Molecular-level studies of organic
tissues and origin of organic matter.
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Chronologies
Setting and origin of organic matter.
Structure, absolute or relative abundance,
Fourth feature, the radiocarbon content,
Are specific to individual or a restricted
A wealth of information on the carbon
Cycle in past and present-day oceans as
Organic compounds are currently
Lipid biomarkers that
Independent of
Influence on the carbon-14 ages of purified, source-specific
Biomarker) sources can be
MultIPLE
Inputs on carbon-14-based sediment
Chronologies of different source inputs to the Arabian
Carbon-14 ages have remained elusive.
Measurement of total organic carbon
Depend on being able to
Individual fossil and contemporary inputs (5) in order
Evaluate the magnitude and source of age variation in these components of sedimentary
Organic matter.
We selected a series of long chain (C27-39) 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
Prymnesiophyceae 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 813C values (Table 1), which are consistent with values for lipids from
Marine phytoplankton (7). The similarity in both 813C values and the conventional
14C ages (8) (Table 1) between the alkenes and TOC (813C = -25.5 per mil; 950 years before the present (B.P.),
respectively) and TOC (813C = -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 14C ages between
Prymnesiophyceae alkenes and TOC also suggests that, contrary to previous assumptions (9), older detrital OC inputs have a minimal influence on the 14CTOC age of late Holocene Black Sea sediments. Conversion of conventional radiocarbon ages to reservoir-corrected ages for marine carbon re-

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21. We thank the Pew Charitable Trust, the Blandin Foundation, the Huron Mountain Wildlife
Foundation, and NSF for grants EAR 90-04181 and ACS-PRF-27461-ACS. Comments by R. Van der Voo and
Three anonymous reviewers are greatly appreciated.

31 March 1997; accepted 2 June 1997

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 signal radiocarbon 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 14C content provides a means to evaluate the source and fate of natural and anthropogenic organic compounds in the biosphere.

Organic materials from various sources

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quires that the reservoir age be accounted for before calibration against tree-ring records of atmospheric 14C abundance (10). The reservoir age describes the difference in 14C activity between atmospheric CO2 and surface-dissolved inorganic carbon (DIC) in marine systems resulting from the mixing of older waters from deep into the surface layer of the ocean. For a reservoir correction of 400 years (9), the alkaline yields a revised 14C 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 210Pb and 14C 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 14C measurements of individual C29 and C31 n-alkanes (compounds v and vi, respectively) (Fig. 1A). The chain length distribution, odd over even carbon number predominance (OEP), and 813C compositions (Table 1) of these hydrocarbons are highly characteristic of leaf wax inputs from C3 vascular (land) plants (plants in which the first product of photosynthesis is a three-carbon acid) (12). The young conventional 14C ages for the C29 and C31 homologs relative to bulk OC (Fig. 2A) demonstrate corrections that the reservoir correction to Black Sea sediments should not necessarily invoke older OC inputs. Indeed, accounting for the reservoir age correction for the hynesiophyte algae (vascular plants fix atmospheric CO2 directly, so their 14C compositions are not subject to any reservoir correction), we find that the n-C29 and n-C31 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 (C23 to C27) n-alkanes (compounds ii through iv) as well as the total saturated hydrocarbon (HC) fraction exhibit significantly older 14C ages than either the vascular plant n-alkanes or TOC (Fig. 2A and Table 1). Given the similarity in 813C values to those of the longer chain alkane, an independent source for the shorter chain n-alkanes seems unlikely. Indeed, 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 the 14C values (8) (Table 1) into an isotopic mass balance (1) to estimate the proportion of fossil hydrocarbon required to produce the observed radiocarbon values. For a 14C-free signature (Δ14C = -100 per mil) for the fossil component and -66 per mil for a fresh higher plant component (n-C31 alkane, Table 1), we measured the Δ14C value for the C23 n-alkane (-153 per mil) would correspond to 9% fossil n-alkane. Similarly, given the Δ14C 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 813C values but is clearly revealed by 14C 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 (C23 to C27). If a similar input was responsible for the fossil hydrocarbons we observed, the C23 and C25 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 14C ages of these compounds (mean = 680 years B.P.) are significantly younger than the TOC age (990 years B.P.). Consequently, in contrast to the Black Sea, the offset between sterene and TOC conventional 14C ages likely reflects contributions of older OC to the sediment. This age discrepancy is amplified further when

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**Table 1.** Isotopic composition of bulk fractions and isolated compounds. The 813C values were determined by IRMS (5), except when noted, and were calculated relative to PDB. The 14C age is the conventional radiocarbon age (8, 10). Pyrm., prymnesiophytes; Vas., vascular (higher) plant; Fos., fossil carbon; Dist., diatoms; Phyt., phytoplankton; Bac., bacteria; ID, compound identification; n.d., not determined (813C assumed as -26 per mil in these instances).

| Compound or fraction | Inferred source | ID | 813C (per mil) | Δ14C (per mil) | 14C age (years B.P.) |
|----------------------|-----------------|----|---------------|---------------|----------------------|
| **Black Sea core BC4, 4 to 7 cm** | | | | | |
| TOC | | | | | |
| TLE† | | | | | |
| Saturated HC | | | | | |
| Autochthonous biomarkers
| C27-C31 alkane† | Pyrm. | i | -116 ± 10 | 950 ± 100 |
| Allomagnococcal biomarkers
| n-C29 alkane | Vas./Fos. | ii | -131 ± 13 | 1,290 ± 130 |
| n-C31 alkane | Vas./Fos. | iii | -152 ± 17 | 1,340 ± 170 |
| n-C27 alkane | Vas./Fos. | iv | -158 ± 9 | 1,130 ± 90 |
| n-C25 alkane | Vas. | v | -164 ± 9 | 610 ± 90 |
| n-C29 alkane | Vas. | vi | -172 ± 9 | 500 ± 90 |
| **Arabian Sea core 60B, 2 to 4 cm** | | | | | |
| TOC | | | | | |
| TLE | | | | | |
| Autochthonous biomarkers
| C25-C27 HBI alkene | Dist. | a | -23.2 ± 15 | 270 ± 130 |
| C25-C27 HIE alkene | Dist. | b | -20.2 ± 15 | 350 ± 50 |
| C25-C27 HBI alkene | Dist. | c | -20.2 ± 15 | 350 ± 50 |
| C31 sterene | Phyt. | e | -13.6 ± 13 | 550 ± 130 |
| Cholesterol-2-ene | Phyt. | f | -13.6 ± 13 | 550 ± 130 |
| 22,29,30-trinorhop-17(21)-ene | Bac. | g | -22.3 ± 12 | 1,170 ± 100 |
| Hop-21-ene | Bac. | h | -20.5 ± 15 | 1,090 ± 100 |
| 30-norhop-17(21)-ene | Bac. | i | -22.3 ± 12 | 1,090 ± 100 |
| Hop-29-ene | Bac. | j | -24.1 ± 12 | 1,240 ± 90 |
| 22,29,30-trinorhop-18(21)-ene† | Bac. | l | -23.2 ± 12 | 7,250 ± 70 |
| Allomagnococcal biomarkers
| 17α,21β-homohopane | Bac./Fos. | m | -21.9 ± 60 | 4,780 ± 80 |
| n-C29 alkane | Vas./Fos. | n | -26.8 ± 12 | 10,300 ± 300 |
| n-C29 alkane | Vas./Fos. | o | -26.8 ± 12 | 10,300 ± 300 |
| n-C29 alkane | Vas./Fos. | p | -28.0 ± 5 | 7,250 ± 70 |

*Also determined by IMS. †Average of two values. ‡C27-C31 alkanes were analyzed as a composite sample to maximize yield and because they were insufficiently resolved to be isolated as pure compounds. §Contains an additional C29 hydrocarbon. ¶Contains a small portion (~10%) of unresolved material.
a series of highly branched isoprenoid (HBI) alkenes (compounds a through d), characteristic diatom biomarkers (17), are examined (Fig. 2B). The C23 HBI alkenes exhibit substantially younger 14C ages (mean = 280 years B.P.) than both the sterenes and TOC. Their 14C compositions would yield present-day 14C 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 14C 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 14C activity) and the physical invasion or biologically driven draw-down of atmospheric CO2 (high 14C activity) into the surface ocean may give rise to spatial and temporal variability in 14C ages (and, consequently, planktonic 14C). Consequently, differences in 14C and 13C composition, such as those between the C23 and C30 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 14C 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 I), which were chosen as bacterial biomarkers (21), yielded with one exception (22) conventional 14C 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 813C compositions (Table 1) clearly point to a marine origin. Deep-dwelling cyanobacteria could yield older 14C ages as a result of uptake of respired DIC emanating from the O2-depleted waters underlying the Oman upwelling zone (7), whereas benthic heterotrophic or chemosynthetic bacteria may consume older carbon associated with bottom waters or sediments (23).

We determined the 14C 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
much older conventional 14C ages ranging from 7200 to 10,000 years B.P. (Fig. 2B). As for the Black Sea sample, a pronounced OEP for the C32 to C31 n-alkanes indicates that OC from higher plants was supplied to the sediments (Fig. 1B). Plant detritus is likely delivered to this region by eolian processes, primarily the Somali Jet, which entrains dust from the Arabian Peninsula and the Horn of Africa (4). Older ages for the n-alkanes could be expected because the OC in dust plumes from this region are believed to arise from desiccated lacustrine sediments and paleosols formed at times when the climate in eastern Africa was less arid (before ~6000 years B.P.) (24). The hopanoid alkane (compound m) may derive from similar sources (soil or lacustrine bacteria); however, the similarity of its δ13C value to the photoautotrophic biomarkers suggests that is has a marine origin. We suspect that the old 14C ages of the n-alkanes and hopane are a result in part of the presence of fossil OC.

Support for this interpretation is provided by the lack of OEP in a series of n-alkanes extending to C41 (Fig. 1B), indicating the presence of thermogenic hydrocarbons. The lack of an associated unresolved envelope suggests that these fossil hydrocarbons are protected from microbial degradation, possibly through association with mineral matrices (25). The overlap in the n-alkane envelopes from the higher plant and fossil inputs (Fig. 1B) provides an opportunity to estimate the 14C age for the plant wax contribution. For infinite 14C age petrogenic contributions of 30, 40, and 50% (26) to the C31, C32, and C33 n-alkane, respectively, application of a similar mass balance approach to that described above for the Black Sea n-alkanes yields a 14C age of between 4000 and 5000 years B.P. for the land plant component, quite consistent with the timing for the onset of deterioration of climatic conditions in East Africa (24).

In both sediments, the maximal variation in radiocarbon ages observed between compounds exceeds the estimated <300-year age span (based on published sedimentation rates) for either of the intervals sampled. Our results reveal that compounds of the same class and belonging to the same homologous series (Black Sea n-alkanes) can exhibit distinctly different radiocarbon ages. Compounds having similar δ13C values may display significantly different 14C ages (Black Sea n-alkanes) or, conversely, compounds of similar 14C age may have various δ13C values (Arabian Sea HBI alkenes). These molecular isotopic measurements thus illustrate how different sources can affect sedimentary 14C composition.

Differences in 14C age can now be explained in the context of isotopic characteristics of specific source inputs and hence can be used to interpret the biogeochemical processes that govern their provenance in sediments. Two examples of long-standing issues in biogeochemistry that benefit from molecular 14C measurements are the origin of non-zero 14C ages commonly observed for marine surface sediments (27), and the development of refined chronostatigraphies free of interferences due to detrital OC inputs and selective degradation of different organic components. The latter also holds promise for other disciplines where accurate 14C measurements are important (such as archaeology) but may be compromised by the presence of extraneous carbon-containing material.

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24. We thank M. Kashgarian, J. Southon, I. Forder, and L. Osborne for assistance with AMS analyses, J. Primack and J. Hayes for irn-3GC-MS analyses, and D. K. Barlow and J. E. Southon for assistance with AMS samples. This work was supported in part by NSF grants (CCE-94155088; OCE-8010198) and a Woods Hole Oceanographic Institution (WHOI) Independent Study Award. This is WHOI contribution no. 9476.
25. 23 April 1997; accepted 13 June 1997.

www.sciencemag.org — SCIENCE — VOL. 277 — 8 AUGUST 1997