# A Survey of Modern Radiocarbon Dating

Kirk Bertsche

Stanford Linear Accelerator Center

Stanford University

Views presented here are those of the author, and do not necessarily reflect the positions of either Stanford University or the US Department of Energy.

# Radiocarbon Dating

- What is it?
- How well does it work?
- What is it good for?

# Willard F. Libby

- 1948: First radiocarbon date
- 1950: First “date list” (148 samples)
- 1960: Nobel Prize in Chemistry “for his method to use Carbon-14 for age determinations in archaeology, geology, geophysics and other sciences”

# Isotopes of Carbon

- $^{12}C$: “Normal” carbon (6 protons, 6 neutrons)
- $^{13}C$: Stable, about 1.1% of natural carbon (6 protons, 7 neutrons)
- $^{14}C$: Unstable “radiocarbon”, about $10^{-12}$ of modern carbon (6 protons, 8 neutrons)
  - Decays to $^{14}N$ by beta decay (electron emission)

$$^{14}_{6}C \rightarrow ^{14}_{7}N + \beta^{-} + \bar{\nu}_{e}$$

# $^{14}C$ Decay

- Decay is random, with fixed probability independent of time, environment, etc.

$$P_{decay} = \lambda$$

- Decay rate is constant

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

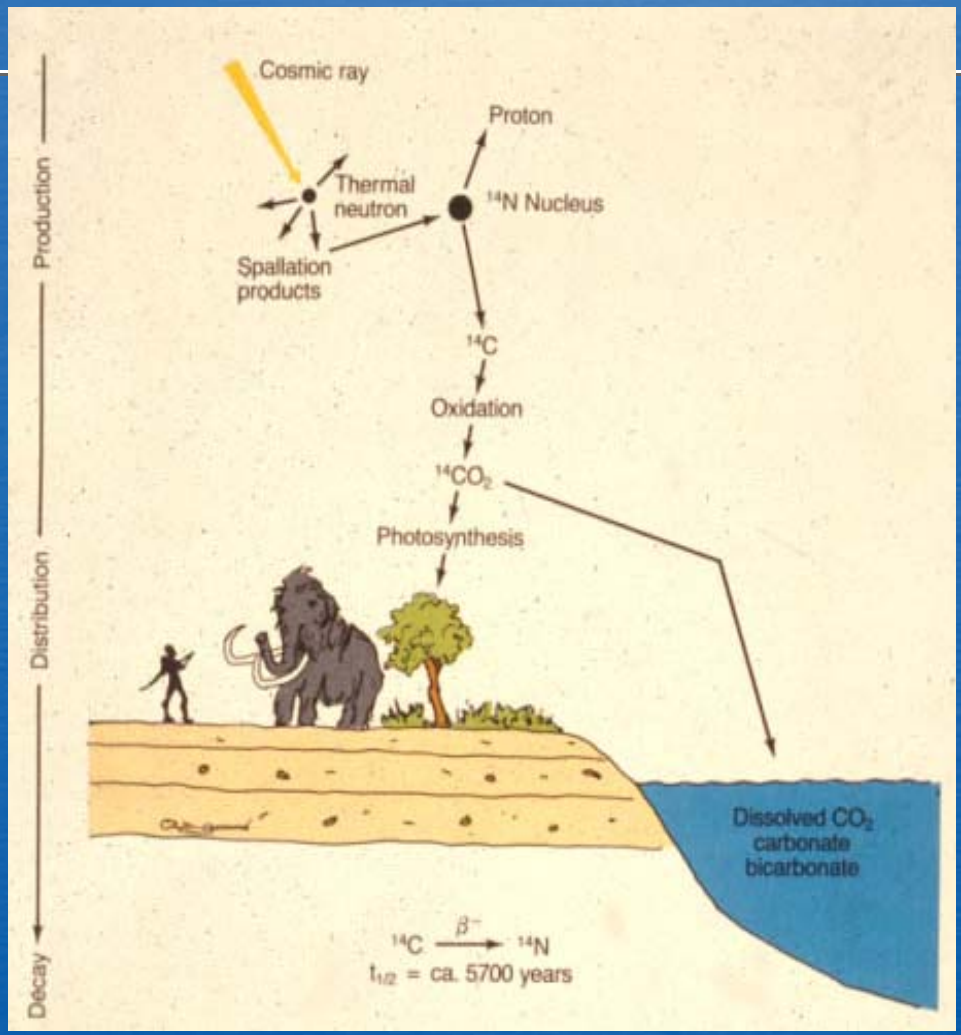
$$N_t = N_0 e^{-\lambda t}$$

- Often expressed as “half-life”

$$t_{1/2} = \frac{\ln 2}{\lambda} \approx 5730 \text{ years (5568 Libby value)}$$

# $^{14}C$ Production

- Cosmogenic
- (n,p): $^{14}_{7}N + n \rightarrow ^{14}_{6}C + p$
- Atmosphere and ocean buffers production variations




(after Taylor 1987 fig. 1.1)

# Principle of $^{14}C$ Dating

- Living ("modern") organisms in equilibrium with atmosphere ($^{14}C/^{12}C$ about $10^{-12}$)
- Current radiocarbon content is measured (typically expressed as Fraction or % Modern)
- Decay equation gives time of organism death

$$N_t = N_0 e^{-\lambda t} = N_0 e^{-\frac{t \ln 2}{t_{1/2}}} = N_0 e^{-\frac{t \ln 2}{5568\ yrs}}$$

- "Radiocarbon age" is generally expressed in years BP ("before present")
- "modern" = "present" = 1950 AD; based on NIST Oxalic Acid 1 standard, or secondary IAEA standards

# Mass Fractionation

- Chemical and biological processes (e.g. diffusion) affect ratio due to $^{14}C/^{12}C$ mass difference
- Fractionation can be characterized and corrected based on measured $\delta^{13}C$
  - $CO_2$ in air: $\delta^{13}C \sim -8$ ‰
  - C in tree: $\delta^{13}C \sim -28$ ‰
- "modern" or "present" is further defined as having $\delta^{13}C = -25$ ‰; $^{14}C$ measurements are corrected to this value

# $^{14}C$ Calibration

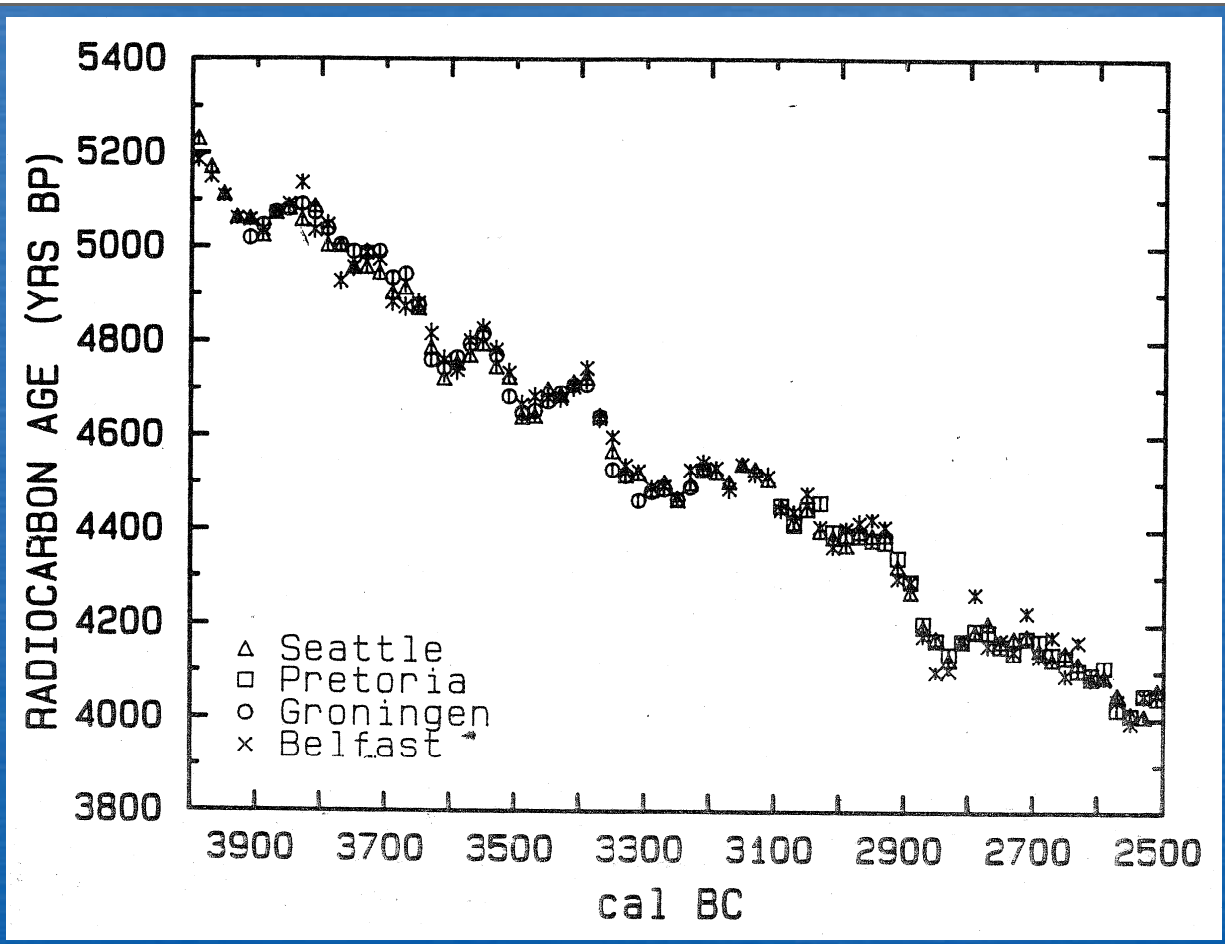
- A “Second Radiocarbon Revolution” (R.E. Taylor)
- Tree Rings or Lake Varves are counted to give give independent date
- Allows correction for and characterization of atmospheric variations in radiocarbon
  - (Basic method assumed atmospheric level is constant)

# Tree Rings

- Bristlecone Pine, European Oak, etc.
- Oldest *living* tree ~4,600 years
- Record extended using fossil trunks to ~12,400 years
- Cross-comparisons (different species & labs) show excellent agreement

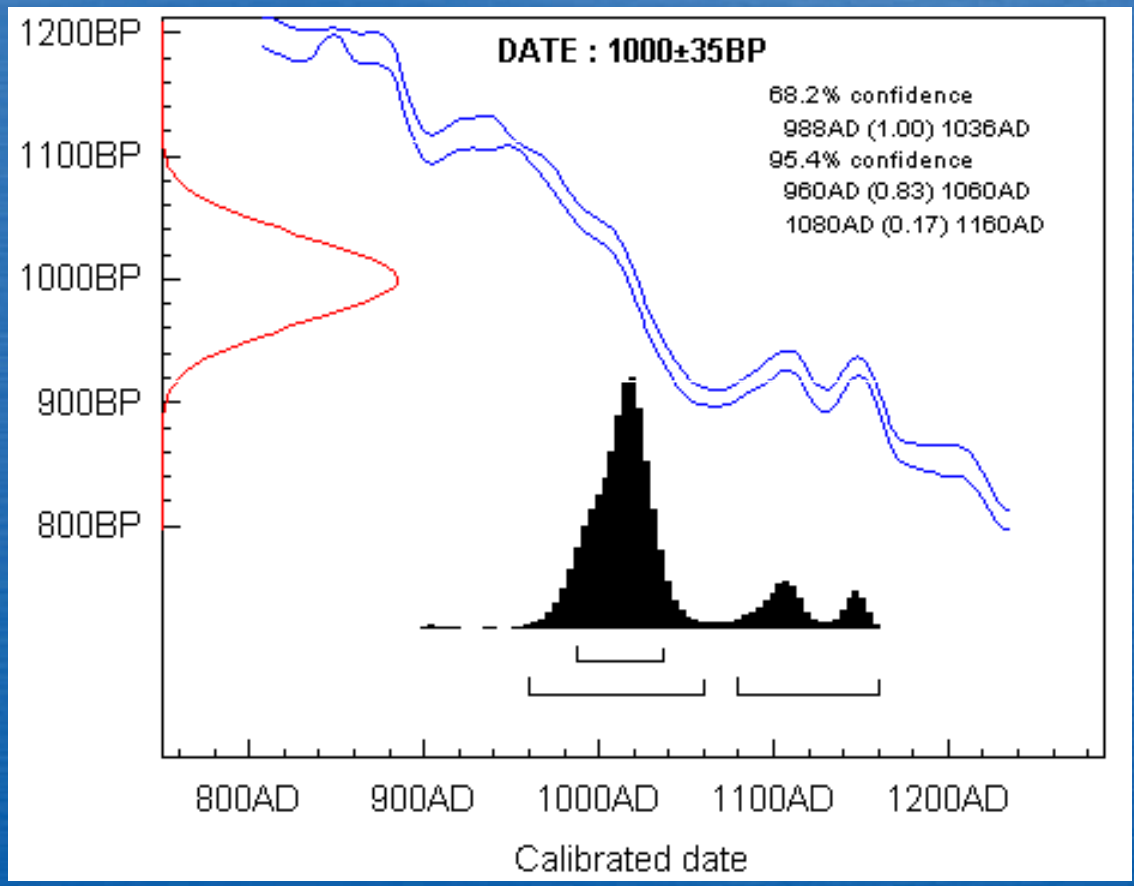
# Tree Ring Calibration Curve

- Msmts by four different labs on two different species show excellent agreement
- Correction at 5200 BP is ~15%




(Stuiver & Pearson 1992 fig. 3.2)

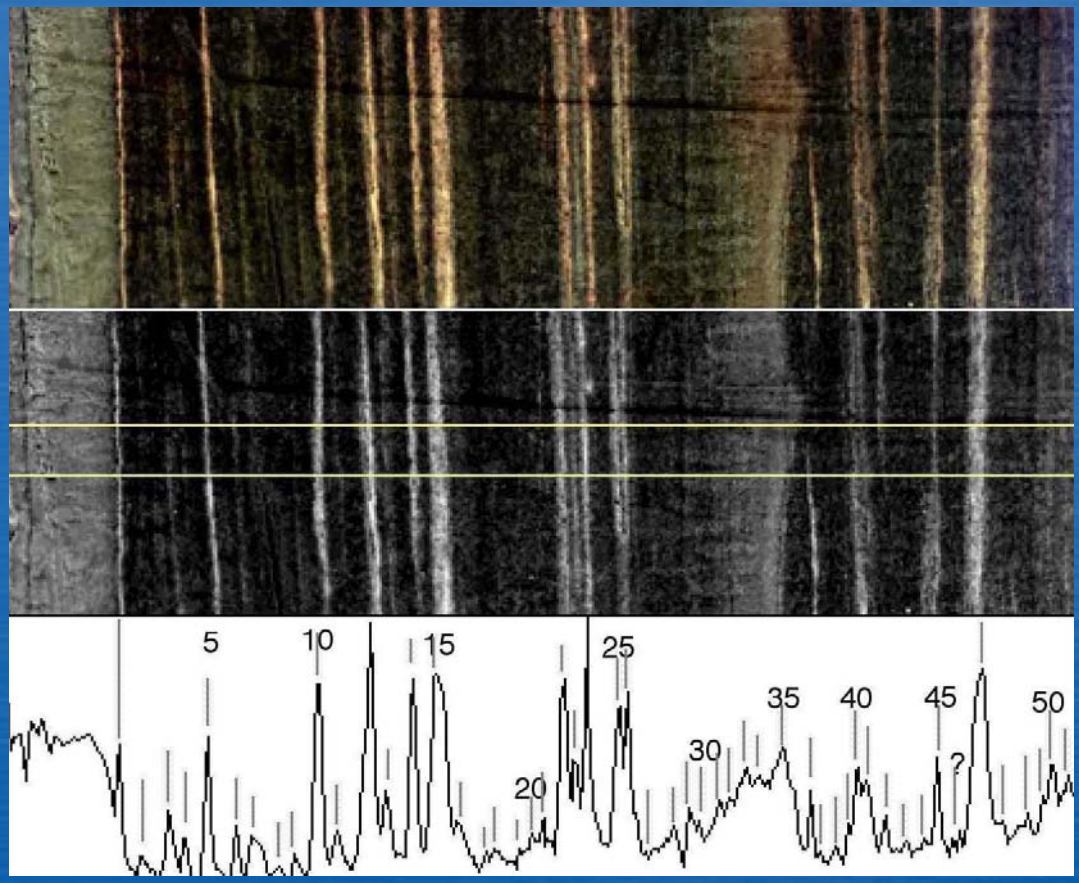
# Tree Ring Calibration Curve




(Courtesy J. Southon and S. Trumbore, UCI)

# Lake Varves

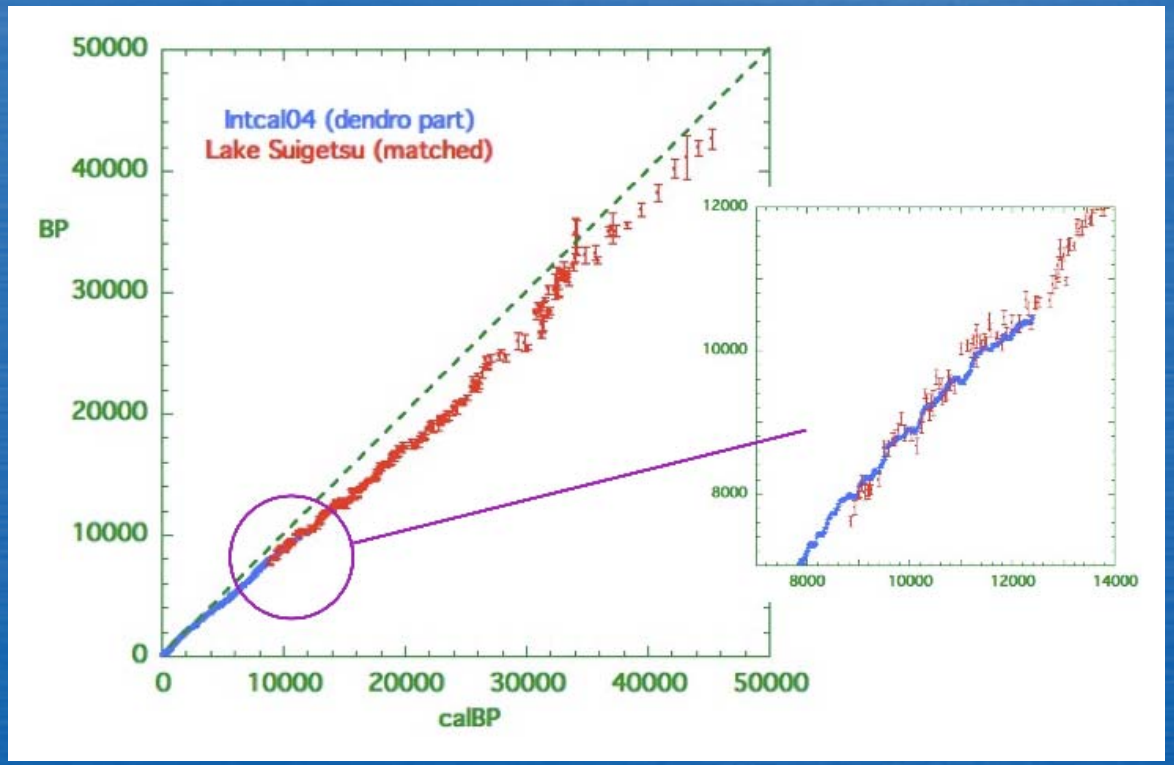
- Annual layers
  - Light layers from springtime diatoms (Japan)
  - Fine silt and lower $^{18}O/^{16}O$ from glacial meltwater (Scandanavia)
- Layers are counted
- Organic inclusions are dated




(Lake Suigetsu, Japan. Courtesy J. van der Plicht, Groningen)

# Lake Varve Calibration

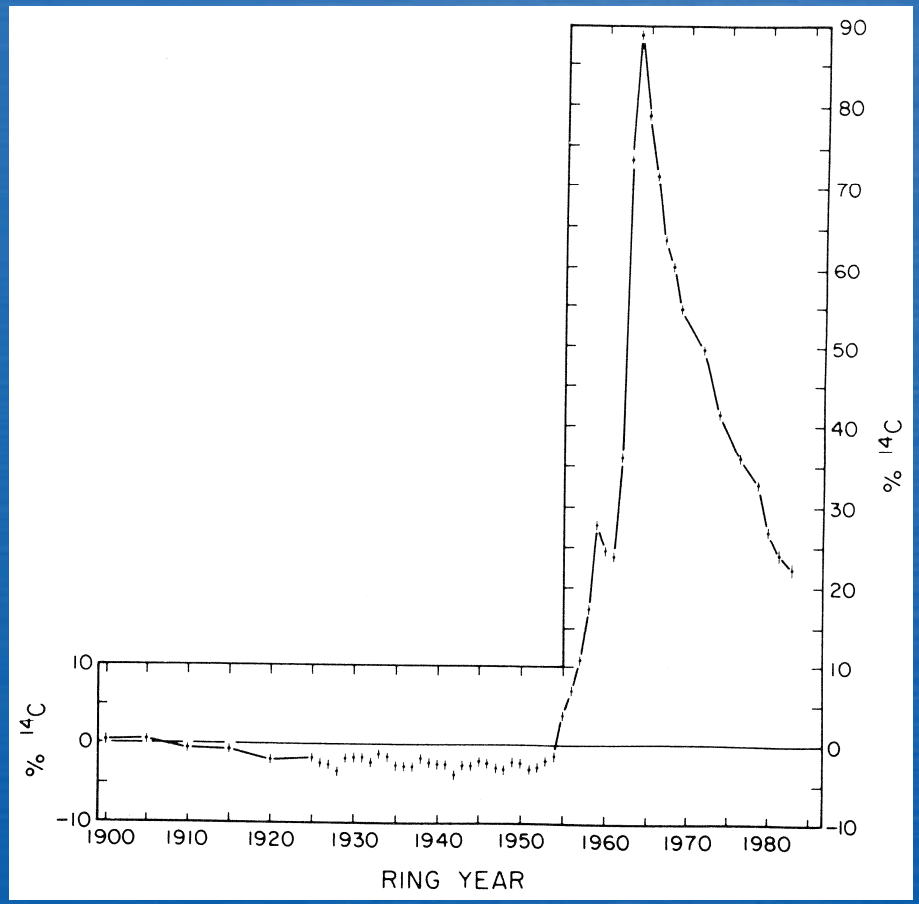
- Statistical "Wiggle-match" to tree ring calibration curve
- Extends calibration to ~45,000 years




(Courtesy J. van der Plicht, Groningen)

# Recent $^{14}C$ Anomolies

- Suess effect:
  - Fossil fuels dilute atmospheric $^{14}C$
  - Evident thru ~1955
- Bomb radiocarbon:
  - Nearly doubled $^{14}C$ concentration




(Taylor 1987 fig. 2.14)

# Accelerator Mass Spectrometry (AMS)

- Comprised a “Third Radiocarbon Revolution” (R.E. Taylor)
- Invented by R.A. Muller, 1976
  - Followup to Alvarez, 1939
  - Particle accelerator used as a mass spectrometer
  - Counts atoms rather than decay electrons
- ~1000x less material than beta counting
  - ~0.1 to 1 mg of carbon vs ~1 g
- ~1000x faster than beta counting
  - A few minutes vs a few days for +/- 20 year precision on modern carbon

# Why an Accelerator?

- $^{14}C$ has extremely low abundance
- Instrument needs extremely high rejection of interferences
- Nuclear physics techniques allow this

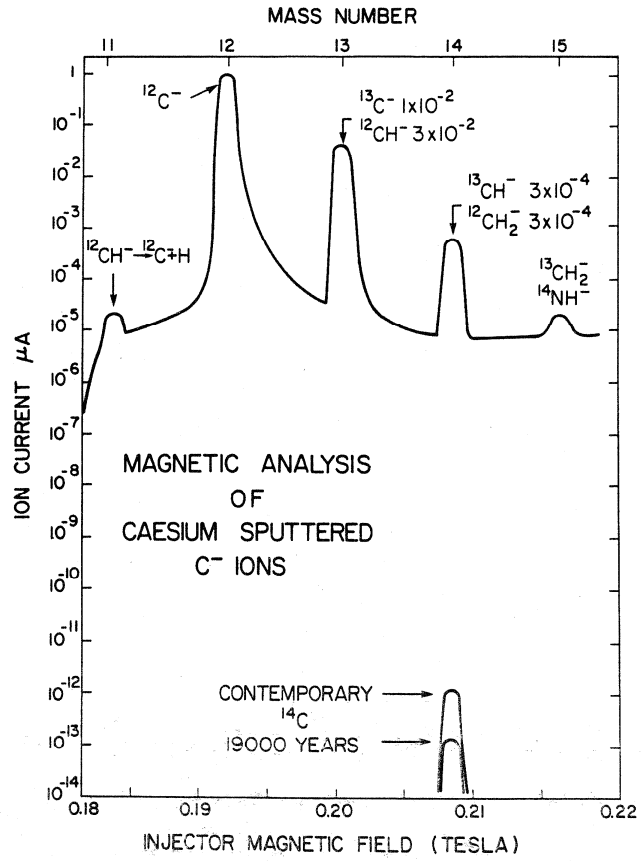



Fig 16.2. Magnetic analysis of the negative ions sputtered from a carbon target

(Beukens 1992 fig. 16.2)

# Typical Sample Preparation

- Pre-treatment
  - Mechanical cleaning
  - Acid (HCl), or acid-alkali(NaOH)-acid rinse
  - Sometimes more complex chemistry
- Conversion to $CO_2$
  - Organic C: combustion (oxidation) with CuO in sealed tube
  - Carbonates: acid hydrolysis in sealed tube
- Reduction to graphite
  - Hydrogen reduction with Fe catalyst

# Graphitization Line

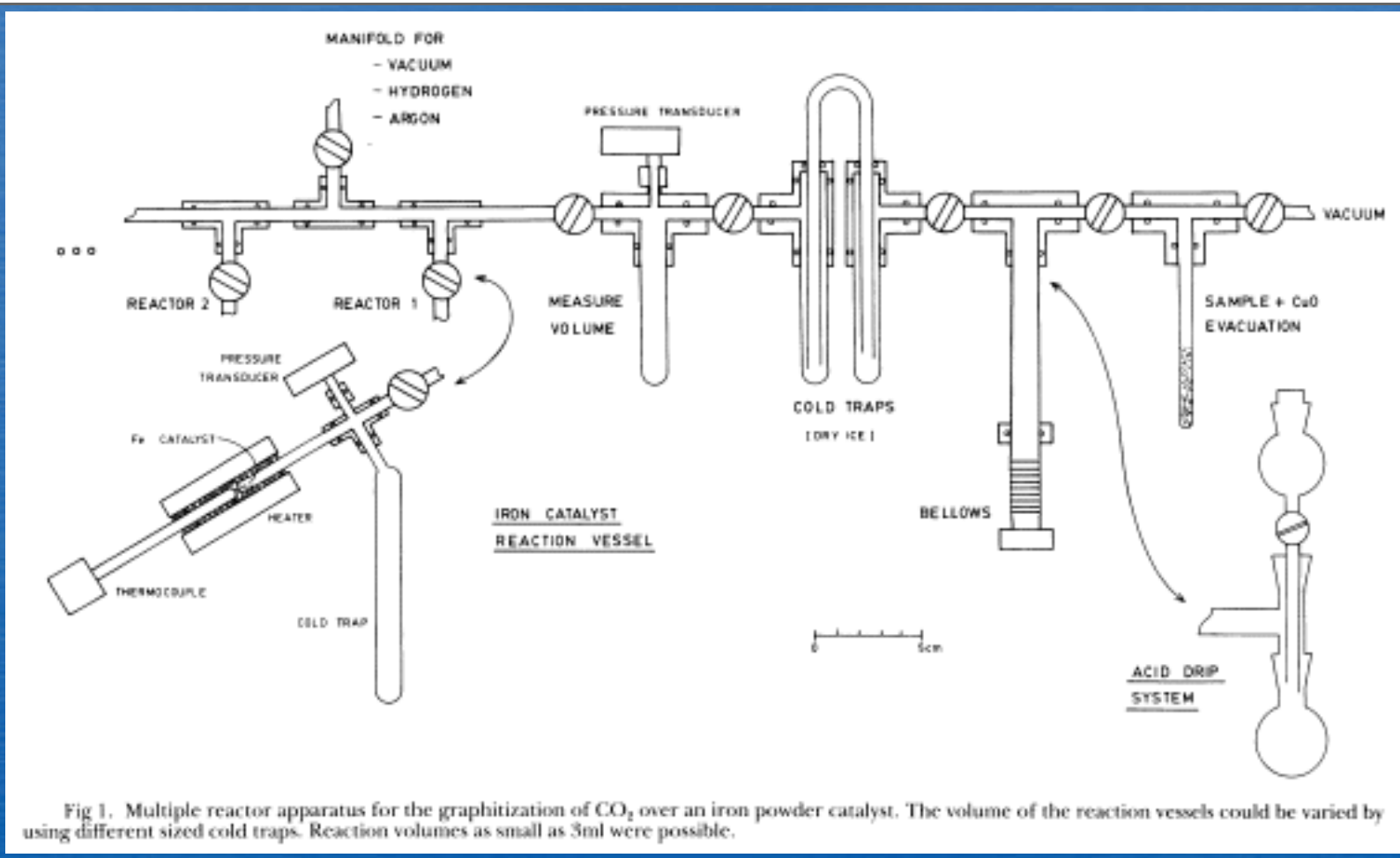


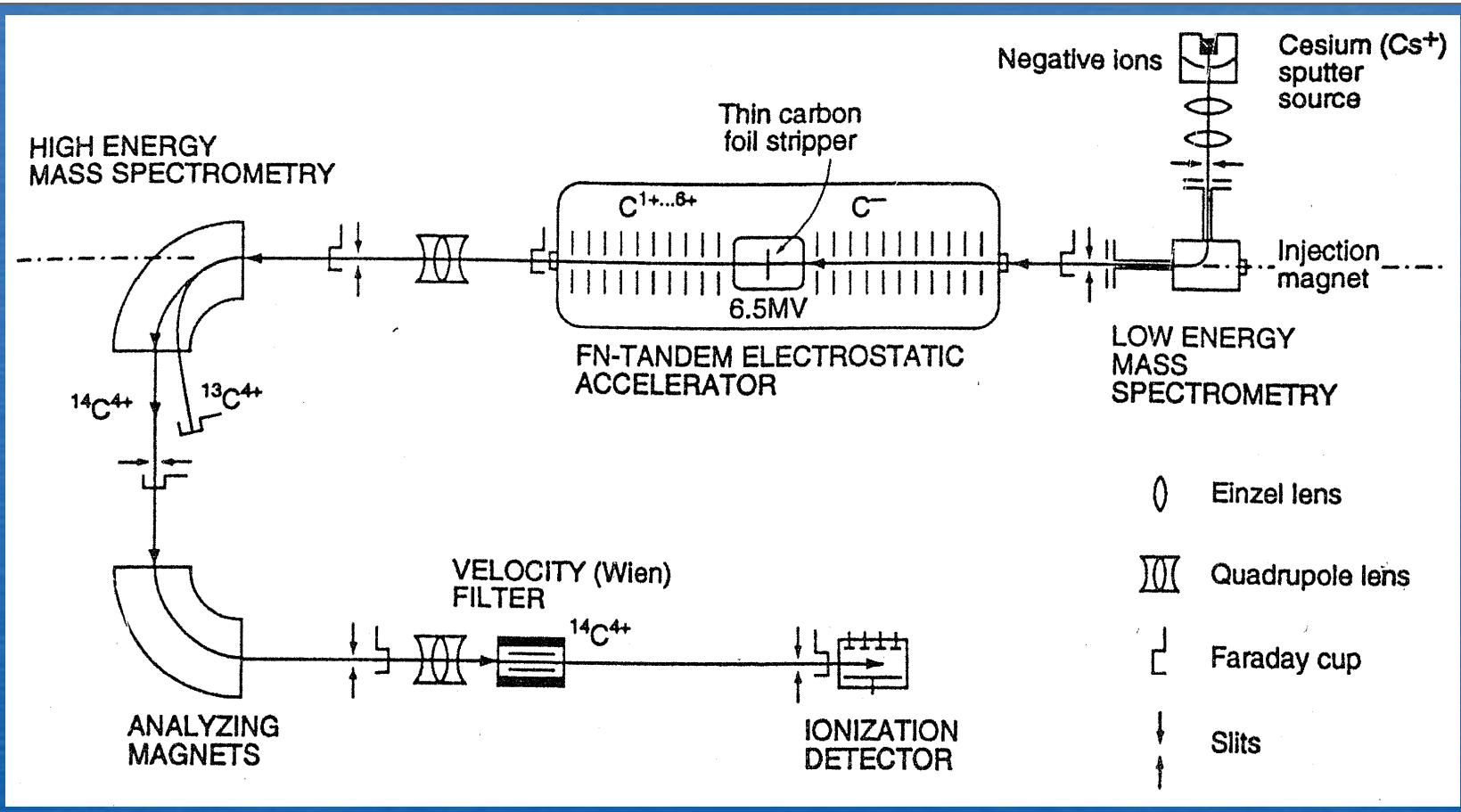

Fig 1. Multiple reactor apparatus for the graphitization of $CO_2$ over an iron powder catalyst. The volume of the reaction vessels could be varied by using different sized cold traps. Reaction volumes as small as 3ml were possible.

(Vogel et al 1987)

# Graphitization Lines

(U. AZ)

# Accelerator Diagram




(LLNL CAMS laboratory; Taylor & Aitken 1997 fig. 3.5)

# Accelerator Examples

(CAMS, LLNL)

(Isotrace lab, U Toronto)

# Contamination and Background

- Sources
  - 1) In-situ (or collection or storage) contamination
  - 2) Processing Background
    - Tube and graphitization line surfaces
    - Lab chemicals
  - 3) Instrument background
    - Ion source memory
    - Mass spectrometer background
    - Detector background
- Characterization and correction
  - Parallel-process known radiocarbon-free material
  - Use as process blank

# ICR RATE Project

- RATE claim:
  - Background and contamination are really intrinsic radiocarbon left over from Creation
  - Evidence: bio vs geo samples, shells, coal, diamond
- Specific problems with claim:
  - RATE assumes essentially zero process background
    - Erroneously compares processed to unprocessed samples
  - RATE assumes unrealistically small instrument background
    - High sensitivity analytical equipment generally has non-zero (and variable) levels
  - Shells: frequently anomalous, probably due to carbon exchange in situ
  - Coal: probably in situ contamination (known mechanisms)
  - Diamond: probably instrument background
- More: <http://www.asa3.org/ASA/education/origins/rate.htm>

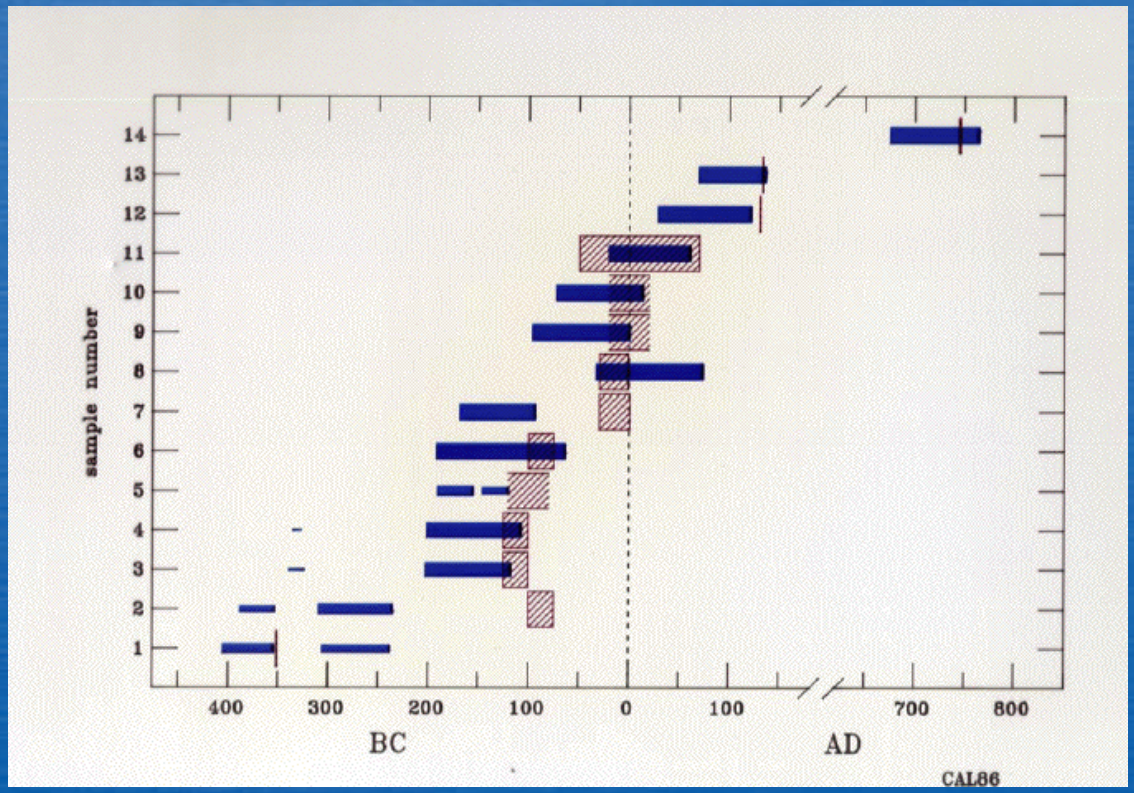
# Modern Capabilities

- ~ 1mg C sample size
- Range:
  - ~ 12,000 years cal to tree rings
  - ~ 45,000 years cal to lake varves
  - ~ 60,000 years uncal without heroics
  - > 75,000 years uncal with isotopic enrichment
- ~ 0.25% msmt error (~ +/-20 years uncalibrated error [1$\sigma$])

# Applications

- Archaeology
  - Prehistory
  - Peopling of New World
  - Near East
  - Iron artifacts (pre-industrial revolution)
- Geoscience
- Climatology
- Bioscience

# Dead Sea Scrolls




(after Bonani 1992)

- Red: paleographic dates
- Blue: 1σ calibrated $^{14}C$ dates
  - On avg ~35 yrs older
  - Difference may be real
  - Some may have had glue contamination

# Turin Shroud

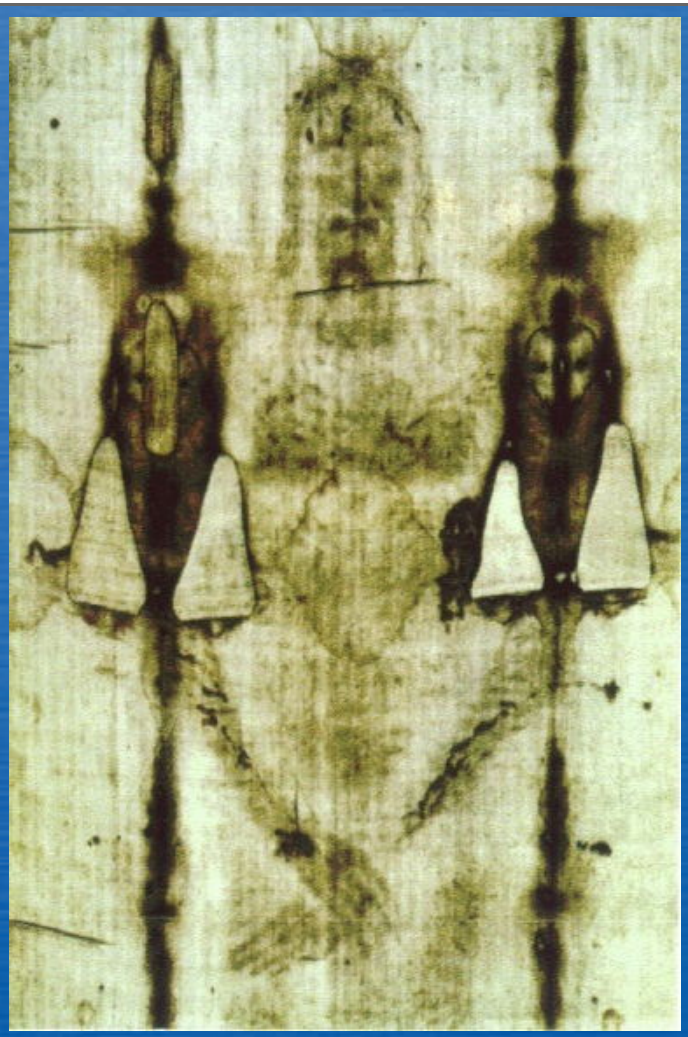


**Table 3.3.** AMS $^{14}$C Dating of the Shroud of Turin[a]

| Laboratory | Known age Egyptian linen AMS $^{14}$C age (yrs. BP)<br><br>2,010±80<br>110 BC-AD 75 | Shroud AMS $^{14}$C (yrs. BP) |
|---|---|---|
| Arizona AMS | 1,838±47<br>2,041±43<br>1,960±55<br>1,983±37<br>2,137±46 | 591±30<br>690±35<br>606±41<br>701±33 |
| | Mean = 1,995±46 | Mean = 646±31 |
| Oxford AMS | 1,955±70<br>1,975±55<br>1,990±50 | 795±65<br>730±45<br>745±55 |
| | Mean = 1,980±35 | Mean = 750±30 |
| Zurich AMS | 1,984±50<br>1,886±48<br>1,954±50 | 733±61<br>722±56<br>635±57<br>639±45<br>679±51 |
| | Mean = 1,940±30 | Mean = 676±24 |
| Combined | Mean $^{14}$C age = 1,964±20<br><br>Calibrated age = 10 BC-AD 80[b] | Mean $^{14}$C age = 689±16<br><br>Calibrated age = AD 1260-1390[b] |

[a] Based on data from Damon *et al.* 1989.
[b] 95% confidence interval.

(Taylor & Aitken 1997 tbl 3.3)

# Applications

- Archaeology
- Geoscience
  - Ocean Circulation
  - Hydrology (groundwater)
  - Earthquake and volcano dating
- Climatology
- Bioscience

# Ocean Circulation

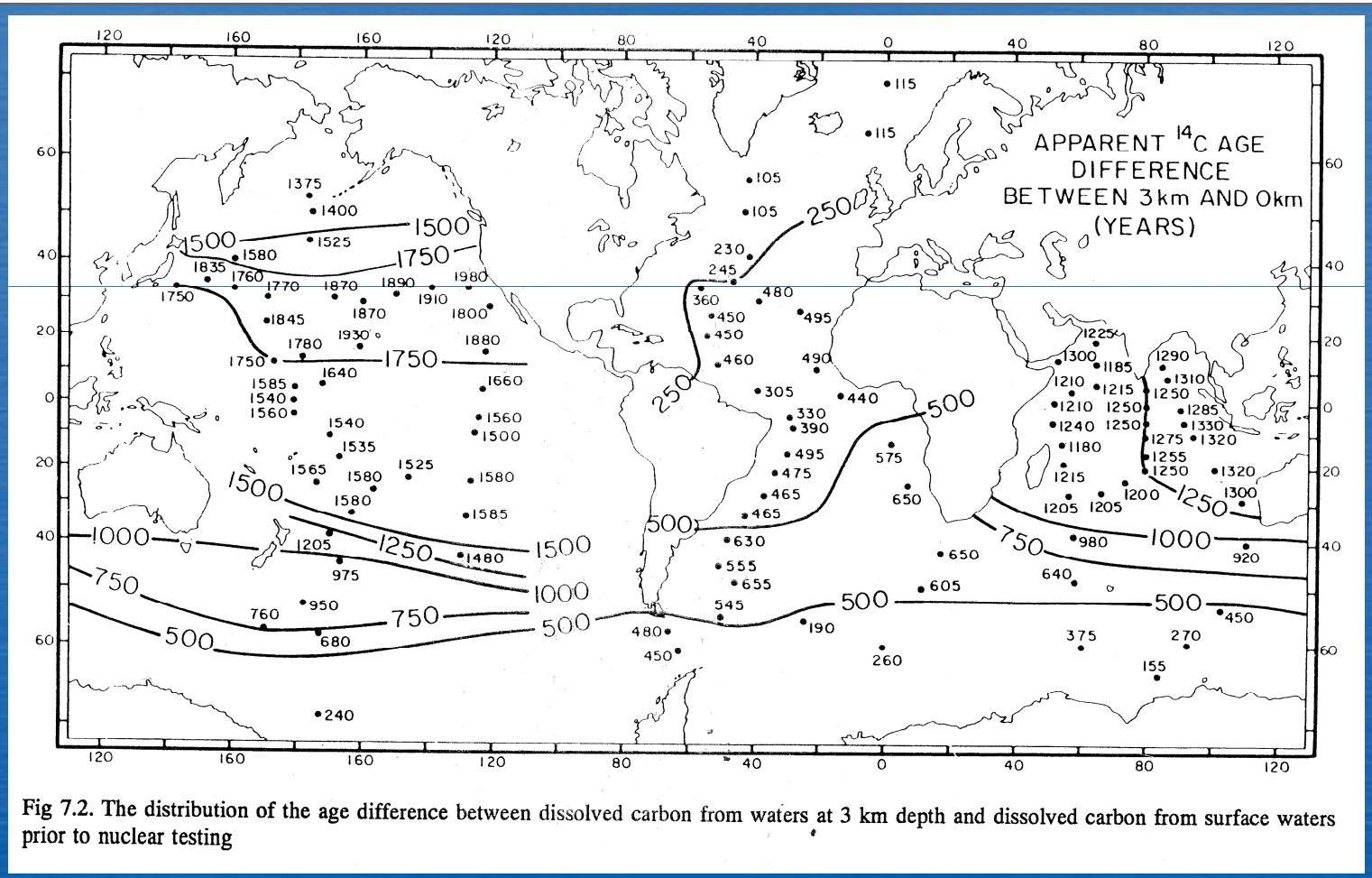



Fig 7.2. The distribution of the age difference between dissolved carbon from waters at 3 km depth and dissolved carbon from surface waters prior to nuclear testing

(Peng & Broecker 1992 fig. 7.2)

# Applications

- Archaeology
- Geoscience
- Climatology
  - Carbon cycle research
  - Palynology (fossil pollen)
  - Glacial meltwater plumes (foraminifera correlated to $\delta^{18}O$)
- Bioscience

# Applications

- Archaeology
- Geoscience
- Climatology
- Bioscience
  - Biochemical pathways
  - Carcinogen metabolism
  - Radiocarbon-depleted mice

# Summary

- $^{14}C$ has been calibrated to ~45,000 years
- AMS allows very small samples
- Lots of interesting applications

# References


Beukens, RP 1992 “Radiocarbon accelerator mass spectrometry: background, precision and accuracy” *In* Taylor, RE, Long, A and Kra, RS, eds, *Radiocarbon After Four Decades: An Interdisciplinary Perspective*. New York, Springer-Verlag, 230-240.

G. Bonani et al 1992 “Radiocarbon dating of fourteen dead sea scrolls” *Radiocarbon* 34(3) 843-849.

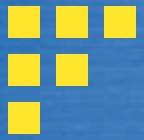
Peng, TH and Broecker, WS 1992 “Reconstruction of radiocarbon distribution in the glacial ocean” *In* Taylor, RE, Long, A and Kra, RS, eds, *Radiocarbon After Four Decades: An Interdisciplinary Perspective*. New York, Springer-Verlag, 75-92.

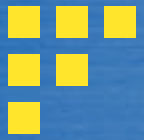
Taylor, RE 1987 *Radiocarbon Dating: An Archaeological Perspective*. New York, Academic Press.

Taylor, RE and Aitken, MJ 1997 *Chronometric Dating in Archaeology*. New York, Plenum Press.

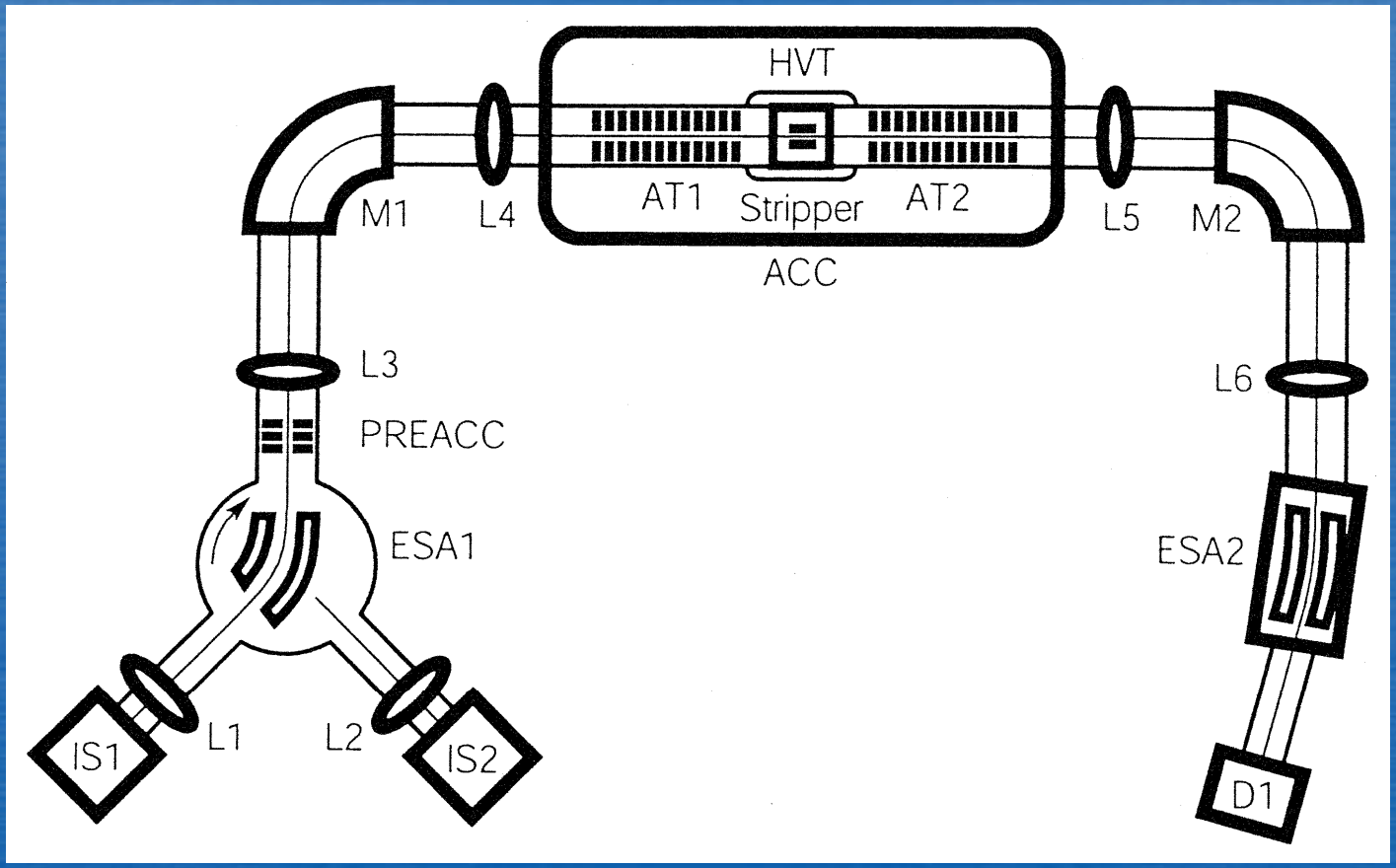
Tuniz, C, Bird, JR, Fink, D and Herzog, GF 1998 *Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science*. New York, CRC Press.

Vogel, JS, Nelson, DE and Southon, JR 1987 “$^{14}$C background levels in an accelerator mass spectrometry system” *Radiocarbon* 29(3) 323-333.





# Accelerator Diagram




(Tuniz 1998 fig. 3.1)

# Ionization of graphite

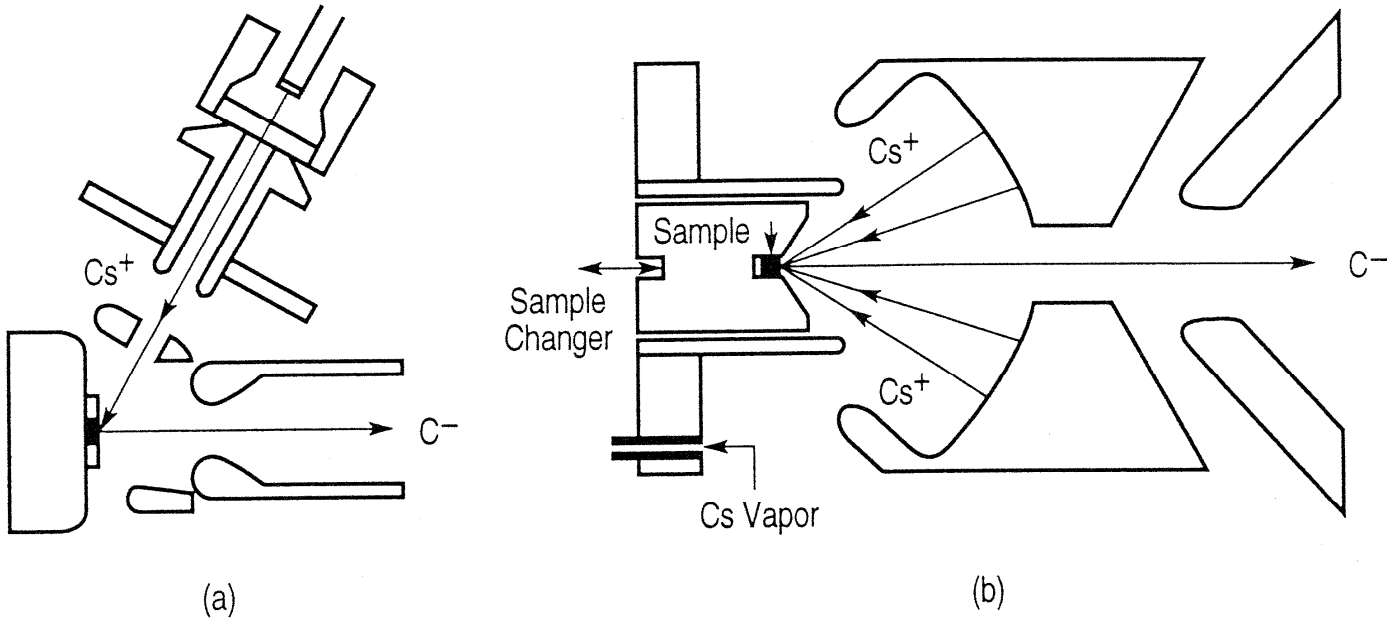
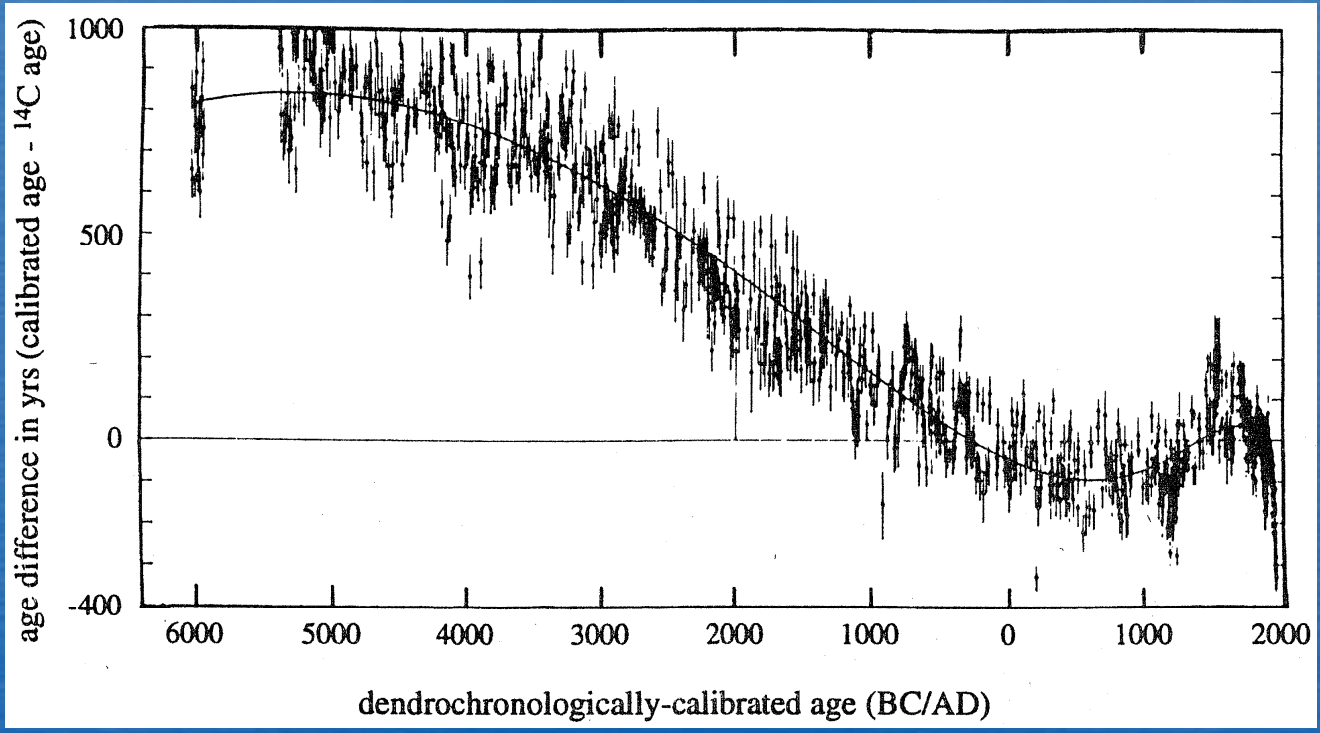



**Figure 3.2** Ion source geometries: (a) focused Cs source, and (b) high-intensity source.

- Cs-sputter sources are standard (Tuniz fig 3.2)
- Ongoing research on gas sources

# Tree Ring Calibration Corrections




(Taylor & Aitken 1997 fig. 3.2)

- Max correction ~10% over past 8000 years (~7% with correct half-life)
- Could calibrated dates be in error by large factors?
  - Would require independent parameters to vary in coupled manner (pathological)