

Geochemistry of Radiocarbon in Organic Materials

Suggested Reading:

Eglinton T.I., Benitez-Nelson B.C., Pearson A., McNichol A.P., Bauer J.E. and Druffel E.R.M. (1997) Variability in radiocarbon ages of individual organic compounds from marine sediments. *Science* **277**, 796-799.

Pearson A., Eglinton T.I. and McNichol A.P. (2000) An organic tracer for surface ocean radiocarbon. *Paleoceanog.* **15**, 541-550.

Wang X.-C., Druffel E.R.M., Griffin S., Lee C. and Kashgarian M. (1998) Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean. *Geochim. Cosmochim. Acta* **62**, 1365-1378.

Raymond P.A. and Bauer J.E. (2001) Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. *Nature* **409**, 497-500.

Blair N.E. *et al.* (2003) The persistence of memory: The fate of ancient sedimentary organic carbon in a modern sedimentary system. *Geochim. Cosmochim. Acta* **67**, 63-73.

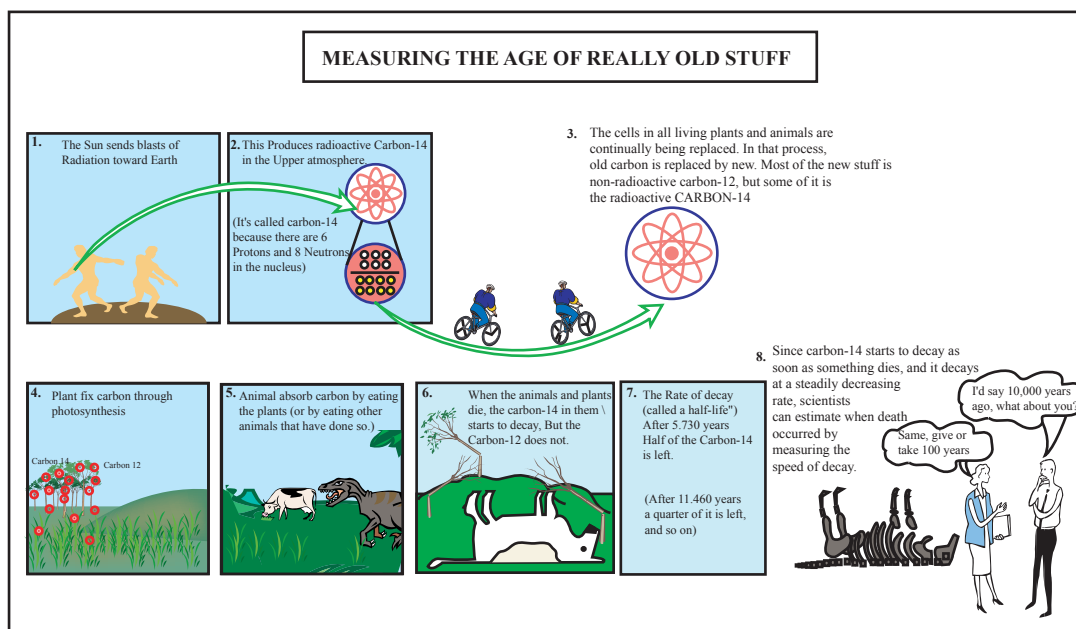
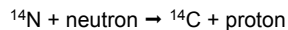


Figure by MIT OCW.

Geochemistry of Radiocarbon in Organic Materials

- *Natural abundance of stable and radio isotopes of carbon*
 - ^{12}C - 99%
 - ^{13}C - 1%
 - ^{14}C - 1 part per trillion (10^{-12}) in modern carbon
- ^{14}C is a cosmogenic nuclide - continually formed in the upper atmosphere (lower stratosphere/upper troposphere) by interaction of neutrons (produced by cosmic rays) and nitrogen atoms.



- After formation, ^{14}C atoms rapidly combine with oxygen to form CO_2 which mixes throughout atmosphere, dissolves in the oceans, and enters the biosphere via photosynthetic carbon fixation.

Geochemistry of Radiocarbon in Organic Materials

- There is a dynamic equilibrium between ^{14}C formation and decay leading to an approximately constant level in the atmosphere.
- Current best estimate for half-life, $T_{1/2}$, of ^{14}C = 5730 yr
- Conventional (Libby) half-life adopted for reporting ^{14}C ages = 5568 yr (3% smaller than true half-life).
- The half-life is related to the meanlife, τ , by:

$$T_{1/2} = (\ln 2)\tau \quad (\text{or } T_{1/2} = 0.693\tau)$$

- Corresponding meanlife, τ , for Libby half-life is 8033yr.
- The radiocarbon age, t , can be determined from:

$$t = -\tau \ln(A/A_0) \quad (\text{or } t = -8033 \ln(A/A_0))$$

- where A is the number of atoms left after time t and A_0 is the initial number of atoms.

Key attribute: 5730 yr half life of ^{14}C is suitable for studying processes and dating carbonaceous materials over 10^2 – 10^3 yr time-scales.

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Methods of ^{14}C measurement

1. Conventional method - Determination of ^{14}C activity of a weighed sample by counting the number of electrons (beta particles) emitted from nucleus per unit time by the decay of ^{14}C .
 - Beta-counting can be performed by samples combusted to CO_2 (gas proportional beta counting) or on samples converted to benzene and measured photometrically after addition of a scintillator (liquid scintillation counting).
 - Sample size requirements: > 1 g C and long counting times (days).
2. Direct measurement of the proportion of ^{14}C atoms (relative to ^{13}C or ^{12}C) by accelerator mass spectrometry (AMS).
 - Measurements are typically made on graphite (CO_2 also possible). Graphite is formed by combustion of sample to CO_2 and then reduction of CO_2 to graphite.
 - Measurement times as short as 20 min.
 - Key attribute of AMS - Isobar rejection:
 - Negative ions (Cs sputter source) remove ($^{14}\text{N}^+$)
 - Electron stripping (accelerator) to remove hydrides ($^{13}\text{CH}^-$)
 - Sensitivity of AMS = 6×10^{-16} ($\equiv 60,000$ yr; $\equiv 10$ half-lives).
 - Sample size requirements:
 - "Standard" targets < 1 milligram C* (as little as 300 μg C) for full precision (± 4 ‰)
 - As low as 25 μg C possible at reduced precision (± 15 -20 ‰).
 - Standards:
 - Oxalic acid (HOxI, HOxII)
 - *Small sample size has opened up many new applications for ^{14}C .

Accelerator Mass Spectrometer



Courtesy of Lawrence Livermore National Laboratories.
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¹⁴C systematics

- The absolute international standard of ¹⁴C activity (A_{abs}) is defined as 95% of the ¹⁴C activity of the original oxalic acid standard (HOxI), in the year 1950. This is equivalent to the activity of 19th century wood, and represents the ¹⁴C concentration of the atmosphere prior to anthropogenic influence (fossil fuel combustion, atomic weapons testing).
- The measured activity of HOxI (A_{ox}) is corrected from fractionation effects using a defined $\delta^{13}C_{ox}$ value of -19‰ to yield the fractionation-normalized activity (A_{ON}):
- This is corrected to account for radioactive decay between 1950 and the year of measurement:

$$A_{ON} = 0.95 A_{ox} \left(1 - \frac{2(19 + \delta^{13}C)}{1000} \right)$$

$$A_{abs} = A_{ON} e^{\lambda(y-1950)}$$

¹⁴C systematics

- The measured ¹⁴C activity of a sample (A_s) is normalized (A_{sn}) to a constant $\delta^{13}C$ value of -25‰ to remove the influence of isotopic fractionation on the reported concentration:

$$A_{sn} = A_s \left(1 - \frac{2(25 + \delta^{13}C_{sample})}{1000} \right)$$

- To a first approximation, the above equation treats the ¹⁴C fractionation as twice the ¹³C fractionation (to account for the greater mass difference). This is based on physical-chemical derivations that suggest the ¹⁴C fractionation is approximately equal to the square of the ¹³C fractionation. The mean age correction is about 16 years for every 1 ‰ difference from -25‰ . This may be simplified to:

$$A_{sn} = A_s \left[\frac{\left(1 + \frac{-25}{1000} \right)^2}{\left(1 + \frac{\delta^{13}C_{sample}}{1000} \right)^2} \right]$$

¹⁴C systematics

- The above equations were first developed for ¹⁴C measurements from decay counting techniques.
- AMS yields absolute ratios of ¹⁴C/¹²C in a sample, rather than the rate of decay. The above equations are still applicable, as activity and R^{14/12} are proportional via the decay constant, λ. AMS data are reported as fraction modern (f_m) values, rather than activities:

$$f_m = \frac{A_{sn}}{A_{ON}} = \frac{R^{14/12}_{sn}}{R^{14/12}_{ON}}$$

- When a radiocarbon age (year date) is not desired, data are reported as Δ¹⁴C values in one of two forms.
- For samples with no age correction, where y is the year of measurement:

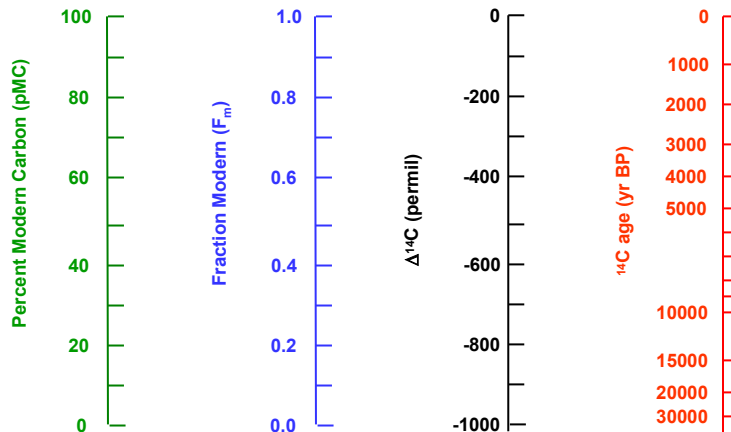
$$\Delta^{14}C = \left(\frac{A_{sn}}{A_{ON} e^{\lambda(y-1950)}} - 1 \right) * 1000 = (f_m e^{-\lambda(y-1950)} - 1) * 1000$$

- For samples of known geochronological age, where y is the year of measurement, and x is the year of sample formation:

$$\Delta^{14}C = \left(\frac{A_{sn} e^{\lambda(y-x)}}{A_{ON} e^{\lambda(y-1950)}} - 1 \right) * 1000 = (f_m e^{-\lambda(1950-x)} - 1) * 1000$$

- The “radiocarbon age” of a sample is strictly defined as the age calculated using the Libby half-life (5568 y) for radiocarbon.
- In classical radiocarbon dating applications, the calculated radiocarbon ages are converted to calendar ages using calibration curves.

Reporting of Radiocarbon Data



Radiocarbon age versus $\Delta^{14}\text{C}$

$\Delta^{14}\text{C}$ is useful for isotopic mass
balance calculations

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$\Delta^{14}\text{C}$ originally defined by Broecker and Olson (1959). Am. J. Sci. Radiocarbon Suppl. 1, 111-132.

Factors influencing radiocarbon abundances:

1. Atmospheric ^{14}C variations

- Variations in solar (cosmic ray flux) activity (long-term, $\sim 10^3$ yr variations in production rate).
- Variations in Earth's geomagnetic field strength (short-term, $< 10^2$ yr variation in production rate)
- Climate induced variations - solubility of CO_2 in water a function of temperature.
- Volcanic activity
- Anthropogenic activity.
 - Fossil fuel burning ("Suess effect").
 - Nuclear weapons testing ("Bomb spike").

2. Fractionation effects

- The fractionation effect for ^{14}C is assumed to be double that for ^{13}C (reflecting mass difference relative to ^{12}C).
- *Conventional* radiocarbon ages are corrected to a single $\delta^{13}\text{C}$ value (-25 ‰ = approximate value for wood).

3. Source or reservoir effects.

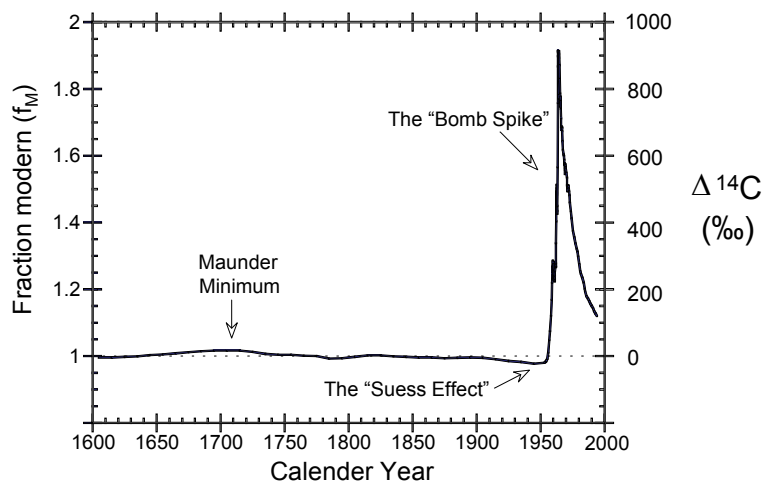
- There is rapid global mixing between the atmosphere and the terrestrial biosphere.
- However, mixing rates in deep ocean are slow. Mixing between surface mixed layer (high ^{14}C) and deeper layers (lower ^{14}C) gives rise to an offset between mixed layer and atmosphere. This offset ("reservoir effect") for the pre-bomb era is on average ca. 400 yr, but varies spatially and temporally. Thus organic matter synthesized in the oceans will have an *apparent* age which is 400 yr older than terrestrial biomass synthesized at the same time.

^{14}C variations and radiocarbon calibration

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High precision ^{14}C calibration curve for the past 7000 yr (from Irish Oak). Straight line is the 1:1 correspondence between ^{14}C age and dendrochronological age. Short-term (10^2 yr) variations are due to geomagnetic field variations. Long-term (10^3 yr) variations are due to variations in cosmic ray flux.

Recent variations of ^{14}C in atmospheric CO_2



Wiggle-matching, dendrochronologies and varve chronologies

^{14}C variations vs varve age for Cariaco basin sediments, compared to those from tree rings

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Hughen et al., 1998 Nature, v391

Potential limitations in assigning Calendar ages from ^{14}C data

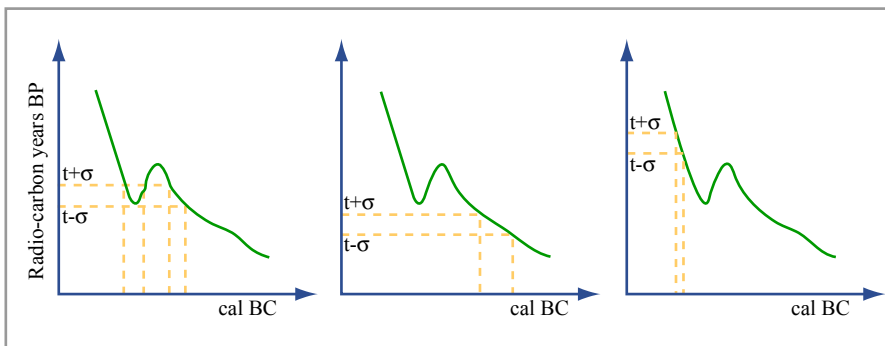
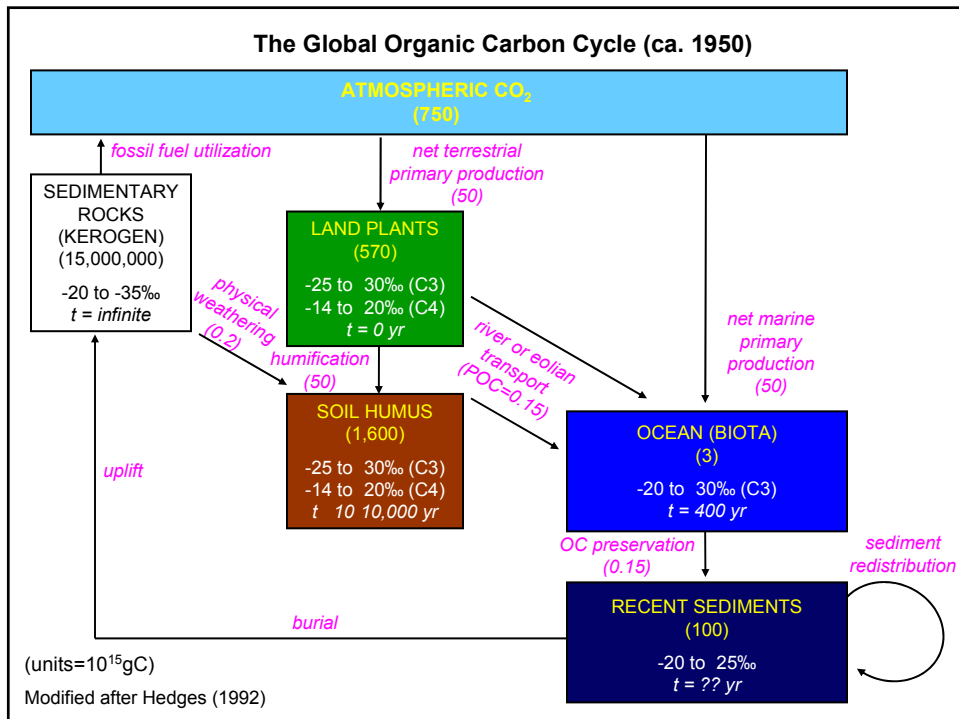


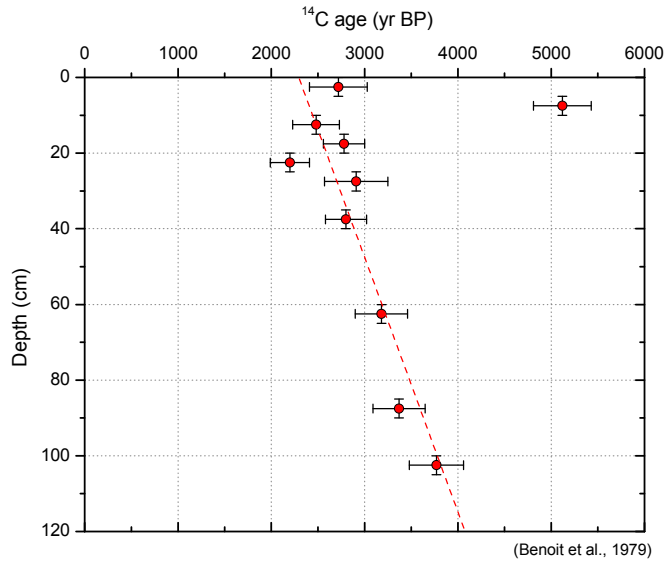
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Geochemical Applications of Radiocarbon

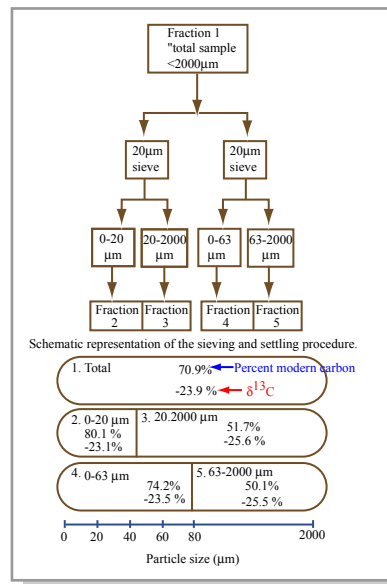
- Development of sediment chronologies
- Tracer studies (e.g., bomb-spike)
- Isotopic mass balance



Radiocarbon age of bulk OC in Long Island Sound sediments



Variations in stable carbon isotopic and radiocarbon composition of organic matter as a function of particle size



Variations in stable carbon isotopic and radiocarbon composition of organic matter as a function of chemical compound class

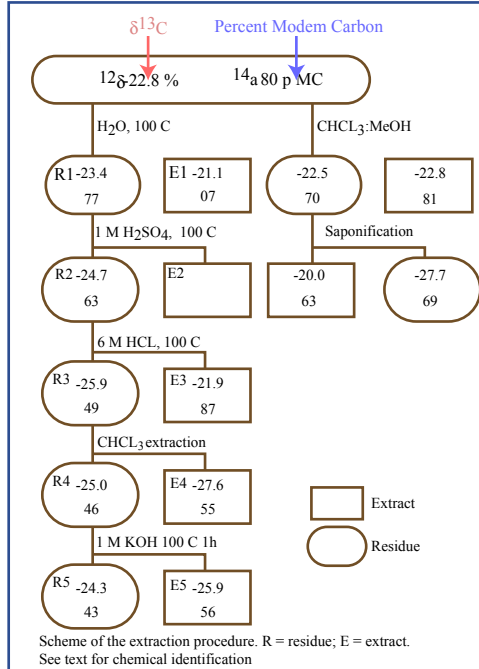
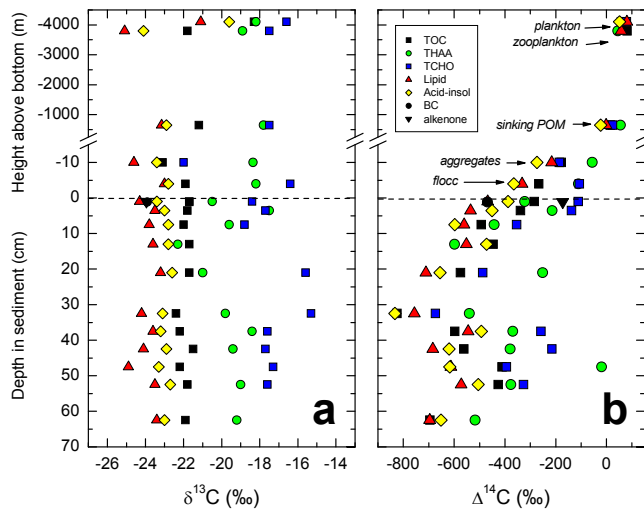


Figure by MIT OCW.

Megens et al.

Variations in stable carbon isotopic and radiocarbon composition of organic matter as a function of chemical compound class



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Wang, Druffel et al.

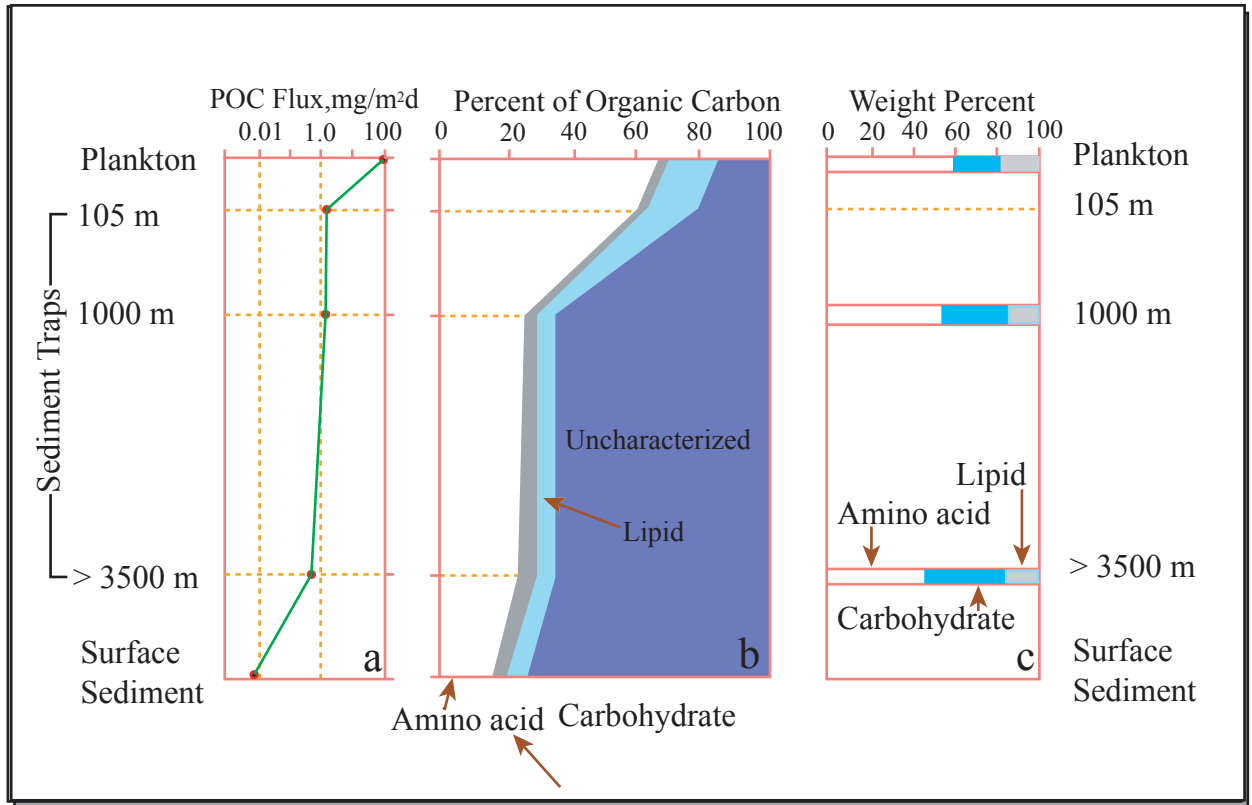


Figure by MIT OCW.

Isotopic (¹³C, ¹⁴C) evidence for a lipid-like source for acid insoluble macromolecular organic matter in sinking POM

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Molecular-level Radiocarbon Analysis

The Problem:

- Many samples contain heterogeneous mixtures of organic compounds of diverse origin (and age).
- Age variability can be a source of interference, or information.

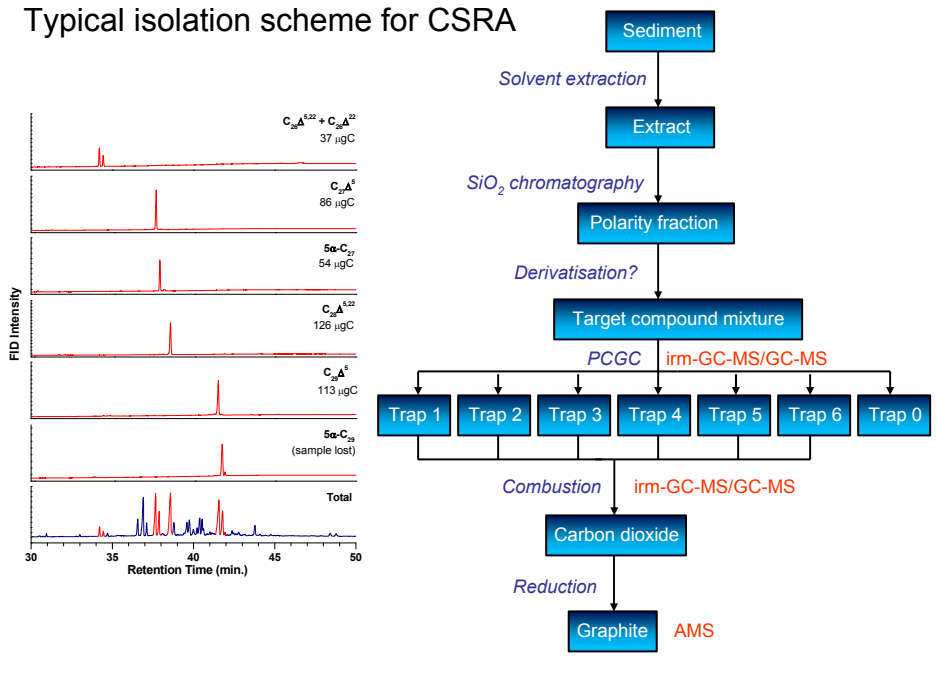
The Approach:

- Structurally diverse organic compounds are preserved in sediments and carry a wealth of biogeochemical information.
- Measure the stable- and radio- carbon isotopic composition of individual organic compounds in order to constrain the origin of OC buried in sediments.
- Isotopic mass balance using both ^{14}C and ^{13}C allows for three OC source inputs (phytoplankton, vascular plant, relict organic matter) to be defined.
- Select compounds for ^{14}C and ^{13}C analysis using biochemical criteria, rather than characterizing OC pools based on operational definitions.
- Molecular ^{14}C contents also provide apparent ages for assessment of the residence times and cycling rates within (and between) carbon reservoirs.

The Challenge:

- To measure the natural abundance of ^{14}C in individual organic compounds in complex mixtures.
- Greater than 25 $\mu\text{g C}$ required for reliable ^{14}C measurement (by AMS).
- Isolation of target analytes in very high purity.
- Conventional capillary GC resolves < 500ng compound.
- The Approach:
- Automated Preparative Capillary Gas Chromatography (PCGC).

Typical isolation scheme for CSRA



Correction for derivative carbon

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N.B. Derivatives are typically derived from petrochemicals (i.e., $\Delta^{14}\text{C} = -1000\text{‰}$)

Alkenone purification methodology

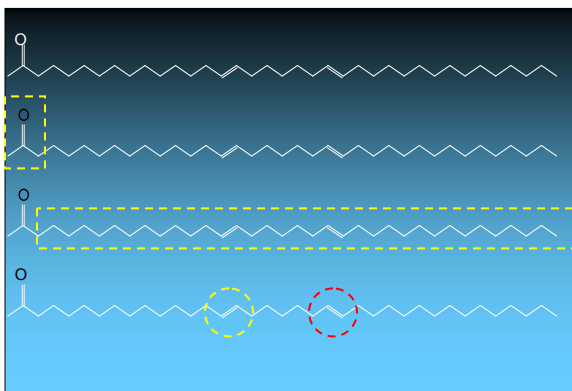
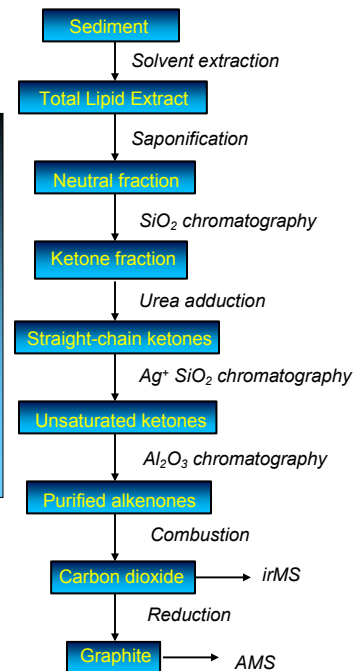


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Bulk vs molecular ^{14}C - isotopically homogeneous samples

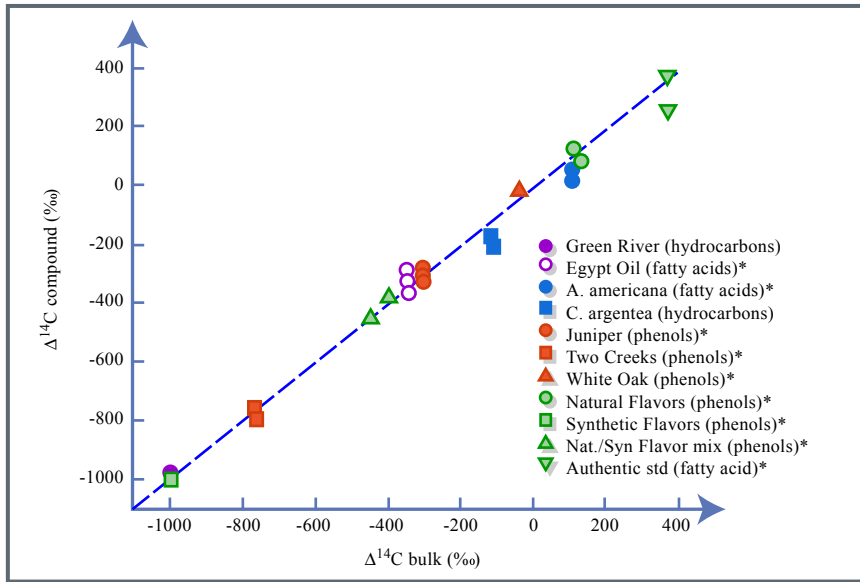


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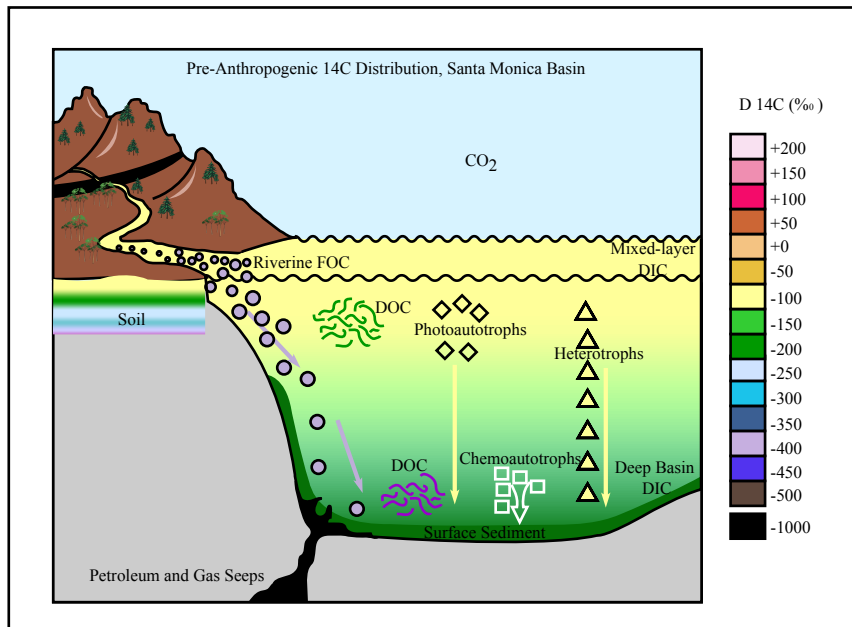


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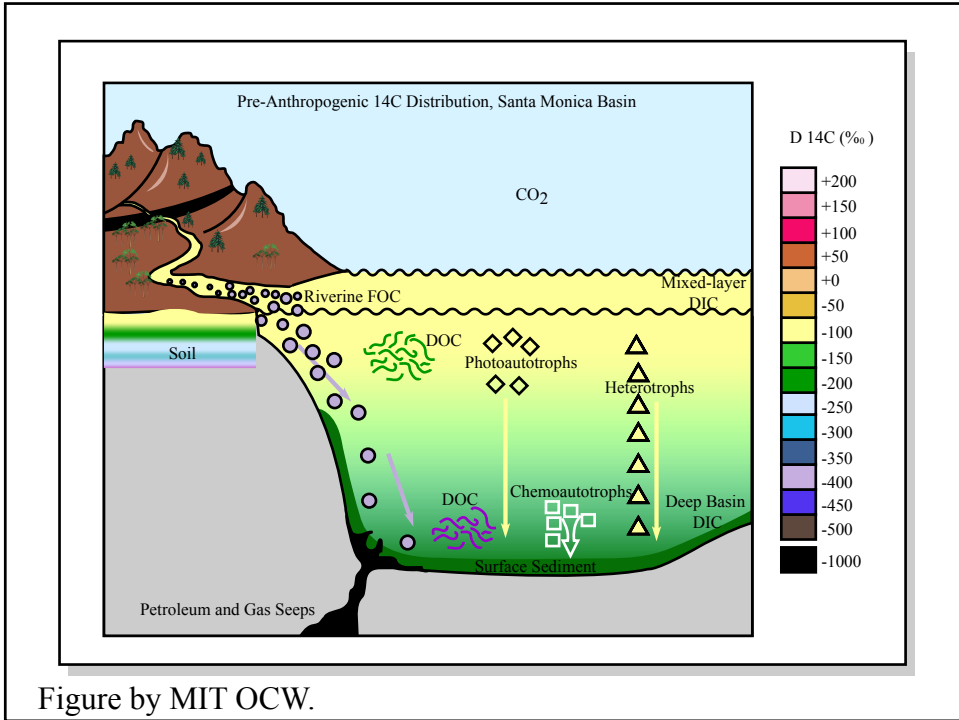


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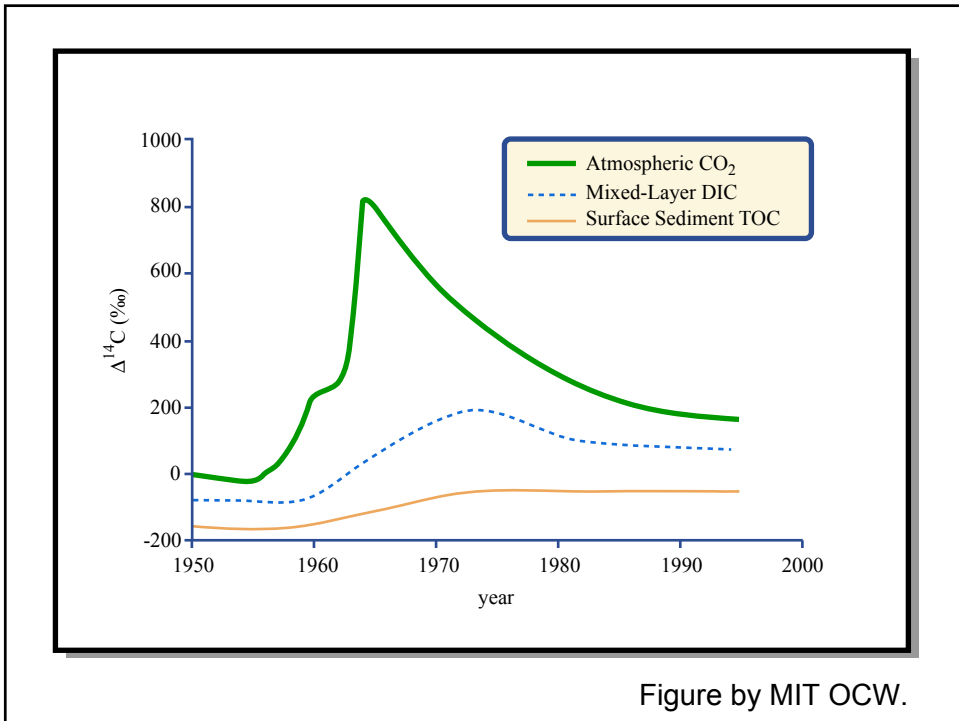
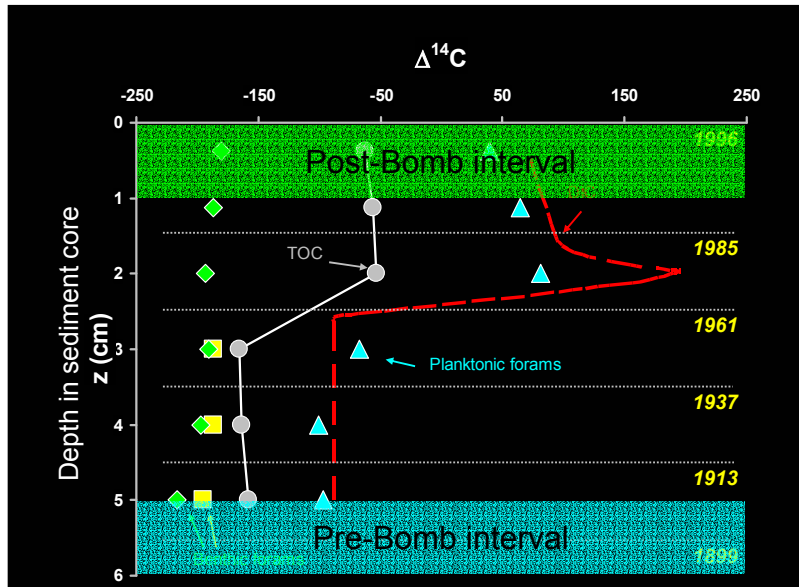
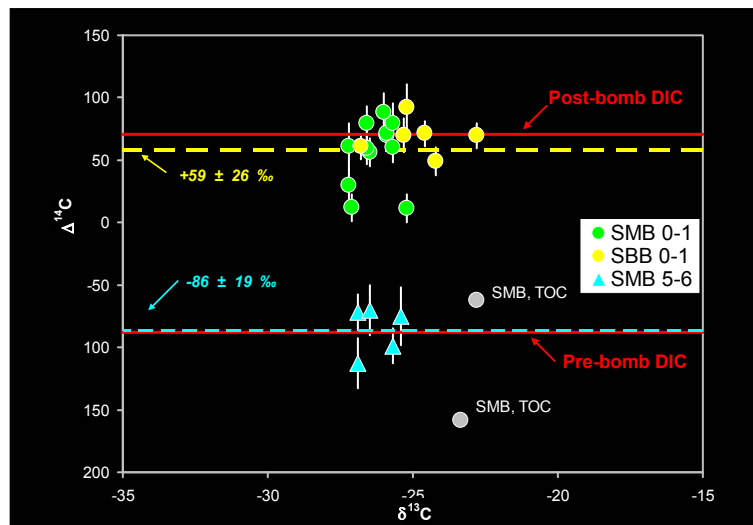


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TOC and foram $\Delta^{14}\text{C}$ in Santa Monica Basin sediments



^{14}C contents of algal sterols in CBB sediments



Data from Pearson et al. (2000)

^{14}C contents of lipid biomarkers in CBB sediments

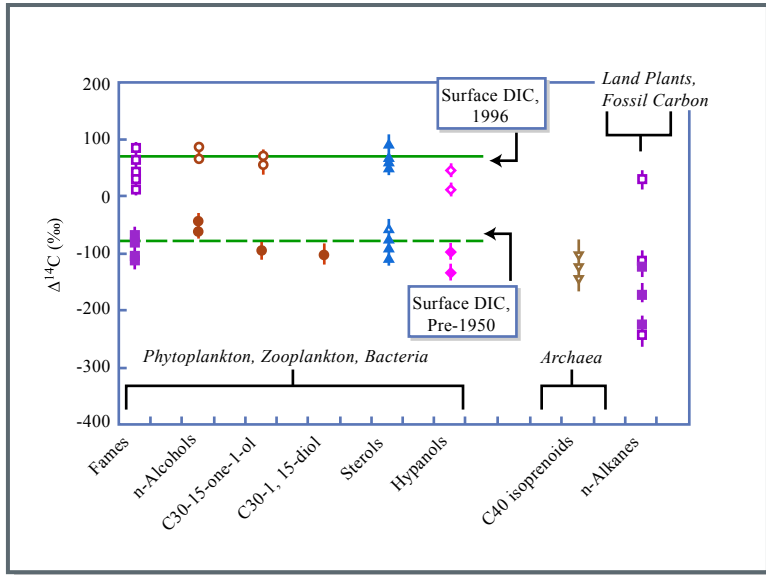


Figure by MIT OCW.

Data from Pearson et al. (2001)