

## Diagenetic and sedimentological controls on the composition of organic matter preserved in California Borderland Basin sediments

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### Abstract

Compound-specific radiocarbon (<sup>14</sup>C) contents, stable carbon isotopes, and abundances of phytoplankton and vascular plant derived lipid biomarkers (alkenones and fatty acids) were obtained from Santa Barbara Basin and Santa Monica Basin sediments, along with radiocarbon contents of planktic foraminifera and total organic carbon. We investigated core-top and prebomb sediment intervals at sites from the flanks and depocenters of the basins deposited under contrasting bottom water oxygen concentrations. Bulk organic matter generally has the lowest radiocarbon levels of all sediment constituents measured, whereas planktic foraminifera tend to be the most radiocarbon enriched. Alkenones are systematically depleted in radiocarbon with respect to foraminifera. Short-chain (C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>) fatty acids decrease rapidly in absolute abundance and relative to longer-chain (>C<sub>24</sub>) homologues from core-top to prebomb samples. The loss of short-chain fatty acids with depth is associated with <sup>13</sup>C depletion of short-chain fatty acids, indicating preferential preservation of terrestrially derived fatty acids. Short-chain fatty acids tend to be more <sup>14</sup>C-enriched relative to alkenones in core-top sediments, whereas longer-chain homologues are generally the most radiocarbon depleted of the lipids studied here. Less refractory compounds (e.g., short-chain fatty acids) are thus enriched in radiocarbon with respect to more recalcitrant biomarkers (alkenones, long-chain fatty acids). The lower <sup>14</sup>C content of more refractory compounds reflects a larger proportion of laterally supplied, preaged material. Greater preservation of labile organic compounds observed at the depocenters than in flank sediments results in the presence of “younger” biomarkers, underlining the important influence of selective degradation of labile compounds on their radiocarbon ages.

The reconstruction of past environmental conditions relies to a major extent on the study of marine and lacustrine sediment records because they can provide long and continuous archives. These reconstructions are based on the measurement of physical or chemical properties of the sediments, which vary in response to changes in environmental conditions. Accurate sediment chronologies are a prerequisite for paleoenvironmental studies. For the late Quaternary, age models are most often developed through radiocarbon dating. The most common practice for marine sediments is to measure radiocarbon (<sup>14</sup>C) ages of planktic microfossils, e.g., foraminifera, and to assume identical age of all sediment constituents deposited within that same sediment layer.

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The study of processes affecting carbon cycling within past and present environments often involves the use of molecular organic compounds of known origin, so-called biomarkers. The assumption of coeval deposition of marine organic matter (OM) and microplankton shells was challenged after the first publication of molecular radiocarbon ages of organic compounds in surficial marine sediments (Eglinton et al. 1997), where the various compounds were found to differ in <sup>14</sup>C levels despite their occurrence in the same sediment layer. In a later study, large and variable age offsets between phytoplankton-derived alkenones and planktic foraminifera were reported from the Bermuda Rise and attributed to particle advection to this sediment drift (Ohkouchi et al. 2002). Similar offsets between diatom-bound OM and co-occurring foraminifera in the Southern Ocean have been related to resuspension events (Ingalls et al. 2004b).

It is well known that postdepositional processes (e.g., diagenesis or bioturbation) can affect the fidelity of sedimentary records and thereby reduce their potential for accurately recording past climate conditions (e.g., Thomson et al. 1995; Hedges et al. 1999). In particular, recently produced biogenic materials may be preferentially degraded relative to allochthonous terrigenous and marine organic components as a result of the intrinsic chemical stability of the latter or their physical association with mineral matrices (e.g., Hedges et al. 1999; Mayer 1999; Ingalls et al. 2004a). Diagenetic changes in the proportions of the different components delivered to the sediments shape the sedimentary record and influence interpretation of corresponding proxies (e.g., Canuel and Martens 1996; Arzayus and Canuel 2004; Sun et al. 2004). Moreover,

climate-driven changes in depositional conditions under which sedimentary components are buried likely modulate their degree of preservation (e.g., Sinninghe Damsté et al. 2002).

The degree of OM degradation has been related to bottom water oxygen (BWO) concentrations and the integrated oxygen exposure time of the organic material (Hartnett et al. 1998; Keil et al. 2004). The latter parameter incorporates the amount of time that particles reside within oxygenated environments. BWO levels also determine whether macrobenthic life can be sustained on the seafloor and hence the degree of bioturbation. Best preserved, and least disturbed sediment records are therefore expected in anoxic environments, and the latter are thus targeted for paleoclimate studies (e.g., Kennett and Ingram 1995; Schimmelmann and Lange 1996).

Gong and Hollander (1999) observed differences in alkenone-derived  $U_{37}^{K'}$  values in sediment cores recovered from the flank and the center of the Santa Monica Basin (SMB). These two sites, which are 15 km apart, are overlain by essentially the same water column and vertically separated by only 60 m, but have sharply contrasting BWO contents. These authors and others (Hoefs et al. 1998) have suggested that preferential oxic degradation of alkenones with greater unsaturation may result, on the basis of the  $U_{37}^{K'}$  method, in higher apparent sea-surface temperatures. Gong and Hollander (1999) reconstructed  $U_{37}^{K'}$ -based sea-surface temperatures of  $\sim 15^{\circ}\text{C}$  and  $\sim 17^{\circ}\text{C}$  in core-top sediments from the depocenter and flank of SMB, respectively. More recent compound-specific isotopic studies have revealed, however, that different source-specific biomarkers in depocenter surficial sediments exhibit a wide spectrum of radiocarbon ages (Pearson et al. 2000; Pearson et al. 2001). Although alkenones were not measured in these studies, the results imply varied predepositional histories for organic constituents residing in the sediments.

In order to study the influence of BWO content, bioturbation, and other sedimentary processes on the composition and age distribution of biomarkers relative to other sedimentary components, we contrast nearby sites deposited above and below the sill depths from the flanks and depocenters of two of the California Borderland Basins (Santa Barbara Basin [SBB] and SMB). At the depocenters, bottom waters are suboxic inhibiting bioturbation and sediments are laminated. At the sites from the flanks of the basins, bottom waters are less oxygen deficient and sediments show no laminations. Assuming identical inputs, differences in preserved radiocarbon ages of biomarkers between flank and depocenter sites must reflect differences in postdepositional processes (Hedges et al. 1999; Bard 2001).

Molecular-level radiocarbon and stable carbon isotope data were obtained on alkenones and fatty acids representing phytoplankton and vascular plant derived biomarkers. We investigated core-top and pre-1960 sediment intervals at each site to examine differences in the uptake of "bomb"  $^{14}\text{C}$ . Radiocarbon values of lipids were also compared with those of co-occurring planktic foraminifera and bulk organic carbon from corresponding sediment intervals.

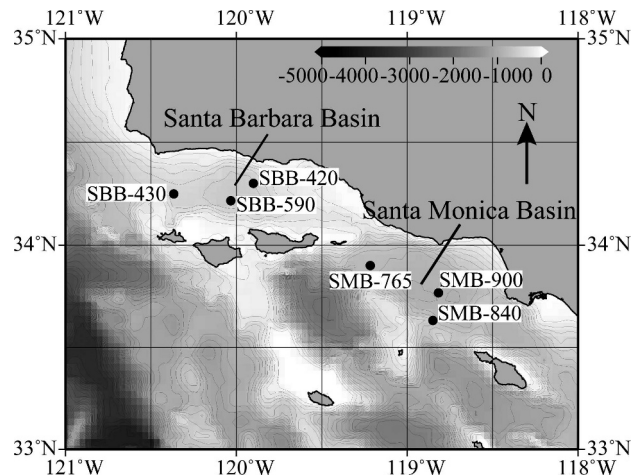


Fig. 1. Study area and core locations. Core sites are named SBB for Santa Barbara Basin and SMB for Santa Monica Basin, followed by the respective water depth (m).

Our results imply a strong advective control on the age distribution of OM in these sedimentary environments, with reactivity being strongly linked to age. Specifically, refractory lipids, such as alkenones can survive and be supplied by lateral transport. In contrast, labile compounds (e.g., short-chain fatty acids) are less able to survive lateral transport and therefore more strongly reflect inputs from the overlying water column. Terrigenous lipids (e.g., long-chain fatty acids) are preaged at the time of delivery to the marine sediments. Selective degradation during subsequent diagenesis has the effect of increasing the importance of laterally delivered biomarkers at the expense of autochthonous, relatively reactive compounds. Together these processes appear to shape the lipid biomarker records of California Borderland Basin sediments. Differential bioturbational processes could not be detected as a factor influencing the radiocarbon signature of lipid biomarkers in these sediments.

*The study area*—The California Borderland, is characterized by a series of sills bordered by San Diego, Santa Barbara, and the Channel Islands (Fig. 1; for a very detailed map of SBB, see Bernhard et al. 2003). Two of these basins, SBB and SMB, have been extensively studied in the past (cf. Schimmelmann and Lange 1996). Maximum sill and basin depths are approximately 475 m and 590 m in SBB, and 740 m and 940 m in SMB, respectively. In both basins, prevailing BWO concentrations in the deepest parts are at or below  $0.1 \text{ mL L}^{-1}$  so that bioturbation is inhibited and primary sedimentary structures of fine laminations are preserved. Conditions leading to the deposition of laminated sediments have persisted in SBB for most of the Holocene, though intermittent intervals of oxygen levels in bottom waters high enough to allow bioturbation have occurred during this period (Schimmelmann et al. 2006). In contrast, conditions with  $\text{BWO} < 0.1 \text{ mL L}^{-1}$  in SMB only developed approximately 350 to 400 yr ago, at the onset of the Little Ice Age, and has since expanded in area (e.g.,

Table 1. Core locations of sediment samples used for this study. For reference, locations of California Borderland Basin cores studied previously are also given. Sedimentation rates are based on excess  $^{210}\text{Pb}$  activity ( $^{210}\text{Pb}_{\text{xs}}$ ) analyses. They are calculated from the slope of the regressions of  $\ln(^{210}\text{Pb}_{\text{xs}})$  versus depth ( $r^2$  values also given) divided by  $\lambda$ , where  $\lambda = (\ln 2)/22.3 \text{ yr} =$  decay constant of  $^{210}\text{Pb}$ . Uncertainties in the sedimentation rates are calculated from the standard deviations of detrended  $\ln(^{210}\text{Pb}_{\text{xs}})$  values.

Station	Latitude N	Longitude W	Water depth (m)	Sedimentation rate ( $\text{cm yr}^{-1}$ )	$r^2$	Reference
SBB-430	34°15'	120°22'	430	0.41±0.05	0.98	This study
SBB-420	34°18'	119°54'	420	0.24±0.05	0.93	This study
SBB-590	34°13'	120°02'	590	0.39±0.07	0.98	This study
SMB-765	33°54'	119°13'	765	0.040±0.006	0.97	This study
SMB-900	33°46'	118°49'	900	0.057±0.002	0.99	This study
SMB-840	33°38'	118°51'	840	0.062±0.014	0.95	This study
SABA87-1	34°14'	120°01'	590	0.3–0.5		Schimmelmann and Tegner (1991)
Pulse-32	33°44'	118°50'	905	0.041		Pearson et al. (2001)
	33°44'	118°50'	902			Masiello and Druffel (2003)

Gorsline 1992; Christensen et al. 1994; Masiello and Druffel 2003). Fine-scale laminations in SBB are interpreted to reflect annual variations in sediment supply or depositional conditions (varves) (e.g., Schimmelmann and Tegner 1991; Thunell 1998; Berger et al. 2004). In contrast, laminations in SMB have been shown to be nonannual but result from cyclic variability on scales of several years (~7 yr; Christensen et al. 1994). In addition, BWO levels in SMB are often high enough to support shallow and mild bioturbation.

Sediment is supplied to the basins by a combination of processes, including sinking of bioaggregates from surface waters, nepheloid plumes at the surface, middepth and near bottom, turbidity currents, and mass movements (Hülsemann and Emery 1961; Gorsline 1992; Thunell 1998). Most of the uppermost decimeters of sediment in SMB have been derived from vertical rain and nepheloid plumes, but sporadic turbidity flows by distinct channels entering SMB have also occurred in the recent geological past in this tectonically active region (Gorsline 1992). The mainland facing slope of SBB is gentler than those of other basins in the region and is uncut by submarine canyons, showing only traces of a few small sea gullies (Emery and Hülsemann 1962). However, detailed studies of thickness and composition of the individual sediment layers suggested that intermediate storage on the shelf, where sediment can be remobilized by waves, currents, and tides, must be taken into account when interpreting the sedimentary records in this basin (Schimmelmann and Tegner 1991; Berger et al. 2004).

## Material and methods

**Samples**—Sediment material was retrieved by multicoring during RV *New Horizon* cruise NH01-12 in 2001. Three multicore sites from SBB (SBB-430, SBB-420, and SBB-590) and SMB (SMB-765, SMB-900, and SMB-840) were chosen (Fig. 1, Table 1). Two sites in each basin were located on the flanks at depths above the sill depths (<500 m in SBB and <850 m in SMB); one was from the corresponding depocenters, where oxygen concentrations are below  $0.1 \text{ mL L}^{-1}$ . Oxygen penetration into the sediments is negligible at all sites (A. Dickens, unpubl.

data). Multicore subcores were sectioned in 1-cm intervals (0–20 cm) and 2-cm intervals (<20 cm) on board ship and stored frozen in precombusted glass jars or in heat-sealed Kapak geochemical bags. At each site, core tops and one sediment horizon deposited before 1960 (“prebomb”) were selected. The depths of the prebomb horizons were estimated on the basis of published sedimentation rates in SBB and SMB (e.g., Schimmelmann and Tegner 1991; Christensen et al. 1994). Corresponding 1-cm intervals from three subcores were combined. An additional sample horizon was selected from the SMB depocenter core at a depth where total organic matter contents were much lower than near the surface. Analogous to the work by Masiello and Druffel (2003), we consider this interval to represent sediment deposited before the development of suboxic conditions in SMB.

**Bulk analyses**—Freeze-dried and homogenized 1- and 2-cm-interval samples from one subcore of each of the six multicores were analyzed for bulk sediment geochemistry. Contents of total nitrogen, total carbon, total organic carbon (TOC), and total carbonate (calculated from the difference of total carbon and TOC) were determined. Reported data are average values of duplicate analyses, with reproducibility typically better than  $\pm 0.1\%$  dry weight for TOC and total carbon. No correction was made for the salt content in the sediments. Stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of TOC were measured as well. These analyses were carried out in triplicate with an average standard deviation of <0.1‰.

**Stratigraphy**—Stratigraphy is based on measurement of unsupported  $^{210}\text{Pb}$  (half-life 22.3 yr) (Koide et al. 1972). Samples of dry and homogenized sediment (5 g) were gamma counted for at least 24 h after equilibration in sealed plastic containers for at least 4 weeks. Activities of  $^{210}\text{Pb}$  (46.52 keV) and  $^{214}\text{Pb}$  (351.99 keV) were determined with a high-purity germanium detector (Canberra model GCW 4023S) and reported as disintegrations per minute (dpm). Unsupported  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}$ ) was calculated by subtracting  $^{226}\text{Ra}$  activity approximated by the activity of its very short-lived daughter isotope  $^{214}\text{Pb}$ . We assumed uniform relative salt content within the individual cores.

Sedimentation rates were calculated assuming constant rate of supply of  $^{210}\text{Pb}_{\text{xs}}$  from decay of atmospheric  $^{222}\text{Rn}$  (Appleby and Oldfield 1978), constant sedimentation rate within the core interval of interest, no migration of  $^{210}\text{Pb}$  in the sediment, and production of supported  $^{210}\text{Pb}$  entirely due to decay of  $^{226}\text{Ra}$ . Sedimentation rate was calculated by fitting a linear regression of  $\ln(^{210}\text{Pb}_{\text{xs}})$  and core depth and dividing its slope by the decay constant ( $\lambda = (\ln 2) \times \text{half-life}^{-1}$ ).

*Biomarker extraction, analyses, and purification*—Alkenones and fatty acids were purified from total lipid extracts of core-top and prebomb samples combined from three multicore subcores. Samples were freeze-dried, homogenized, and a total lipid extract was obtained by Soxhlet extraction with a mixture of dichloromethane and methanol (93:7; 48 h). Solvent was eliminated by rotary evaporation, and extracts were saponified in 0.5 mol L<sup>-1</sup> KOH in methanol (80°C; 2 h). After saponification, methanol was evaporated to a small volume (~5 mL), 10 mL Milli-Q water was added, and neutral lipids were recovered by liquid-liquid extraction by using hexane. Alkenones were further purified from the neutral lipid fraction by a sequence of wet chemical separation steps including silica-gel column chromatography, urea adduction, and silver nitrate column chromatography following the methods described by Ohkouchi et al. (2005). Sample purity was checked by analyzing 1% splits of the samples on a HP 5890 series II gas chromatograph equipped with a flame-ionization detector (GC-FID). Purified C<sub>37</sub>, C<sub>38</sub>, and C<sub>39</sub> alkenones were quantified by an external standard (behenic acid myristyl ester).

After recovery of neutral lipids from the saponified extracts, the pH was reduced to 1 by using 12 mol L<sup>-1</sup> HCl and fatty acids (FAs) were extracted into dichloromethane. FAs were converted to methyl ester derivatives (FAMES) with 5% hydrochloric acid in methanol under a N<sub>2</sub> atmosphere (80°C, 12 h) (Christie 2003). FAMES were extracted with *n*-hexane and further purified by using small silica gel columns, with the FAMES eluting with dichloromethane and hexane (2:1). Straight-chain FAMES were further separated by urea adduction (Marlowe et al. 1984). Abundances of FAMES were determined by peak integration on GC-FID chromatograms of urea-adducted samples.

Purified individual FAMES were collected by using a preparative capillary gas chromatography system as described in detail by Eglinton et al. (1996). In brief, a HP 5890 series II gas chromatograph, equipped with a HP 7673 autoinjector, a Gerstel CIS-3 injection system, and a Gerstel preparative trapping device, was fitted with a J&W Scientific DB-XLB column (60 m × 0.53 mm × 0.5 μm). The injection volume was 5 μL, and the gas chromatograph temperature program was 50°C (1 min), 20°C min<sup>-1</sup> to 150°C, 8°C min<sup>-1</sup> to 320°C (15 min). Approximately 1% of the effluent was diverted to a flame ionization detector, and the remaining 99% was collected in a series of seven glass U-traps. Traps 1–3 were cooled (0°C) and programmed to collect C<sub>14</sub>, C<sub>16</sub>, and C<sub>18</sub> FAMES; traps 4–6 were left at room temperature and programmed to collect C<sub>24</sub>, C<sub>26</sub>, and C<sub>28</sub> FAMES. The content of each trap was recovered by

using dichloromethane, and any column bleed was removed by subsequent elution through small silica gel columns immediately before transfer to quartz combustion tubes. Sample purity was checked on a GC-FID system, and FAMES were quantified by an external FAME standard.

*Radiocarbon measurements*—Radiocarbon ( $^{14}\text{C}$ ) measurements were performed at the National Ocean Science Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution. Techniques for the analyses of planktic foraminifera, which were handpicked after wet-sieving of solvent extracted sediment residues, and TOC followed standard procedures (McNichol et al. 1994). For radiocarbon measurement of TOC, subsamples of homogenized bulk sediments containing approximately 1 mg of organic carbon were hydrolyzed with 10% hydrochloric acid and combusted in evacuated precombusted quartz tubes with copper oxide and silver. Resulting CO<sub>2</sub> was purified and graphitized over an iron catalyst; graphite targets were then pressed for analysis by accelerator mass spectrometry (AMS). Foraminiferal shells were acidified in vacuo with 100% H<sub>3</sub>PO<sub>4</sub> in a 60°C bath overnight. Resulting gas was purified, converted to graphite, and analyzed by AMS by using identical procedures as for TOC.

Purified alkenones and FAMES samples were sealed with copper oxide in precombusted evacuated quartz tubes and combusted at 850°C. Resulting CO<sub>2</sub> gas was purified, quantified, and converted to graphite with cobalt used as a catalyst for radiocarbon analysis by AMS (Pearson et al. 1998). AMS analyses of samples smaller than 300 μg carbon (most compound-specific samples) were carried out on dedicated small sample wheels with size-matched standards in order to correct for different ion beam behavior (Pearson et al. 1998). Small samples (<300 μg C) of alkenones have been shown to be accurate with a precision better than 17‰ (Mollenhauer et al. 2005). The good agreement between replicate measurements of alkenones confirms this (Table 2). All radiocarbon values of FAMES were corrected for isotopic contribution of the methyl-group carbon obtained during derivatization by use of a simple mass balance equation.

Radiocarbon data are reported as fraction modern carbon (fMC), which involves a fractionation correction that uses simultaneously measured  $\delta^{13}\text{C}$  values of the samples (Stuiver and Polach 1977). This correction ensures comparability of radiocarbon results regardless of possible carbon isotopic fractionation of the different carbon containing materials. Second, we report initial  $\Delta^{14}\text{C}$  ( $\Delta^{14}\text{C}_{\text{initial}}$ ) as per mil (‰) difference to atmospheric radiocarbon levels of 1950 at the time of deposition (Mook and Van Der Plicht 1999). This term involves correction for  $^{14}\text{C}$  decay that has occurred since the time of deposition and requires accurate knowledge of the depositional age of the sediment. We used sediment ages derived from  $^{210}\text{Pb}$  stratigraphy for the latter.

*Compound-specific stable carbon isotopic ( $\delta^{13}\text{C}$ ) analysis*—Molecular-level stable carbon isotopic compositions of FAMES were determined by a Finnigan Delta<sup>plus</sup>

Table 2. Radiocarbon results of planktic foraminifera, TOC and alkenones given in fraction modern carbon (fMC; Stuiver and Polach, 1977). Year of deposition is derived from  $^{210}\text{Pb}$  stratigraphy. Planktic foraminifera data were obtained from samples of mixed planktic species, except SBB-590, 19–20 cm, where *G. bulloides* and *N. pachyderma* were used. fMC values for alkenones are corrected assuming a constant blank contribution of  $0.08 \pm 0.02 \mu\text{mol C}$  with a radiocarbon concentration of blank C of 0.25 fMC. The decay-corrected radiocarbon level of samples at the time of deposition  $\Delta^{14}\text{C}_{\text{initial}}$  is calculated as  $\Delta^{14}\text{C}_{\text{initial}} = (\Delta^{14}\text{C}_{\text{meas}} + 1)\exp(\lambda_p\tau) - 1$ , where  $\Delta^{14}\text{C}_{\text{meas}} = \exp(-\lambda_p \times \Delta t - \lambda_L \times t)$ ,  $\tau =$  time interval between deposition and measurement in calendar years (year of measurement = year of deposition from  $^{210}\text{Pb}$  stratigraphy),  $t = -8,033 \times \ln(\text{fMC}) =$  conventional radiocarbon age,  $\Delta t =$  interval between 1950 and the year of measurement,  $\lambda_p = (\ln 2)/5,730 \text{ yr}^{-1} =$  true decay constant,  $\lambda_L = (\ln 2)/5,568 \text{ yr}^{-1} =$  Libby decay constant. Sea-surface temperatures (SST) are reconstructed from  $\text{U}_{37}^K$  measurements by using the temperature calibration from Prahl et al. (1988).

Core	Sample interval (cm)	Year of deposition (A.D.)	Foraminifera		TOC		Alkenones			SST (°C)
			fMC	$\Delta^{14}\text{C}_{\text{initial}}$	fMC	$\Delta^{14}\text{C}_{\text{initial}}$	Sample size ( $\mu\text{mol}$ )	fMC	$\Delta^{14}\text{C}_{\text{initial}}$	
Santa Barbara Basin flank sites										
SBB-430	0–1	2000			0.795 $\pm$ 0.003	–210.2	8.8	0.876 $\pm$ 0.007	–129.5	15.2
SBB-430	19–20	1954			0.734 $\pm$ 0.003	–266.8	14.0	0.860 $\pm$ 0.006	–140.7	15.4
SBB-420	0–1	1999	1.031 $\pm$ 0.003	25.4	0.852 $\pm$ 0.004	–153.3	5.5	0.886 $\pm$ 0.009	–119.7	15.1
SBB-420	19–20	1909			0.730 $\pm$ 0.004	–266.6	12.0	0.832 $\pm$ 0.007	–163.6	15.6
							26.8	0.822 $\pm$ 0.012	–178.2	
Santa Barbara Basin depocenter										
SBB-590	0–1	2000	1.041 $\pm$ 0.003	34.8	0.922 $\pm$ 0.005	–83.6	7.3	0.997 $\pm$ 0.009	–9.4	13.2
SBB-590	19–20	1951	0.915 $\pm$ 0.003	–85.4	0.788 $\pm$ 0.004	–212.3	19.7	0.871 $\pm$ 0.006	–129.1	14.4
Santa Monica Basin flank sites										
SMB-765	0–1	1988	1.051 $\pm$ 0.004	46.3	0.847 $\pm$ 0.005	–156.4	14.9	0.960 $\pm$ 0.006	–44.6	15.3
SMB-765	5–6	~1860	0.949 $\pm$ 0.003	–40.6	0.727 $\pm$ 0.003	–264.8	16	0.833 $\pm$ 0.007	–158.7	14.7
SMB-840	0–1	1993	1.036 $\pm$ 0.003	30.4	0.906 $\pm$ 0.004	–98.6	18.7	0.897 $\pm$ 0.006	–108.2	14.3
SMB-840	5–6	1913	0.942 $\pm$ 0.004	–53.9	0.797 $\pm$ 0.004	–199.4	11.2	0.864 $\pm$ 0.007	–132.3	15.5
							22.1	0.875 $\pm$ 0.007	–121.2	
							30.1	0.851 $\pm$ 0.012	–145.6	
Santa Monica Basin depocenter										
SMB-900	0–1	1992	1.055 $\pm$ 0.005	49.9	0.931 $\pm$ 0.005	–74.0	9.8	0.983 $\pm$ 0.006	–22.6	14.7
							19.3	1.018 $\pm$ 0.007	1.3	
SMB-900	6–7	~1890	0.913 $\pm$ 0.004	–80.0	0.821 $\pm$ 0.004	–172.8	10.1	0.873 $\pm$ 0.006	–120.8	15.3
							20.8	0.890 $\pm$ 0.007	–103.9	
							28.9	0.8694 $\pm$ 0.10	–121.2	
SMB-900	32–34				0.533 $\pm$ 0.002		3.0	0.641 $\pm$ 0.016		16.0

GCirmMS system. Results are reported in per mil (‰) relative to the PeeDee Belemnite (PDB) standard and referred to as  $\delta^{13}\text{C}_{\text{GCirmMS}}$ . We also report stable carbon isotopic composition determined from a split of the  $\text{CO}_2$  gas resulting from combustion of purified samples and submitted for radiocarbon analysis. These measurements were carried out at the NOSAMS facility with a VG Optima irMS, and results are referred to as  $\delta^{13}\text{C}_{\text{NOSAMS}}$ . Comparison of these two independent measurements provides an additional control on purity of combusted and radiocarbon dated samples. A mass balance approach was used to correct all  $\delta^{13}\text{C}$  values of FAMEs for the isotopic contribution of the methyl-group carbon obtained during derivatization.

## Results

**Bulk parameters**—Carbonate contents in SBB and SMB sediments were generally low ( $\leq 20\%$  dry weight), with higher values in SMB than SBB. TOC contents range from approximately 1 to 5% dry weight (Figs. 2 and 3). In both basins, TOC contents are slightly higher (SBB: average  $3.2\% \pm 0.2\%$  in the upper 20 cm; SMB: average  $4\% \pm$

$0.2\%$  in the upper 20 cm) in the depocenter sediments than at the periphery (SBB: avg.  $2.5\% \pm 0.1\%$  to  $2.7\% \pm 0.1\%$ ; SMB: avg.  $1.2\% \pm 0.9\%$  to  $3\% \pm 0.9\%$ ).  $\text{C}_{\text{org}}:\text{N}$  ratios range between  $7.9 \pm 0.4$  (SBB-590) and  $9.3 \pm 1$  (SMB-900), and display variable values for SMB-765 from the SMB flank ( $7.2 \pm 2$ ).

The stable carbon isotopic composition of TOC is fairly constant down-core in both of the cores from SBB flanks, with  $\delta^{13}\text{C}$  values between  $-21.5$  and  $-22.5\%$  (Figs. 2 and 3). At the SBB depocenter, TOC  $\delta^{13}\text{C}$  values are slightly less negative and also more variable than in the sediments deposited on the basin flanks. More negative and variable  $\delta^{13}\text{C}$  values ( $-22\%$  to  $-23.5\%$ ) are observed in sediments from SMB, again with a tendency to slightly higher values in near-surface depocenter samples. The depocenter core SMB-900 shows an abrupt change in bulk sediment parameters between core depths of 22–24 cm and 24–26 cm, where TOC and carbonate contents decrease sharply and  $\delta^{13}\text{C}$  values of TOC become more depleted by approximately  $1\%$  (Fig. 3).

**Unsupported  $^{210}\text{Pb}$  stratigraphy**—In all cores, an almost linear decrease of  $\ln^{210}\text{Pb}_{\text{xs}}$  with core depth is observed,

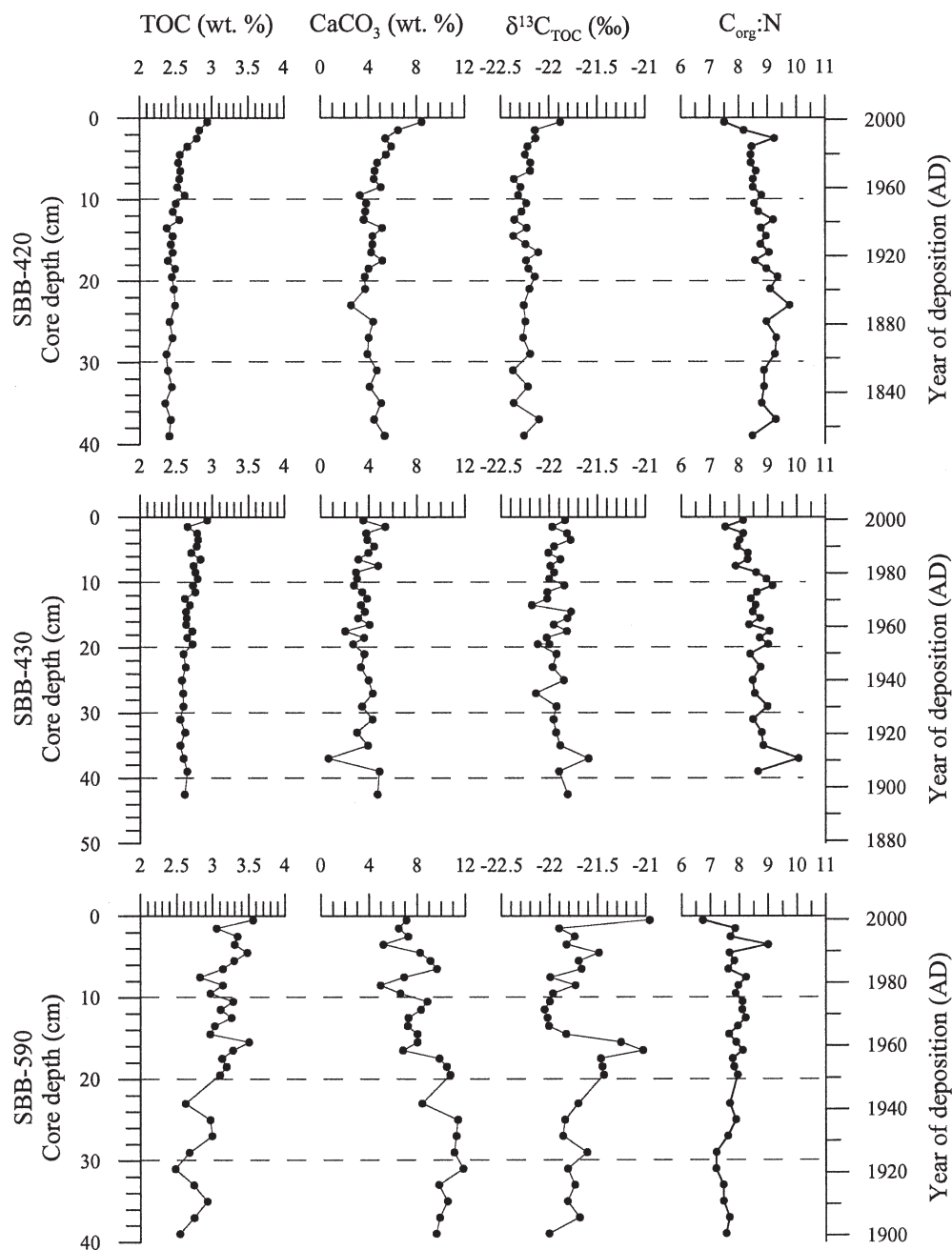


Fig. 2. Bulk sediment properties of cores from Santa Barbara Basin. SBB-590 (bottom panels) was taken at the depocenter.

including the cores from the basin flanks, suggesting the absence of bioturbation and of a homogenized mixed layer. Sedimentation rates on the order of 0.2 to 0.4 cm yr<sup>-1</sup> were calculated for SBB, whereas calculated sedimentation rates in SMB were lower (0.04 to 0.06 cm yr<sup>-1</sup>). These values agree well with published data (Table 1).

*Δ<sup>14</sup>C values of foraminifera, alkenones, and TOC*—Radiocarbon measurements revealed a characteristic age relationship between foraminifera, alkenones, and TOC in all of the cores from the California Borderland Basins (Table 2). Where present, foraminifera are the youngest

and most enriched in radiocarbon of these three sediment constituents, whereas TOC is the oldest (most <sup>14</sup>C depleted). Alkenones are intermediate in age, and replicate analyses generally agreed within 2σ errors. Organic matter samples (i.e., TOC and alkenones) from the depocenters were generally enriched in radiocarbon compared with the flank samples from the respective basin (Fig. 4). Core-top foraminifera, in contrast, have similar radiocarbon signatures both in flank and depocenter sediment environments. Prebomb foraminiferal radiocarbon ages of flank samples from SBB could not be obtained because of the paucity of planktic foraminifera.

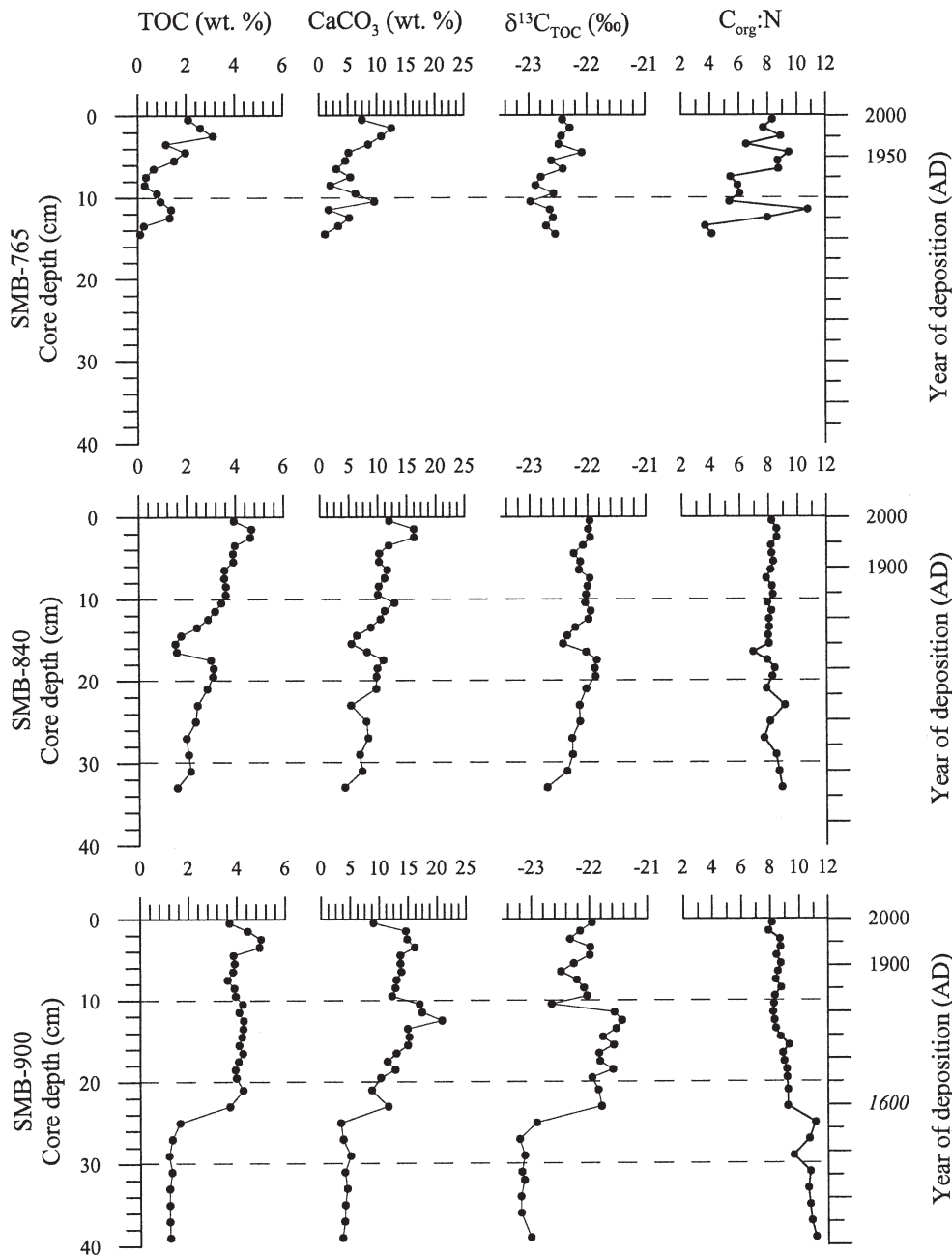


Fig. 3. Bulk sediment properties of cores from Santa Monica Basin. SMB-900 (bottom panels) was taken at the depocenter.

*Isotopic compositions of fatty acids*—FAs have very heterogeneous radiocarbon and stable carbon isotopic signatures (Table 3, Figs. 5–7). Although some of the short-chain ( $C_{14}$ ,  $C_{16}$ , and  $C_{18}$ ) FAs are similarly enriched in  $^{14}C$  in core-top samples as foraminifera, long-chain ( $>C_{22}$ ) FAs tend to be more depleted. In the prebomb samples,  $\Delta^{14}C$  of short-chain FAs tend to be more similar to that of long-chain FAs than to that of foraminifera. In addition, FA radiocarbon levels are less variable in SMB depocenter sediments than on the basin's flanks.

The FA abundance distribution is typically bimodal (Fig. 7), where  $C_{16}$  is the most abundant homologue in all

samples except for the prebomb samples from SMB-900 and SMB-840. Of the long-chain homologues,  $C_{24}$  FA and  $C_{26}$  FA dominate. Short-chain FAs are less abundant in prebomb sediments than at the core tops. Long-chain FAs, in contrast, contribute a larger proportion to total FA in prebomb samples than in core tops.

The  $\delta^{13}C$  values of short-chain FAs from SBB and SMB average  $-23.4\text{‰} \pm 1.4\text{‰}$  in core-top and  $-26.9\text{‰} \pm 1.4\text{‰}$  in prebomb samples (Figs. 6, 7).  $\delta^{13}C$  values of long-chain homologues, in contrast, remain relatively constant between core-top ( $-27.0\text{‰} \pm 2.0\text{‰}$ ) and prebomb samples ( $-26.8\text{‰} \pm 1.3\text{‰}$ ). A good correspondence between

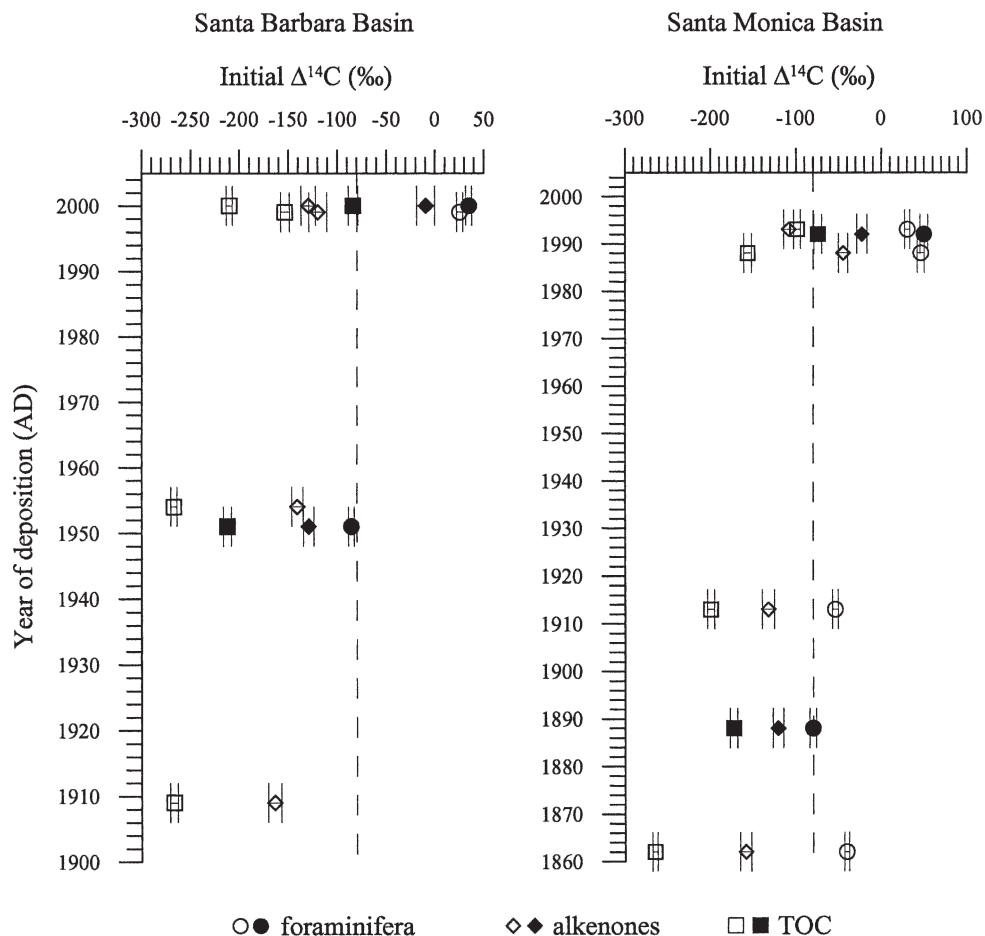


Fig. 4.  $\Delta^{14}\text{C}_{\text{initial}}$  of planktic foraminifera, alkenones, and TOC from flank and depocenter cores from Santa Barbara (SBB) and Santa Monica (SMB) basins. Solid symbols represent data from depocenter sediments (SBB-590 and SMB-900); open symbols are for flank core samples (SBB-430, SBB-420, SMB-765, SMB-840). Error bars are  $1\sigma$  errors. Dashed vertical line indicates prebomb surface water DIC radiocarbon levels, which are assumed to have remained constant between the late 19th century and 1960. Note that alkenones and TOC are more radiocarbon depleted at flank sites than at depocenter sites.

GCirmMS values and those obtained at NOSAMS from combusted purified samples is observed (Table 3).

## Discussion

*Foraminiferal ages*—When discussing radiocarbon age offsets or differences in  $\Delta^{14}\text{C}$  values of co-occurring sediment constituents, planktic foraminifera are generally assumed to most faithfully record the surface water dissolved inorganic carbon (DIC) radiocarbon content, and therefore yield the best estimate of a “depositional age” of the sediment horizon (Pearson et al. 2000; Ohkouchi et al. 2002; Mollenhauer et al. 2003). Indeed, good agreement exists between prebomb foraminiferal radiocarbon levels in our samples from the depocenters ( $-86\text{‰} \pm 3\text{‰}$  and  $-91\text{‰} \pm 4\text{‰}$  in SBB and SMB depocenters, respectively; Table 2, Fig. 4). Values also agree with estimates of prebomb surface ocean radiocarbon levels of DIC ( $\Delta^{14}\text{C}_{\text{DIC}}$ ) which range from  $-63\text{‰} \pm 5\text{‰}$  to  $-88\text{‰} \pm 10\text{‰}$  (Williams et al. 1992; Ingram and Southon

1996). The prebomb foraminiferal samples from the SMB flank sites are slightly enriched in radiocarbon over the corresponding depocenter value, possibly reflecting the occurrence of bioturbation at the flanks, where sediments are not laminated. Burrowing organisms can potentially move younger foraminifera containing bomb radiocarbon downward, resulting in higher radiocarbon levels for mixed versus undisturbed samples. In SMB sediments, this effect would require a downward movement of some foraminiferal tests less than 5 cm.

*Lateral transport and residence times in intermediate reservoirs*—By use of CALIB 5.0.2 (<http://radiocarbon.pa.qub.ac.uk/calib/>), we derived calibrated radiocarbon ages (calendar ages) for alkenones, short-chain ( $\text{C}_{16}$  and  $\text{C}_{18}$ ) fatty acids (FA), and long-chain ( $\text{C}_{24}$ ,  $\text{C}_{26}$ , and  $\text{C}_{28}$ ) fatty acids from prebomb sediments (core-top data were not considered because of the uncertainties in atmospheric and surface water  $\Delta^{14}\text{C}$  levels after above-ground nuclear weapons testing). For this treatment, we assumed  $\text{C}_{16}$  and

Table 3. AMS radiocarbon results given as fraction modern carbon (fMC; Stuiver and Polach 1977) and stable carbon isotope data for fatty acids analyzed as fatty acid methyl esters (FAME). Year of deposition is derived from  $^{210}\text{Pb}$  stratigraphy. fMC data are corrected for blank carbon distribution of  $0.08 \pm 0.02 \mu\text{mol C}$  with a radiocarbon concentration of blank C of 0.25 fMC. Radiocarbon and stable isotope values are corrected for methyl carbon obtained from methanol during derivatization by mass balance (methanol 1: fMC = 0.00227;  $\delta^{13}\text{C} = -47.25\text{‰}$ ; methanol 2: fMC = 0.0105,  $\delta^{13}\text{C} = -39.56\text{‰}$ ; methanol 2 was used for SMB-900, 32–34 cm only).  $\delta^{13}\text{C}$  values were obtained by GCirmMS analysis of samples containing all FAMEs ( $\delta^{13}\text{C}_{\text{GcirmMS}}$ ) and after combustion of single compound samples ( $\delta^{13}\text{C}_{\text{NOSAMS}}$ ) (see text for details).

Sample	Year of deposition (A.D.)	FAME	Sample size ( $\mu\text{mol}$ )	fMC		$\Delta^{14}\text{C}_{\text{initial}} (\text{‰})$	$\delta^{13}\text{C}_{\text{GcirmMS}} (\text{‰ PDB})$	$\delta^{13}\text{C}_{\text{NOSAMS}} (\text{‰ PDB})$
				Corrected	Error			
SBB-420, 0–1 cm	1999	C <sub>14</sub>	6.7	1.007	0.009	1.1	–24.6	–24.3
		C <sub>16</sub>	28.1	1.045	0.004	38.7	–23.9	–24.8
		C <sub>18</sub>	7.5	1.016	0.011	9.9	–23.5	–25.3
		C <sub>24</sub>	7.1	1.001	0.010	–5.2	–26.5	–26.4
		C <sub>26</sub>	6.0	0.931	0.011	–74.6	–26.5	–26.7
		C <sub>28</sub>				–30.0		
SBB-420, 19–20 cm	1909	C <sub>14</sub>					–29.0	
		C <sub>16</sub>	7.6	0.872	0.009	–123.3	–28.3	–28.7
		C <sub>18</sub>					–27.0	
		C <sub>24</sub>	14.5	0.864	0.008	–131.2	–27.3	–27.3
		C <sub>26</sub>					–26.5	
		C <sub>28</sub>				–29.2		
SBB-590, 0–1 cm	2000	C <sub>14</sub>					–23.6	
		C <sub>16</sub>					–22.6	
		C <sub>18</sub>					–24.8	
		C <sub>24</sub>	3.8	0.985	0.017	–20.8	–25.4	–25.4
		C <sub>26</sub>	3.7	0.938	0.017	–67.6	–24.1	–24.3
		C <sub>28</sub>				–29.6		
SBB-590, 19–20 cm	1951	C <sub>14</sub>					–25.1	
		C <sub>16</sub>	8.6	0.931	0.007	–69.1	–25.3	–26.5
		C <sub>18</sub>	2.8	0.836	0.019	–163.9		–26.9
		C <sub>24</sub>					–25.3	
		C <sub>26</sub>	5.8	0.893	0.010	–106.7	–25.5	–25.6
		C <sub>28</sub>	3.5	0.807	0.017	–193.3	–28.7	–29.4
SMB-840, 0–1 cm	1993	C <sub>16</sub>					–20.1	
		C <sub>18</sub>	4.2	1.101	0.012	95.0		–25.7
		C <sub>24</sub>	5.7	0.986	0.019	–19.1	–26.2	–26.2
		C <sub>26</sub>	5.2	1.004	0.011	–1.5	–26.0	–26.2
		C <sub>28</sub>					–28.9	
SMB-840, 5–6 cm	1913	C <sub>14</sub>					–28.1	
		C <sub>16</sub>	11.7	0.877	0.007	–119.5	–26.1	–27.6
		C <sub>18</sub>	4.2	0.911	0.022	–84.8		–26.3
		C <sub>24</sub>	10.9	0.906	0.009	–89.8	–25.7	–26.7
		C <sub>26</sub>	12.8	0.878	0.009	–118.3	–25.9	–25.9
		C <sub>28</sub>	5.3	0.843	0.009	–153.1	–27.5	–27.9
SMB-900, 0–1 cm	1992	C <sub>14</sub>					–23.8	
		C <sub>16</sub>	8.4	1.105	0.010	99.1	–22.9	–24.0
		C <sub>18</sub>					–24.4	
		C <sub>24</sub>	5.4	1.053	0.015	47.7	–25.0	–25.1
		C <sub>26</sub>	3.4	1.011	0.015	5.4	–25.9	–26.1
		C <sub>28</sub>				–29.9		
SMB-900, 6–7 cm	~1890	C <sub>16</sub>	4.6 (?)	0.889	0.015	–103.9	–26.7	–26.9
		C <sub>24</sub>	5.7	0.885	0.010	–108.2	–26.0	–26.4
		C <sub>26</sub>					–26.0	
		C <sub>28</sub>					–28.3	
		C <sub>30</sub>					–30.6	
SMB-900, 32–34 cm		C <sub>14</sub>					–29.2	
		C <sub>16</sub>	5.1	0.785	0.012		–29.0	–28.8
		C <sub>18</sub>					–28.2	
		C <sub>24</sub>	6.8	0.696	0.008		–28.8	–28.7
		C <sub>26</sub>	7.3	0.626	0.008		–28.7	–28.8
		C <sub>28</sub>	6.2	0.621	0.008		–29.9	–29.9
		C <sub>30</sub>				–31.7		

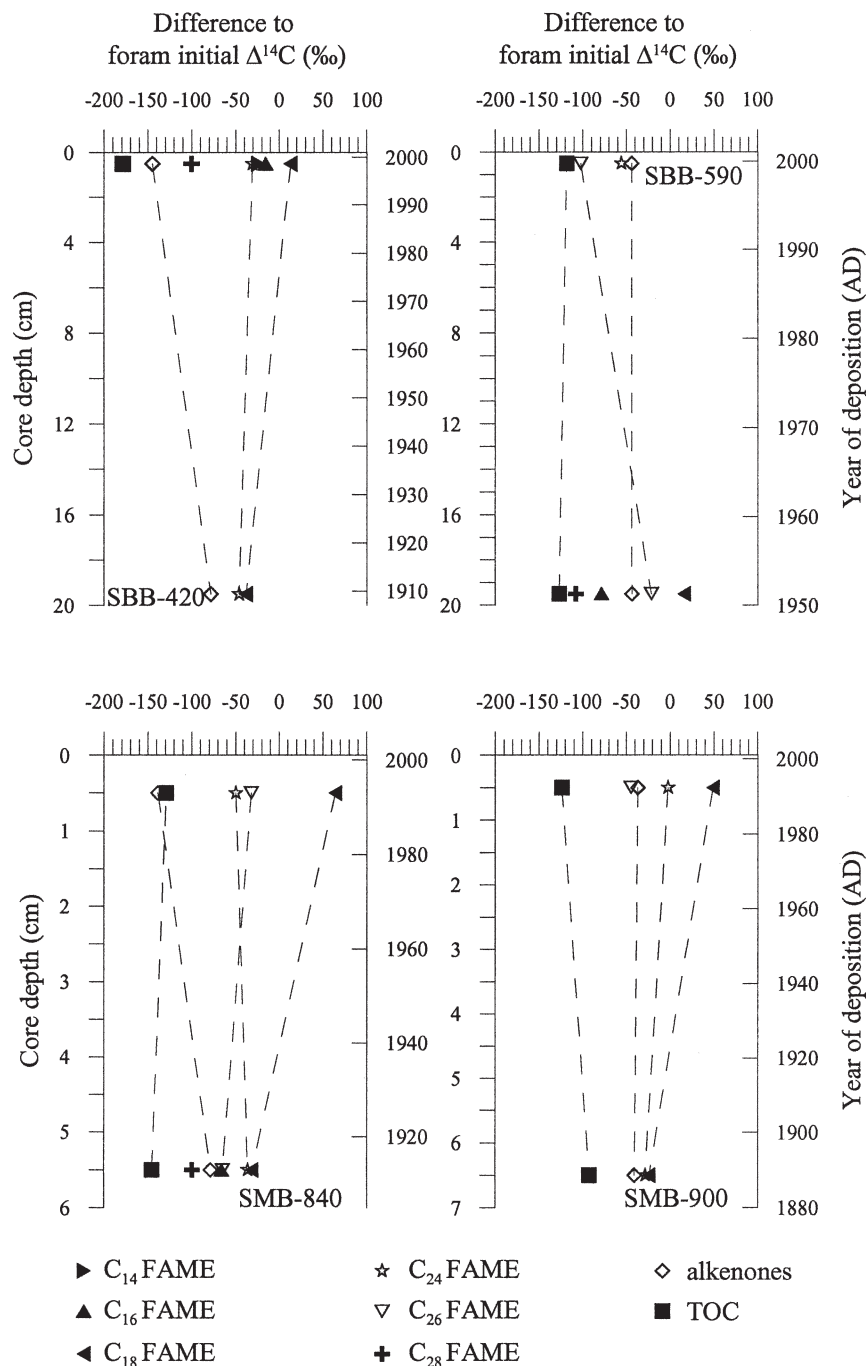


Fig. 5.  $\Delta^{14}\text{C}_{\text{initial}}$  of organic sediment constituents relative to that of planktic foraminifera in samples from flank (left) and depocenter (right) sites from SBB (top) and SMB (bottom). Dashed lines connecting data indicate trends and do not imply interpolation of the values. Where no foraminiferal data were available (SBB-420, 19–20 cm), we assumed the prebomb foraminiferal value of the neighboring core (SBB-590).

$\text{C}_{18}$  FA to be 100% marine, and  $\text{C}_{24}$ ,  $\text{C}_{26}$ , and  $\text{C}_{28}$  to be 100% terrigenous. This source assignment is simplified because there are many different sources for FA, in particular of short-chain FA (cf. Volkman et al. 1998).

In SBB-420, alkenone ages from the prebomb horizon average 810 yr B.P.  $\text{C}_{16}$  FA from the same core depth are

$460 \pm 90$  yr B.P., whereas  $\text{C}_{24}$  FA is older ( $1,110 \pm 70$  yr B.P.). In SBB-590 (depocenter), alkenones are  $480 \pm 60$  yr B.P. old, very similar to  $\text{C}_{16}$  FA in SBB-420. Long-chain FAs in this core are older ( $840 \pm 80$  and  $1,660 \pm 160$  yr B.P. for  $\text{C}_{26}$  and  $\text{C}_{28}$ , respectively). Similar differences in molecular-level radiocarbon ages of short-chain and long-

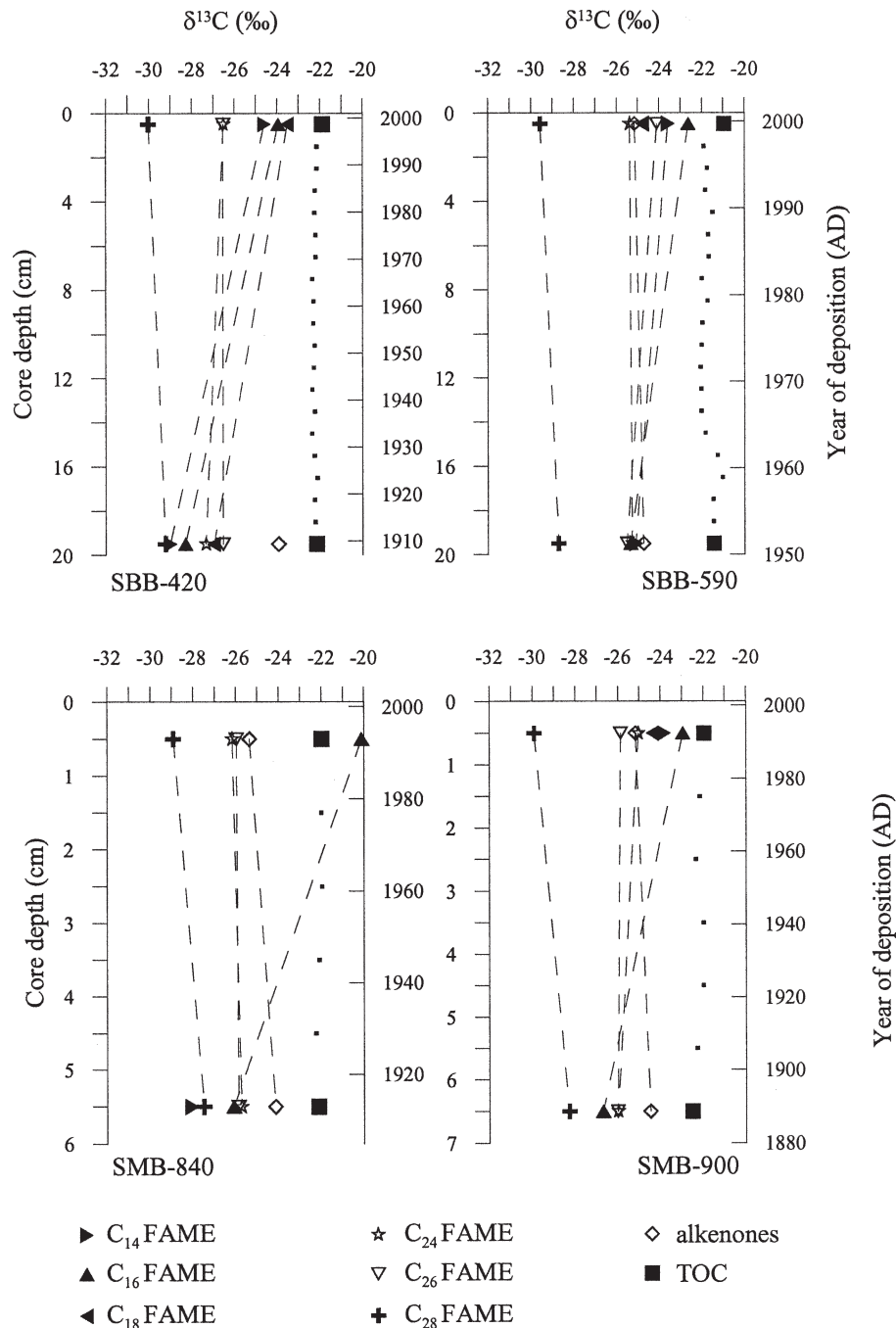


Fig. 6. Stable carbon isotopic composition of alkenones, fatty acids, and TOC in SBB (top) and SMB (bottom). (Left) Flank cores. (Right) Data from depocenter cores. TOC  $\delta^{13}\text{C}$  from intermediate core depths are also shown with small squares at the midpoint of the 1-cm intervals measured. Dashed lines connecting core-top and prebomb data points indicate trends and do not imply interpolation.

chain fatty acids have been observed before, both in aerosols and in marine sediments (Matsumoto et al. 2001; Uchida et al. 2001).

Calibrated radiocarbon ages for the 6–7-cm sediment interval in the SMB depocenter are  $440 \pm 75$  yr B.P. for alkenones (average of three values), and  $340 \pm 140$  and  $880 \pm 90$  yr B.P. for C<sub>16</sub> and C<sub>24</sub> FA, respectively. Similar values can be derived when initial  $\Delta^{14}\text{C}$  values of long-chain FA in

prebomb sediments published by Pearson et al. (2001) are converted to calendar ages ( $\sim 550$  yr and  $\sim 820$  yr for C<sub>24</sub> and C<sub>26</sub> FA, respectively).

All biomarkers in the prebomb intervals are thus older than the  $^{210}\text{Pb}$ -derived sediment age ( $\sim 0$  yr B.P. in SBB and  $\sim 60$  yr B.P. in SMB). Because bioturbation in the depocenter sediments is expected to be minimal, the older C<sub>16</sub> FA and alkenone  $^{14}\text{C}$  ages suggest input of preaged

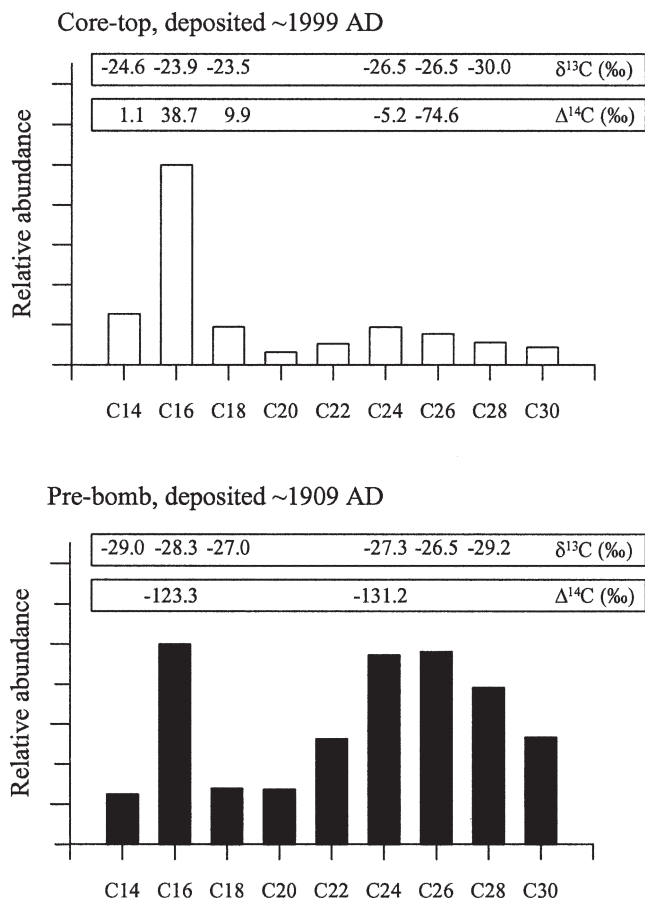


Fig. 7. Abundances of saturated fatty acids (normalized to the abundance of  $\text{C}_{16:0}$ ) in core-top and prebomb samples from SBB-420 and corresponding isotopic compositions ( $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ ) of the individual homologues.

remobilized material to both basins. For marine compounds, this preaging could occur at sites of intermediate storage, and for terrestrial OM, preaging can also take place on land (e.g., in soils). Alternatively, radiocarbon ages of biomarkers older than the depositional age could result from input of fossil material eroded elsewhere. Indeed, in SBB there is evidence for outcrops of sediments up to 500,000 yr old (Kennett et al. 2005), which may be a possible source for preaged organic material.

A large fraction of the sediment accumulating in the California Borderland Basins is likely supplied from the adjacent shelf areas. Mechanisms for sediment remobilization include flood events, storm waves, and tidal currents (Soutar and Crill 1977; Schimmelmann and Tegner 1991; Berger et al. 2004). It is known that much of the terrigenous OM in SMB is nonfossil organic material and does not derive from hydrocarbon seeps or sedimentary rocks (Pearson and Eglinton 2000). Furthermore, 24–60% of extractable lipids in marine sediments from the shelf off California were estimated to consist of preaged terrigenous material (Hwang et al. 2005). Little is known about absolute residence times of particles and associated organic material on the shelf, including marine OM. Schimmelmann and Tegner (1991) detect a lag of 1 or 2 yr between El

Niño-associated phenomena, such as destruction of kelp forest and storm events, and deposition of  $^{13}\text{C}$ -enriched kelp-derived organic matter in laminated sediments in central SBB. The age of storm-wave or tidally remobilized sediment, however, may be much different from the relatively fresh large kelp debris.

Our alkenone data suggest that intermediate storage of marine OM can last up to several centuries. Making the simplified assumption that all alkenones have been supplied to the core sites laterally, we would estimate the residence time on the shelf to be on the order of 380 to 480 yr. This estimate is based on the two calibrated radiocarbon ages of alkenones from prebomb depocenter samples ( $440 \pm 75$  yr B.P. for SMB-900 [mean value], and  $480 \pm 60$  yr B.P. for SBB-590), from which the depositional ages were subtracted. The depocenter samples were taken as the ones with the least potential for bioturbational or diagenetic alteration. Short-chain fatty acids, assumed to be 100% marine derived, were dated as  $340 \pm 140$  yr B.P. ( $\text{C}_{16}$  FA) SMB and  $760 \pm 160$  B.P. ( $\text{C}_{18}$  FA) in SBB prebomb samples, which suggests residence times for these compounds in intermediate storage on the same order of magnitude as for the alkenones.  $\text{C}_{16}$  FA in the SBB prebomb sample was near modern, however, indicating that it contains only a small preaged, allochthonous component. The same is true for a published prebomb  $\text{C}_{16}$  value from SMB (Pearson et al. 2001).

Bomb radiocarbon ( $\Delta^{14}\text{C}_{\text{initial}} > -88\text{‰} \pm 10\text{‰}$  for marine compounds; Tables 2 and 3) is also present in alkenones from the depocenter core-top samples and from one sample from the flank of the SMB (SMB-765). This indicates that a substantial proportion of fresh alkenones is present in the samples, which presumably is mostly supplied directly from the overlying surface waters. Therefore, the average age of preaged laterally supplied alkenones must be greater than 380 to 480 yr. Bomb radiocarbon is also detectable in all short-chain FA in core-top samples, and core-top radiocarbon levels of these compounds are even higher than those of the co-occurring alkenones. The samples therefore likely contain a greater proportion of vertically derived “fresh” short-chain fatty acids than alkenones. The systematically older radiocarbon ages of terrigenous FA, manifested by  $\Delta^{14}\text{C}$  values below the atmospheric  $\Delta^{14}\text{C}$  value of the time of deposition ( $\sim 100\text{‰}$  in the late 1990s; Levin and Kromer 2004) in core-top sediments and lower  $\Delta^{14}\text{C}$  in prebomb samples, imply at first glance that residence times of these compounds in intermediate reservoirs such as shelf sediments and on the continent are much higher than for the marine OM. The radiocarbon age difference between short-chain and long-chain FA, in a simple approach, could thus be interpreted as the amount of preaging occurring in soils and other terrestrial reservoirs. Long-chain FAs likely have limited marine sources (Volkman et al. 1998), so that vertical input of fresh material can be assumed to be minimal. Marine compounds accumulating in depocenters, in contrast, are composed of a mixture of laterally supplied preaged material and vertically supplied fresh OM. The radiocarbon age of long-chain FA deposited in the SBB and SMB depocenters, however, likely reflects the cumulative resi-

dence times of the compounds on land and in intermediate storage on the shelf.

Interestingly, the  $\Delta^{14}\text{C}_{\text{initial}}$  values of prebomb long-chain FA are similar to those of odd-numbered long-chain *n*-alkanes reported by Pearson and Eglinton (2000), but are higher than those of combined even-numbered *n*-alkanes (Pearson and Eglinton 2000) and total extractable lipids from particulate organic carbon in small mountainous rivers draining the adjacent coastal areas (Hwang et al. 2005). We conclude that long-chain fatty acids and odd-numbered long-chain *n*-alkanes are derived from similar sources, namely vascular plant material. These materials are likely transported to the ocean by eolian or riverine processes with minimal preaging, whereas substantial proportions of fossil material (e.g., fossil even numbered *n*-alkanes; Pearson and Eglinton 2000) contribute to the total pool of particulate organic carbon in rivers.

If the lowest  $\Delta^{14}\text{C}_{\text{initial}}$  of terrigenous compounds at each site is regarded as an estimate for the age of laterally supplied biomarkers, estimates for the proportion of autochthonous fresh material and preaged allochthonous material can be made by simple mass balance. These estimates were made for prebomb samples assuming a  $\Delta^{14}\text{C}_{\text{initial}}$  value for fresh, vertically supplied material equal to the prebomb  $\Delta^{14}\text{C}$ -value of DIC ( $= -88\% \pm 10\%$ ) and the  $\Delta^{14}\text{C}_{\text{initial}}$  value for allochthonous material equal to that of the most  $^{14}\text{C}$ -depleted (i.e., "oldest") long-chain FA plus the  $\Delta^{14}\text{C}$  value of DIC. Relative proportions of "fresh" alkenones were estimated at 43–71% and 70–79% in basin flank and depocenter samples, respectively. For  $\text{C}_{16}$  FA, the autochthonous proportions were estimated at around 70% for samples from the basin periphery and >80% for the depocenter.

The differing contributions of "fresh" alkenones to total alkenones in basin depocenter versus flank sediments offer an alternative explanation of the observed differences in alkenone-derived  $\text{U}_{37}^{\text{K}'}$  values for sediments recovered from these regions of the SMB (Gong and Hollander 1999). If the preaged material introduced alkenones produced during a previous period with warmer average sea-surface temperatures, a larger preaged proportion in flank sediments would bias the  $\text{U}_{37}^{\text{K}'}$ -derived temperature estimates toward higher values compared with the depocenter site. Indeed, there is evidence that several centuries ago, average sea-surface temperatures may have been warmer than today (Gong and Hollander 1999). We also observe differences of  $\sim 1\text{--}2^\circ\text{C}$  between sea-surface temperatures reconstructed from flank sediments and depocenter sediments of SBB (Table 2). Alternatively, the preaged laterally supplied portion of alkenones preserved in the sediments could be derived from a site with warmer sea-surface temperatures. This is considered less likely in the California Borderland because the adjacent shelf areas are likely the dominant source of advected particles.

Transport-related radiocarbon age offsets between organic matter and co-occurring foraminifera can only be explained if the transport process affects the organic sediment fraction to a much greater extent that the coarser-grained foraminifera. This can only be the case if resuspension is due to currents within a narrow range of

current velocities (cf. Thomsen and Gust 2000). Alternatively, the composition of the sediments in the source area must be much different than that in the basins, i.e., it must contain less planktic foraminifera. The consistent  $^{14}\text{C}$  depletion in alkenones with respect to co-occurring foraminifera in all of the studied samples has important implications for the reconstruction of high-frequency paleoenvironmental variability based on lipid biomarkers from these laminated sediments. Even though annually deposited laminations can be identified in SBB, samples of alkenones and other lipid biomarkers known to be susceptible to transport may contain contributions from a preaged component.

*Selective degradation*—In all depocenter sediments, alkenones have higher  $^{14}\text{C}$  contents than in corresponding flank sediments, likely reflecting the preservation of a greater proportion of autochthonous material in sediments overlain by oxygen-depleted bottom waters. In accordance with Gong and Hollander (1997), we propose that this is related to the degree to which fresh OM is decomposed upon arrival at the seafloor, rather than to differences in supply between flank and depocenter sites. A scenario invoking selective degradation of autochthonous material as the cause for this implies that the advected portion of alkenones (and other marine biomarkers) would be less susceptible to degradation than the same compounds delivered from the overlying surface waters. This requires protection of the allochthonous material from degradation, and could result from intimate association with mineral grains (e.g., Keil et al. 1994; Mayer 1994; Hedges et al. 2001).

The differences between  $\Delta^{14}\text{C}$  of codeposited compounds of different classes (Fig. 8, Table 3) would be explained in this scenario of selective degradation by their different reaction rates and resulting likelihood to survive lateral transport (Fig. 9). A more labile compound would be less likely to be preserved during intermediate storage and transport, involving several hundred years of possible oxygen exposure, than a more refractory compound. Consequently, the allochthonous component of such a labile compound would be smaller at a given site than of a more refractory compound, assuming uniform initial production of both compounds over the area of interest. This would result in higher  $\Delta^{14}\text{C}$  for the preserved labile compound than for the more refractory compound (Fig. 9).

Preferential in situ degradation of a labile compound could also be expected relative to the same compound introduced by lateral advection. The result would not only be a strong down-core decrease in abundance but also a change in the proportions of compounds derived from allochthonous versus autochthonous inputs. Importantly, these variations would be manifested as an artificially rapid "aging" of the compound down core (Fig. 9).

Isotopic differences between short-chain FAs from core tops and prebomb samples are consistent with this pattern (Figs. 5 and 7). In Fig. 5, we show  $\Delta^{14}\text{C}$  differences between co-occurring foraminifera and biomarkers. This difference is a better measure for the initial radiocarbon content of the biomarkers at the time of deposition than

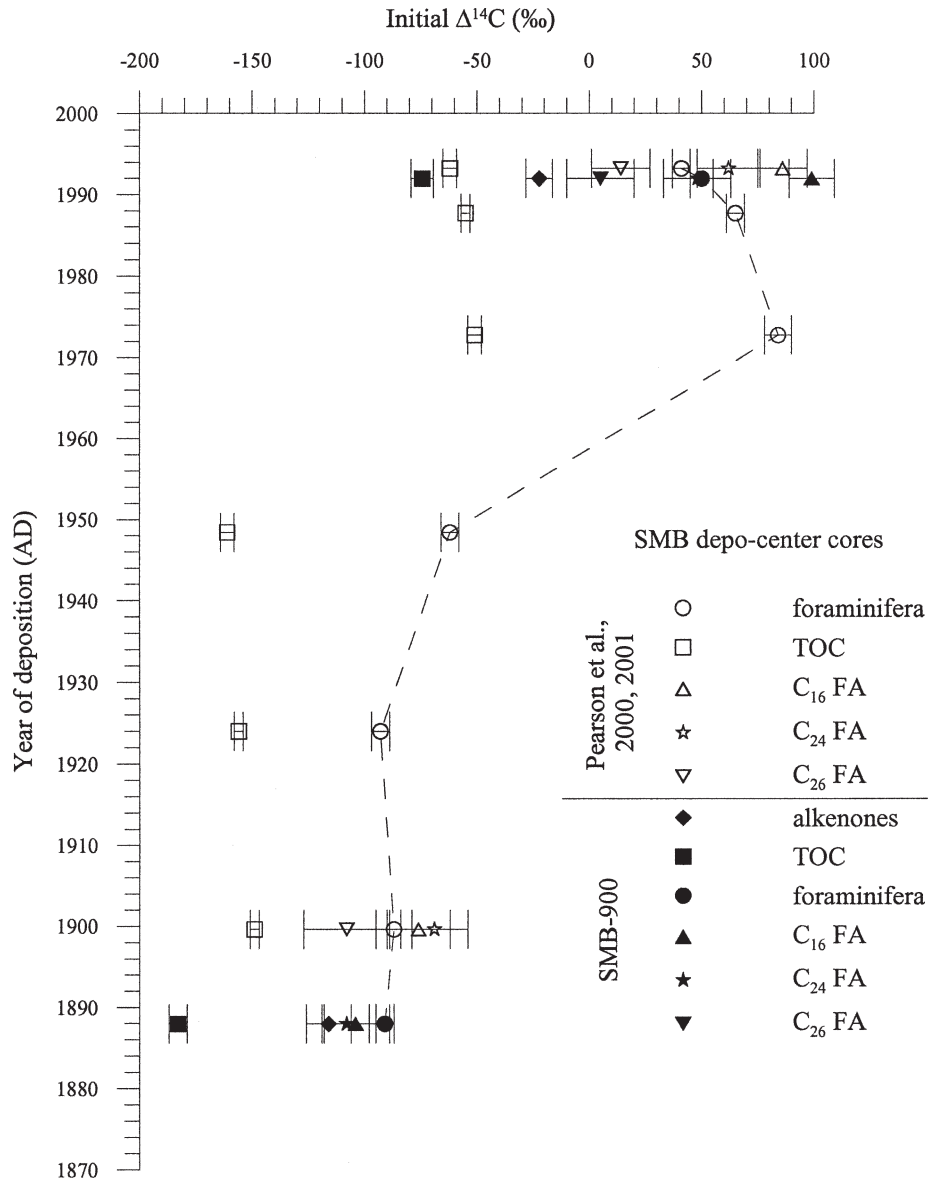


Fig. 8. Compilation of molecular-level radiocarbon data for fatty acids, planktic foraminifera, and TOC from SMB depocenter cores. Open symbols represent data from Pearson et al. (2000, 2001) (core Pulse-32, Table 1); solid symbols are from this study (core SMB-900). Data are provided as  $\Delta^{14}\text{C}_{\text{initial}}$ , which involves correction for decay between deposition and measurement (Table 2). Year of deposition is derived from  $^{210}\text{Pb}$  stratigraphy. Dashed line connecting foraminiferal  $\Delta^{14}\text{C}$  traces the increase in their radiocarbon content related to the "bomb spike." All foraminiferal  $\Delta^{14}\text{C}$  data are obtained from planktic foraminifera.

$\Delta^{14}\text{C}_{\text{initial}}$  values because of the bomb-related changes in reservoir age over the time period covered by the sediment interval. Performing the correction, however, involves the risk of overcorrecting for samples, a main portion of which was formed before 1960, as is the case, for example, for alkenones and terrigenous fatty acids. This overcorrection results in an apparent increase in  $\Delta^{14}\text{C}_{\text{initial}}$  of these compounds between core-top and prebomb samples (Fig. 5).

The occurrence of bomb radiocarbon (i.e.,  $\Delta^{14}\text{C}$  of biomarkers  $> -88\% \pm 10\%$ , prebomb  $\Delta^{14}\text{C}$  of DIC) in core-top sediments also fits the proposed scenario. Whereas

in alkenones, bomb radiocarbon is only present in core-top samples from the depocenters and one additional core top from SMB, short-chain FA contain bomb radiocarbon in all core tops, both from basin flanks and depocenters (Tables 2 and 3). Moreover, short-chain FA radiocarbon values are much higher than alkenone values, implying that the samples contain a much higher fraction of labile autochthonous fatty acids.

Compound-specific stable carbon isotope data likewise agree with the above scenario (Fig. 6). However, an important additional aspect is revealed by differences in  $\delta^{13}\text{C}$  of fatty acids between core-top and prebomb samples.

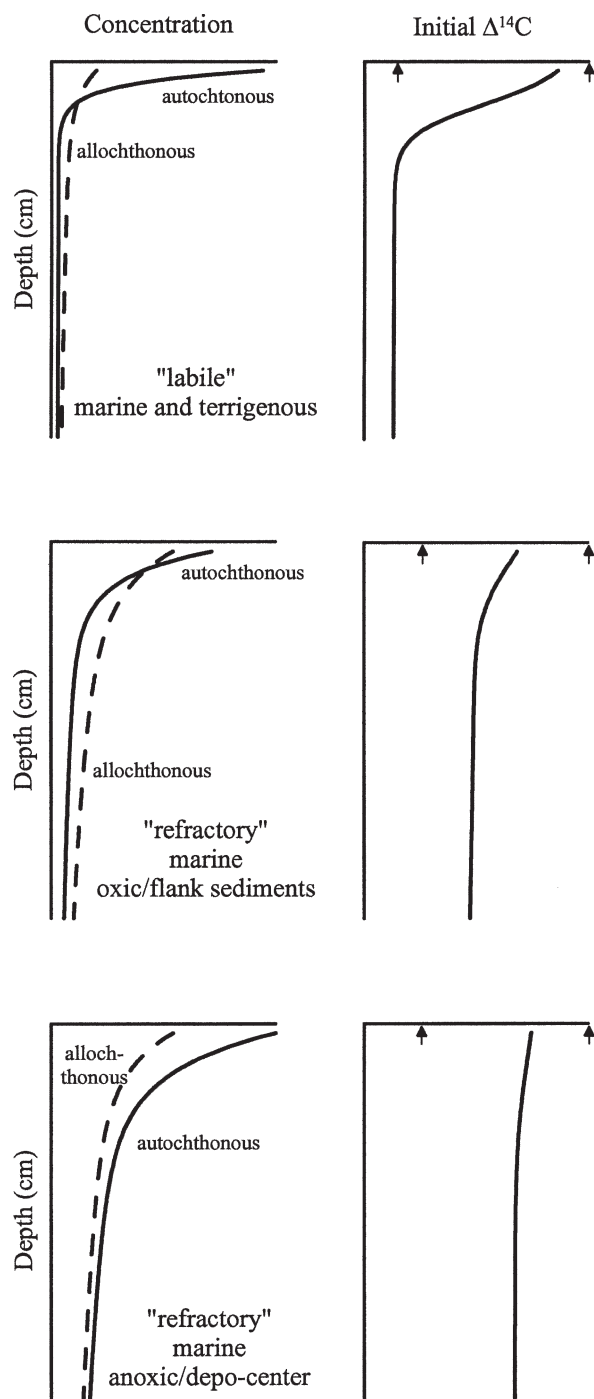


Fig. 9. Conceptual models of selective degradation of organic compounds. (Left) Down-core changes in concentration of a labile compound with marine (autochthonous) and preaged terrestrial (allochthonous) sources (e.g.,  $C_{16}$  FA, top), a more refractory marine compound (e.g., alkenones) in a more oxygenated depositional setting (middle), and in an oxygen-depleted depocenter (bottom). Dashed lines represent preaged allochthonous proportions of the respective biomarker; solid lines represent the autochthonous, fresh biomarkers. (Right) Preserved  $\Delta^{14}C_{\text{initial}}$  that would be measured, resulting from mixing of the preaged and fresh proportions; upward-pointing arrows depict approximate  $\Delta^{14}C$  values of the two end members.

Short-chain FA in core tops are relatively enriched in  $^{13}C$  ( $-20$  to  $-24\%$ ), but are more depleted in the prebomb samples (values of approximately  $-22.5$  to  $-30\%$ ). Long-chain fatty acids are more  $^{13}C$  depleted than the corresponding short-chain homologues in core tops ( $-26$  to  $-30\%$ ) and are practically invariant with depth. Long-chain fatty acids have very limited marine sources (Volkman et al. 1998). Short-chain fatty acids, in contrast, occur ubiquitously and may even be produced in situ by bacteria (Volkman et al. 1998). Assuming that the long-chain fatty acid  $\delta^{13}C$  values are typical of terrestrial FA, the tendency of short-chain fatty acid  $\delta^{13}C$  values to approach these terrestrial values in prebomb samples may therefore reflect selective degradation of the marine,  $^{13}C$ -enriched fraction of short-chain fatty acids.

In order to survive lateral transport to the site of deposition, the terrigenous FA fraction must be protected from degradation. As a result, terrigenous short-chain fatty acids may be better preserved in deeper sediment layers than their marine counterparts and thus constitute a larger fraction of total short-chain fatty acids in prebomb (i.e., more diagenetically processed) sediments. This process would also lead to the apparent "aging" of short-chain fatty acids between core tops and the prebomb horizon, as described above (Figs. 5 and 7). An alternative explanation is that the system is not in steady state. Specifically, the amount of terrigenous FA delivered to the basins could have decreased or other changes in sources (e.g., input of short-chain FA from sea grasses or aquatic plants; Canuel et al., 1997) could have occurred between deposition of the prebomb samples and present. However, the former would be expected to result in lower abundance of long-chain terrigenous FA in core tops than in prebomb sediments as well, which is not in agreement with observed FA profiles (cf. Gong and Hollander 1997; Pearson et al. 2001).

*Continental residence times*— $\Delta^{14}C_{\text{initial}}$  values of long-chain fatty acids, representing integrated storage times on land and in intermediate storage in the ocean, were used to estimate the fraction of preaged, allochthonous compounds present in the sediment. For this exercise, terrigenous compounds were assumed to be delivered to the oceans immediately after production. However, these estimates must be considered minimum values for the proportion of allochthonous material because some temporary storage of allochthonous compounds on land is likely. For example, aerosol studies have shown that plant wax-derived compounds such as long-chain fatty acids can be preaged even when compounds are rapidly transported to distal locations (Matsumoto et al. 2001; Eglinton et al. 2002), and continental residence times can be longer than 10,000 yr for riverine transport (Drenzek et al. 2007). Furthermore, this approach requires the assumption of concurrent transport of terrigenous and marine organic matter in the oceans. Considering the evidence for differential transport of terrigenous organic matter from different sources (Goñi et al. 1998), this assumption must be regarded a simplification, even though the small size of our study area allows us to assume comparable inputs to the individual sites. Therefore, we attempt to reconstruct continental residence times from

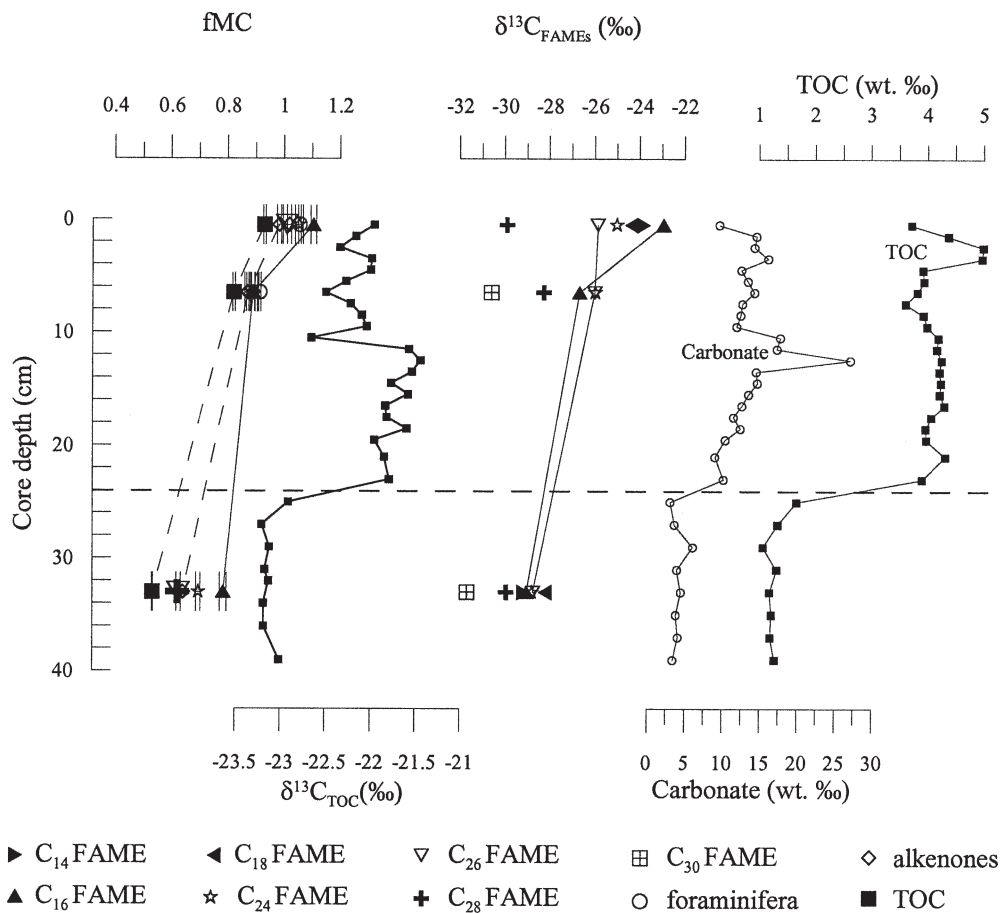


Fig. 10. Summary of all available sediment data from the Santa Monica Basin depocenter (SMB-900), including compound-specific radiocarbon and stable carbon isotope data from before the oxic–suboxic transition at approximately 350 to 400 yr B.P. Data are shown on a core-depth axis rather than versus time of deposition. This is because the oxic–anoxic transition likely involved a change in sedimentation rate. Extrapolation of the <sup>210</sup>Pb-derived age model is therefore not feasible. As a result, radiocarbon data could not be decay corrected and are therefore shown as fraction modern carbon (fMC), where fMC of 1950 = 1. The dashed horizontal line indicates the oxic–anoxic transition.

the integrated signal by comparison of calibrated radiocarbon ages of alkenones and long-chain FA.

By use of data from the SBB depocenter, the continental residence times of C<sub>26</sub> FA calculated by subtracting the calibrated alkenone age from the calibrated FA age, is 380 ± 190 yr. C<sub>28</sub> FA is more <sup>14</sup>C-depleted than C<sub>26</sub> FA, corresponding to a longer continental residence time of 1,200 ± 250 yr. This difference may reflect a greater recalcitrance of C<sub>28</sub> FA than the shorter homologue (*see* discussion above). The two compounds may also derive from different sources and be supplied by different pathways.

Results for SMB sediments are more variable. In prebomb sediments, continental residence times for C<sub>26</sub> FA are calculated as 440 ± 170 yr (SMB-840, 5–6 cm), and 1,000 ± 410 yr (SMB-900, 32–34 cm, below the oxic–anoxic transition zone). Continental residence time of C<sub>28</sub> FA was calculated as 750 ± 170 yr (SMB-840, 5–6 cm) and 1,090 ± 320 yr (SMB-900, 32–34 cm), similar to values from SBB. Previous radiocarbon measurements of C<sub>26</sub> FA from the SMB depocenter are identical within errors to our

core-top data, and in the prebomb horizon, the C<sub>26</sub> FA conventional radiocarbon age was older than corresponding foraminifera (Pearson et al. 2001).

Generally speaking, the calculations indicate that in the California Borderland area, long-chain fatty acids have an average continental residence time on the order of 360–1,200 yr. This is longer than the decadal continental residence time estimated from plant-wax *n*-alkane data (Pearson and Eglinton 2000), even though the measured Δ<sup>14</sup>C values are similar. Our estimate is much shorter than implied by the age of extractable lipids in riverine particulate OM delivered to the California Borderland basins, which were on the order of 15,000 yr (Komada et al. 2005). However, this old organic material at least partly reflects supply of fossil OM derived from ancient sedimentary rocks.

*Timescales of degradation*—The process of selective degradation is not a new concept and has been discussed extensively in the literature (e.g., Cranwell 1981; Sun and Wakeham 1994; Canuel and Martens 1996). Although

superior preservation of terrigenous organic biomarkers over their marine counterparts is well documented (e.g., Prahl et al. 2003), the effect of selective degradation on radiocarbon ages has not been previously considered. Our data reveal that selective degradation of labile short-chain fatty acids and other compounds in sediments occurs within decades, and that this imparts shifts in the age distribution of OM observed at the molecular level. Quantitative estimates of the amount of remineralized carbon cannot be made on the basis of our data. Higher resolution quantitative studies, ideally performed in concert with isotopic analyses of carbon pools in sediment pore waters, are necessary for this purpose.

One important implication of these results is that both chemical stability and physical protection are important factors determining the preservation of organic compounds in the sedimentary record (Goñi et al. 1998). For mixed-source compounds (e.g.,  $C_{16}$  FA for terrestrial versus marine sources, or advected versus autochthonous sources), this may result in selective preservation of one signature over another.

*Oxic-suboxic transition in SMB*—Down-core bulk sediment parameters for SMB-900 clearly reflect a dramatic change in the depositional regime in central SMB at approximately A.D. 1600 (corresponding to ~24 cm, Fig. 10). This abrupt change in sediment composition has previously been observed in cores from the SMB depocenter and is attributed to a transition from oxic to suboxic conditions at ~350 to 400 yr B.P. (e.g., Gorsline 1992; Christensen et al. 1994). Our data agree very well with the data obtained from a nearby core published by Masiello and Druffel (2003), who report almost identical isotopic values and transition depths.

All studied fatty acids from below the transition are further depleted in  $^{13}C$  with respect to the prebomb sample at 6–7 cm (A.D. ~1890) core depth. This is in agreement with our model of selective degradation. Studies in lake sediments and peats have shown that free fatty acids are rapidly decomposed within several years to a few decades (Stefanova and Disnar 2000; Disnar et al. 2005). These authors have found increasing concentrations of slowly accumulating fatty acids from microbial activity, which, however, were only extractable from sediments after acid and base treatment. Therefore, we do not expect to see a large contribution of this pool of bound FA in our samples. The larger range of radiocarbon levels in fatty acids from the pre-A.D. 1600 section than in the A.D. ~1890 sample (Fig. 10) suggests, however, that this fatty acid fraction may contain some recently produced fatty acids.

Our study of California Borderland basin sediments has revealed several important influences on the composition and radiocarbon age of lipid biomarkers accumulating in marine sediments. Advection of preaged material, together with preferential degradation of freshly produced OM, most strongly influence the radiocarbon age of preserved lipids. These findings have important implications for the use of molecular proxies for the reconstruction of paleoenvironmental conditions.

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