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Variability in Radiocarbon Ages of Individual Organic Compounds from Marine Sediments

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Organic carbon (OC) from multiple sources can be delivered contemporaneously to aquatic sediments. The influence of different OC inputs on carbon-14–based sediment chronologies is illustrated in the carbon-14 ages of purified, source-specific (biomarker) organic compounds from near-surface sediments underlying two contrasting marine systems, the Black Sea and the Arabian Sea. In the Black Sea, isotopic heterogeneity of n-alkanes indicated that OC was contributed from both fossil and contemporary sources. Compounds reflecting different source inputs to the Arabian Sea exhibit a 10,000-year range in conventional carbon-14 ages. Radiocarbon measurements of biomarkers of marine photoautotrophy enable sediment chronologies to be constructed independent of detrital OC influences.

Molecular-level studies of organic compounds in marine sediments can provide a wealth of information on the carbon cycle in past and present-day oceans as well as information on the depositional setting and origin of organic matter. Of greatest utility are lipid biomarkers that are specific to individual or a restricted range of organisms and that are sufficiently refractory to be preserved in sediments. Three characteristic features of individual organic compounds are currently exploited by biogeochemists: precise molecular structure, absolute or relative abundance, and stable carbon isotopic composition. A fourth feature, the radiocarbon content, has been added to the list (1). The ^{14}C content provides a means to evaluate the source and fate of natural and anthropogenic organic compounds in the biogeosphere.

Organic materials from various sources and with different ages are deposited concurrently in marine sediments. This is particularly the case near continents where fresh vascular plant debris, soil organic matter, and OC eroded from sedimentary rocks may be deposited together with autochthonous biomass synthesized in the water column. The construction of carbon budgets and sediment chronologies based on ^{14}C measurements of total organic carbon (TOC) depends on being able to accurately quantify these inputs. The ages of specific OC inputs and their influence on TOC ^{14}C ages have remained elusive. Measurements of different compound classes in sediments have indicated that ^{14}C contents are heterogeneous (2), but it is only at the biomarker level that these variations are fully expressed and can be attributed to specific inputs.

Here we present an assessment of radiocarbon ages measured in individual biomarkers from two contrasting marine sedimentary systems. The Black Sea is a stratified anoxic marine basin, and the Arabian Sea is a highly productive system supported by intense seasonal upwelling. Organic carbon–rich sediments accumulating in both seas are strongly influenced by terrigenous inputs. Numerous large rivers drain into the western Black Sea and affect the hydrography and geochemistry of this system (3), whereas eolian dust associated with seasonal monsoons is the primary mode of supply of continental OC to the Arabian Sea (4).

In the Black Sea, we studied laminated OC-rich (TOC, 5.5%) sediments at a depth of 4 to 7 cm recovered by a Mk-III box corer (BC4, station 2; 42°51'N, 31°57'E, at a water depth of 2129 m) during leg 134-9 of the 1988 R/V Knorr expedition. In the Arabian Sea, we studied a sediment sample (box core 6BC, depth of 2 to 4 cm; TOC, 6.7%) obtained from the Oman upwelling region in the Arabian Sea (17°48.7'N, 57°30.3'E, at a water depth of 747 m) during leg TN041 of the R/V T.G. Thompson expedition in 1994. We measured the natural ^{14}C content of specific biomarker compounds chosen to reflect both autochthonous and allochthonous inputs (5) in order to evaluate the magnitude and source of age variation in these components of sedimentary organic matter.

We selected a series of long chain (C_{37-39}) alkenes (compounds i in Table 1), the dominant unsaturated hydrocarbons in the Black Sea lipid extract, for radiocarbon dating as biomarkers of marine photoautotrophy. These compounds are derived from prymnesiophyte algae, such as the coccolithophorid Emiliania huxleyi, a major phytoplankter and important contributor to sinking particulate matter in the contemporary Black Sea (6). An autochthonous origin for these compounds is supported by their δ^{13}C values (Table 1), which are consistent with values for lipids from marine phytoplankton (7). The similarity in both ^{13}C values and the conventional ^{14}C ages (8) (Table 1) between the alkenes [average δ^{13}C = −25.5 per mil; 950 years before the present (B.P.), respectively] and TOC (δ^{13}C = −24.2 per mil; 880 years B.P.) suggests that modern photoautotrophic biomass is a major component of the bulk OC in these sediments. The similarity in ^{14}C ages between prymnesiophyte alkenes and TOC also suggests that, contrary to previous assumptions (9), older detrital OC inputs have a minimal influence on the ^{14}C$_{TOC}$ age of late Holocene Black Sea sediments. Conversion of conventional radiocarbon ages to reservoir-corrected ages for marine carbon re-

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quires that the reservoir age be accounted for before calibration against tree-ring records of atmospheric ^{14}C abundance (10). The reservoir age describes the difference in ^{14}C activity between atmospheric CO_2 and surface-dissolved inorganic carbon (DIC) in marine systems resulting from the mixing of older waters from depth into the surface layer of the ocean. For a reservoir correction of 400 years (9), the alkenes yield a revised ^{14}C age for the depth interval of 4 to 7 cm of 550 years B.P. and a calibrated (calendar) age of ~1425 A.D., consistent with published ^{210}Pb and ^{14}C profiles from abyssal Black Sea sediment cores. This age implies that sedimentation rates were 10 to 20 cm per thousand years during the late Holocene (9, 11).

We assessed directly the allochthonous OC inputs from ^{14}C measurements of individual C_{29} and C_{31} n-alkanes (compounds v and vi, respectively) (Fig. 1A). The chain length distribution, odd over even carbon number predominance (OEP), and $\delta^{13}C$ compositions (Table 1) of these hydrocarbons are highly characteristic of leaf wax inputs from C_3 vascular (land) plants (plants in which the first product of photosynthesis is a three-carbon acid) (12). The young conventional ^{14}C ages for the C_{29} and C_{31} homologs relative to bulk OC (Fig. 2A) demonstrate that corrections for detrital contributions to Black Sea sediments should not necessarily invoke older OC inputs. Indeed, accounting for the reservoir age correction for the prymnesiophyte alkenes (vascular plants fix atmospheric CO_2 directly, so their ^{14}C compositions are not subject to any reservoir correction), we find that the n-C_{29} and n-C_{31} alkanes are similar in calendar age to the marine phytoplanktonic biomarkers. Taken together, these data indicate that relatively fresh terrestrial (land plant) debris is deposited with autochthonous OC of similar age in Black Sea sediments.

In contrast, a suite of shorter chain (C_{23} to C_{27}) n-alkanes (compounds ii through iv) as well as the total saturated hydrocarbon (HC) fraction exhibit significantly older ^{14}C ages than either the vascular plant n-alkanes or TOC (Fig. 2A and Table 1). Given the similarity in $\delta^{13}C$ values to those of the longer chain alkanes, an independent source for the shorter chain n-alkanes seems unlikely. Instead, we infer that fossil hydrocarbons partly contribute to the lower molecular weight homologs. Assuming that there was simple mixing of two end members, we can substitute $\Delta^{14}C$ values (8) (Table 1) into an isotopic mass balance (1) to estimate the proportion of fossil hydrocar-

bon required to produce the observed radiocarbon values. For a ^{14}C-free signature ($\Delta^{14}C = -1000$ per mil) for the fossil component and -66 per mil for a fresh higher plant component (n-C_{31} alkane, Table 1), the measured $\Delta^{14}C$ value for the C_{23} n-alkane (-153 per mil) would correspond to 9% fossil n-alkane. Similarly, given the $\Delta^{14}C$ value of the saturated HC fraction (-155 per mil), fossil hydrocarbons likely represent a small but significant component of this fraction. This minor contribution would have little influence on the carbon number distribution or $\delta^{13}C$ values but is clearly revealed by ^{14}C analysis. Thermogenic hydrocarbons have been detected (13) in suspended particles from the Black Sea on the basis of a low OEP n-alkane distribution dominated by lower carbon number homologs (C_{23} to C_{27}). If a similar input was responsible for the fossil hydrocarbons we observed, the C_{23} and C_{25} n-alkanes would be most strongly influenced by the fossil sources.

Because abyssal Black Sea sediments are finely laminated (nonbioturbated) and the depth interval we studied is believed to predate significant human use of fossil fuels (pre-1880), we conclude that these hydrocarbons entered sediments by natural processes such as erosion of petroleum-bearing sediments (14) or seepage from depth (15).

We selected two sterenes (compounds e and f) as generic markers of marine primary productivity from the Arabian Sea sediment sample because sterols, their precursor natural products (16), are biosynthesized by a wide range of phytoplankton and some zooplankton. Conventional ^{14}C ages of these compounds (mean = 680 years B.P.) are significantly younger than the TOC age (890 years B.P.). Consequently, in contrast to the Black Sea, the offset between sterene and TOC conventional ^{14}C ages likely reflects contributions of older OC to the sediment. This age discrepancy is amplified further when

Table 1. Isotopic composition of bulk fractions and isolated compounds. The $\delta^{13}C$ values were determined by irm-GC-MS (5), except when noted, and were calculated relative to PDB. The ^{14}C age is the conventional radiocarbon age (8, 10). Prym., prymnesiophytes; Vas., vascular (higher) plant; Fos., fossil carbon; Diat., diatoms; Phyt., phytoplankton; Bac., bacteria; ID, compound identification; n.d., not determined ($\delta^{13}C$ assumed as -25 per mil in these instances).

Compound or fraction	Inferred source	ID	$\delta^{13}C$ (per mil)	$\Delta^{14}C$ (per mil)	^{14}C age (years B.P.)
Black Sea core BC4, 4 to 7 cm					
TOC	–	–	−24.2*	−108 ± 3	880 ± 25
TLE†	–	–	n.d.	−113 ± 7	925 ± 65
Saturated HC	–	–	n.d.	−155 ± 15	1,310 ± 150
Autochthonous biomarkers					
C_{37-39} alkenes‡	Prym.	i	−25.5	−116 ± 10	950 ± 100
Allochthonous biomarkers					
n-C_{23} alkane	Vas./Fos.	ii	−30.7	−153 ± 13	1,290 ± 130
n-C_{25} alkane	Vas./Fos.	iii	−29.5	−158 ± 17	1,340 ± 170
n-C_{27} alkane§	Vas./Fos.	iv	−31.1	−136 ± 9	1,130 ± 90
n-C_{29} alkane	Vas.	v	−32.2	−78 ± 9	610 ± 90
n-C_{31} alkane	Vas.	vi	−30.2	−66 ± 11	500 ± 100
Arabian Sea core 6BC, 2 to 4 cm					
TOC	–	–	−21.7*	−109 ± 3	890 ± 30
TLE	–	–	n.d.	−100 ± 6	800 ± 60
Autochthonous biomarkers					
$C_{25:4}$ HBI alkene	Diat.	a	−23.2	−40 ± 15	270 ± 130
$C_{25:3}$ HBI alkene	Diat.	b	−20.2	−47 ± 6	350 ± 50
$C_{25:2}$ HBI alkene	Diat.	c	−19.9	−33 ± 8	225 ± 70
$C_{30:4}$ HBI alkene	Diat.	d	−37.1	−73 ± 8	570 ± 70
C_{30} sterene	Phyt.	e	−18.5	−81 ± 7	630 ± 70
Cholest-2-ene	Phyt.	f	−25.0	−92 ± 6	735 ± 55
22,29,30-trisnorhop-17(21)-ene	Bac.	g	−22.3	−139 ± 11	1,170 ± 100
Hop-21-ene	Bac.	h	−20.5	−125 ± 13	1,030 ± 110
30-norhop-17(21)-ene	Bac.	i	−22.3	−131 ± 9	1,080 ± 90
C_{30} hopene	Bac.	j	−24.1	−147 ± 9	1,240 ± 90
Hop-22(29)-ene	Bac.	k	−23.9	−120 ± 9	985 ± 85
22,29,30-trisnorhop-13(18)-ene¶	Bac.	l	−23.2	−597 ± 4	7,250 ± 70
Allochthonous biomarkers					
17α,21β-homohopane#	Bac./Fos.	m	−21.9	−608 ± 4	7,480 ± 80
n-C_{23} alkane	Vas./Fos.	n	−26.7	−724 ± 10	10,300 ± 300
n-C_{27} alkane	Vas./Fos.	o	−26.7	−677 ± 6	9,050 ± 160
n-C_{29} alkane	Vas./Fos.	p	−28.0	−594 ± 5	7,200 ± 90

*Determined by irMS.   †Average of two values.   ‡C_{37-39} alkenes were analyzed as a composite sample to maximize yield and because they were insufficiently resolved to be isolated as pure compounds.   §Contains an additional C_{27} hydrocarbon.   ¶Contains a small portion (~10%) of unresolved material.   #Also contains fernene.

a series of highly branched isoprenoid (HBI) alkenes (compounds a through d), characteristic diatom biomarkers (17), are examined (Fig. 2B). The C_{25} HBI alkenes exhibit substantially younger ^{14}C ages (mean = 280 years B.P.) than both the sterenes and TOC. Their ^{14}C compositions would yield present-day ^{14}C ages after a 400-year reservoir correction is applied and are likely the result of downward mixing of surficial material containing bomb radiocarbon (from nuclear weapons testing). This mixing could result from sediment winnowing, a process that has

been suggested to be a dominant control on the composition of Arabian Sea sediments (18). An alternative explanation giving rise to ^{14}C variations in different photoautotrophic biomarkers is heterogeneity in the reservoir age of the DIC pool. The strong seasonal variations in phytoplankton productivity, community structure, and vertical distribution in the Arabian Sea are related to wind-driven (monsoonal) upwelling and mixing of the water column (19). The balance between the upwelling of deep waters (low ^{14}C activity) and the physical invasion or biologi-

cally driven draw-down of atmospheric CO_2 (high ^{14}C activity) into the surface ocean may give rise to spatial and temporal variability in $^{14}C_{DIC}$ (and, consequently, planktonic ^{14}C). Consequently, differences in ^{14}C and ^{13}C composition, such as those between the C_{25} and C_{30} HBI alkenes, may be a function of the ecological characteristics (such as depth of growth) of their photoautotrophic source—the former having been identified in *Haslea* sp. and the latter in *Rhizosolenia* sp. (20). Such discrepancies between ^{14}C ages of phytoplanktonic markers raise the possibility that information on past variations in water column structure may be carried by the isotopic signatures of different photoautotrophic biomarkers and preserved in the sedimentary record.

The hopanoid alkenes (compounds g through l), which were chosen as bacterial biomarkers (21), yielded with one exception (22) conventional ^{14}C ages that are 300 to 400 years older than the sterenes. The structures of the individual compounds measured do not permit categoric assignment of precursor organisms; however, their relatively uniform $\delta^{13}C$ compositions (Table 1) clearly point to a marine origin. Deep-dwelling cyanobacteria could yield older ^{14}C ages as a result of uptake of respired DIC emanating from the O_2-depleted waters underlying the Oman upwelling zone (7), whereas benthic heterotrophic or chemoautotrophic bacteria may consume older carbon associated with bottom waters or sediments (23).

We determined the ^{14}C compositions of selected saturated hopanoid (compound m) and normal (compounds n through p) hydrocarbons to investigate isotopic characteristics of allochthonous sources of OC. In marked contrast to the sterenes and HBI alkenes, these hydrocarbons display
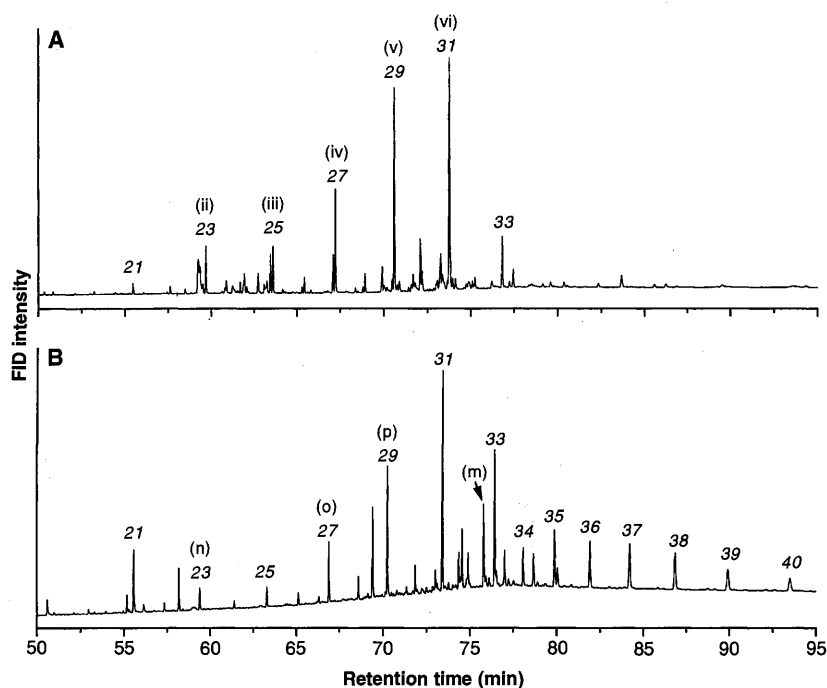
Fig. 1. Partial high-resolution gas chromatograms [with flame ionization detection (FID)] of total saturated hydrocarbon fractions from (**A**) Black Sea core BC4 (4 to 7 cm), and (**B**) Arabian Sea core AS-2 (2 to 4 cm). Numbers in italics indicate carbon chain lengths of n-alkanes. Numbers and letters in parentheses denote compounds isolated for ^{14}C analysis from these fractions (see Table 1).
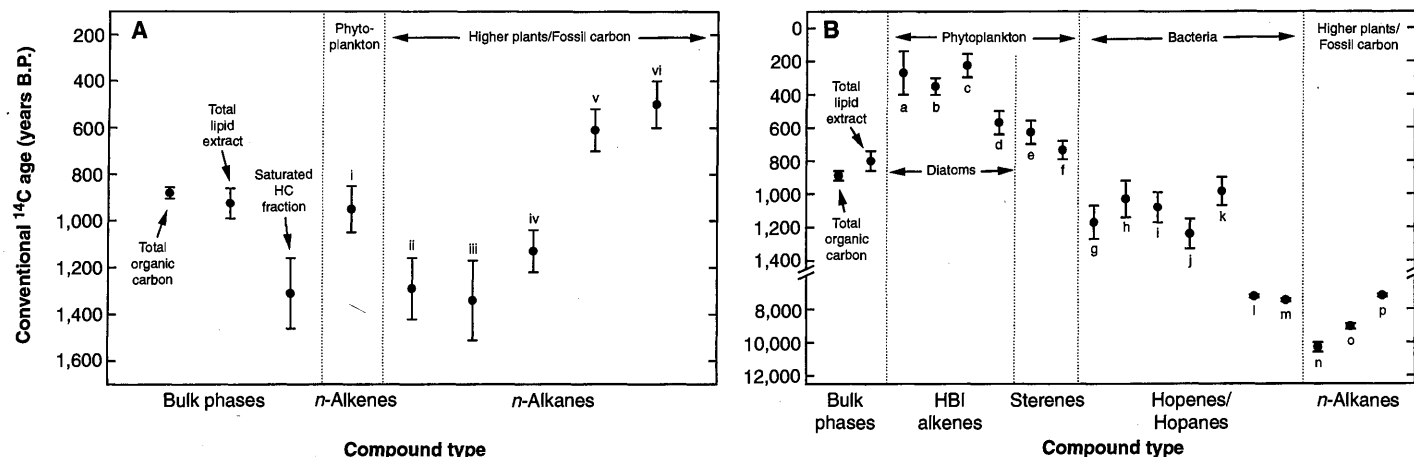
Fig. 2. Plot of conventional ^{14}C ages (determined by AMS) for individual hydrocarbons and bulk fractions: (**A**) Black Sea core BC4, 4 to 7 cm, and (**B**) Arabian Sea core 6BC, 2 to 4 cm. See Table 1 for individual compound identifications. Note break in y axis in (B). Error bars represent uncertainty associated with statistics of the AMS measurement. Overall error is believed to be better than 5% (in $\Delta^{14}C$) (1).