The $^{14}$C Story

12.740 Topic 9 Spring 2008
**$^{14}$C production and inventory**

- cosmic ray (collides with atomic nucleus) -> neutron -> $^{14}$N -> $^{14}$C + proton
- production rate proportional to [$^{14}$N], cosmic ray flux and energy dispersion
- ~600 moles $^{14}$C/year are formed per year
- this production builds up a steady-state inventory of \(~5000 \times 10^3\) moles of $^{14}$C on the earth (where decay = production in the steady state):

  \[
  \frac{dN}{dt} = -\lambda N
  \]

  \[530 \text{ moles/year} = \frac{0.693}{5730 \text{ yrs}} \times N \text{ moles}\]

- $^{14}$C: $t_{1/2} = 5730 \pm 40$ years (Godwin, 1962)

By convention, $^{14}$C dates are reported relative to previously accepted 5568 year half-life (Libby). This convention was decided upon so as not to avoid dividing the literature between dates that are not consistent with the currently-accepted half life, and those that are. In other words, we are consistent by being consistently wrong!
Cosmogenic $^{14}$C production

The "life cycle" of carbon-14 atom. Created in the atmosphere by the collision of a neutron (produced by primary cosmic-ray protons) with a nitrogen atom, the average $^{14}$C atom "lives" for 8200 years. Its life is terminated by the ejection of an electron which returns the atom to its original form, $^{14}$N.

Figure by MIT OpenCourseWare.
If \(^{14}\text{C}/^{12}\text{C}\) in the atmosphere is constant, if the object to be dated obtained its carbon directly from the atmosphere, and if the object to be dated is closed, then

\[
\frac{dN}{dt} = -\lambda N
\]

\[
\frac{N}{N_0} = e^{-\lambda t}
\]
a minor complication:

• Carbon isotopes are fractionated by organisms relative to air and by chemical equilibrium.
  • e.g. $^{13}\text{C}/^{12}\text{C}_{\text{plants}} \sim -20$ permil relative to atmosphere (which is $\sim -7$ permil relative to ocean surface waters);
  $^{14}\text{C}/^{12}\text{C}$ is fractionated by about twice that amount.
  • So you must measure $\delta^{13}\text{C}$ and correct for isotope fractionation of $^{14}\text{C}$:
  • Definition:

$\delta^{13}\text{C} = \left[ \frac{\left( ^{13}\text{C}/^{12}\text{C} \right)_{\text{sample}}}{\left( ^{13}\text{C}/^{12}\text{C} \right)_{\text{standard}}} - 1 \right] \times 1000$

• Definition:

$\delta^{14}\text{C} = \left[ \frac{\text{Activity}_{\text{sample}}}{\text{Activity}_{\text{standard}}} - 1 \right] \times 1000$

where $\text{Activity}_{\text{standard}}$ is taken to be 95% of the NBS oxalic acid standard (to approximate pre-industrial pre-nuclear bomb (PIPN) atmospheric carbon).
\[ \Delta^{14}C \]

- \( \delta^{14}C \) cannot be used to directly calculate the age of a sample; a correction for two effects must be applied:
  
  The first effect is the isotope mass fractionation, so \(^{14}C\) is corrected by subtracting twice the mass fractionation for \(^{13}C\).

  The second effect arises because we want a scale where a sample of pre-industrial, pre-nuclear (PIPN) wood has a "zero" value on the scale; i.e., we want to define the corrected value \(X\) such that \(X/X_0 = e^{-\lambda t}\) gives \(t=0\) for PIPN (together, these require a correction of \(\delta^{14}C\) so that it is equivalent to a constant \(\delta^{13}C = -25\%\)).

So with both corrections, we define a new property:

\[
\Delta^{14}C = \delta^{14}C - (2\delta^{13}C + 50)(1 + \frac{\delta^{14}C}{1000})
\]

The "50" term here arises as an adjustment to make a piece of wood have the correct age; since the \(\delta^{13}C\) of this wood is \(-25\%\), twice that is \(50\%\) (for \(^{14}C\)). This multiplication of \(\delta^{13}C\) by 2 is the "twice-the-isotope fractionation per amu mass difference" correction, which is only approximate but better formulations such as "exponential correction" are not required.

!! Note that \(\Delta^{14}C \neq \delta^{14}C!!

This is probably the source of the use of the diminutive "del" for \(\delta\) to distinguish it from "Delta" for \(\Delta\).
“The Present”

By convention, geological dates are all referenced to the present, which is defined as Jan. 1, 1950 (!)

The reason this has to be done is that the conventional western AD/BC calendar does not have a year zero! (You are either 1 AD or 1 BC). This makes the calculation of time intervals crossing the boundary awkward!

So you are now living in the year -58 BP!

While we’re at it, perhaps it is also worthwhile to note that geological ages before present are reported as “annum”, i.e. we are now living -58 a BP
Δ$^{14}$C transformations:

- Relationship between measured Δ$^{14}$C and radiocarbon age:

\[
1000 \left( e^{\frac{-C14age}{8033}} - 1 \right) = \Delta^{14}C_{measured}
\]

- Relationship between measured Δ$^{14}$C, true age (i.e. based on correct half-life), and initial Δ$^{14}$C:

\[
1000 \left( e^{\frac{-C14age}{8033}} - e^{\frac{-CalAge}{8266}} - 1 \right) = \Delta^{14}C_{initial}
\]

- Relationship between Δ$^{14}$C and the concentration of $^{14}$C in seawater:

\[
[^{14}C] = \left(1.176E-12\right)\left(1 + \frac{\Delta^{14}C}{1000}\right)[\Sigma CO_2]
\]

where ΣCO$_2$ is expressed in terms of μmoles/kg

- “Back of the envelope” estimator: For ocean waters and other relatively "young" (<2500 yr) things: Δ$^{14}$C decreases by 10% every 80 years.
$^{14}$C measurement I:

- Counting measurement ($\beta$ gas counting or liquid scintillation). Requires tens of grams, low background counters (anticoincidence), and time (for enough decays to count).

  Convert: $\text{CaCO}_3 \rightarrow \text{CO}_2 \rightarrow \text{C}_2\text{H}_2$ (acetylene)

  Gas (proportional) counting:

  $\beta$ decay leads to gas discharge across high voltage gradient (count discharges)

  Liquid scintillation counting

  Convert $\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$ (benzene)

  Add 'cocktail' of scintillators which gives off light for each $\beta$ decay
$^{14}$C measurement II:

Accelerator Mass Spectrometer (AMS): counts atoms rather than waiting for them to decay: advantage lies in much smaller sample sizes that can be handled.

- Van de Graf accelerator accelerates ions to high velocities
- Magnetic sector mass spectrometer (separates m/e)
- Stripper (thin sheet of foil or other material) strips electrons from ions (Some ions are unstable; this helps get rid of $^{14}$N)
- Solid State Detector (measures $\Delta E/E$, which is different for each isotope; this is important because it allows for further separation of N and the C isotopes).
- Allows for measurement of much smaller samples (~1 mg of C)

Bennett (1979) American Scientist 67:450-457

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Why simple $^{14}\text{C}$ ages aren’t accurate:

The $^{14}\text{C}/^{12}\text{C}$ ratio of the atmosphere isn’t constant!

It varies depending on:

- strength of the earth’s magnetic field
- solar activity
- changes in the operation of the earth’s carbon system
- nuclear bombs and reactors

In order to get an accurate $^{14}\text{C}$ age, you must “calibrate” ancient $^{14}\text{C}$ samples by reference to an independent absolute chronology (e.g. tree rings, varved sediments, $^{230}\text{Th}/\text{U}$ dates).
The effect of nuclear bomb testing:

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The Suess* Effect:

The burning of ancient fossil fuels decreases the $^{14}\text{C}/^{12}\text{C}$ ratio of the atmosphere
(note it also decreases $^{13}\text{C}/^{12}\text{C}$)

* That’s Dr. Hans Suess, not Dr. Seuss
The effect of the earth’s magnetic field

Recall: $^{14}$C is produced (indirectly) by thermal neutrons created by the interaction of cosmic rays with the upper atmosphere.

1. Cosmic rays: 92% protons; 6% helium nuclei; 1% electrons; 1% gamma rays, heavier nuclei, and other elementary particles. Their origin is outside solar system; we will assume that their flux is constant, but this is a question for astrophysicists, not paleoceanographers! What is the origin of cosmic rays? It appears that there are many potential sources; perhaps none of them is dominant. (An object thought to be a black hole (Cygnus X-3) is emitting cosmic rays; it would take only about 30 of these in the galaxy to account for the cosmic ray flux. A recent study (Physics Today, Jan. 2005, p. 19-21) attributes most of the cosmic rays to the shock fronts of supernova remnants. Note that only about 0.1% of the cosmic ray flux headed towards the earth reaches the earth's surface at sea level.

2. Cosmic rays are focused by earth's magnetic field [which is variable; e.g westward drift of secular field; its intensity slowly changes (as estimated from the magnetization of dated ceramics and rocks); magnetic reversals] and the field is also influenced by the solar wind. During solar flares (which run in 11 year cycles), the cosmic ray flux changes measurably [and so it is possible to calculate the change in the production rate of carbon 14 from (a) measured neutron flux, which is higher at high latitudes, and (b) known cross-section for reaction. It has been suggested that long-term variations in $^{14}$C/$^{12}$C [as measured in tree rings of known age, as by H. Suess and M. Stuiver] may be related to long-period solar variations.
$^{14}\text{C}$ production in the atmosphere

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D. Lal
Note that solar cycle production variations are not seen in atmospheric $^{14}$C because of efficient mixing and the size of the carbon reservoirs.

Global $^{14}$C production rates derived from neutron fluxes for the years 1937 to 1970. The data are from O'Brien (22). The dashed line gives the long-term change in $^{14}$C production during solar minima. The lower curve gives the inverse sunspot number record.

Figure by MIT OpenCourseWare.

The relationship between conventional radiocarbon ages (5, 568 yr half life) and tree-ring calibrated calendar years. (Different calendar years often have the same radiocarbon age). The width of the curve is twice the counting error in the measurements. The total error in the measurement process is only a few 0.1% larger than the counting error. 0 yr BP is AD 1950.

Figure by MIT OpenCourseWare.

$^{14}$C calibration, AD 1000-1950

Atmospheric $\Delta^{14}$C levels of the current millennium,

data replotted from Stuiver and Quay, 1980
$^{14}$C calibration, 5000 BC - 1950 AD

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Based on varved Cariaco Basin data, assuming constant $^{14}$C surface reservoir.
Reservoir Ages

• $^{14}$C ages are referenced to the atmosphere

• Because the ocean surface water mixes with older deeper waters faster than gas exchange can reset it to the atmospheric value, the $^{14}$C age of tropical surface water is $\sim$400 years.

• In upwelling areas and high latitude regions, the surface $^{14}$C age can be up to $\sim$1000 years (penguins are very old!)

• Benthic organisms assume the $^{14}$C age of deep water.

• In other settings, e.g. continental waters, the "$^{14}$C age" of the water can be affected by sources of old carbon, e.g. the "hard water" effect from ancient calcium carbonates.
Newer $^{14}$C calibration, 15 ka BP - 9 ka BP

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Based on varved Cariaco Basin data, assuming constant $^{14}$C surface reservoir

Hughen et al., 2000
$^{14}$C calibration (detrended), 17 ka BP - 0 ka BP

Image removed due to copyright restrictions.

Stuiver et al. (1998) Radiocarbon 40:1041-1083
Several efforts have been made to calibrate the C14 age scale beyond the LGM. These include pattern-matching climate records to GISP2 millennial events, varved lakes, and U/Th dating of speleothems (Beck et al., 2001) and corals (Fairbanks et al., 2005) . The outcome is somewhat controversial, but here is the Hughen et al. (2004) calibration based on Cariaco Basin – GISP2 correlation.

The very high $\Delta^{14}$C values seen near 40 ka BP are problematical - it’s not clear how the values can become so high.

There was a brief magnetic intensity minimum at $\sim$40 kyrBP, but it did not last long enough to produce the very high $\Delta^{14}$C values on its own.
$^{14}$C calibration, 25 ka BP - 0 ka BP

Figure by MIT OpenCourseWare.

Summary from last time:

- $^{14}$C is created by the collision of cosmic rays with the upper atmosphere
- Atmospheric $^{14}$C/$^{12}$C depends on:
  - The strength of the earth’s magnetic field (a stronger field deflects some cosmic rays away from the earth)
  - Solar activity, via the interaction of solar wind with the earth’s magnetic field (more sunspots, more solar flares, stronger solar wind, fewer incoming cosmic rays)
  - The earth’s carbon cycle (how $^{14}$C is distributed between carbon reservoirs)
- We can establish the fluctuations in atmospheric $^{14}$C/$^{12}$C by measurements on samples with independent chronologies (tree ring sequences, varved sediments, $^{230}$Th/$^{238}$U dated corals).
- From the known variations in solar activity over the past 500 years and $^{14}$C and $^{10}$Be data from before that, we infer that solar activity goes through minima lasting of a few decades every few centuries, resulting in a build-up of $^{14}$C in the atmosphere during that period.
- Over periods of thousands of years, paleomagnetic data show that the geomagnetic field intensity varies between something comparable to that seen at present, and near-zero. The weaker magnetic field at times in the past led to higher $^{14}$C and $^{10}$Be production rates.
\[ ^{14}C \text{ calibration, 25 ka BP - 0 ka BP} \]

Figure by MIT OpenCourseWare.

Changes in the earth’s magnetic field strength from rock magnetism

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Tric et al. (1992) JGR 97:9337-9351
(A) Past changes in the intensity of the virtual axial dipole moment over the last 75 kyr. This curve is constructed on the basis of weighted archeomagnetic and volcanic data from present to 19.5 kyr and on NAPIS-75 between 21 and 75 kyr. (B) $^{14}$C production for the last 75 kyr calculated using the model of Masarik and Beer with a value $\Phi = 550$ MeV for the solar modulation parameter.

GLOPIS-75 (Laj et al., 2004)

Mono Lake
Laschamp Excursion

Figure by MIT OpenCourseWare.
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Can we understand the changes in atmospheric $^{14}$C?

The possible causes for changes in atmospheric $^{14}$C are:
(a) variations in the earth's magnetic field (production rate changes)
(b) variations in the solar magnetic field (production rate changes)
(c) redistribution of radiocarbon between its reservoirs (variations in reservoir sizes and exchange rates).

In addition, there are ~200 units of $^{14}$C in oceanic sediments.
The distribution of $^{14}$C on earth

- In each "box", $^{14}$C builds up until decay = renewal rate

- Total production $\approx 600$ moles/year, so total steady-state reservoir must be

  \[ N \sim 5 \times 10^6 \text{ moles} \; ^{14}\text{C}. \]

- Most vegetation, humus, mixed layer, is radiocarbon "young" relative to atmosphere. Total carbon reservoir is

  \[ (100 + 70 + 60 + 50 + 3000) = 3280 \times 10^{15} \text{ moles} \]

  humus  veg  Atm  mixed  deep
  layer  ocean

  So the average carbon-14 specific activity in these reservoirs is about 100 dpm/g
The distribution of $^{14}$C on earth

- There are hold-up times for carbon transfer between reservoirs:
  - $^{14}$C "age" of surface ocean water is 400 years; deep Pacific ocean "age" is 2500 years

Using pre-industrial pre-nuclear atmosphere (PIPN) as a standard

- $\Delta^{14}$C -50‰ surface ocean (400 years)
- $\Delta^{14}$C -210‰ deep ocean (2000 years)

so the storage of $^{14}$C in the reservoirs is as follows:

$^{14}$C/$^{14}$C$_{atm}$

- 1.00 Atmosphere (0 years, $\delta^{13}$C=-7‰) : 2% of total $^{14}$C
- 0.97 Vegetation (0 years old, $\delta^{13}$C=-27‰) : 3%
- 0.96 Humus (100 years old, $\delta^{13}$C=-27‰) : 4%
- 0.95 Mixed layer (400 yrs old, $\delta^{13}$C=+2‰) : 2%
- 0.87 Deep ocean (2000 yrs old, $\delta^{13}$C=+0.7‰) : 90%
Changes in the $^{14}$C distribution on earth

- If all the carbon were homogenized, the $^{14}$C “age” would be 940 yrs old relative to the previous atmosphere.

- Reductions in reservoir mixing rates could be even more significant: if a "lid" was placed between the surface ocean and the deep ocean for a sufficient time interval:
  
  Total C in atm.+mixed layer : $280 \times 10^{15}$ moles
  
  Total $^{14}$C in " " : $550 \times 10^3$ moles (11% of total $^{14}$C)
  
  $^{14}$C Decay rate in " " : 70 moles/year
  
  $^{14}$C Production rate : $\sim 600$ moles/year

- So: $^{14}$C in the atmosphere and mixed layer could double in 1000 years!!!!

  $dn/dt = 0$; production = decay = 530 moles/yr
  
  (or in $10^3$ yrs, $5.3 \times 10^5$ moles)

  Is there any evidence for such an extreme event? No, but it shows how easily smaller reductions in ocean mixing can influence atmospheric $^{14}$C levels.
Distribution of $^{14}$C in the waters of the ocean: 'aging' of water masses moving from Atlantic into Pacific

Image removed due to copyright restrictions.

Broecker and Peng. Figure 5-3.
Distribution of $^{14}$C in the Atlantic Ocean

Image removed due to copyright restrictions.

Broecker and Peng. Figure 5-5.
Mixing of waters of different ages is a major influence on oceanic $^{14}$C

Concept of Transit Time distribution: suppose we could attach a clock to each atom of water as it left the surface mixed layer and moved into the interior. Because of vertical and horizontal mixing, each water sample will be a mixture of water that sank at different times, best described as a probability distribution.
Transit Time Distribution Concept (a la Kawatihala, Haines)

A water sample is composed of a mixture of water that has left the surface at different times in the past - hence the "age" of water sample is best expressed as a distribution rather than as an average.
Problem: how do we know what the transit time distribution is?

There isn’t any theoretical reason for it to assume a particular shape for the distribution. In fact, it may be a discontinuous function (e.g. deep water forms some years, not others).

Ocean circulation models can generate transit time distributions as part of their output. However, we suspect that these results may not be accurate because of limited resolution imposed by current computer capabilities.

If we had a series of tracers with temporally different surface boundary conditions, we could potentially estimate the transit time distribution, at least to a first approximation. This has not been done yet.

BOTTOM LINE: the meaning of a $^{14}$C “age” for water depends on the conceptual or mathematical model within which you choose to interpret it.
Planktonic-Benthic $^{14}$C age differences as a tracer of past deep water

Planktonic foraminifera will record the $^{14}$C age of the near-surface waters (a few hundred years $+$, depending on upwelling and mixing).

Benthic foraminifera will record the $^{14}$C age of bottom waters.

After incorporation, the $^{14}$C/$^{12}$C ratio decays according to the radiodecay law. The benthic-planktonic $^{14}$C age difference will reflect the age difference of the deep and surface waters.

Surface sediment mixing will create a mixture of specimen ages until the sediment passes through the bottom of the sedimentary bioturbation layer.

AMS $^{14}$C determination requires $\sim$1000 individual foraminifera. The foraminifera will have a range of ages and the measurement will record the average.
Deepwater-Surface $^{14}$C Age Differences in the Modern Ocean

Image removed due to copyright restrictions.
Early B-P 14C results: Sonne I

Sonne 50  37 KL
South China Sea

AMS C14 Age, yrs bp

Depth, cm
B-P results: TR163-31b

- AMS C14 Age, kyr.
  - Benthic: $y = 7.4239 + 9.5322 \times 10^{-2} x$, $R^2 = 0.982$
  - Planktonic: $y = 5.6227 + 9.1462 \times 10^{-2} x$, $R^2 = 0.994$

Shackleton, Duplessy, Arnold Maurice, Hall, & Cartlidge, 1988

Figure by MIT OpenCourseWare.
Changes in the ventilation rate of the deep ocean

**PACIFIC**

- Modern
- Glacial

**ATLANTIC**

- Modern
- Glacial

Radiocarbon Age, kyr relative to surface ocean
The role of sampling statistics in foraminiferal property analysis
Example of discrete vs crush & split reproducibility

Deviation of individual analysis from mean, \( \mu\text{mol/mol} \)

TR163 - 31b (Eastern Equatorial Pacific)

Triplicates of Separate Picks (pooled Std. Dev. = .023)

Crushed and Split Triplicates (pooled Std. Dev. = .009)

Effect of bioturbation on sedimentary signals and discrete analysis reproducibility

- Berger-Heath sedimentary mixed layer model
Effect of bioturbation on sedimentary $^{14}$C
Keigwin’s strategy for minimizing the effect of bioturbation:

• Use high accumulation rate cores (minimize age range of mixture)

• pick from abundance (per gram) maxima (so foraminifera from outside the zone reflect minimal contamination)
Summary of apparent ventilation ages for (a) the YD and LGM time slices, and (b) benthic foram dates during the YD and planktonic dates on the LGM benthic peaks. For each panel, YD data are solid squares, and LGM data are open squares.


Reading (2)
