12.740 Paleoceanography

Spring 2008

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The ^{14}C story.

I. Production and simple age calculation

A. Produced by cosmic ray -> 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. This builds up a steady-state inventory of ~5000 x 10^3 moles of ^{14}C on the earth:

$$\frac{dN}{dt} = -\lambda N$$

$$530 \text{ moles/year} = \frac{-.693}{5730 \text{ yrs}} \times N \text{ moles}$$

B. ^{14}C: $t_{1/2}$ = 5730 ± 40 years (Godwin, 1962).

1. 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!

C. If ($^{14}C/^{12}C$) 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

$$\frac{dN}{dt} = -\lambda N$$

$$N/N_O = e^{-\lambda t}$$

II. A minor complication: Carbon isotopes are fractionated by organisms relative to air: $^{13}C/^{12}C_{plants}$ ~ -20 permil relative to atmosphere (which is -7 permil relative to ocean surface waters), and $^{14}C/^{12}C$ is fractionated by about twice that amount. So you must measure $\delta^{13}C$ and correct for isotope fractionation of ^{14}C:

A. Definition: $$\delta^{13}C = \left[\frac{\left(^{13}C/^{12}C\right)_{sample}}{\left(^{13}C/^{12}C\right)_{standard}} - 1 \right] * 1000$$

B. Definition: $$\delta^{14}C = \left[\frac{Activity_{sample}}{Activity_{standard}} - 1 \right] * 1000$$

where $Activity_{std}$ is taken to be 95% of the NBS oxalic acid standard (to approximate pre-industrial pre-nuclear bomb (PIPN) atmospheric carbon).

C. $\Delta^{14}C$

1. $\delta^{14}C$ cannot be used to directly calculate the age of a sample; it must be corrected for two effects. 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 $X/X_o = e^{-\lambda t}$ 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‰).

2. Then:

$$\mathbf{\Delta^{14}C = \delta^{14}C - (2\delta^{13}C + 50)(1 + \delta^{14}C/1000)}$$

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.

Relationship between measured $\Delta^{14}C$ and radiocarbon age:

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

Relationship between measured $\Delta^{14}C$, true age, and initial $\Delta^{14}C$:

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

D. For some purposes, we need to know the absolute concentration of ^{14}C (moles per kg, for example). For seawater, the conversion is:

$$\mathbf{[^{14}C] = 1.176 \times 10^{-12} (1 + \Delta^{14}C/1000)\, \Sigma CO_2}$$

where ΣCO_2 is expressed in terms of μmoles/kg.

E. For ocean waters and other relatively "young" (<2500 yr) things: $\Delta^{14}C$ decreases by 10‰ every 80 years.

III. ^{14}C measurement:

A. Counting measurement (β gas counting or liquid scintillation), need tens of grams,

low background (anticoincidence counters), and time.

1. Convert $CaCO_3$ --> CO_2 --> C_2H_2 (acetylene)

   a. Gas (proportional) counting

   β decay leads to gas discharge (count)

   b. liquid scintillation

   C_2H_2 --> C_6H_6 (benzene)

   add 'cocktail' of scintillators which gives off light for each β decay

B. Accelerator measurement: 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)
   -->Mass spectrometer (separates m/e)
   -->Stripper (thin sheet) which strips electrons from ions
   (Some ions are unstable; this is important because it helps get rid of N)
   -->Solid State Detector (measures ΔE/E, which is different for each isotope; this is important because it allows for further separation of N and the C isotopes).

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Source for above illustrations: Bennett (1979) American Scientist 67:450-457, figure 4.

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C. Where sample contamination and size is not limiting, samples may be enriched by thermal diffusion separation.

IV. What regulates ^{14}C /^{12}C in the atmosphere?

A. Most recently, the burning of (very old) fossil fuels with no radiocarbon has been diluting the ^{14}C concentration of the atmosphere (Suess Effect):

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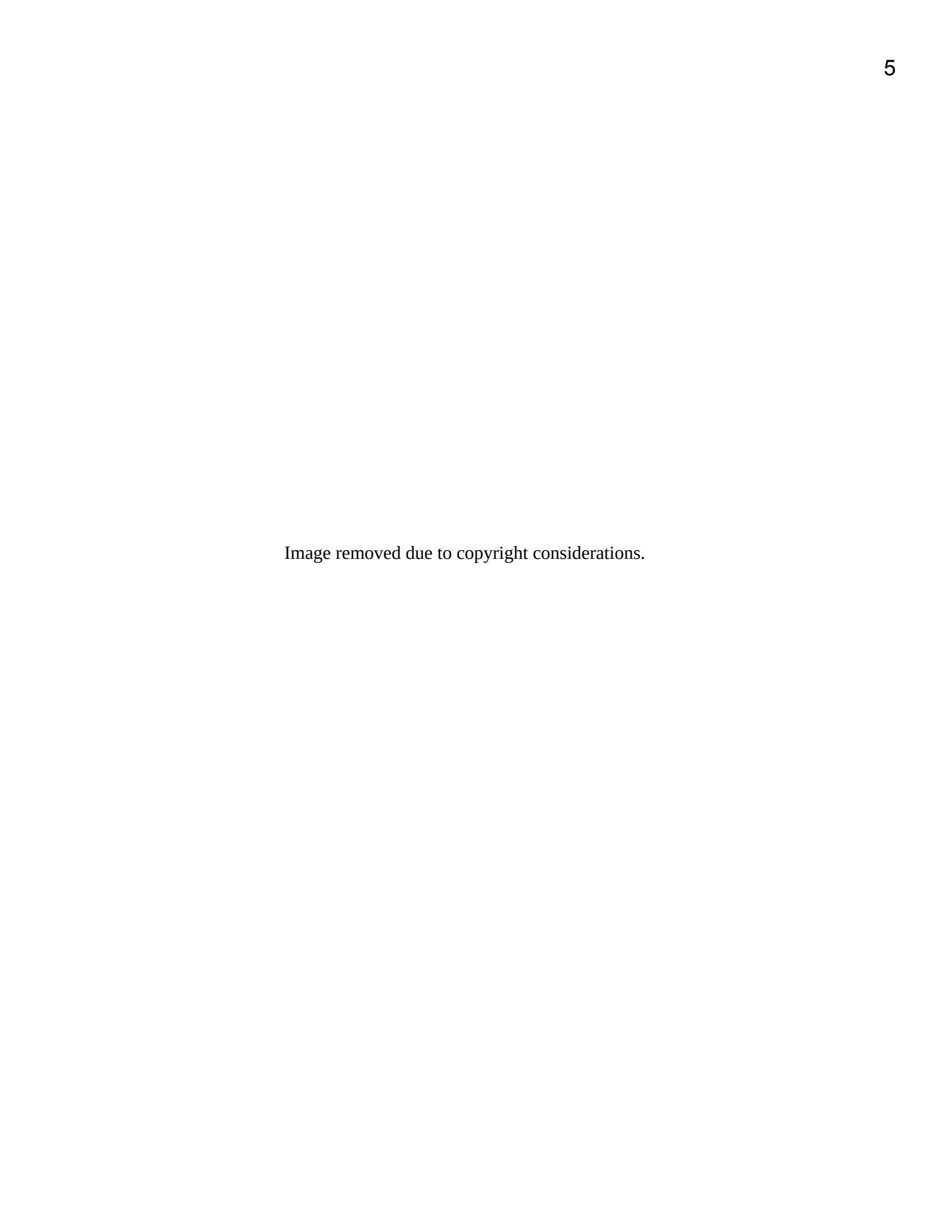
Source: Stuiver and Quay (1981) EPSL 53:349-362.

B. ^{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. Origin is outside solar system; flux is assumed 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 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; slow changes in intensity (as estimated from the magnetization of dated ceramics and rocks); magnetic reversals] which in turn are influenced by 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.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Source: Stuiver and Quay (1980) Science 207: 11-19, figure 1.

Solar cycle production variations are not seen in the atmosphere because of the size of carbon reservoirs.

C. Measurement of tree rings of known age can tell us the initial carbon 14 content of the atmosphere during its growth year.

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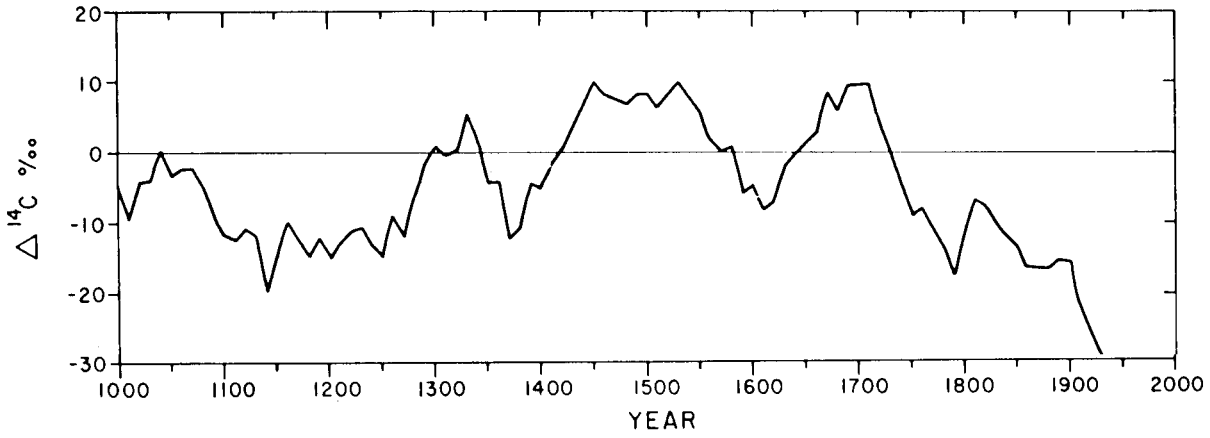
Source: Stuiver (1978) Nature 273:271-274.

2. During the last 1000 years, fluctuations in the initial activity have occurred, although the changes are small (less than 2%):



Atmospheric $\Delta^{14}C$ levels of the current millennium,
Source: data replotted from Stuiver and Quary, 1980.

2. Over the last 9000 years, larger changes have occurred (up to 9%):

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Source: Neftel, Oeschger, and Suess (1981) EPSL 56: 127-147.

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Source: Hughen et al., 1998, figure 4.

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Source: Hughen et al., 2000, figure 2.

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Source: Stuiver et al. (1998) Radiocarbon 40:1041-1083, figure 12.

4. 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 . The outcome is somewhat controversial, but the odds probably favor the recent reconstruction (based on Cariaco Basin – GISP2 correlations) of Hughen et al. (2004):

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Source: Hughen et al. (2004).

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Source: Hughen et al. (2004), figure 3.

5. IntCal 04 (Reimer et al., 2004)

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Source: Reimer et al. (2006).

Note: Fairbanks et al. (2005) and Chiu et al. 2005) argue for a different sample selection of corals

6. Measurements of corals which grew during the last glacial maximum 18000 years ago (as dated by the ingrowth of ^{230}Th from ^{234}U in the coral skeletons) also show that the ^{14}C activity of the atmosphere was about 30% higher than at present. This is thought to be due to changes in the earth's magnetic field. These magnetic field changes are observable by measuring the (calibrated) intensity of lavas which have cooled through the Curie Point at times in the past.

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Source: Tric et al. (1992) JGR 97:9337-9351

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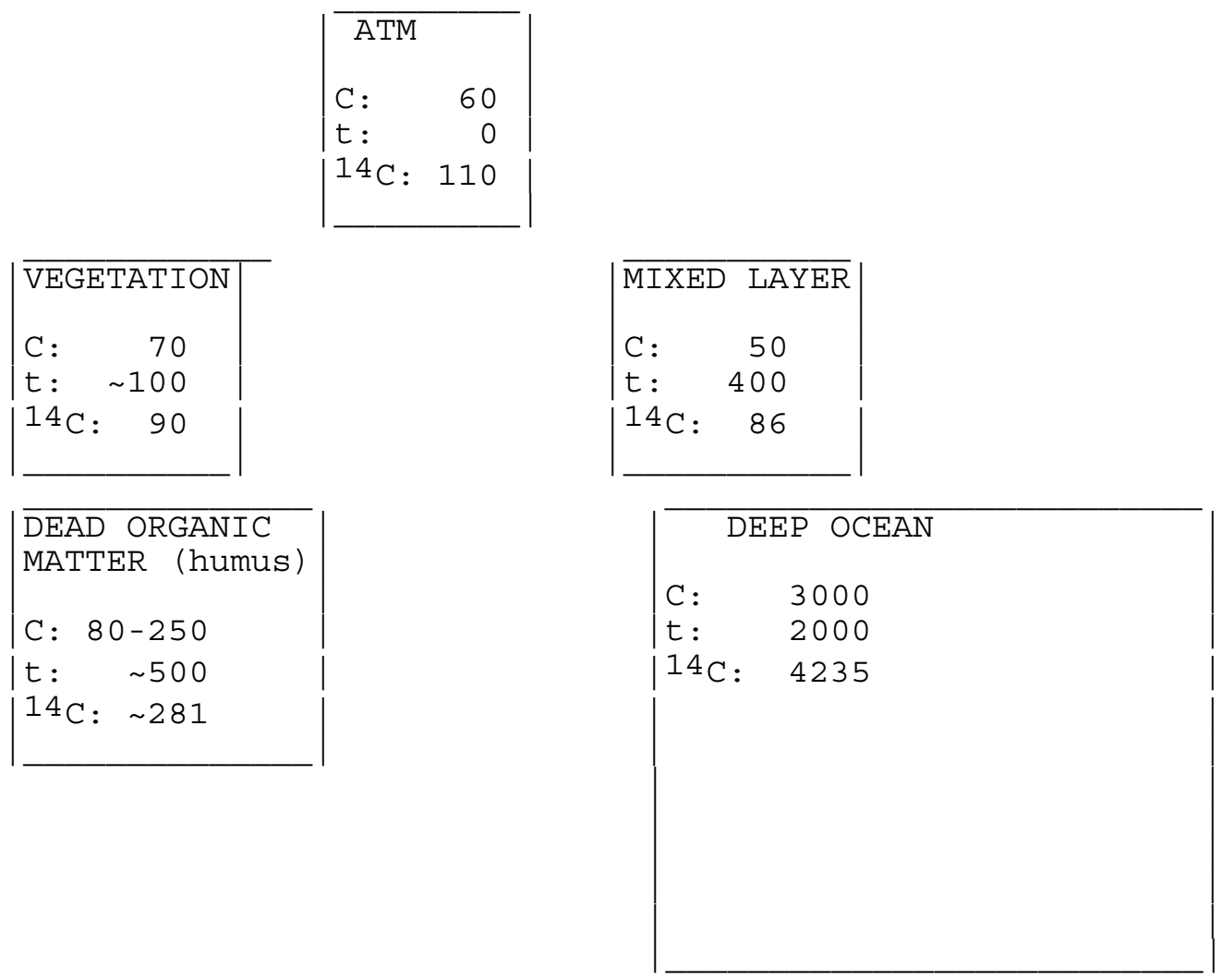
Source: C. Laj et al. Earth and Planetary Science Letters 200 (2002) 177-190.

5. 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).

D. Carbon reservoirs, carbon-14 ages, and carbon-14 reservoirs

Units:

10^{15} moles of carbon
radiocarbon years (relative to atmosphere)
10^{3} moles of carbon 14.



(in addition, there are ~200 units of ^{14}C in oceanic sediments)

1. In each "box", ^{14}C builds up until decay = renewal rate
2. Total production ≈ 600 moles/year, so total <u>steady-state</u> reservoir must be

   $N \simeq 5 \times 10^{6}$ moles ^{14}C.

3. <u>Most</u> vegetation, humus, mixed layer, is radiocarbon "young" relative to atmosphere. <u>Total</u> reservoir is

(100 + 70 + 60 + 50 + 3000) = 3280 x 10^{15} moles

humus veg Atm mixed layer deep ocean

So average carbon-14 specific activity is about 100 dpm/g

4. There are hold-up times for carbon transfer between reservoirs:

a. ^{14}C "age" of surface ocean water is 400 years; deep Pacific ocean "age" is 3000 years

b. 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:

$^{14}C/^{14}C_{atm}$		tot ^{14}C
1.00	Atmosphere (0 years, $\delta^{13}C$=-7‰ : 2% of	
0.97	Veg (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%	

5. If all the carbon were homogenized, it would become (suddenly) 940 yrs old relative to previous atmosphere.

6. 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: 280×10^{15} moles

Total ^{14}C in " " : 550×10^{3} moles (11% of total ^{14}C)

^{14}C Decay rate in " " : 70 moles/year

^{14}C Production rate : ~600 moles/year

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

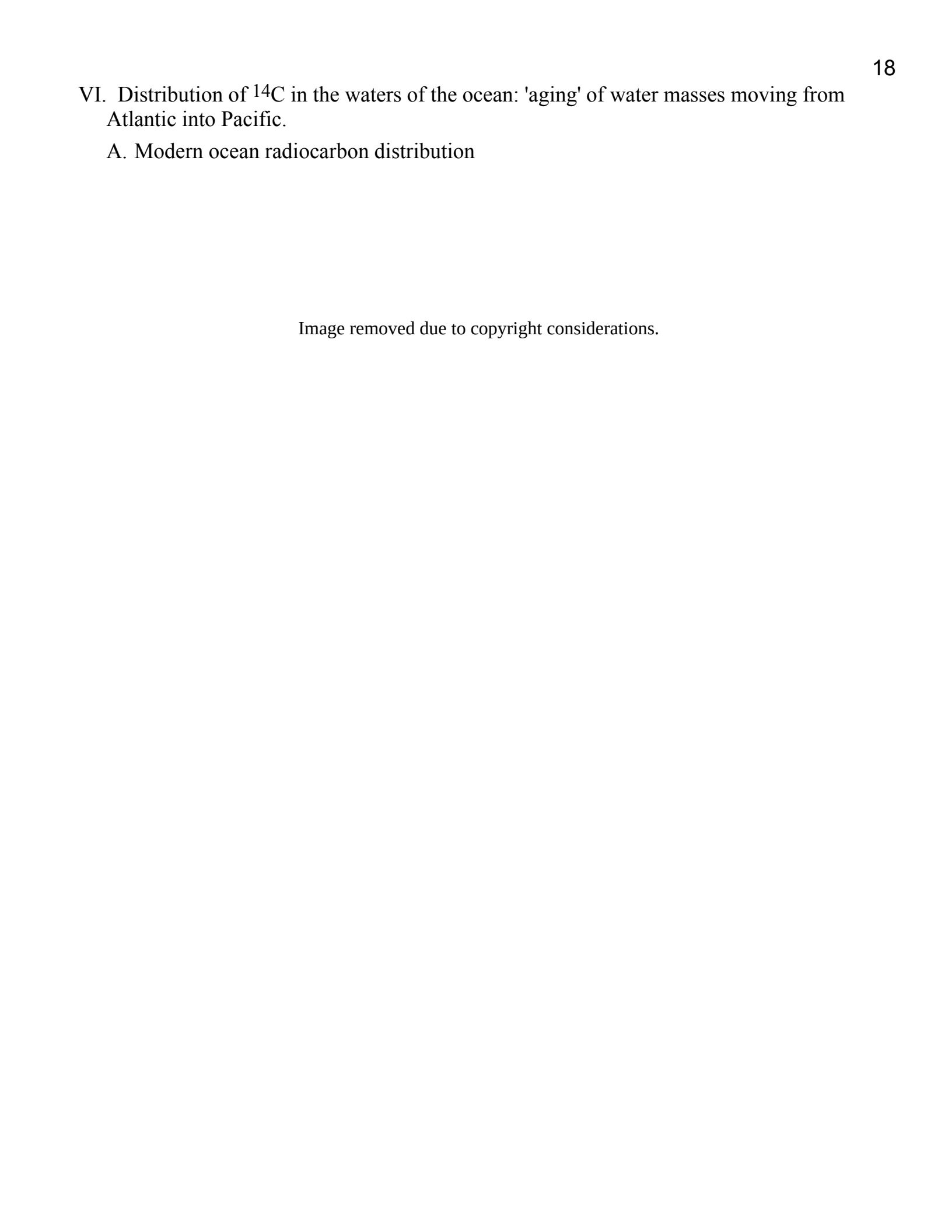
dn/dt =0; production = decay = 530 moles/yr

(or in 10^{3}yrs, 5.3×10^{5} moles)

a. Is there any evidence for such an extreme event? No, but it shows how easily smaller mixing reductions can influence atmospheric ^{14}C levels.

VI. Distribution of ^{14}C in the waters of the ocean: 'aging' of water masses moving from Atlantic into Pacific.

A. Modern ocean radiocarbon distribution



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Source: Broecker and Peng (1984), figure 5.5.

Problem: the ocean is not a mummy: water masses mix horizontally and vertically, and particles move ^{14}C from the surface to deep waters. Carbon is transferred vertically in the ocean as organic carbon and inorganic carbonate precipitated by organisms from material obtained from solution in seawater. Deep-sea ^{14}C ages need to be interpreted by a model that takes mixing into account; raw deepwater ^{14}C ages must not be interpreted literally as a transit time from the atmosphere.

B. Planktonic-Benthic ^{14}C differences as a measure of the radiocarbon distribution in the past.

1. Planktonic foraminifera incorporate ^{14}C of surface waters; benthic foraminifera incorporate ^{14}C of deep waters. Then, buried in the sediment, the ^{14}C decays in both, preserving a record of the difference in surface and deep radiocarbon values.

2. Originally, this difference was used directly to assess changes in the deep water ^{14}C age (e.g. Broecker, Duplessy and Shackleton). But because the transit time of ^{14}C into the deep sea is long compared to the rate at which ^{14}C can change in the atmosphere (see above), one has to interpret the ^{14}C of benthic foraminifera relative to the ^{14}C of the atmosphere at the time the water left the surface – rather than the ^{14}C of the atmosphere recorded by the coexisting planktonic foraminifera (Adkins and Boyle, 1997).

For further details:

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