Geochemistry of Radiocarbon in Organic Materials

Suggested Reading:

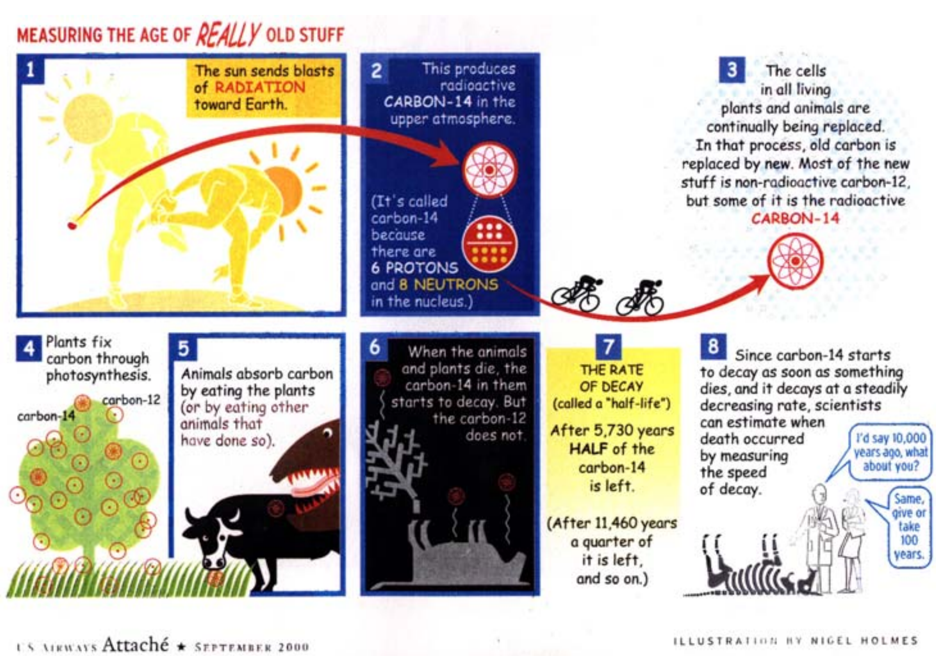
Eglinton T.I., Benitez-Nelson B.C., Pearson A., McNichol A.P., Bauer J.E. and Druffel E.R.M. (1997) Variability in radiocarbon ages of individual organic compounds from marine sediments. *Science* **277**, 796-799.

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.



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.

$$^{14}N + \text{neutron} \rightarrow {}^{14}C + \text{proton}$$

- 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, $T½$, 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:

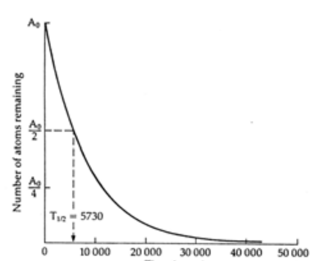
$$T½ = (\ln 2)\tau \qquad (\text{or } T½ = 0.693\tau)$$

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

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

- 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.



Methods of ^{14}C measurement

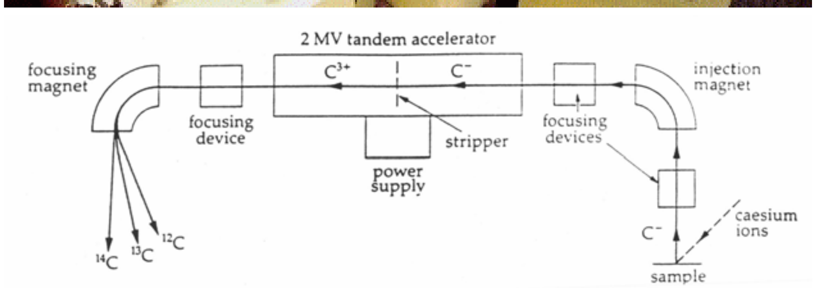
1. Conventional method - Determination of ^{14}C activity of a weighed sample by counting the number of electrons (beta particles) emitted from nucleus per unit time by the decay of ^{14}C.

- 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 ($^{14}N^+$)
  - Electron stripping (accelerator) to remove hydrides ($^{13}CH^-$)
- Sensitivity of AMS = 6×10^{-16} (≡ 60,000 yr; ≡ 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



^{14}C systematics

- The absolute international standard of ^{14}C activity (A_{abs}) is defined as 95% of the ^{14}C 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 ^{14}C 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}):

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

- This is corrected to account for radioactive decay between 1950 and the year of measurement:

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

^{14}C systematics

- The measured ^{14}C 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 ^{14}C fractionation as twice the ^{13}C fractionation (to account for the greater mass difference). This is based on physical-chemical derivations that suggest the ^{14}C fractionation is approximately equal to the square of the ^{13}C fractionation. The mean age correction is about 16 years for every 1 ‰ difference from -25 ‰. This may be simplified to:

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

^{14}C systematics

- The above equations were first developed for ^{14}C measurements from decay counting techniques.
- AMS yields absolute ratios of $^{14}C/^{12}C$ 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 $\Delta^{14}C$ values in one of two forms.
- For samples with no age correction , where *y* is the year of measurement:

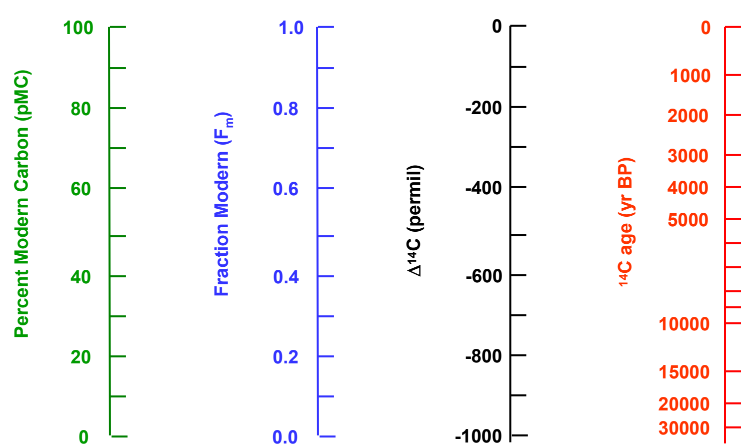
$$\Delta^{14}C = \left(\frac{A_{sn}}{A_{ON}e^{\lambda(y-1950)}} - 1\right) * 1000 = \left(f_m e^{-\lambda(y-1950)} - 1\right) * 1000$$

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

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

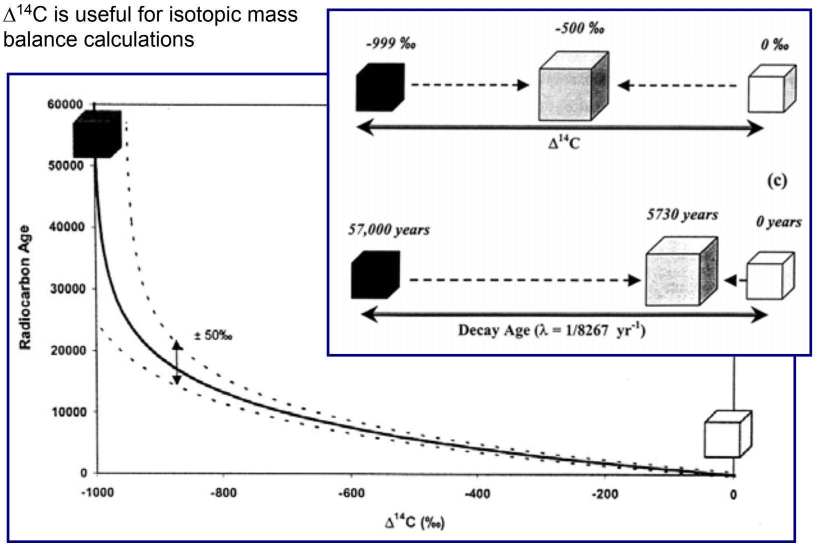
- The “radiocarbon age” of a sample is strictly defined as the age calculated using the Libby half-life (5568 y) for radiocarbon.
- - In classical radiocarbon dating applications, the calculated radiocarbon ages are converted to calendar ages using calibration curves.

Reporting of Radiocarbon Data



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

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



$\Delta^{14}C$ 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, ~ 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").

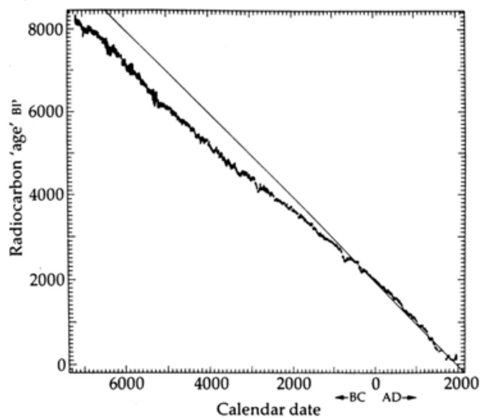
2. Fractionation effects

- 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 $\delta^{13}C$ value (-25 ‰ = approximate value for wood).

3. Source or reservoir effects.

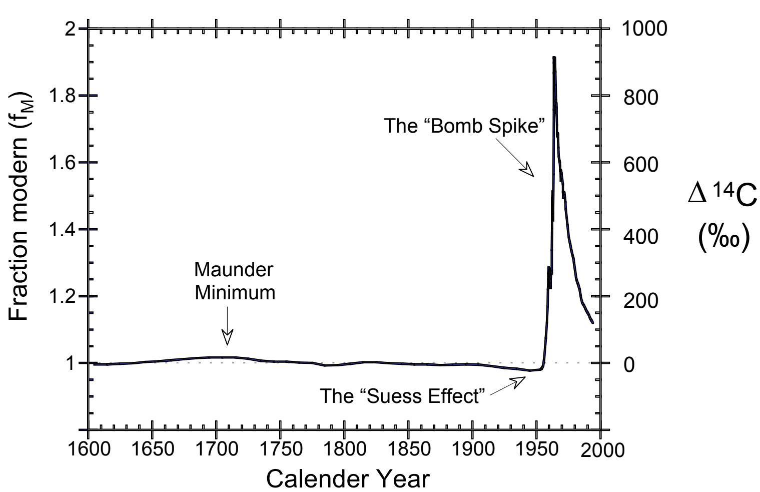
- There is rapid global mixing between the atmosphere and the terrestrial biosphere.
- However, mixing rates in deep ocean are slow. Mixing between surface mixed layer (high ^{14}C) and deeper layers (lower ^{14}C) gives rise to an offset between mixed layer and atmosphere. This offset ("reservoir effect") 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



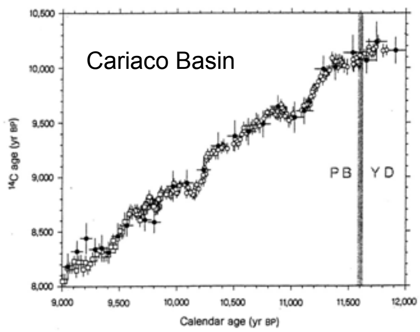
High precision 14C calibration cure for the past 7000 yr (from Irish Oak). Straight line is the 1:1 correspondence between 14C age and dendrochronological age. Short-term (10^2 yr) variations are due to geomagnetic field variations.
Long-term (10^3 yr) variations are due to variations in cosmic ray flux.

Recent variations of ^{14}C in atmospheric CO_2

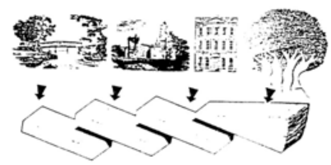


Wiggle-matching, dendrochronologies and varve chronologies

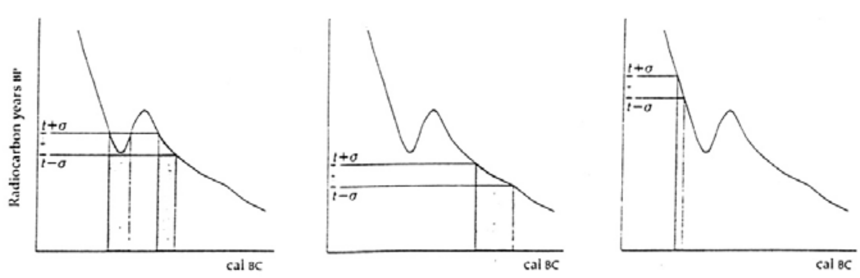
^{14}C variations vs varve age for Cariaco basin sediments, compared to those from tree rings



Hughen et al., 1998 Nature, v391



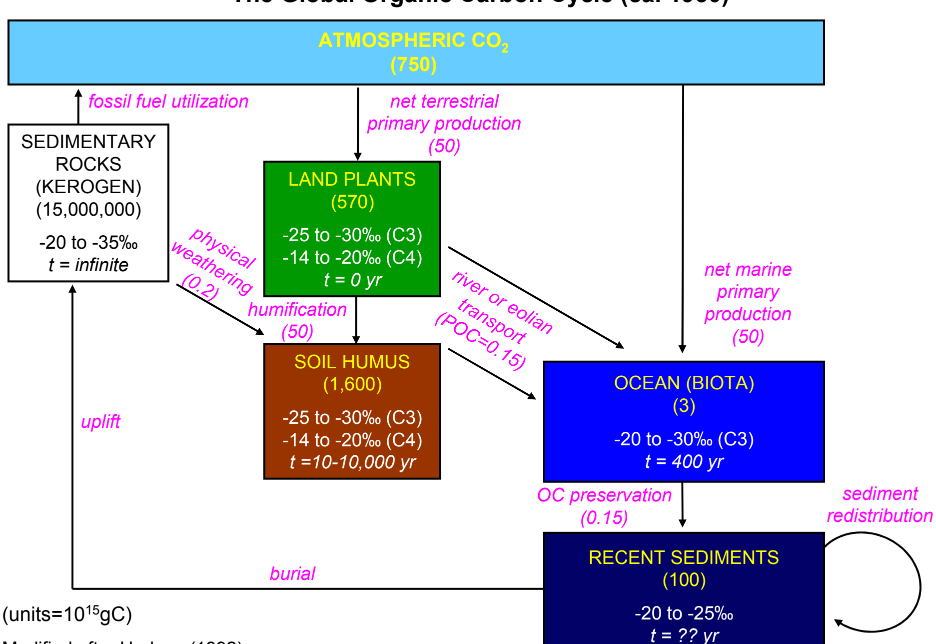
Potential limitations in assigning Calendar ages from ^{14}C data



Geochemical Applications of Radiocarbon

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

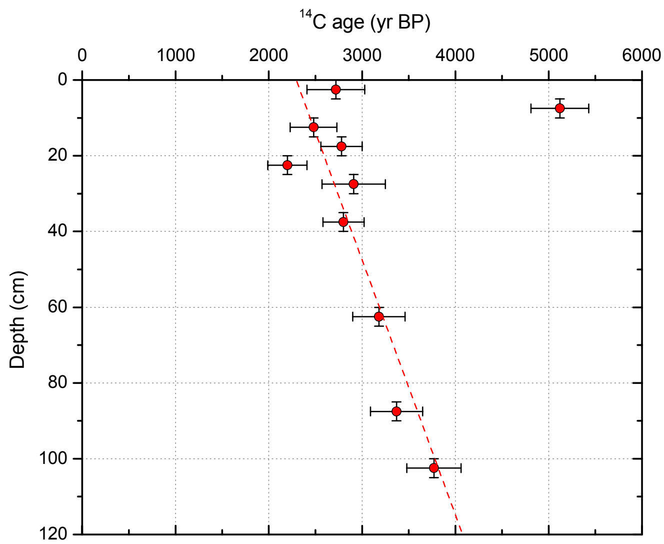
The Global Organic Carbon Cycle (ca. 1950)



(units=10^{15}gC)

Modified after Hedges (1992)

Radiocarbon age of bulk OC in Long Island Sound sediments



(Benoit et al., 1979)

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

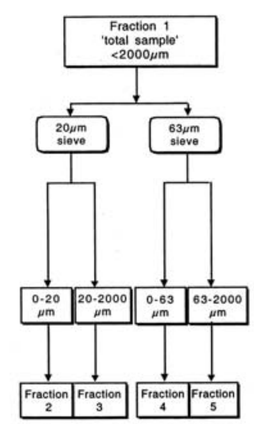
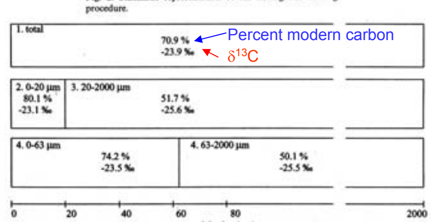


Fig. 2. Schematic representation of the sieving and settling procedure.



Megens et al. (2002) Org. Geochem. 33 945-952.

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

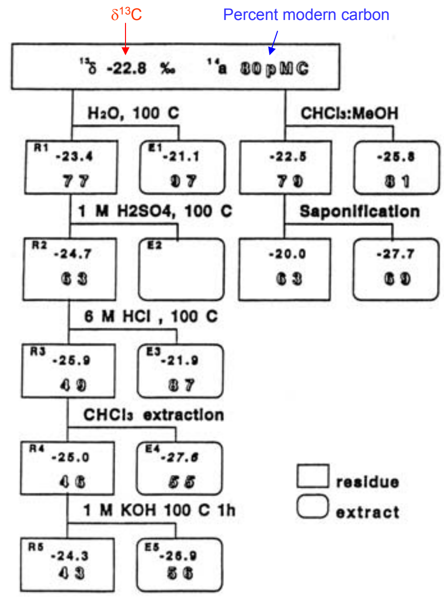
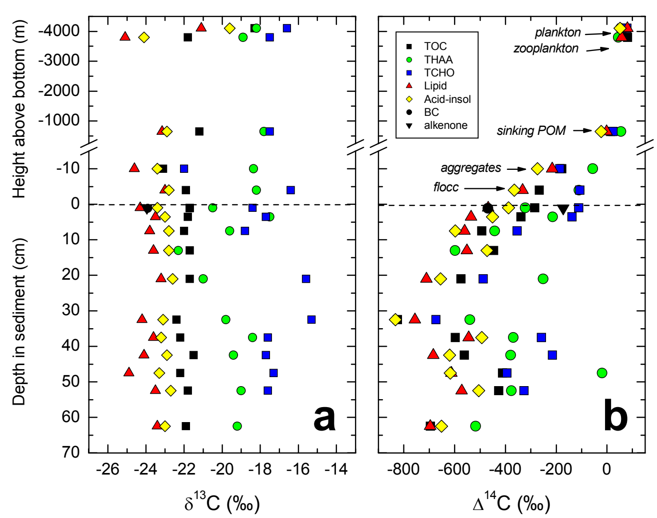


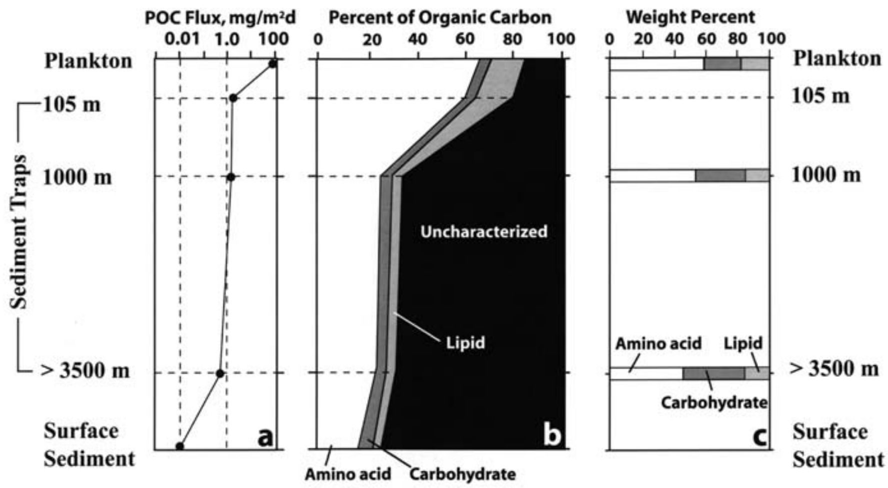
Fig. 2. Scheme of the extraction procedure. R = residue; E = extract. See text for chemical identification.

Megens et al.

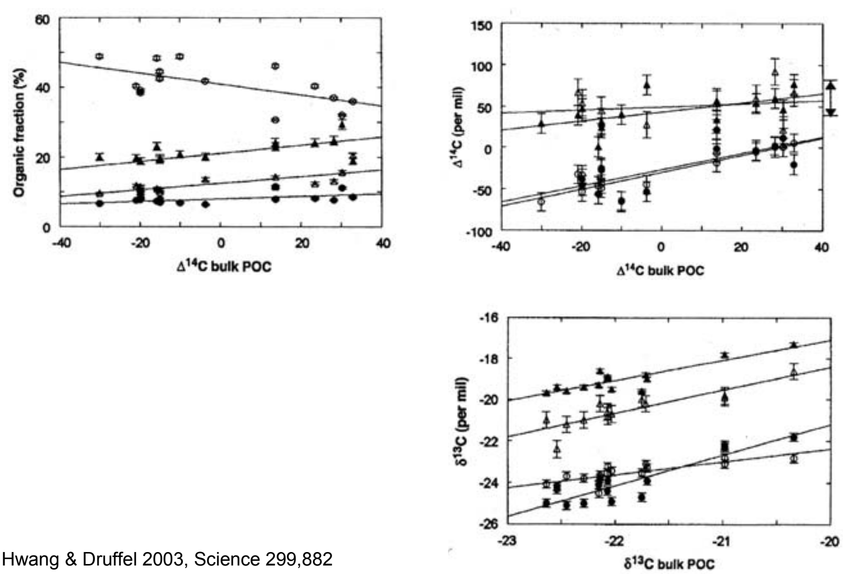
Variations in stable carbon isotopic and radiocarbon composition of organic matter as a function of chemical compound class



Station M
Wang, Druffel et al.



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



Hwang & Druffel 2003, Science 299,882

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.

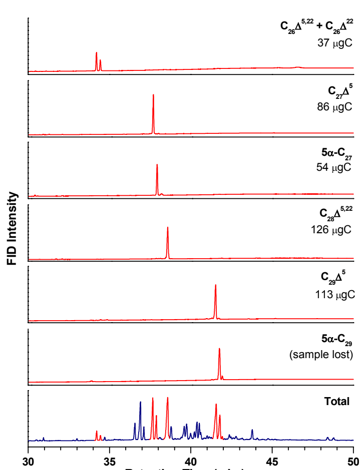
The Approach:

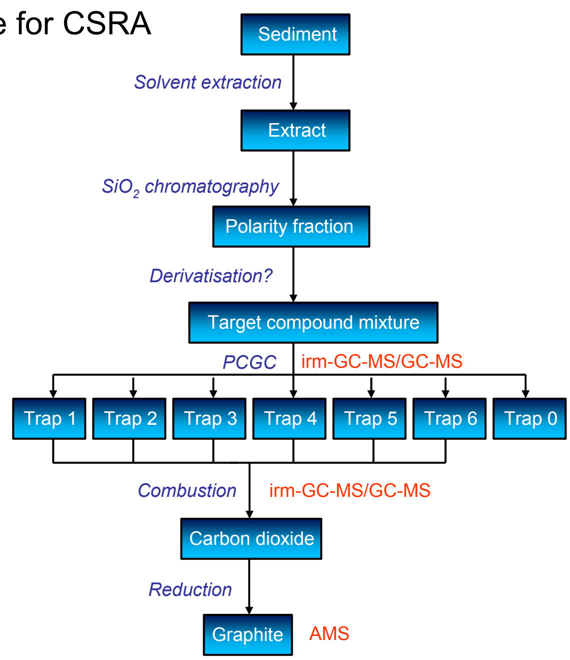
- Structurally diverse organic compounds are preserved in sediments and carry a wealth of biogeochemical information.
- Measure the stable- and radio- carbon isotopic composition of individual organic compounds in order to constrain the origin of OC buried in sediments.
- Isotopic mass balance using 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 μg 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

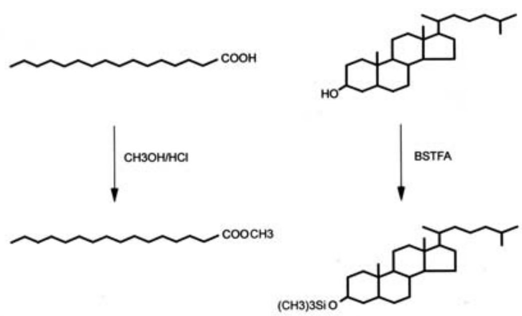




Correction for derivative carbon

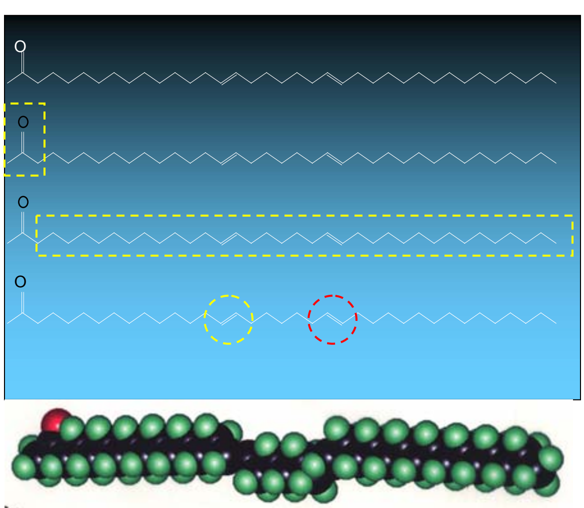
$$\Delta_B = \left[\frac{\Delta_{BD} - (f_D \Delta_D)}{f_B}\right]$$

where Δ_B, Δ_{BD} and Δ_D are the $\Delta^{14}C$ values of the parent biomarker (**underivatized**), the derivatized molecule and the derivative carbon atom(s) respectively, and f_B and f_D are the fractions of biomarker carbon and derivative carbon in the derivatized molecule.

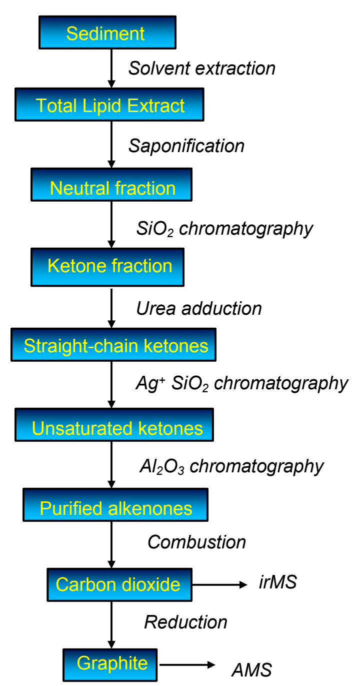


N.B. Derivatives are typically derived from petrochemicals (i.e., $\Delta^{14}C$ = -1000 ‰)

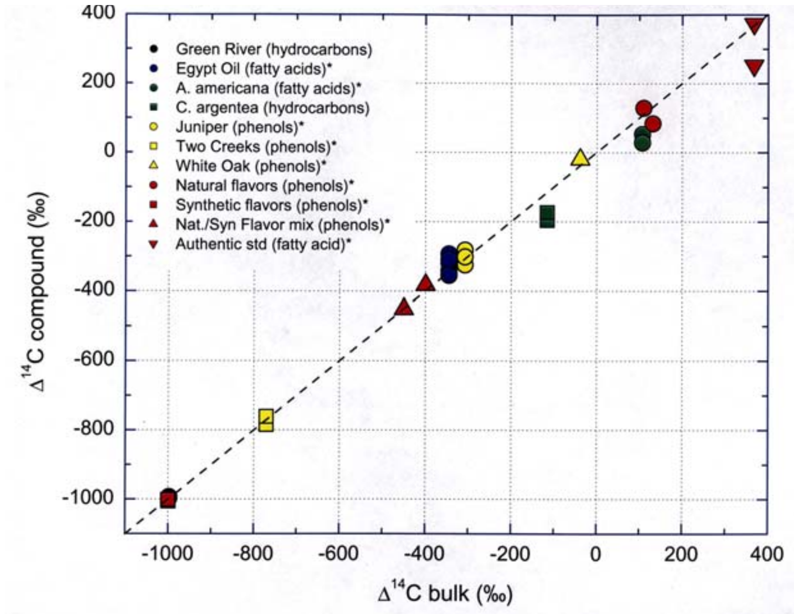
Alkenone purification methodology

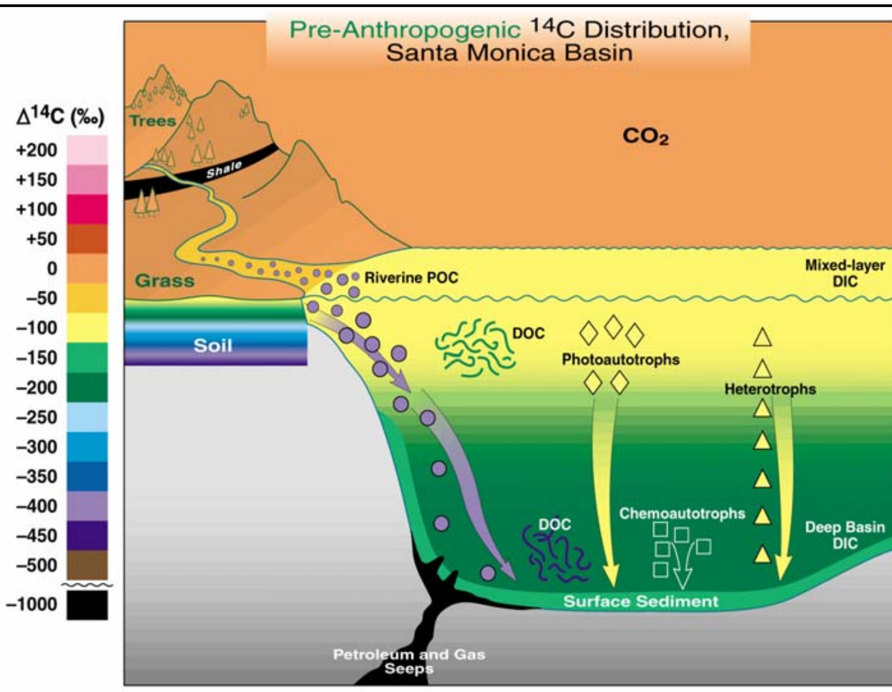


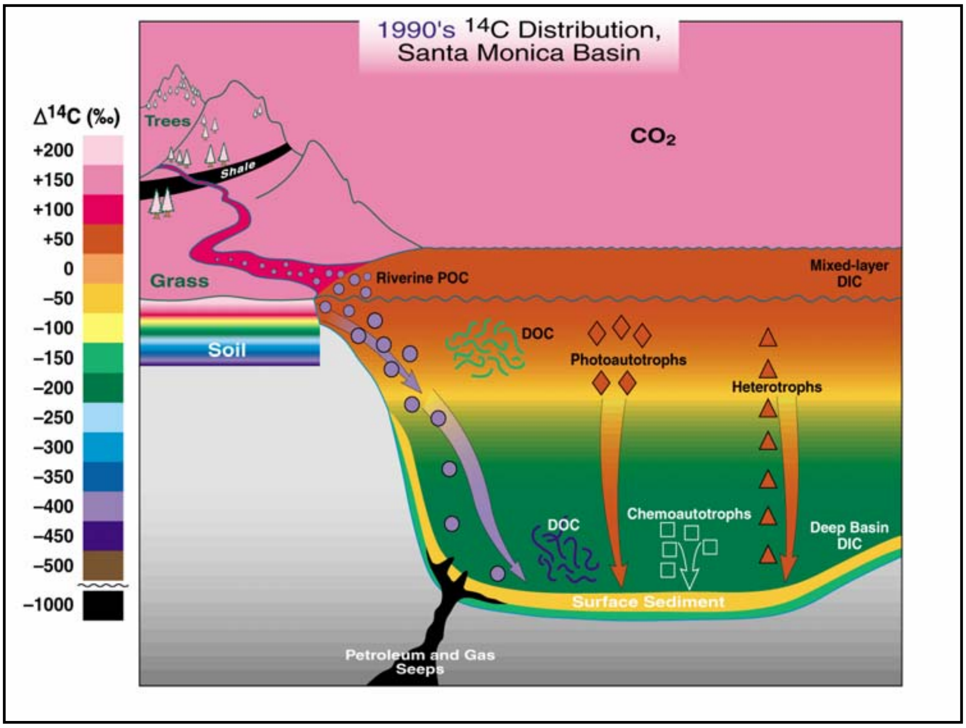
C_{37} alkadienone

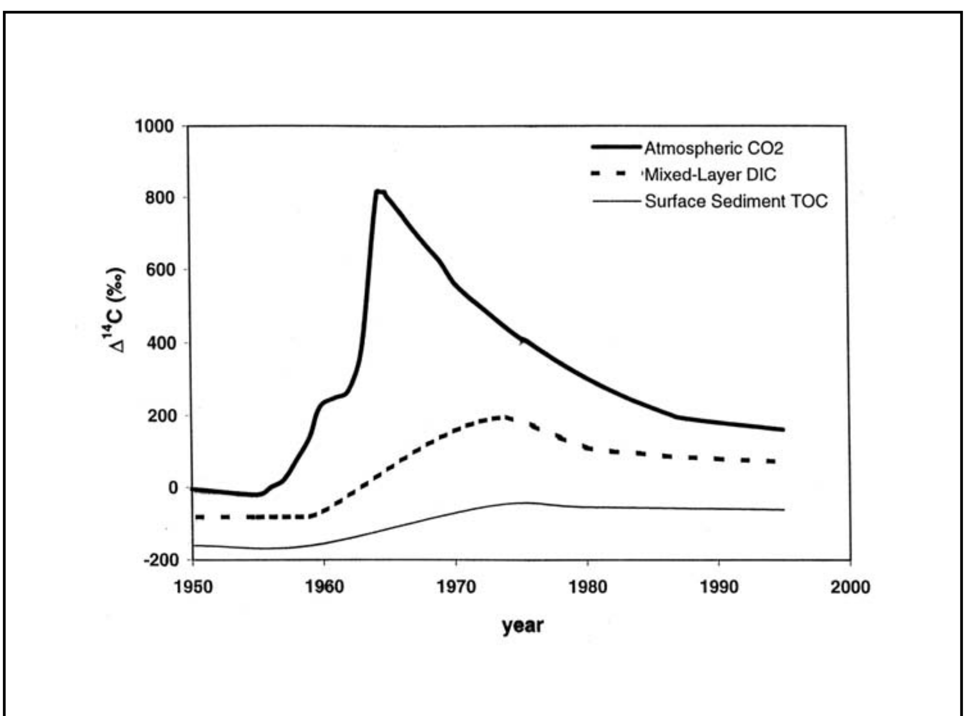


Bulk vs molecular ^{14}C - isotopically homogeneous samples

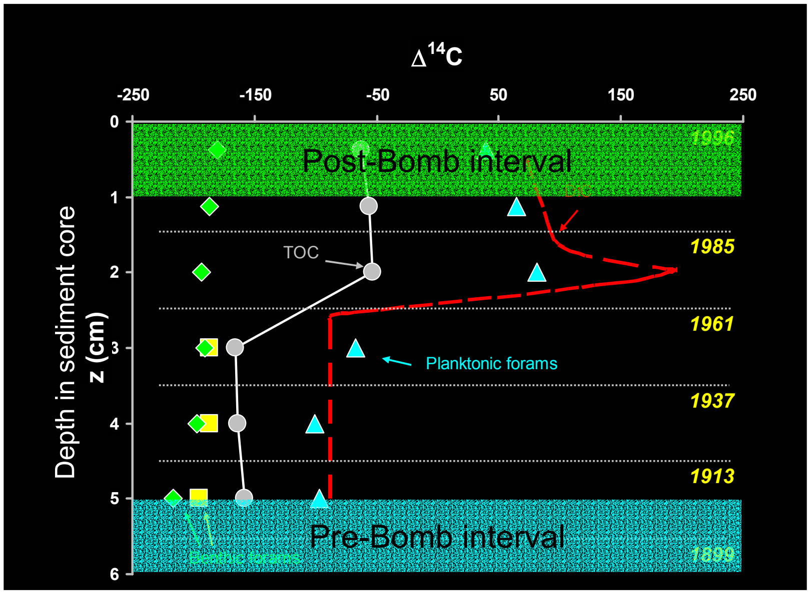




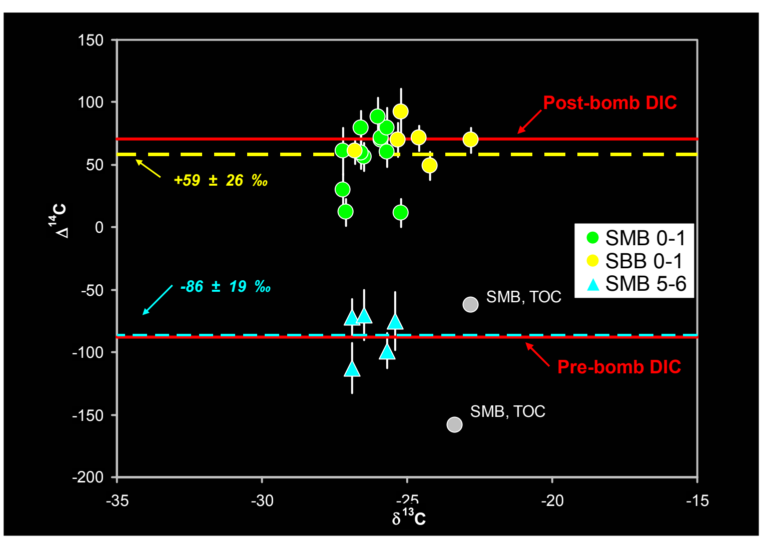

1990's ^{14}C Distribution, Santa Monica Basin
$\Delta^{14}C$ (‰)
+200
+150
+100
+50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
−500
−1000
Trees
Shale
Grass
Soil
CO_2
Riverine POC
Mixed-layer DIC
DOC
Photoautotrophs
Heterotrophs
DOC
Chemoautotrophs
Deep Basin DIC
Surface Sediment
Petroleum and Gas Seeps


Atmospheric CO2
Mixed-Layer DIC
Surface Sediment TOC
$\Delta^{14}C$ (‰)
1000
800
600
400
200
0
-200
1950
1960
1970
1980
1990
2000
year

TOC and foram Δ14C in Santa Monica Basin sediments

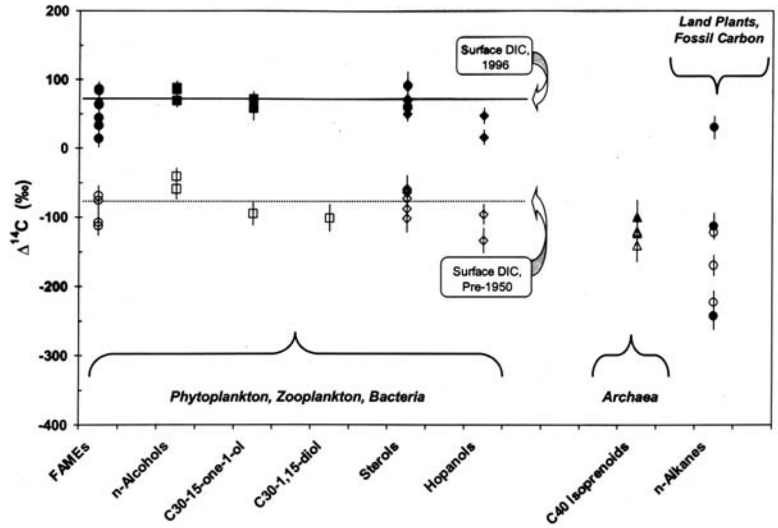


14C contents of algal sterols in CBB sediments



Data from Pearson et al. (2000)

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



Data from Pearson et al. (2001)