Radiocarbon Dating

Archeological Chemistry Seminar

2023 AAS/ARAS Training Program

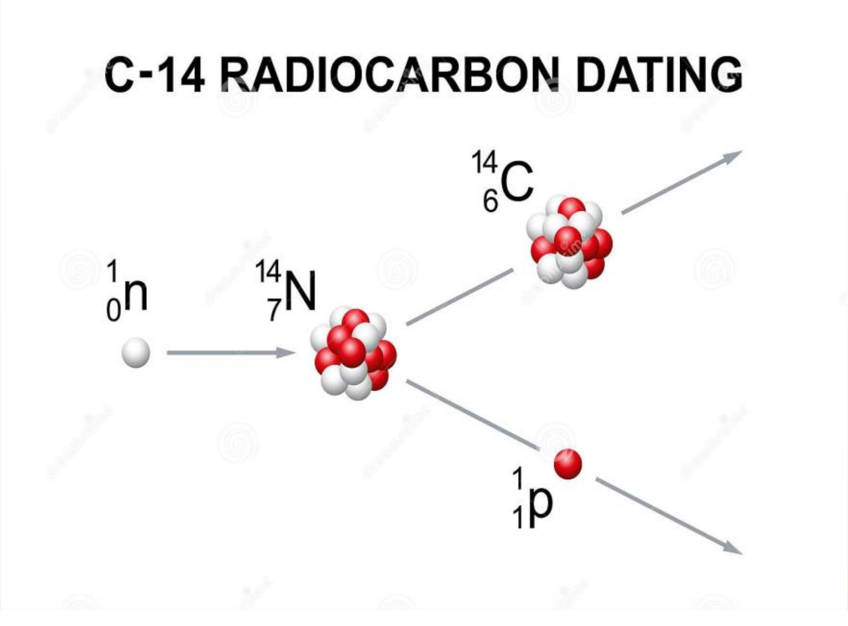
Early History

- C-14 dating was developed by Willard Libby at the University of Chicago
  - Important collaborators:
    - James Richard Arnold – Research Assistant
    - Ernest Carl Anderson – Graduate Student
  - Research began in 1946 looking at the difference in abundance of C-14 in fossil and living organic material
  - Libby was aware of archeological implications and later professed his own avocational interest in archeology
  - Was awarded Nobel Prize in Chemistry (1960)

Willard Libby

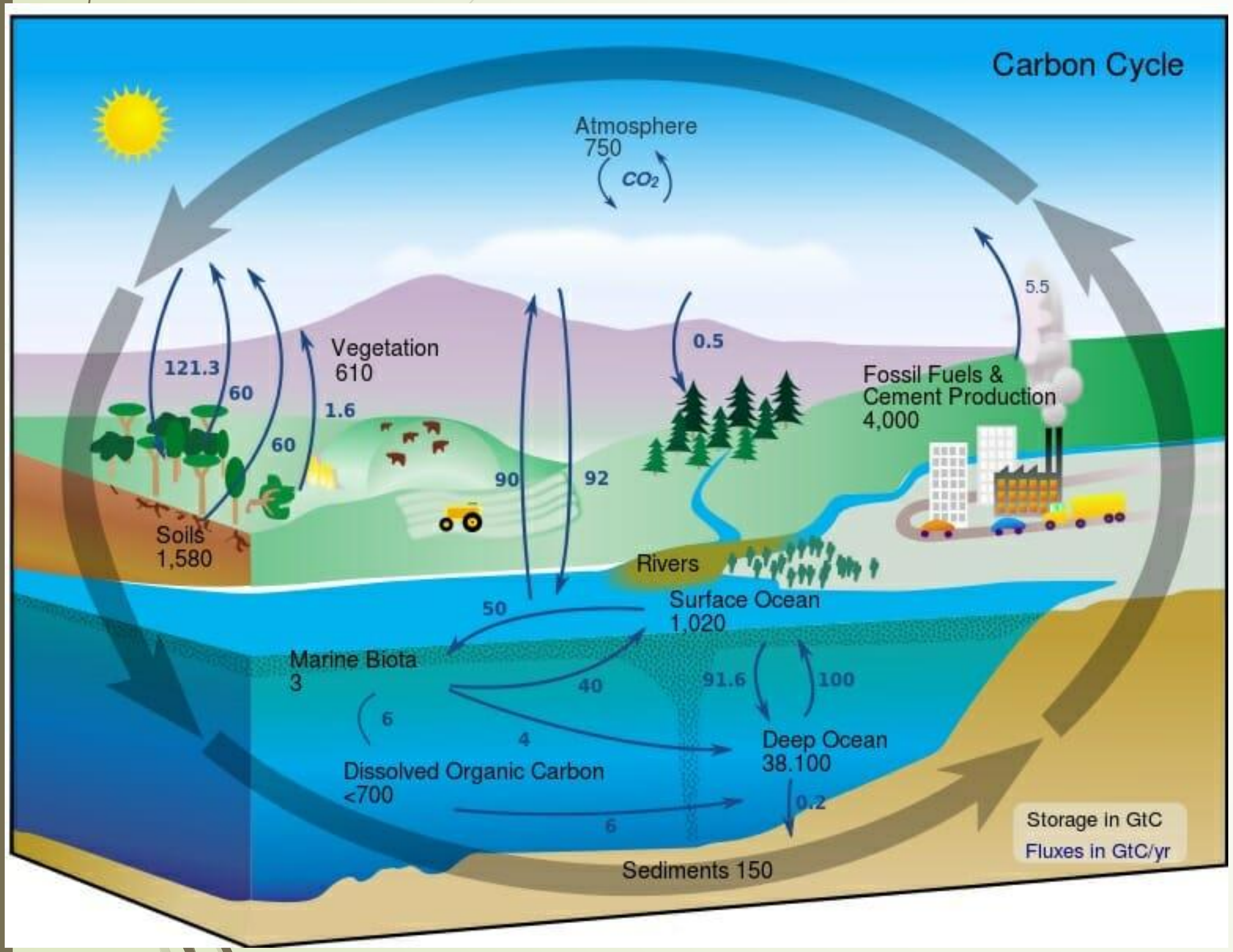
How C-14 is made

- 99% of C-14 occurs through collisions of cosmic radiation with atmospheric gas
  - Cosmic radiation (H^+, He^{+2}) collisions create spallation products (including thermal neutrons)
  - Neutrons then collide with nitrogen atoms to produce radioactive C-14
  - Process primarily occurs 10-13 miles above Earth (stratosphere)



Production rate of ^{14}C has ranged from 1.8 – 2.5 ^{14}C atoms/cm^2/s

Distribution of C-14



- Initial ^{14}C atoms combine with oxygen to form carbon monoxide (^{14}CO)
- Days later ^{14}CO combines with another oxygen to form $^{14}CO_2$
- This process converts 95% within two weeks

$$^{14}C \rightarrow {}^{14}CO \rightarrow {}^{14}CO_2$$

- Production rate depends only on
  - Cosmic radiation flux
  - Strength of Earth's magnetic field
- Production rate is 4x higher at geomagnetic poles than at equator
  - At poles, magnetic field dips toward the surface bringing cosmic radiation to lower altitudes

A few considerations for use in dating

- Terrestrial and marine plants incorporate $^{14}CO_2$ during photosynthesis
- Thus, it enters the food chain
- People and animals incorporate ^{14}C through food and respiration
- Organisms have both input and output of ^{14}C leading to a constant equilibrium concentration while the organism is alive
- Upon death, there is no more input
  - Remaining ^{14}C will eventually decay back to ^{14}N

$$^{14}C \rightarrow {}^{14}N + B^- + \nu$$

By-products are beta particle and neutrino

- By counting remaining ^{14}C in a sample, the time since death can be calculated

The math of radioactive decay

- All radioactive decay (including C-14) follows "1st order kinetics"
- 1st order decay equation (written three ways):
  - $[A]_t = [A]_0 e^{-kt}$
  - $\ln[A]_t = \ln[A]_0 - kt$
  - $\ln\frac{[A]_t}{[A]_0} = -kt$
    - $[A]_0$ = initial amount of radiogenic substance (atoms, percentage, molarity, etc…)
    - $[A]_t$ = amount of radiogenic substance remaining after some time has passed
    - k = rate constant for radiogenic decay
    - t = time passed since death

    - ln (natural log) and e (exponential) are calculator functions

Half-life ($t_{1/2}$)

- The rate of radioactive decay depends on the isotope
- Some radiogenic isotopes decay very fast and others are very slow
  - Milliseconds to billions of years
  - Rate of decay depends on rate constant (k)
  - The rate of decay is often expressed with the half-life ($t_{1/2}$)
  - Half-life is the amount of time it takes for the original amount to be cut in half
  - $t_{1/2} = \frac{\ln 2}{k}$
- For C-14, there are two quoted half-lives in the literature
  - Libby value: 5568 ± 30 years
  - Cambridge value: 5730 ± 40 years (modern accepted value)

C-14 Dating Notes

- To determine a C-14 age, the amount of C-14 remaining $[A]_t$ must be measured in a laboratory
  - Beta counting
  - Accelerated Mass Spectrometry (AMS)
- Some knowledge of the original amount of C-14 $[A]_0$ must be known
- Solve for time t in the first order kinetics formula

- Half-life $_{t1/2}$ sets a limit to how old a sample can be dated
  - Generally, samples must be within 10 $t_{1/2}$ to be reliably dated
  - Thus, C-14 samples must be less than about 60,000 years
  - Samples older than 60,000 years do not have enough C-14 left to be reliable measured

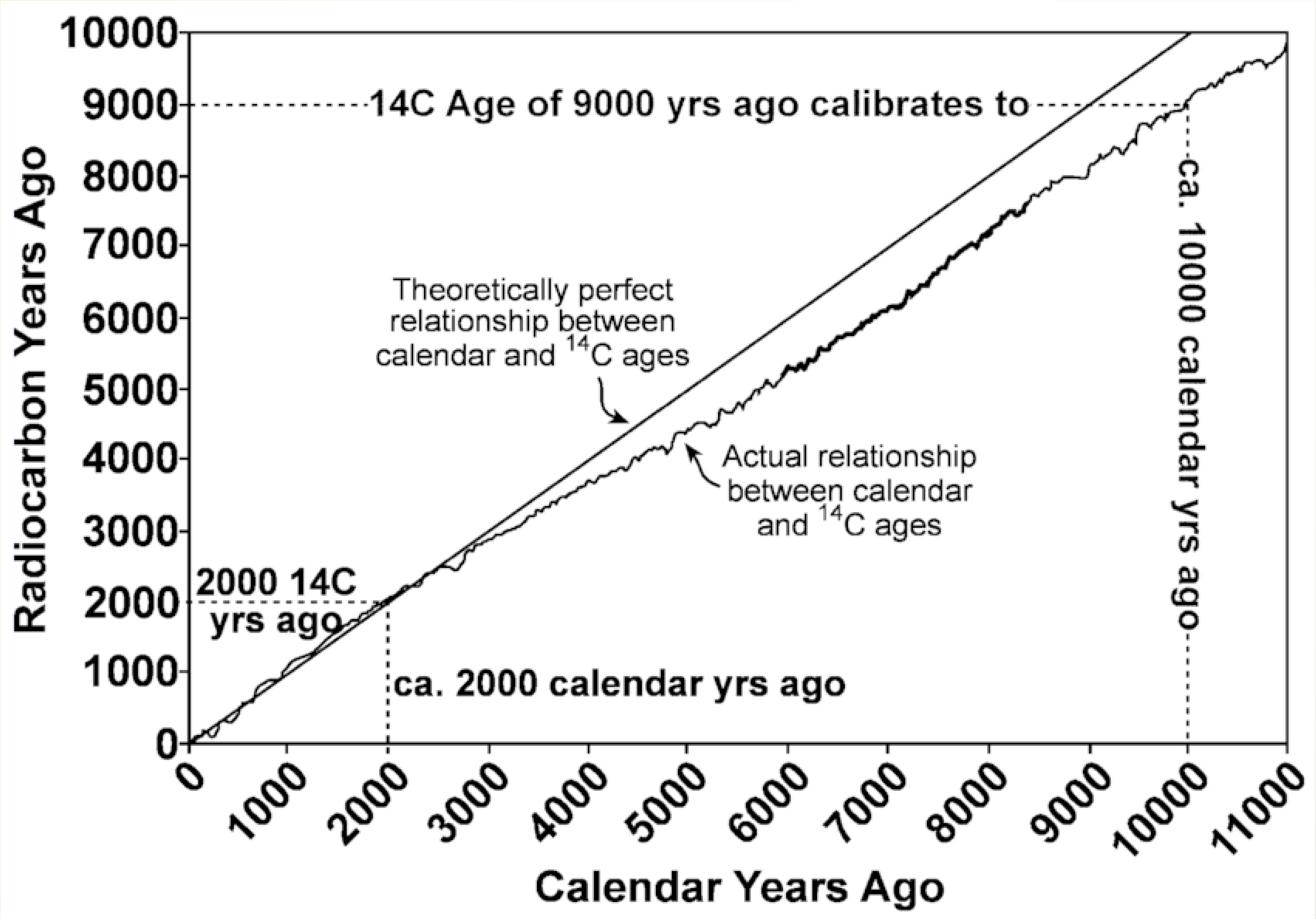
Secular Variation Effects

- Three types:
  - Geophysical mechanisms controlling worldwide ^{14}C production rate
  - Distribution rate mechanisms of ^{14}C
  - Variability in carbon isotopes due to reservoir effects
- Biosphere carbon comes from atmospheric carbon
  - But there is a lag time between changes in atmospheric carbon and changes in biosphere carbon
  - Assuming a 10% sudden increase in the production of C-14 in the atmosphere
    - It would take the atmosphere 20,000 years to reach a new equilibrium value
    - Biosphere would take a bit longer to reach equilibrium for C-14
  - This complicates our estimate of $[A]_0$ and creates error
  - Age calculation could be off by hundreds of years

Calibrating Radiocarbon Ages

- Willard Libby initially used Egyptian artifacts of known ages and tree ring data to test for secular variation effects
    - He concluded there was good (± 10%) agreement between radiocarbon ages and known ages back to 4000 BP
    - Other researchers found notable discrepancies in radiocarbon vs. expected ages for older samples
- In the 1970s, California bristlecone pine trees were used to extend the radiocarbon calibration back to 7000 BP
    - The results show ever increasing divergence when dating the oldest tree ring layers

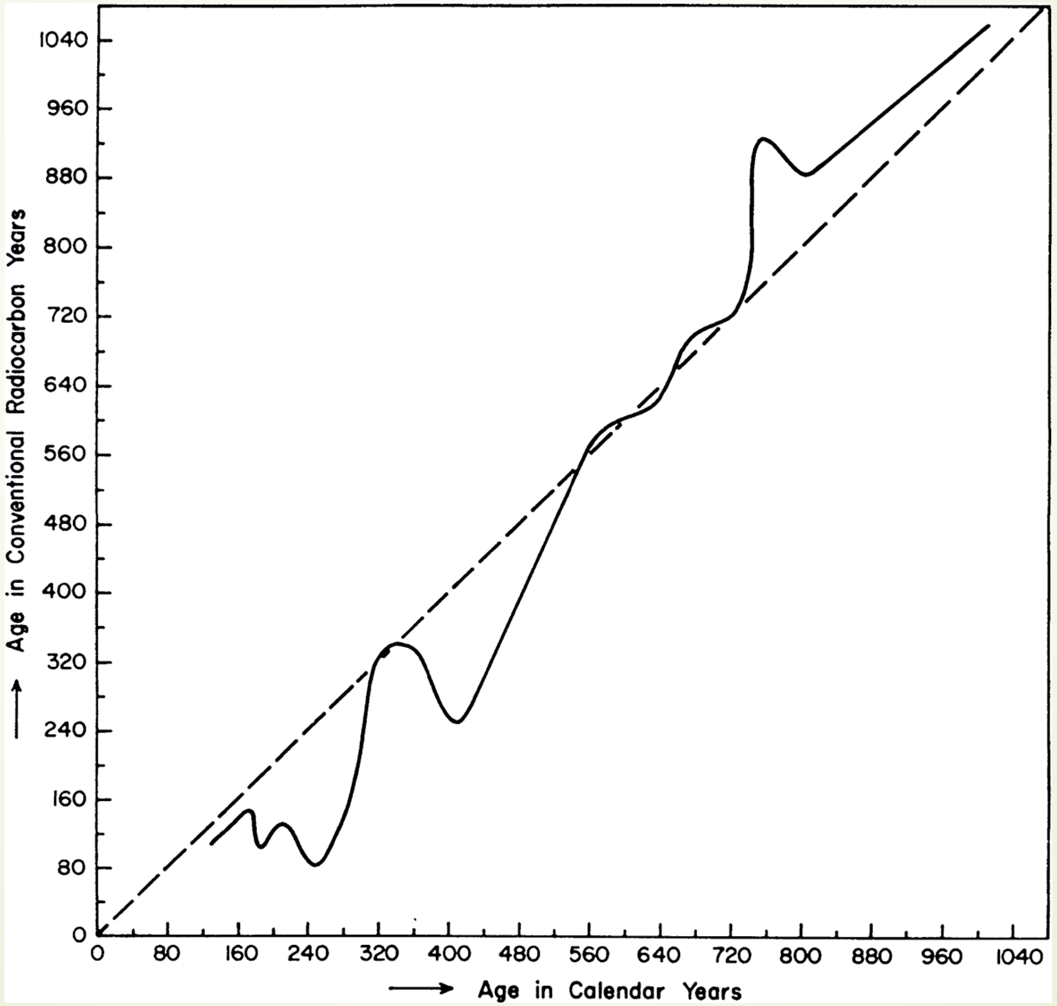
Radiocarbon Age vs Tree Ring Age



Biggest discrepancy = 1700 years

^{14}C Age of 10,000 BP =
11,700 years cal BP

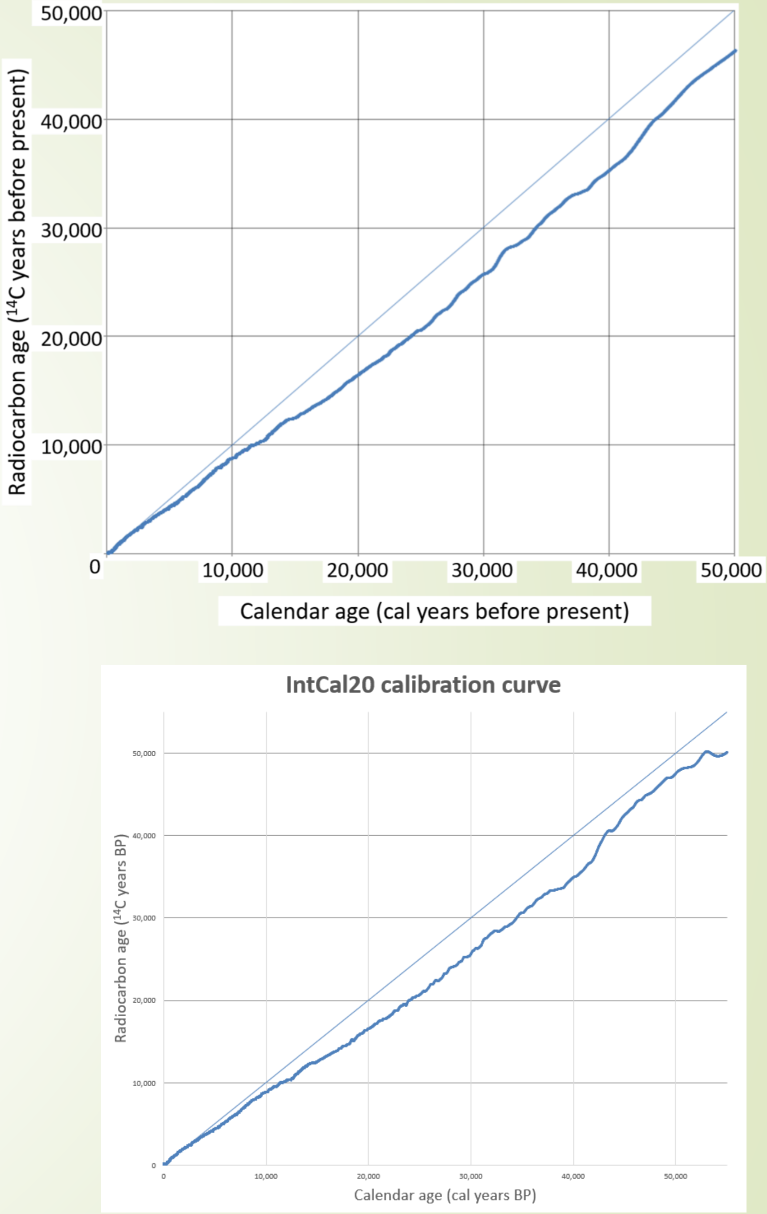
Significant Age Variations over Shorter Time Scales



Cambridge
Calibration Scale

Calibration Databases

- Since the 1980s, there have been several C-14 calibration databases created
  - Use different statistical models and geographic data
  - Published in the journal Radiocarbon
  - In chronological order:
    - Calibration Issue (1986)
    - Calibration 1993
    - IntCal98: Calibration Issue
    - 14C Varve/Comparison Issue
    - IntCal04
    - IntCal09
    - IntCal 13
    - IntCal20



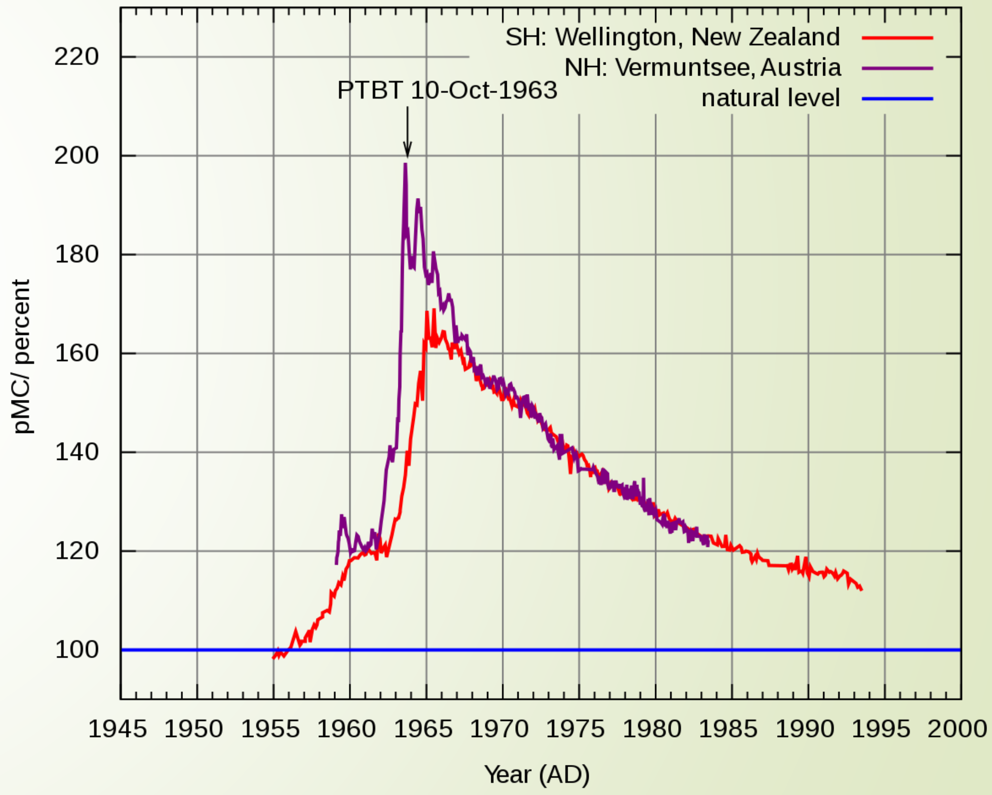
Differences between IntCal13 (top) and IntCal20 (bottom)

Computer Programs for Calibration

- Computer programs take the current calibration models and apply it to specific samples of interest
- These programs include:
  - Calib
  - OxCal
  - CAL
  - CalibETH
  - CALPal

Anomalies affecting C-14 abundance in the atmosphere

- De Vries Effects – Secular variations (wiggles) caused by changes in solar heliophysics
- Suess Effect – Burning of fossil fuels is adding abundant ^{14}C-free carbon to the atmosphere
- Libby Effect – Atomic bomb testing has added significant ^{14}C to the atmosphere
  - Mixing rates of ^{14}C between stratosphere and troposphere is less than 5 years for 95% of ^{14}C
- When radiocarbon ages are less than 200 years, samples are simply reported as "modern"



C-14 in the atmosphere due to atomic bomb testing

Ways to measure C-14 (or any $[A]_0$)

- Beta Counting
  - Every decay of ^{14}C to ^{14}N releases a beta particle
  - Young samples have more ^{14}C and thus more decays/minute
  - Used by Libby (gas proportional counting and liquid scintillation)
  - Requires destruction of 5-20 g
  - Measurement time days to months
- Accelerator Mass Spectrometry (AMS)
  - Uses mass spec to separate carbon isotopes by mass
  - Counts ^{14}C atoms and ratios it to ^{12}C (i.e. $^{14}C/^{12}C$)
  - Requires 3-100 mg of sample
  - Measurement time 15 minutes

Sample Pretreatment before AMS

- The goal of pretreatment is to remove carbon containing contaminants
- Most samples are treated with the following steps
  - Physical examination – removal of rootlets and other non-sample debris
  - Acid extraction – treated with hydrochloric acids to remove carbonate compounds
  - Base extraction – treated with sodium hydroxide to dissolve humic and fulvic acids, followed by repeated rinsing with water. Humic acid component is sometimes tested to see if it has a ^{14}C activity different from sample.
  - Solvent extraction – non-sample organics are removed by treatment with methanol, toluene, ether, etc…

- Samples are then burned to convert material into carbon dioxide and nitrogen gas for stable isotopes
- ^{14}C is determined by converting carbon dioxide into graphite

Mean lifetime of ^{14}C and Conventional Radiocarbon Age

- Use 1st order decay equation
- Also requires the "mean" lifetime T of a ^{14}C radionuclide
  - Recall the half-life is 5568 years (Conventional radiocarbon ages use the Libby value)
  - But, half of the ^{14}C will last much longer
  - Can be calculated from the decay constant k, $t_{1/2} = \ln 2/k$
  - Thus, $k = \frac{\ln 2}{t_{1/2}} = \frac{0.69315}{5568} = 1.2449x10^{-4}yr$
  - Mean lifetime of ^{14}C = 1/k = 8033 years

- Inserting into 1st order equation gives:

$$t\ (\text{years}) = 8033 * \ln(A_0/A) \qquad \text{(conventional age)}$$

Determining Conventional ^{14}C Ages

- First, a modern standard sample for carbon must be used
  - NBS oxalic acid (OXI) – used as instrumental standard sample
  - Has "percent modern carbon" (pMC) where 100 pMC = 0 BP = AD 1950

- Next, ^{14}C result must be converted to per mil

$$d^{14}C = [(A/A_0)-1]*1000$$

- Then, $d^{14}C$ must be normalized onto a common $d^{13}C$ scale

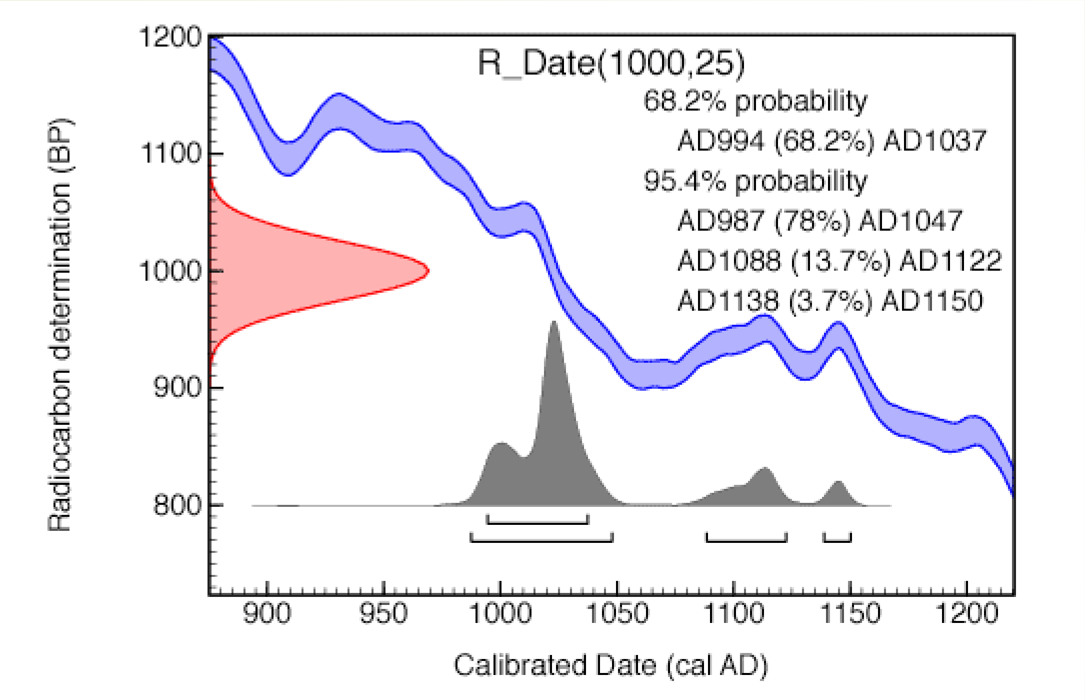
$$D^{14}C(‰) = d^{14}C - 2(\delta^{13}C + 25)\left(1 + \frac{d^{14}C}{1000}\right)$$

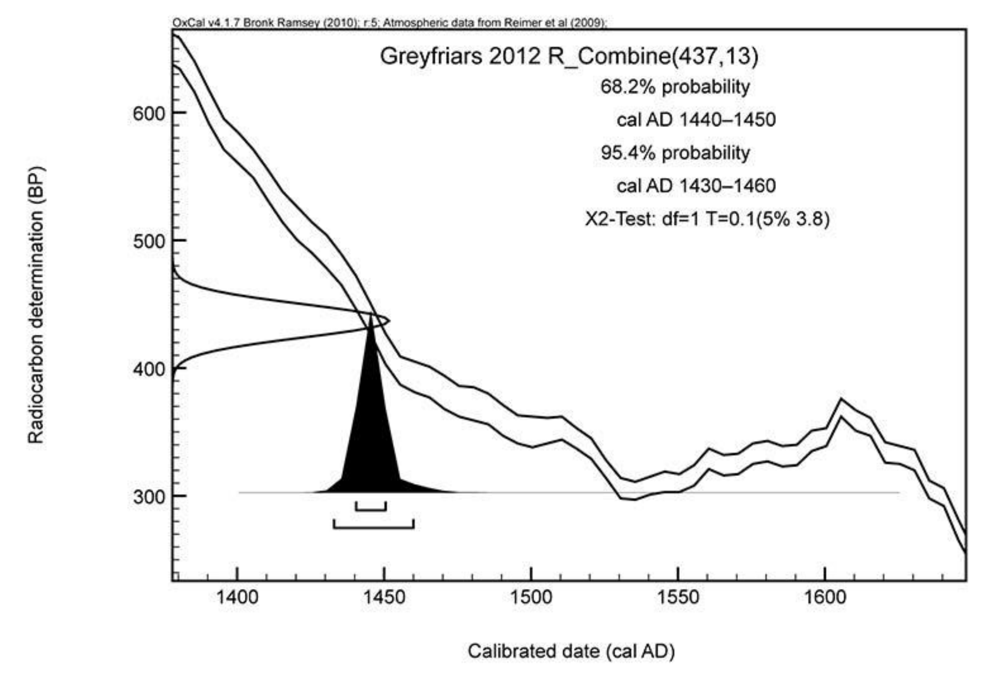
- Finally, radiocarbon age is calculated by:

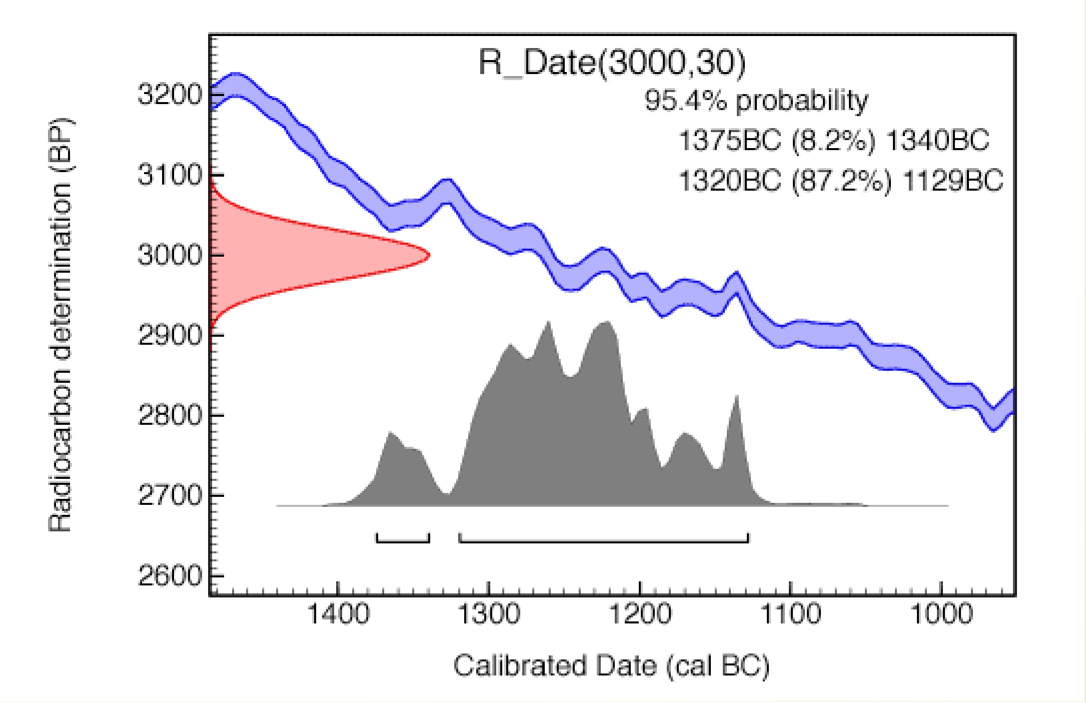
$$t\text{ (years)} = 8033 \ln \frac{1}{1+D^{14}C/1000}$$

Please note: Here we have not applied any statistical error analysis

Radiocarbon Examples







Radiocarbon Age and Calendar Age - I

- Conventional radiocarbon age should be reported as radiocarbon years before present and to a 1 sigma σ precision
  - Example: 3560 ± 30 RCYBP (1σ)
- $\delta^{13}C$ values should also be reported
  - Used to calculate conventional age and can be used for diet studies
- Calendar ages should be reported as AD/BC with "cal" included
  - 1 or 2 sigma precision is also included
  - Example: Cal AD 1160 to 1280 (2σ)
- Calibrated dates cannot be recalibrated
  - Conventional dates can be recalibrated in the future with new calibration curves

Radiocarbon Age and Calendar Age - II

- Measured Age – raw age measured by the lab using AMS or other techniques
- Conventional Age – measured age adjusted for isotopic fractionation
  - Prior to the late 1970s, reported ages were rarely corrected for isotopic fractionation
- Calibrated Age – conventional age corrected with tree-ring or varve calibration curves for ^{14}C variations over time
  - Sometimes called “radiocarbon date”

Image References

page #		
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