.*, 2000b]. Crenarchaeol and GDGT-0 were present in the Saanich Inlet sediments in comparable quantities at concentrations as high as 50–150 μg/g sediment with invariant δ^{13}C values of −21 ± 0.5‰ (Table 2). Because of the worldwide ubiquity of marine crenarchaeol and the largely marine origin of the Saanich Inlet sedimentary organic carbon, as discussed above, while reports of terrigenously sourced crenarchaeol have so far been scarce, it is anticipated that all crenarchaeol is sourced by marine *Crenarchaeota*. Because of the similarity of the abundance and the carbon isotopic composition of crenarchaeol and GDGT-0, both compounds are anticipated to have the same source. However, a minor contribution of GDGT-0 by other archaea, e.g., methanogenic archaea, can not be excluded. The δ^{13}C values of the GDGTs (Table 2) are consistent with practically all earlier measured δ^{13}C values for present-day crenarchaeol from marine sediments, which are almost invariant [*Hoefs et al.*, 1997; *Schouten et al.*, 1998a; *Pearson et al.*, 2001]. This invariance was partly the basis for the assumption that marine *Crenarchaeota* are chemoautotrophs which assimilate DIC independent from the availability of oxygen and light [*Hoefs et al.*, 1997; *Pearson et al.*, 2001; *Sinninghe Damsté et al.*, 2002a], and this was recently demonstrated by in situ labeling experiments [*Wuchter et al.*, 2003]. It is furthermore observed that marine *Crenarchaeota* are most abundant at depths with highest nitrate concentrations below an oxygen minimum zone or chemocline, e.g., in the Black sea (unpublished data), and it was hypothesized that reduction of nitrate may be their energy source [*Sinninghe Damsté et al.*, 2002a]. During most of the year this is at intermediate depths between 30 and 100 m in Saanich Inlet, around the chemocline [*Anderson and Devol*, 1973; *Timothy and Soon*, 2001], and it is therefore anticipated that the bulk of crenarchaeol and GDGT-0 is produced from DIC by *Crenarchaeota* residing at these depths. Because both GDGTs occur in abundant quantities, and because they are anticipated to reflect the ^{14}C contents of DIC, they are also considered as good candidates for compound-specific radiocarbon dating.

5.1.6. Long-Chain *n*-Alkanes

[27] To substantiate any difference between the radiocarbon contents of marine biomarkers and that of the total organic carbon (TOC), terrestrial derived biomarkers were also selected for radiocarbon analysis. Straight-chain C_{27}, C_{29} and C_{31} *n*-alkanes were isolated in combined fractions from a series of *n*-alkanes exhibiting a carbon preference index of 3–4.5. This carbon preference index suggests that they originate from higher plant waxes [*Eglinton and Hamilton*, 1967] and thus are almost exclusively of terrestrial origin. In Saanich Inlet, terrestrial derived compounds are assumed to be mainly derived from soils in the catchment areas of the Fraser river and Cowichan river, the major source of sediment for the Saanich Inlet [*Gucluer and Gross*, 1964; *Blais-Stevens et al.*, 2001], although an aeolian contribution of plant-waxes can not be completely discounted.

5.2. Radiocarbon Contents

5.2.1. Radiocarbon Ages of Marine and Terrestrial Biomarkers, Macrofossils, and TOC

[28] The calibrated radiocarbon ages of the leaf remains in the prebomb sediment (1932–1950 AD) and the seed in the sediment of ∼500 BP, matched the sediment ages (Tables 4a and 4b), which substantiates the varve-based age model, at least for the most recent sediments. This becomes also clear when measured radiocarbon ages are plotted against the sediment ages, together with the calibration curves of *Stuiver et al.* [1998b] (Figure 3). This plot also shows that the ages of TOC are substantially greater than their parent sediments throughout the investigated cores, and also greater than the marine derived biomarkers (Tables 4a and 4b). The ages of the marine biomarkers show on average an offset with the sediment age in reasonable agreement with the proposed reservoir age of ∼800 years in this area [*Bornhold et al.*, 1998]. However, the spread in age between the different marine biomarkers is sometimes substantial and will be discussed below. The *n*-alkanes, representing terrestrial, vascular plant derived organic carbon, exhibit calibrated

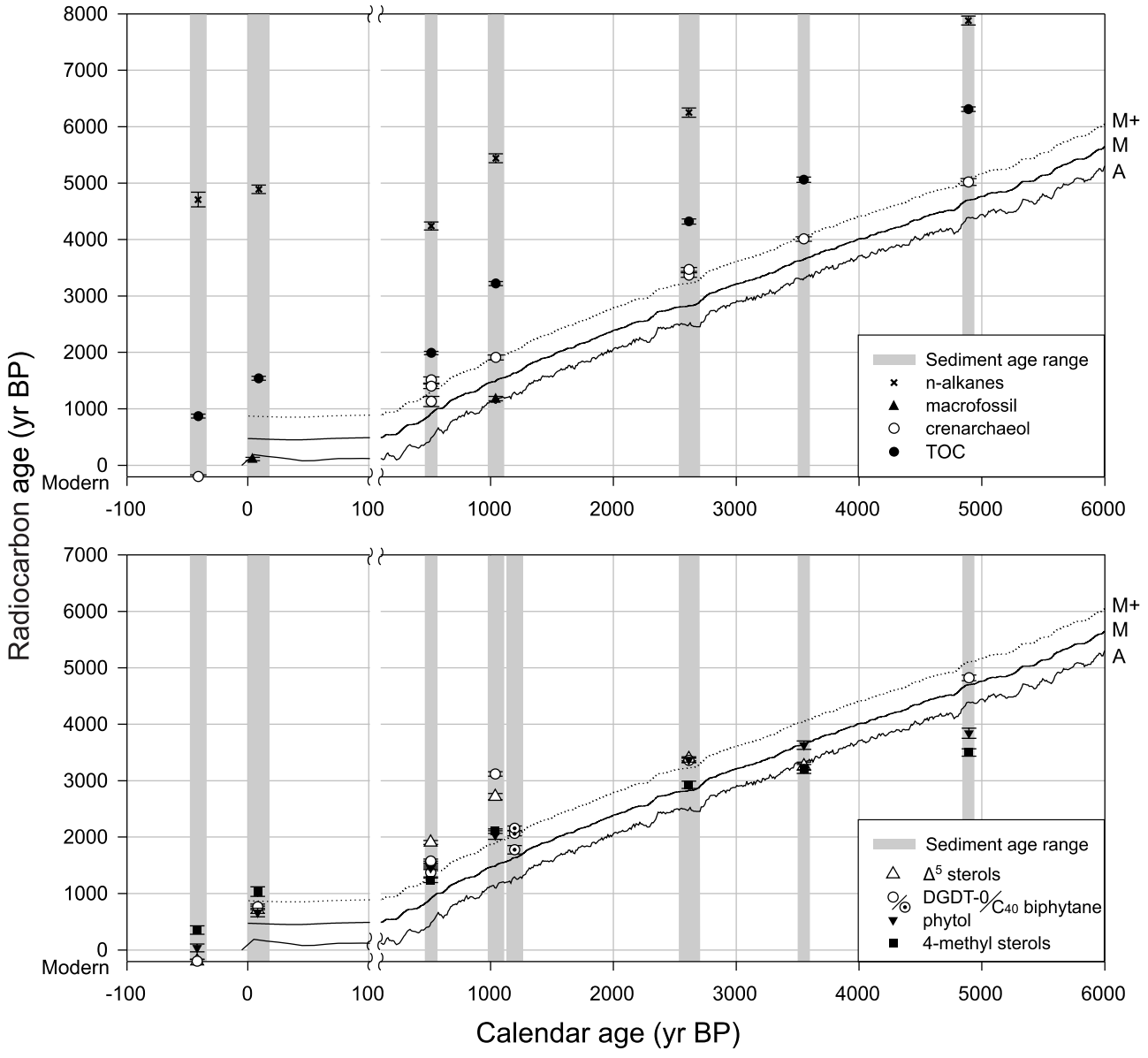

Figure 3. Radiocarbon ages of TOC, *n*-alkanes, macrofossils and crenarchaeol (upper panel), and GDGT-0 or corresponding biphytanes, Δ^5 sterols, 4-methyl sterols, and chlorophyll derived phytol (lower panel) against sediment calendar ages and the calibration curves of *Stuiver et al.* [1998a]. A: Atmospheric calibration curve. M: Marine calibration curve. M+: Marine calibration curve +401 years (ΔR). Note the change of scale at 100 cal years BP.

ages that are 4000–5500 years older than the sediments (Figure 3), which may partly explain the offset of the TOC ages from the marine biomarker ages and the sediment ages. Thus as already anticipated, the radiocarbon content of TOC can not be used for dating purposes, due to the admixture of preaged terrestrial organic carbon with autochtonous organic carbon. A detailed account on the radiocarbon contents of TOC and the *n*-alkanes, in comparison with the marine derived biomarkers, will be discussed elsewhere.

5.2.2. Prebomb and Postbomb Radiocarbon Contents: A Carbon Source Evaluation

[29] Comparison of the initial Δ^{14}C values (Figure 4) of the biomarkers sedimented before aboveground nuclear weapon testing in the early 1960s (prebomb sample, 1932–1950 AD), and those deposited afterward (postbomb sample, 1984–1998 AD), yields insights into the carbon sources of the various biomarkers used in this study. Owing to these tests, the atmospheric radiocarbon concentration increased dramatically [*Nydal and Gislefoss*, 1996] with a subsequent dissemination of this "spike" into the carbon cycle, including the ocean's DIC-pool [*Guilderson*, 2000; *Levin and Hesshaimer*, 2000]. The *n*-alkane postbomb Δ^{14}C value shows no influence of bomb-^{14}C when compared to the prebomb value (Table 3), indicating that aeolian sources of terrestrial higher plant-derived carbon are insignificant compared to riverine transported terrestrial (soil organic)

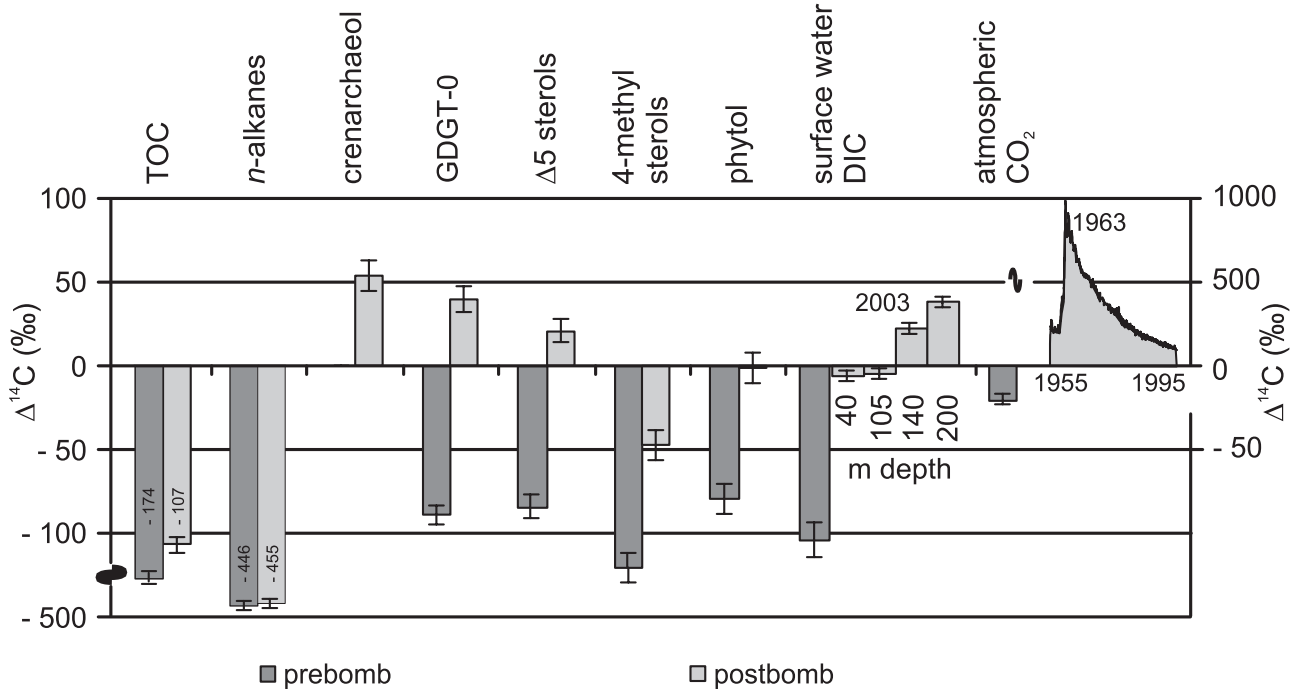

Figure 4. Prebomb (1932–1950 AD) and postbomb (1984–1998 AD) $\Delta^{14}C$ values of TOC and the various biomarkers, together with those of NE Pacific ocean surface water DIC (prebomb), Saanich Inlet water DIC from four different depths as measured in 2003, and atmospheric CO_2 (postbomb data from *Levin et al.* [1997]). Note the changes in the $\Delta^{14}C$ scale.

carbon. In contrast, postbomb TOC is substantially enriched in ^{14}C compared to prebomb TOC. This must thus primarily be due to the contribution of marine derived carbon that was ^{14}C enriched due to the bomb-spike. The results of the world ocean circulation experiment [*Key et al.*, 1996] and other investigations [*Druffel et al.*, 1996] indicate that currently DIC-$\Delta^{14}C$ values in the mixed water layer (0–75 m) along the British Columbian coast are between +25‰ an +75‰, while prebomb values must have been −90 ± 10‰, according to reservoir ages reported previously for the northeastern Pacific [*Southon et al.*, 1990]. Indeed, the deeper parts of the Saanich Inlet water DIC exhibited $\Delta^{14}C$ values of 22‰ and 38‰ in August 2003 (140 and 200 m respectively, Table 3; Figure 4). The postbomb $\Delta^{14}C$ values of +54‰ and +40‰ for crenarchaeol and GDGT-0 respectively, and the prebomb GDGT-0 value of −89‰ (Table 3) are in good agreement with these observations. This strongly suggests that marine planktonic Crenarchaeota make use of DIC that enters the lower parts of the fjord via yearly bottom water renewals. The ∼20‰ difference can be explained by the fact that the ^{14}C content of the biosphere has been decreasing since the cease of nuclear bomb testing, and that current DIC-$\Delta^{14}C$ values should be lower than a decade ago. The postbomb $\Delta^{14}C$ values of the phytoplankton-derived biomarkers (Δ^5-sterols, 4-methyl sterols and phytol) show relatively lower postbomb ^{14}C contents than those of the archaeal biomarkers, and also show a high variance compared with each other (Table 3; Figure 4). They compare, however, on average well with the surface water DIC $\Delta^{14}C$ values of around −5‰ (40 and 105 m; Table 3; Figure 4), values that indicate a more immediate relationship with the decreasing atmospheric ^{14}C content. These data point toward different carbon sources for phytoplankton and the marine archaea, the phytoplankton using surface water DIC from the photic zone, and the archaea using DIC from deeper waters. The observed variation is furthermore in good agreement with *Heier-Nielsen et al.* [1995], who found that ^{14}C concentrations in fjord surface waters in Denmark were highly variable due to varying concentrations of dissolved old soil carbonate entrained with fresh water inputs. This so-called "hard water effect" is regularly observed in fresh water [*Goodfriend*, 1997; *Siani et al.*, 2000] and may also play a role in the surface water in the Saanich Inlet area. Although there is, to the best of our knowledge, no information available on the ^{14}C contents of the Cowichan an Fraser river, the main contributors of fresh water to the Saanich Inlet, it is known that two limestone quarries were active near the shores of Saanich Inlet throughout most of the 20th century [*Kharé et al.*, 2001], as well as in the Georgia Strait [*Stiles*, 1995], which may have increased any possible natural hard water effects considerably. Furthermore, the ^{14}C concentration in coastal surface waters may also vary due to seasonal upwelling events, varying ocean-atmospheric exchange through the year [*Goodfriend*, 1997] or varying fresh water inputs [*Ingram and Southon*, 1996]. In Saanich Inlet, surface water characteristics like salinity and nutrient concentrations are indeed considerably influenced by these effects [*Takahashi et al.*, 1977]. It can be assumed that this is also the case for the ^{14}C concentration, which is reflected in the variable ^{14}C content of the phytoplankton biomarkers. Comparatively, even in the more open ocean

Table 4a. Calibrated Age Ranges (Years BP) Obtained With the Atmospheric Calibration Curve Using a ΔR of 401 ± 25 Years, of Sedimentary Total Organic Carbon (TOC), Terrestrial Macrofossils, and Isolated Biomarkers Originating From Differently Aged Sediment Layers

Sediment Age	TOC	Terrestrial Macrofossils	*n*-Alkanes	Crenarchaeol	GDGT-0	Δ5 Sterols	4-Methyl Sterols	Phytol[a]
1984–1998 AD	877–732		5592–5307	modern	modern	modern	514–319	92–0
1932–1950 AD	1512–1385	139–0	5659–5586		727–663	724–656	1057–922	671–553
568–465 BP	1965–1899		4846–4699	1454–1338	1466–1375	1898–1832	1238–1107	1351–1306
				1331–1281	1510–1397			
1111–977 BP	3481–3401	1171–1055	6327–6203	1891–1803	3389–3313	2873–2785	2125–2032	2084–1889
1273–1125 BP					2082–1954[b]			
					2172–2084[b]			
2707–2533 BP	4912–4859		7249–7026	3653–3549	3634–3526	3637–3587	3256–3027	3665–3511
				3784–3672				
3600–3500 BP	5889–5754			4528–4425		3629–3454	3595–3400	4028–3837
4940–4840 BP	7280–7206		8664–8420	5876–5677	5610–5530		3918–3727	4391–4100

[a]Phytol, chlorophyll-derived phytol.
[b]Measured on corresponding biphytanes.

setting off the coast of California the ^{14}C ages of different isolated sterols varied more than desirable [*Pearson et al.*, 2000], although these authors contributed this to relatively poor AMS precision obtained for these samples.

[30] The correlation of the Δ^{14}C values of the archaeal biomarkers with the Δ^{14}C value of the deeper layers below the chemocline in the Saanich Inlet, where the water properties are primarily influenced by the yearly water renewals, indicate that the bulk of the archaeal lipids is produced in these deeper water layers. Such a conclusion is in agreement with crenarchaeol maxima observed just below the chemocline in e.g., the Black Sea (unpublished data) and with the observation of *Pearson et al.* [2001] that archaeal lipids present in postbomb sediments of the Santa Barbara basin were produced with old DIC present in the subsurface California current. The renewal water is thought to be derived from intermediate water masses formed in the region of the San Juan Islands by the mixing of warm, low salinity water from the Strait of Georgia with cold, saline water that has upwelled off the coast and moved into the Strait of Juan de Fuca [*Anderson and Devol*, 1973]. Thus the ^{14}C concentration of DIC present below the dynamic surface water layer will be influenced to a much lesser extent by fresh water inputs and by ocean-atmosphere exchange than the upper surface water. Consequently the ^{14}C contents of the biomarkers produced using this deeper water DIC are much closer to that of the open ocean's mixed layer, and thus also less variable.

5.2.3. Archaeal Lipid Radiocarbon Contents: A Reservoir Age Evaluation

[31] The marine calibrated ages of crenarchaeol are very comparable with the sediment ages (Tables 4a and 4b). However, although the 1σ uncertainty of calibrated ages overlaps in all cases with the age range of the sediments, the agreement is sometimes marginal. A perfect match of the average calibrated age with the mean sediment age is only obtained for the sample of 1111-977 cal years BP (Tables 4a and 4b), and for the comparison between the postbomb crenarchaeol with postbomb ocean surface water, as described above. The remaining samples exhibit on average an offset of >100 years. Errors in the ^{14}C analysis can not be excluded, but this is already accounted for in the calibration uncertainty. It is therefore more likely that the offsets these ages from the varve ages are the result of inconsistencies in the calibration procedure, or more specifically, of varying reservoir ages through time.

[32] The marine calibration curve of *Stuiver et al.* [1998b] is based upon the atmospheric calibration curve and a simple box model that incorporates ocean circulation, air-sea exchange and atmosphere/terrestrial biosphere CO_2 fluxes. It is corrected for a reservoir age, $R_g(t)$, of the global ocean relative to the atmosphere. $R_g(t)$ is determined at 400 ^{14}C years in preindustrial times (1850 AD), but varies

Table 4b. Calibrated Age Ranges (Years BP) Obtained With the Marine Calibration Curve Using a ΔR of 401 ± 25 Years, of Sedimentary Total Organic Carbon (TOC), Terrestrial Macrofossils, and Isolated Biomarkers Originating From Differently Aged Sediment Layers

Sediment Age	Crenarchaeol	GDGT-0	Δ5 Sterols	4-Methyl Sterols	Phytol[a]
1984–1998 AD	modern	modern	modern	>0	>0
1932–1950 AD		>0	>0	411–249	>0
568–465 BP	700–624	705–668	1117–1012	503–465	648–602
	623–537	734–678			
1273–1125 BP		1280–1163[b]			
		1332–1272[b]			
1111–977 BP	1113–994	2485–2353	2014–1865	1303–1234	1274–1101
2707–2533 BP	2777–2701	2760–2691	2789–2718	2318–2151	2786–2681
	2870–2782				
3600–3500 BP	3552–3444		2745–2640	2729–2498	3142–2903

[a]Phytol, chlorophyll-derived phytol.
[b]Measured on corresponding biphytanes.

Table 5. Reservoir Ages in ^{14}C Years BP and Reservoir Age Offsets ΔR as Calculated With the Values Given in Table 2[a]

Sediment Age	Crenarchaeol	GDGT-0	Δ5 Sterols	4-Methyl Sterols	Phytol
		Reservoir Age			
1932–1950 AD		590	540	860	490
568–465 BP	920	1060	1420	750	970
1111–977 BP	760	1980	1560	950	880
1273–1125 BP		850[b]			
2707–2533 BP	940	870	900	440	880
3600–3500 BP	690		−70	−120	300
4940–4840 BP	660	450		−870	−530
Average ± SD	794 ± 130				
		ΔR			
1932–1950 AD		290	240	560	190
568–465 BP	490	630	990	320	540
1111–977 BP	410	1630	1210	600	530
1273–1125 BP		480[b]			
2707–2533 BP	590	520	550	90	530
3600–3500 BP	360		−400	−450	−30
4940–4840 BP	330	120		−1200	−860
Average ± SD	436 ± 105				

[a]The reservoir age is the biomarker age minus the atmospheric age and ΔR is the biomarker age minus the global ocean model age [*Stuiver and Braziunas*, 1993]. Phytol, chlorophyll-derived phytol.
[b]Measured on corresponding biphytanes.

over time because of the relative inertia of the ocean water ^{14}C content compared to fluctuations in the atmospheric ^{14}C production caused by heliomagnetic variations. Furthermore, the reservoir age varies geographically [*Stuiver and Braziunas*, 1993]. A reservoir age at a certain site can be expressed as R(t, s), with s = space, and t = time, or as ΔR(s) when compared to the marine calibration curve that includes R_g(t). Implied in this definition is the notion that the time-dependent changes of a local environment parallel those of the global ocean, thus yielding a time-independent ΔR(s). For northeastern Pacific coastal waters, the reservoir age has been determined at 788 ± 33 ^{14}C year [*Southon et al.*, 1990], mainly based upon shell and wood pairs recovered from approximately the same depth. On a local scale, *Bornhold et al.* [1998] determined a reservoir age of 798 ± 50 ^{14}C years for the Saanich Inlet, based upon a wood/shell pair from approximately the same depth, similar to an earlier determined reservoir age of 801 ± 23 years [*Robinson and Thomson*, 1981], which may also be read as a ΔR of 401 years. This local value has been used for the calibration of the various marine biomarkers (Tables 4a and 4b). The subtraction of the atmospheric radiocarbon ages from the measured biomarker radiocarbon ages results in the reservoir ages of the different samples (Table 5) while the local offset ΔR(Saanich) from the marine calibration curve is determined in the same way by taking the marine calibration curve as a reference (Table 5). The reservoir ages show a spread of ±130 years, while the ΔR values exhibit a standard deviation of 105 years. This indicates that indeed part of the variation in reservoir age results from the variation in the atmospheric radiocarbon concentration through time compared with a relatively inert ocean. This is also apparent when the initial radiocarbon contents of crenarchaeol are contrasted with the sediment ages in the context of both calibration curves (Figure 3). This allows an evaluation of the radiocarbon age of the biomarker in comparison with both calibration curves through time.

[33] The ΔR spread of >100 years may be a naturally occurring effect, and the assumption that the temporal variation of the reservoir effect modeled for the global ocean is practically the same for all regions, may not entirely be true, especially for coastal sites where upwelling or significant fresh water inputs occurs [*Stuiver and Braziunas*, 1993]. Natural variations in the DIC-^{14}C concentration on a regional to local scale, like variations in air-sea CO_2 exchange or upwelling strength can also play an important role. For instance, the (mixed layer) DIC radiocarbon ages of the North Atlantic, the Mediterranean and the Black Sea decreased by some 150 years between 1900 and 1930 AD. This change was due to a temporary increase of air-sea CO_2 exchange resulting from a high North Atlantic Oscillation index and related average wind strengths [*Siani et al.*, 2000]. Observations on mollusk shells found in sediments along the British Columbia coast also suggests that coastal surface water DIC-^{14}C contents can be variable [*Southon et al.*, 1990]. These authors suggest that variations in upwelling or ocean current strength may have played a role, thus affecting the relative contribution of upwelled old oceanic bottom water to the surface. Furthermore the extent and frequency of water renewals, possibly linked with climatic variations, could also be important in the case of Saanich Inlet.

[34] Another factor that may play a role is a delay of the marine calibration curve at sites with high reservoir ages, like the NE Pacific coastal waters. Together with the dissemination of atmospheric ^{14}C into the oceanic DIC pool, atmospheric ^{14}C variations are also entrained. At upwelling sites, these "stored" variations will come to the surface only after considerable time, and will have its influence on the local temporal variation in the reservoir age. *Stuiver and Braziunas* [1993] included the effect of "storage" of ^{14}C variations ocean water only to a minor extent in their model, and they argue that the major part of short-term variations in the marine calibration curve is

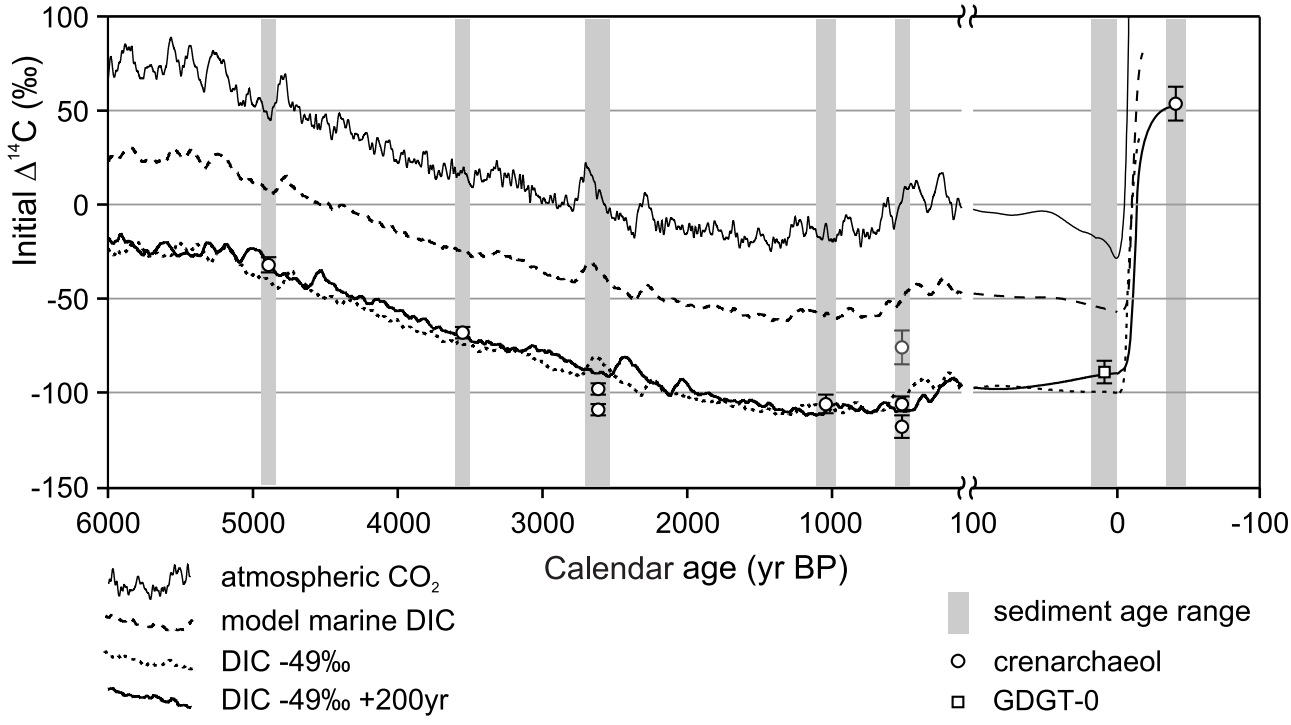

Figure 5. Initial $\Delta^{14}C$ values of crenarchaeol, together with various calibration curves. Because the prebomb sediment crenarchaeol measurement was corrupted, the GDGT-0 radiocarbon content is plotted as a substitute. The inaccurate (small sized) replicate at ~500 BP is shown by shading. The atmospheric CO_2 (light continuous) and global marine DIC (dashed) curves are taken from *Stuiver et al.* [1998a]. The difference between these two corresponds to the global marine reservoir age $R_g(t)$. The DIC −49‰ curve (dotted) displays this curve adjusted for a local reservoir age offset ΔR of 401 years, according to general calibration practice. A perfect calibration is obtained when a crenarchaeol $\Delta^{14}C$ value is plotted right on top of this curve. This is not the case for most data, but when the reservoir age-corrected calibration curve is shifted with +200 years (thick continuous) an almost perfect match is obtained.

atmospheric driven. However, *Delaygue et al.* [2003] show that timing and amplitude of the reservoir effect are strongly influenced by circulation, and not just a function of atmospheric $\Delta^{14}C$. At upwelling sites the influence of ocean circulation may thus play a more prominent role than is provided in the model of *Stuiver and Braziunas* [1993], due to the relatively large influence of deep-water DIC to surface water ^{14}C concentrations. Instead of simply adding a certain reservoir age offset, ΔR, to the global reservoir age, $R_g(t)$, it may be appropriate to include a temporal shift of the marine calibration curve. Indeed, a shift of 200 years of the marine calibration curve toward the future results in an almost perfect match for all the crenarchaeol initial $\Delta^{14}C$ values (Figure 5). This suggests that variations in the marine radiocarbon pool may indeed play a more important role on reservoir age variations then the calibration model allows, at least for upwelling areas with high reservoir ages. Obviously, the data provided here are only indicative, and evaluation of larger data set and thorough modeling like that of *Delaygue et al.* [2003] needs to be performed before any conclusions can be drawn.

[35] GDGT-0 yields approximately the same results as crenarchaeol, except for one outlier at 1111-977 BP, which is considerably older. Possibly some of this GDGT-0 was produced by methanotrophic or methanogenic archaea assimilating respectively methane or simple organic molecules derived from sedimentary organic matter [*Schouten et al.*, 2000b]. This interpretation is supported by the coincidence with the TOC ^{14}C age for this interval (Table 3). However, the $\delta^{13}C$ value of this sample does not differ from the general archaeal value of 21‰ (Table 2), and why such a methane-related signal would be absent in the other samples is also not clear. Furthermore, the age of the GDGT-0 derived biphytane fraction of the sediment of 1273-1125 BP, directly below, is an excellent match with the sediment age (Tables 4a and 4b). This also suggests that biphytanes derived from GDGTs can be used as an alternative for intact GDGTs, although analysis of the latter is more laborious. Thus, while radiocarbon analysis of GDGT-0 may yield the same results as that of crenarchaeol, its less well constrained origin renders the use of GDGT-0 less reliable.

5.2.4. Phytoplankton Biomarker Radiocarbon Contents: Surface Water Variability

[36] The radiocarbon contents and calibrated ages of phytol, Δ^5 sterols and 4-methyl sterols isolated from the ODP sediments (Tables 3 and 4, respectively, while also visible in Figure 3) show considerable variation, both

between the different biomarkers isolated from the same sediment layer, as well as in terms of the age difference with the sediments through time. As discussed above, relatively young phytoplankton biomarkers ages compared to the archaeal biomarker ages are likely the result of algal growth in well-mixed, stratified surface water with a high contribution of atmospheric ^{14}C, while old ages may be caused by hard-water effects introduced by run-off and fluvial inputs. Phytol is in general 100–150 years older than the sediment ages for the upper three intervals of the ODP-core (568-465 BP; 1111-977 BP and 2707-2533 BP), and thus quite comparable with crenarchaeol. In contrast, 4-methyl sterols and Δ^5 sterols show a larger spread of −400 to +900 years compared to the sediment age. The phytoplankton biomarkers from the two lowermost sediment intervals (3500–3600 and 4840–4949 BP) show relatively high ^{14}C contents. This is especially the case for the phytoplankton biomarkers of the oldest sediment, which appear to be younger than the sediments even before a reservoir age correction (Figure 3). This suggests that they have either been synthesized from substantially ^{14}C enriched carbon, that they are indeed younger than the sediment and mixed downward by some mechanism, or that the samples have been contaminated with modern carbon. Because the sediments show no sign of redistribution (e.g., bioturbation), the second explanation does not seem plausible. Similarly, contamination of all phytoplankton biomarkers with approximately the same amounts of modern carbon also seems unlikely for several reasons: first, carbon abundances based on the CO_2 yields after combustion of these samples were not larger than estimated abundances determined by gas chromatography, indicating the absence of additional carbon. Second, the phytoplankton biomarkers isolated from the younger sediment intervals do, in contrast, not show unexpected young ages, nor do the archaeal biomarkers, while all samples were isolated and prepared for AMS in exactly the same way. Third, systematic large errors in the ^{14}C determination of several biomarkers from one sediment layer are also unlikely, because the biomarkers have not all been analyzed in the same batch. More specifically, the phytol fractions were isolated using a different procedure from the sterols and were analyzed more than 8 months later. We conclude, therefore, that another mechanism(s) must be responsible for the unexpectedly high ^{14}C concentrations. As discussed above, lesser reservoir ages may stem from higher contributions of atmospheric ^{14}C in photic zone resulting from a well-mixed stratified surface water layer. Alternatively, errors associated with varve counting for deeper sediment layers may give rise to artificially old ages. This would imply that difference in age between the archaeal biomarker ages and the sediments are even greater than is now estimated, suggesting that reservoir ages were larger at that time. Coincidentally, *Southon et al.* [1990], observed significantly higher reservoir ages around 6000 ^{14}C years BP. However, the uncertainties in the varve-based sediment age determination allow at most a 200 year shift toward a younger age (i.e., ∼4700 BP) [*Nederbragt and Thurow*, 2001; A. J. Nederbragt, personal communication, 2003]. Furthermore, the factors ''sediment age'' and ''atmospheric radiocarbon'' can not by far account for the observed offset of the phytoplankton biomarkers. The oldest sediment age would need to be around 4000 BP for the initial $\Delta^{14}C$ value of 4-methyl sterol to be equal to the atmospheric $\Delta^{14}C$ value. To a lesser extent the same is true for phytol. A final but highly speculative hypothesis is that the enigmatic low values may be caused by a flaw in the calibration curve, exhibiting larger ''spikes'' of elevated atmospheric ^{14}C concentrations than is currently thought. However, it seems far more likely that the radiocarbon contents of the oldest phytoplankton biomarkers are ''off'' due to some unexplained error. Would future measurements also result in the same young algal biomarkers at the given time-frame, then it would be worthwhile to investigate a scenario which combines a sediment age that is estimated to old with algal growth under conditions with highly elevated ^{14}C concentrations. Such a scenario would imply that the Saanich Inlet surface water used to be more influenced by stratification and atmospheric-ocean mixing than is nowadays the case, and furthermore that the atmospheric and marine radiocarbon contents experienced substantially larger variations in the past than is currently acknowledged.

6. Conclusions

[37] Calibrated ages obtained from compound-specific radiocarbon analysis of the marine pelagic archaeal biomarker crenarchaeol, extracted from sediments of Saanich Inlet, Canada, compare favorably with independently determined ages from varve-counting. The same applies for the more generic archaeal biomarker GDGT-0, although the less specific origin of this biomarker renders it slightly less reliable. An average reservoir age offset from the marine calibration curve, ΔR, of 430 ± 110 years is consistent with previous measurements, and thus demonstrating for the first time that compound-specific radiocarbon dating can be successfully applied. The results are in good agreement with earlier conclusions in the literature that marine crenarchaeota use DIC as their carbon source.

[38] Although the calibrated crenarchaeol ages match closely with the sediment ages, the reservoir age varies by more than 100 years. This can either be attributed to a variability of the local or regional reservoir age resulting from natural processes like a variation in upwelling through time, or to inconsistencies in the marine calibration curve for sites such as the Saanich Inlet that exhibit high reservoir ages. Both explanations imply that ideally both spatial and temporal variations in reservoir age should be assessed when radiocarbon dating is performed with marine derived samples.

[39] In contrast to crenarchaeol, the radiocarbon ages of phytoplankton derived biomarkers Δ^5 sterols, 4-methyl sterols and chlorophyll-derived phytol, were quite variable. This is likely related in part to highly variable ^{14}C contents in the surface waters of the fjord, resulting from temporal variations in stratification, ocean-atmosphere CO_2 exchange and fresh water input with associated hard-water effects. The radiocarbon contents of the phytoplankton biomarkers of the oldest sediment exhibited anomalously high values

(i.e., young ages). Determining the reason for these discrepancies would require further measurements and error assessment.

[40] While the marine pelagic *Crenarchaeota* have been shown to be present throughout the water column, it is likely that they are concentrated in the waters immediately below the photic zone, where higher nutrient levels prevail. Correspondingly, they are less sensitive to the variations in surface water DIC-^{14}C that apparently influenced the phytoplankton biomarkers, which resulted in more consistent reservoir ages. However, this also implies that in open ocean settings crenarchaeol may reflect a mixture of surface water and subsurface water DIC-^{14}C contents. Crenarchaeol is abundant in marine sediments worldwide [*Karner et al.*, 2001], implying that smaller amounts of sediment are needed for radiocarbon dating. For example, while the used subsamples from Saanich Inlet corresponded to ages spanning 100–150 years, the recovered amounts of crenarchaeol would have allowed a resolution of 10–20 years. Thus crenarchaeol may be an ideal biomarker for compound-specific radiocarbon dating of marine sediments. A continuous profile of radiocarbon contents of crenarchaeol, combined with the varve-based age model, would allow for a site-specific marine calibration curve to be obtained.

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