

# RADIOCARBON NOMENCLATURE

Radiocarbon Book Chapter 3:  
Radiocarbon Nomenclature, Theory, Models,  
and Interpretation: Measuring Age,  
Determining Cycling Rates, and Tracing Source  
Pools

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Radiocarbon in the Earth System  
Sep 24-29 2017, Jena



# Carbon Isotopes: Stable and Radioactive

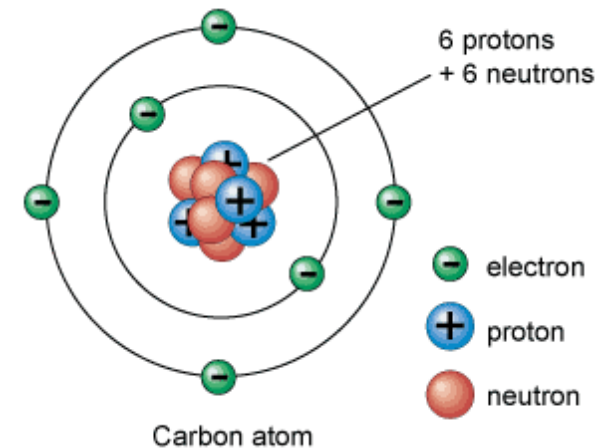
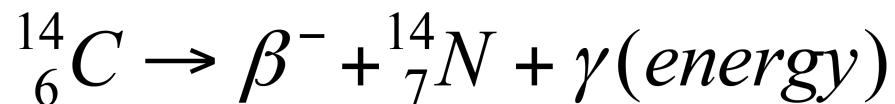
- The naturally occurring isotope of carbon: Same number of protons => same chemistry, but different mass

Stable             $^{12}\text{C}$  (98.8%)            6 protons, 6 neutrons

Stable             $^{13}\text{C}$  (1.1%)            6 protons, 7 neutrons

Radioactive     $^{14}\text{C}$  (<  $10^{-10}$  %)            6 protons, 8 neutrons

- $^{14}\text{C}$  decays to  $^{14}\text{N}$  by emitting a  $\beta$  particle (electron), with a half-life of 5730 years:



# Isotopes of C contain independent information



- $^{13}\text{C}$  – patterns in the environment reflect mass-dependent fractionation (partitioning among phases at equilibrium and differences in reaction rates)
- $^{14}\text{C}$  – Reflects time (closed system) or mixing (open system). Mass-dependent fractionation is corrected out in reported data using  $^{13}\text{C}$

# Stable isotope ( $^{13}\text{C}$ ) fractionation:

- **Kinetic reactions** (non-reversible):

- $^{13}\text{CO}_2$  diffuses more slowly than  $^{12}\text{CO}_2$
- $^{13}\text{C}$  reacts more slowly than  $^{12}\text{C}$

- **Equilibrium reactions** (reversible):



*$^{13}\text{C}$  will partition into the species where overall energy is lowest (strongest bond or phase with least randomness).*

*Reaction rates and equilibrium partitioning coefficients are dependent on state variables like  $T$ ,  $P$*

# $^{13}\text{C}$ Nomenclature

$$R = \frac{\textit{rare}}{\textit{abundant}} = \frac{\textit{heavy}}{\textit{light}} = \frac{^{13}\text{C}}{^{12}\text{C}}$$

$$\delta = \left[ \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000 = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$$

Element	Standard	R
Carbon	Pee Dee Belemnite (calcium carbonate)	$^{13}\text{C}/^{12}\text{C} = 0.0112372$ $^{18}\text{O}/^{16}\text{O} = 0.002671$



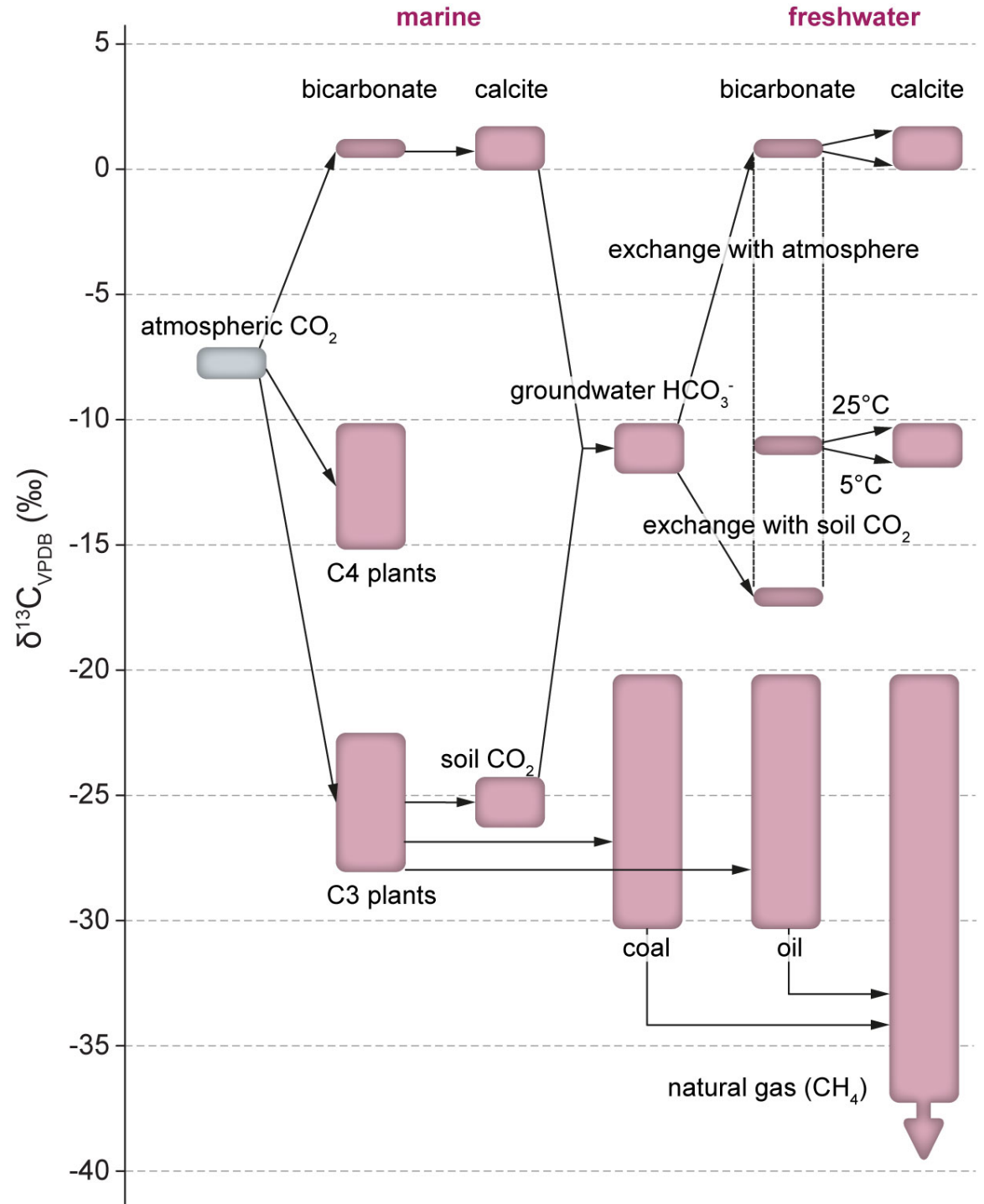
# Why Reporting Isotope Data Relative to a Standard?

- **Difficult** to measure the absolute abundances of isotopes accurately, so measure differences in relative abundance between sample and an accepted standard material
- For measurements made by different laboratories to be **comparable**, there is agreement on what those standard materials are
- **Convenient** - R are small numbers, and their variation are small too, e.g.

$$^{13}\text{C}/^{12}\text{C}_{\text{sample}} = 0.0109563, \quad ^{13}\text{C}/^{12}\text{C}_{\text{PDB}} = 0.0112372$$

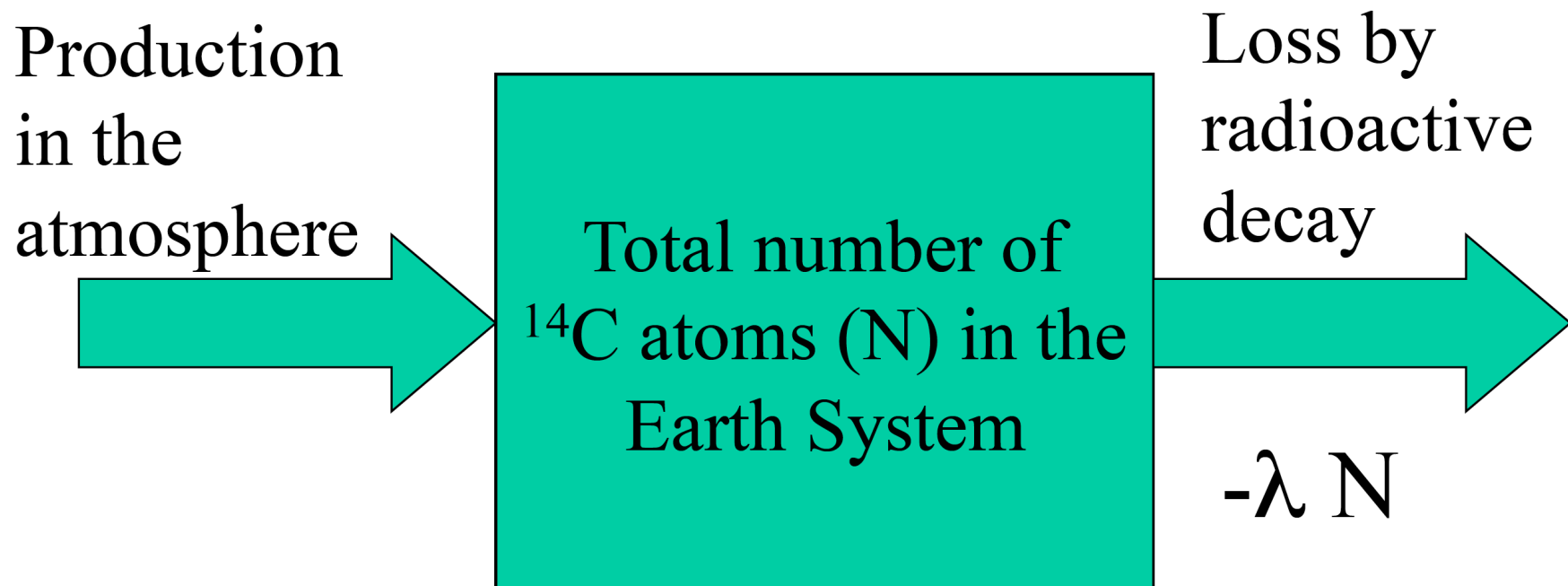
$$\delta^{13}\text{C} = [(0.0109563/0.0112372) - 1] \times 1000 = -25.00\text{‰}$$

# $\delta^{13}\text{C}$ Variation found in the Earth's major C reservoirs



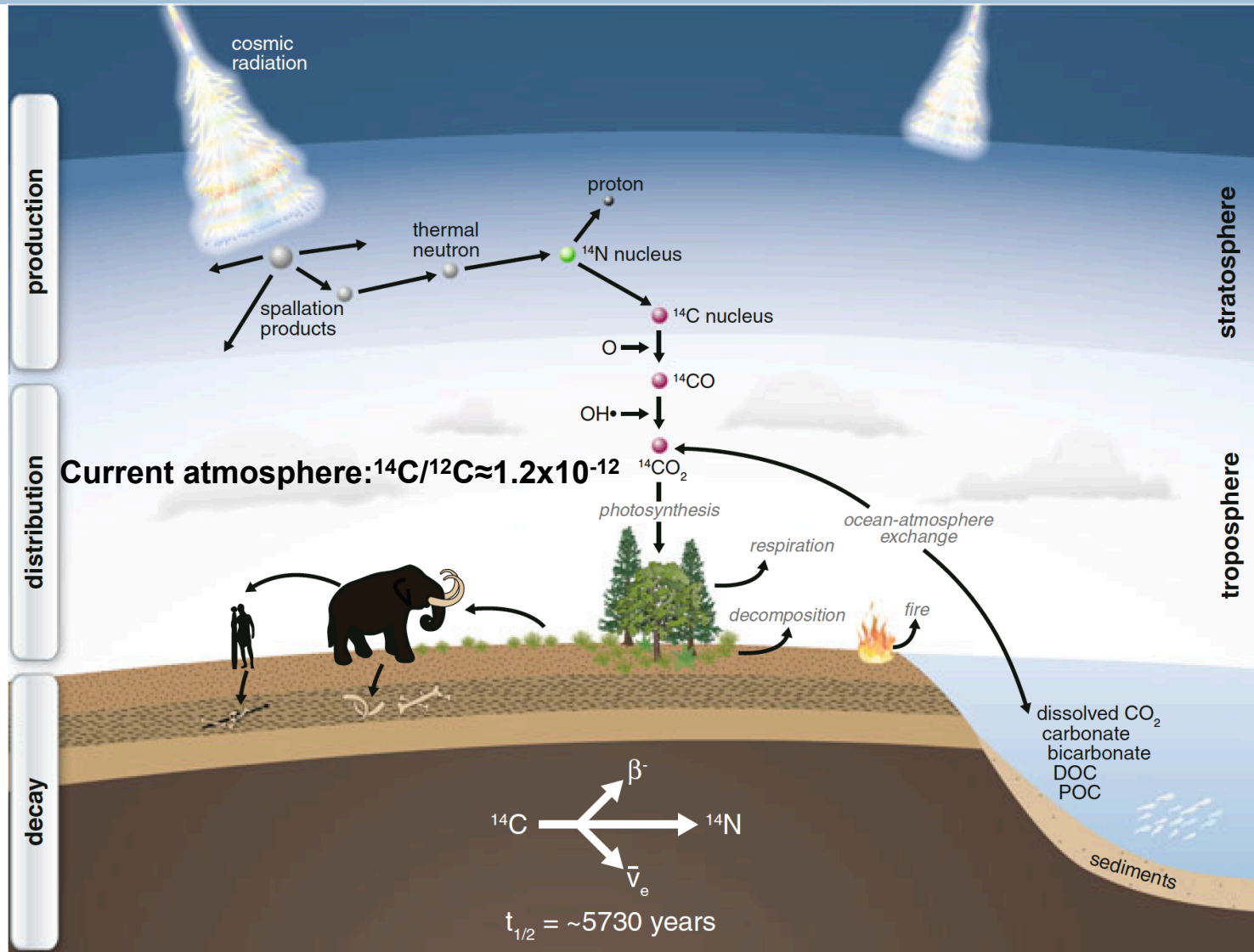
# Stable C isotopes vs. Radiocarbon

- Stable C isotopes are conserved
- Radiocarbon is constantly created and destroyed





# Cosmogenic Production of $^{14}\text{C}$



# Different ways of expressing $^{14}\text{C}$ data



For each of these applications:

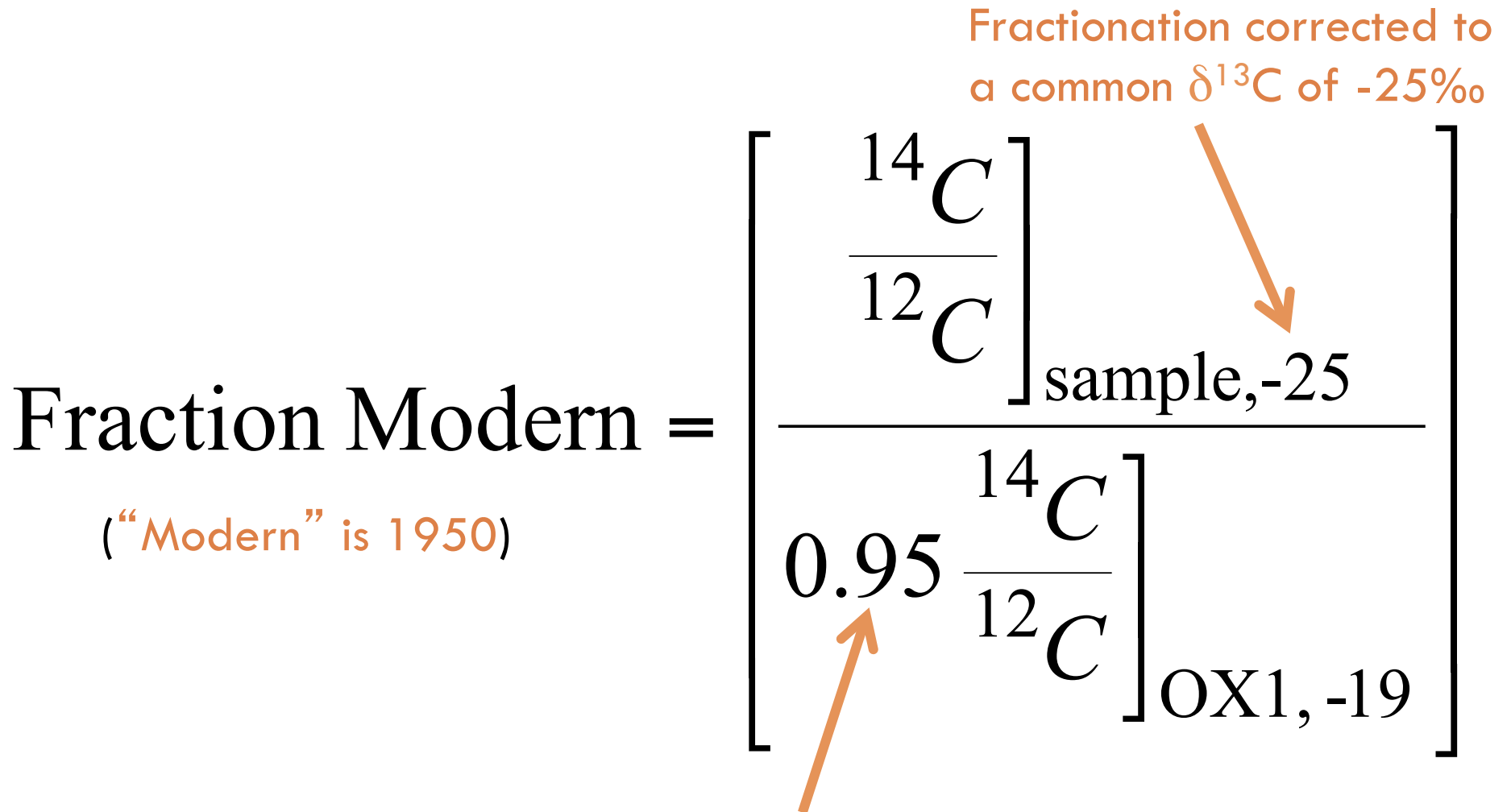
- **Determining the age of C in a closed system:** age of pollen, foraminifera, seeds
- **As a source tracer:** mixing of sources with different  $^{14}\text{C}$  signatures
- For open systems, a measure of the **rate of exchange of C** with other reservoirs (Flux of C)
- As a **purposeful tracer** tracing pathways (allocation) or rates

Reporting of  $^{14}\text{C}$  data: as the ratio  $^{14}\text{C}/^{12}\text{C}$  with respect to a standard with known  $^{14}\text{C}/^{12}\text{C}$  ratio

Fractionation corrected to a common  $\delta^{13}\text{C}$  of  $-25\text{‰}$

$$\text{Fraction Modern} = \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25}}{0.95 \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19}}$$

(“Modern” is 1950)

The diagram shows the equation for Fraction Modern. An orange arrow points from the text 'Fractionation corrected to a common δ¹³C of -25‰' to the sample term in the numerator, [¹⁴C/¹²C]sample, -25. Another orange arrow points from the text '95% the activity of Oxalic Acid I in the year 1950 = 1890 wood standard' to the 0.95 multiplier in the denominator.

95% the activity of Oxalic Acid I in the year 1950 = 1890 wood standard

# Why must there be a correction for mass dependent fractionation?

## Why?

$^{14}\text{C}/^{12}\text{C}$  in your samples changes by (assuming the initial ratio is the same)

- 1) decay with time
- 2) mass dependent fractionation, which is twice that of  $^{13}\text{C}$

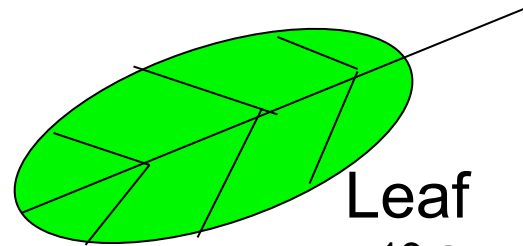
But you only want the “Time”, so you would want to remove the change introduced by mass dependent fractionation

## How?

- 1) Force to one common  $\delta^{13}\text{C}$  of -25‰
- 2) use  $\delta^{13}\text{C}$  and assume  $^{14}\text{C}$  fractionates twice that of  $^{13}\text{C}$

# Why must there be a correction for mass dependent fractionation?

CO<sub>2</sub> in air  
 $\delta^{13}\text{C} = -8 \text{ ‰}$



Leaf  
 $\delta^{13}\text{C} = -28 \text{ ‰}$

<sup>14</sup>C - <sup>12</sup>C mass difference is twice that of <sup>13</sup>C - <sup>12</sup>C =>

**<sup>14</sup>C fractionation is twice that of <sup>13</sup>C**

Therefore a 20 ‰ difference in <sup>13</sup>C means a 40 ‰ difference in <sup>14</sup>C

Expressed as an 'age' this is  $-8033 \cdot \ln(.96) = 330$  years

Force the  $\delta^{13}\text{C}$  to  $-25 \text{ ‰}$ , what will the  $^{14}\text{C}/^{12}\text{C}$  be based on mass dependent fractionation?

$$\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}[-25\text{‰}]} = \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, \delta \text{‰}} \left\{ \frac{1 - \frac{25}{1000}}{1 + \frac{\delta}{1000}} \right\}^2$$

Defined  $\delta^{13}\text{C}$  of  $-25 \text{ ‰}$

Actual  $\delta^{13}\text{C}$  of the sample

# What does the fractionation correction really mean for $^{14}\text{C}$ calculation?

- If Sample  $\delta^{13}\text{C}$  is  $> -25\text{‰}$ : **Subtract or Add  $^{14}\text{C}$ ?**
- If Sample  $\delta^{13}\text{C}$  is  $< -25\text{‰}$ : **Subtract or Add  $^{14}\text{C}$ ?**

# What does the fractionation correction really mean for $^{14}\text{C}$ calculation?

- If Sample  $\delta^{13}\text{C}$  is  $> -25\text{‰}$ : **Subtract**  $\sim 2 \times$  difference
- If Sample  $\delta^{13}\text{C}$  is  $< -25\text{‰}$ : **Add**  $\sim 2 \times$  difference
- $^{14}\text{C}$  values reported as fraction Modern, Libby Age, or  $\Delta^{14}\text{C}$  **do not reflect mass-dependent fractionation of isotopes**

Sample	Sample $\delta^{13}\text{C}$ (‰)	Difference (sample $\delta^{13}\text{C} - 25$ ), ‰	$2 \times \delta^{13}\text{C}$ Difference ‰	Measured Uncorrected $^{14}\text{C}/^{12}\text{C}$ ( $10^{-12}$ )	Corrected to $-25\text{‰}$ $^{14}\text{C}/^{12}\text{C}$ ( $10^{-12}$ )	Difference in $^{14}\text{C}/^{12}\text{C}$ (corr-uncorr) ‰
Atm $\text{CO}_2$	-8	17	34	1.0352	<b>1.0000</b>	-35
Biogenic $\text{CH}_4$	-70	-45	-90	0.9089	<b>1.0000</b>	90

# What about $^{13}\text{C}$ Labeled Samples?



Will it affect  $^{14}\text{C}$  calculation ?



# What about $^{13}\text{C}$ Labeled Samples?

It can affect  $^{14}\text{C}$  calculation significantly because it's not mass dependent fractionation – it's mixing! Need to use the **unlabeled** sample  $\delta^{13}\text{C}$  for correction – **Tell the lab!**

Sample	Sample w/o label $\delta^{13}\text{C}$ (‰)	Sample w/ label $\delta^{13}\text{C}$ ‰	Difference (Labeled sample $\delta^{13}\text{C}$ -25), ‰	No correction is needed "Uncorrectd" $^{14}\text{C}/^{12}\text{C}$ ( $10^{-12}$ )	"corrected" to -25‰ $^{14}\text{C}/^{12}\text{C}$ ( $10^{-12}$ )	Difference in $^{14}\text{C}/^{12}\text{C}$ (corr-uncorr) ‰
Soils $\text{CO}_2$ with $^{13}\text{C}$ labeled Cellulose	-25	100	125	1.0000	0.7856	-214
Soil $\text{CO}_2$ in FACE Fossil $\text{CO}_2$	-25	-30	-5	1.0000	1.0103	10

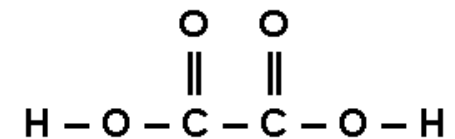
# AMS $\delta^{13}\text{C}$ is preferred over IRMS $\delta^{13}\text{C}$



- AMS  $\delta^{13}\text{C}$  accounts for not only naturally occurred mass dependent fractionation, but also possible fractionation happened during sample preparation (pretreatment and graphitization) and inside the AMS machine (ion source) – **important for high precision measurement!**
- AMS  $\delta^{13}\text{C}$  has to truly reflect fractionation – it needs to be properly calibrated, linear to the entire current range and no beams are cut off inside the AMS.

# The $^{14}\text{C}$ standard: Oxalic Acid I

- The principal modern radiocarbon standard is N.I.S.T Oxalic Acid I ( $\text{C}_2\text{H}_2\text{O}_4$ ), made from a crop of 1955 sugar beets.
- Ninety-five percent of the activity of Oxalic Acid I from the year 1950 is equal to the measured activity of the absolute radiocarbon standard which is 1890 wood (chosen to represent the pre-industrial atmospheric  $^{14}\text{CO}_2$ ), corrected for radioactive decay to 1950. **This is Modern.**
- A range of standards with different  $^{14}\text{C}/^{12}\text{C}$  ratios is maintained by the International Atomic Energy Agency (IAEA).



Oxalic Acid,  $\text{H}_2\text{C}_2\text{O}_4$

# Different ways to report $^{14}\text{C}$ data depend on the application (Stuiver and Polach 1977)

Expressions that **do not depend on the year you make the measurement or take the sample:**

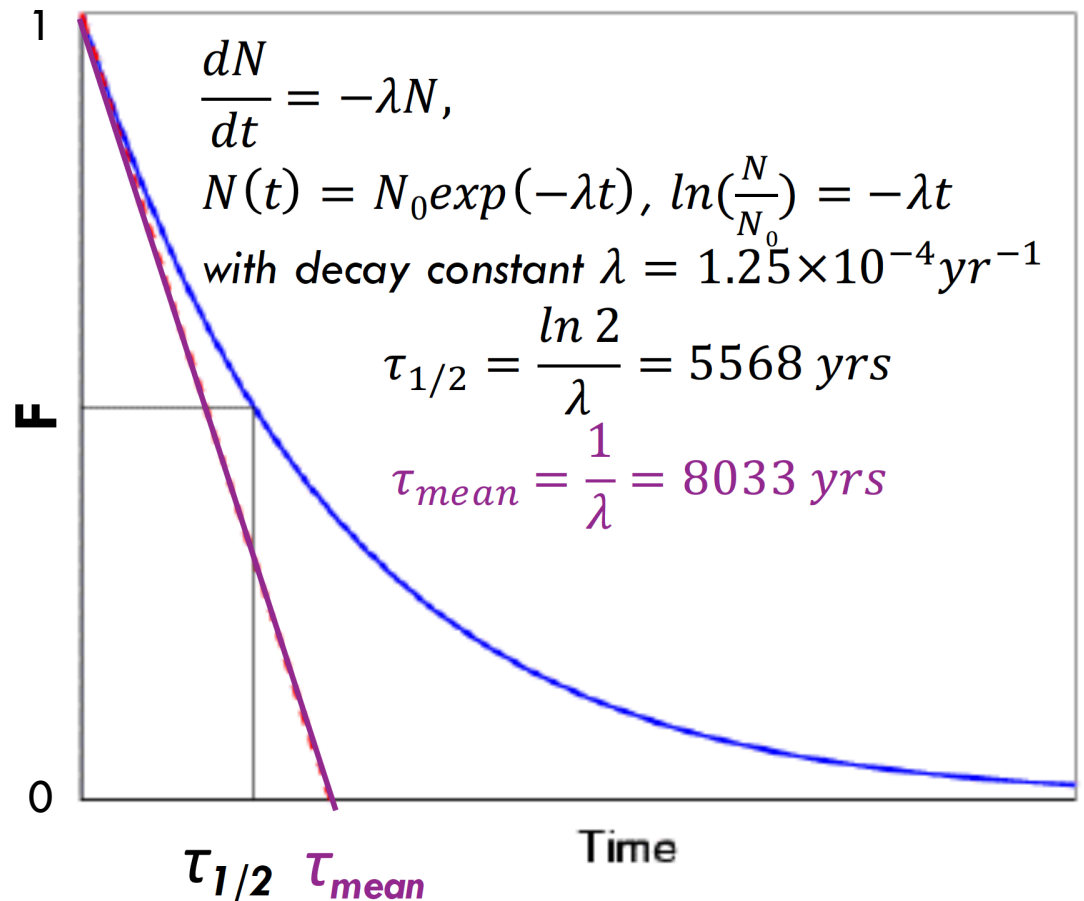
- **Fraction Modern (F)** 0.80
- **Percent modern** (pMC=100\*F) 80%
- **D** = (F - 1) \* 1000 -200 ‰  
(this is equivalent to the stable isotope  $\delta$  notation)
- **Radiocarbon age** (calculated using F)  
 $^{14}\text{C}$  Age =  $-(1/\lambda_{14}) * \ln(F) = -8033 * \ln(F)$

# Conventional Radiocarbon Age

(Libby age, years BP, used for closed systems)

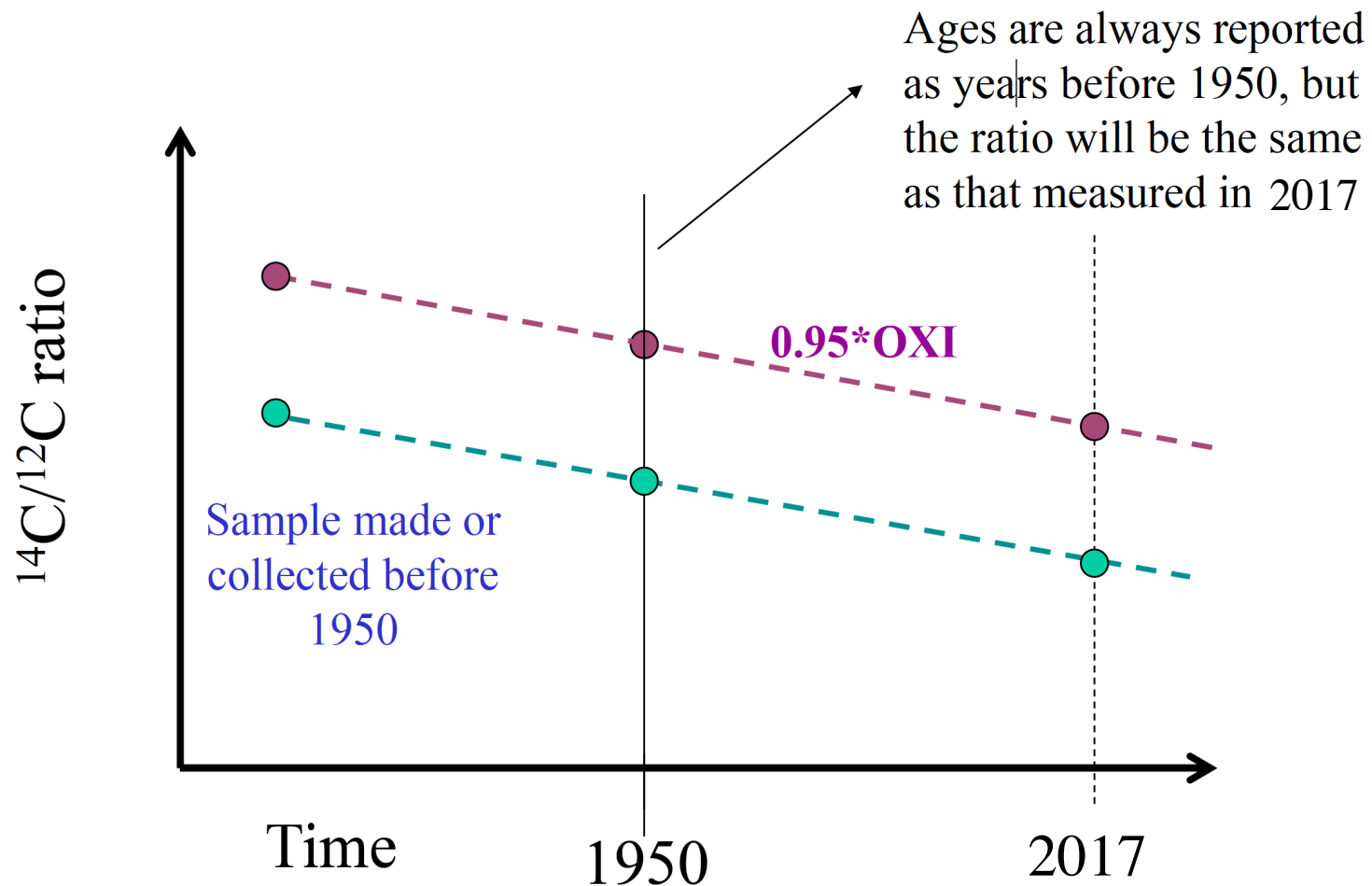
$$^{14}\text{C Age} = -(1/\lambda_{14}) * \ln(F) = -8033 * \ln(F)$$

- Where F is Fraction Modern and  $\lambda_{14}$  is the decay constant for  $^{14}\text{C}$ . When  $F > 1$ ,  $^{14}\text{C}$  Age “> Modern” (negative age)
- The half life ( $\tau_{1/2} = \ln(2)/\lambda_{14}$ ), **Libby half life (5568 years) is used.**
- A more recent and accurate determination of the half-life is **5730 years**. It’s used in decay correction. To convert a radiocarbon age to a calendar age, the **calibration curve** is used.
- Use A.D. 1950 as 0 BP** [BP = “Before Physics”]!
- If radiocarbon production rate and its distribution among atmosphere, ocean and terrestrial reservoirs is constant,  
Then  $N_0 =$  atmospheric  $^{14}\text{CO}_2$  value.



# Fraction Modern, $D$ , $^{14}\text{C}$ age will not vary as time goes

- All report the ratio in the year of measurement, which will not vary as time goes on because radiodecay in standard and sample occurs at the same rate ( $\lambda$ ).



# Past Changes in Atmospheric $^{14}\text{C}$ recorded in tree rings (or ocean $^{14}\text{C}$ in corals)

$T$  = known age (years before 1950)

$\lambda = \ln(2) / 5730 \text{ yr}$  (actual half-life)

=  $1/8267 \text{ yr}$  ('mean life')

$$T = \frac{-1}{\lambda} \ln \left( \frac{F_{\text{sample}}}{F_{\text{atmosphere}}} \right)$$

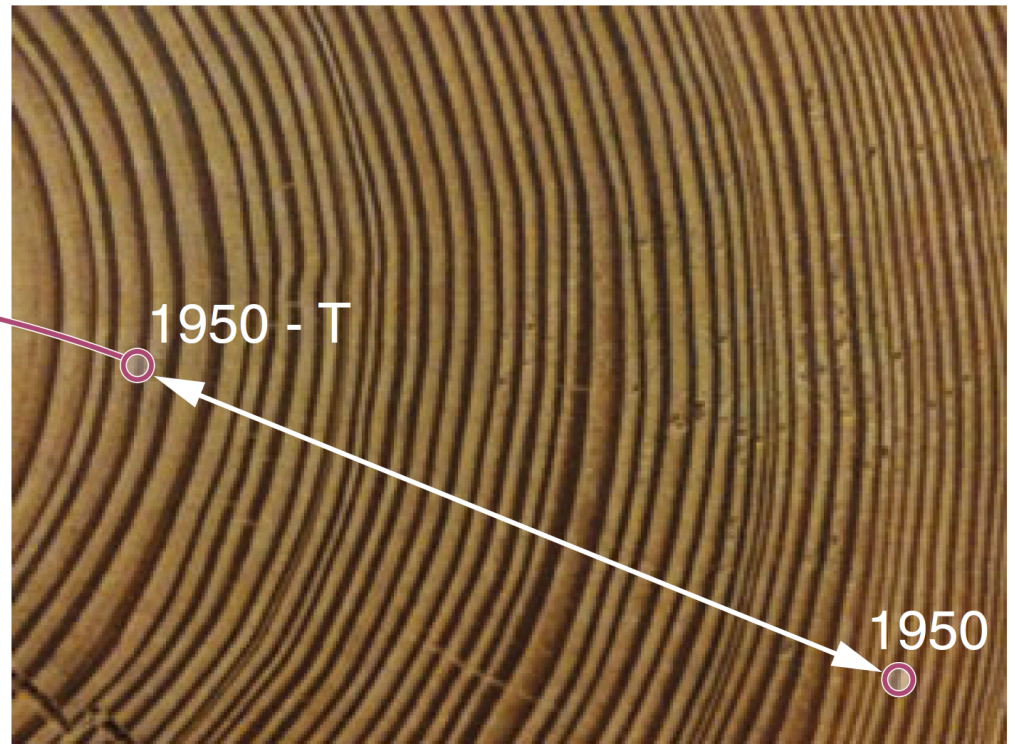
$T$  and  $F_{\text{sample}}$  are known

thus

$$F_{\text{atmosphere}} = F_{\text{sample}} \exp(\lambda T)$$

Corrects for decay of  $^{14}\text{C}$  in the sample from the year of growth (x) to 1950

$$\Delta = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25} \exp\left(\frac{(1950-x)}{8267}\right)}{0.95 \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19}} - 1 \right] 1000$$



# $\Delta$ (known-age corrected sample )

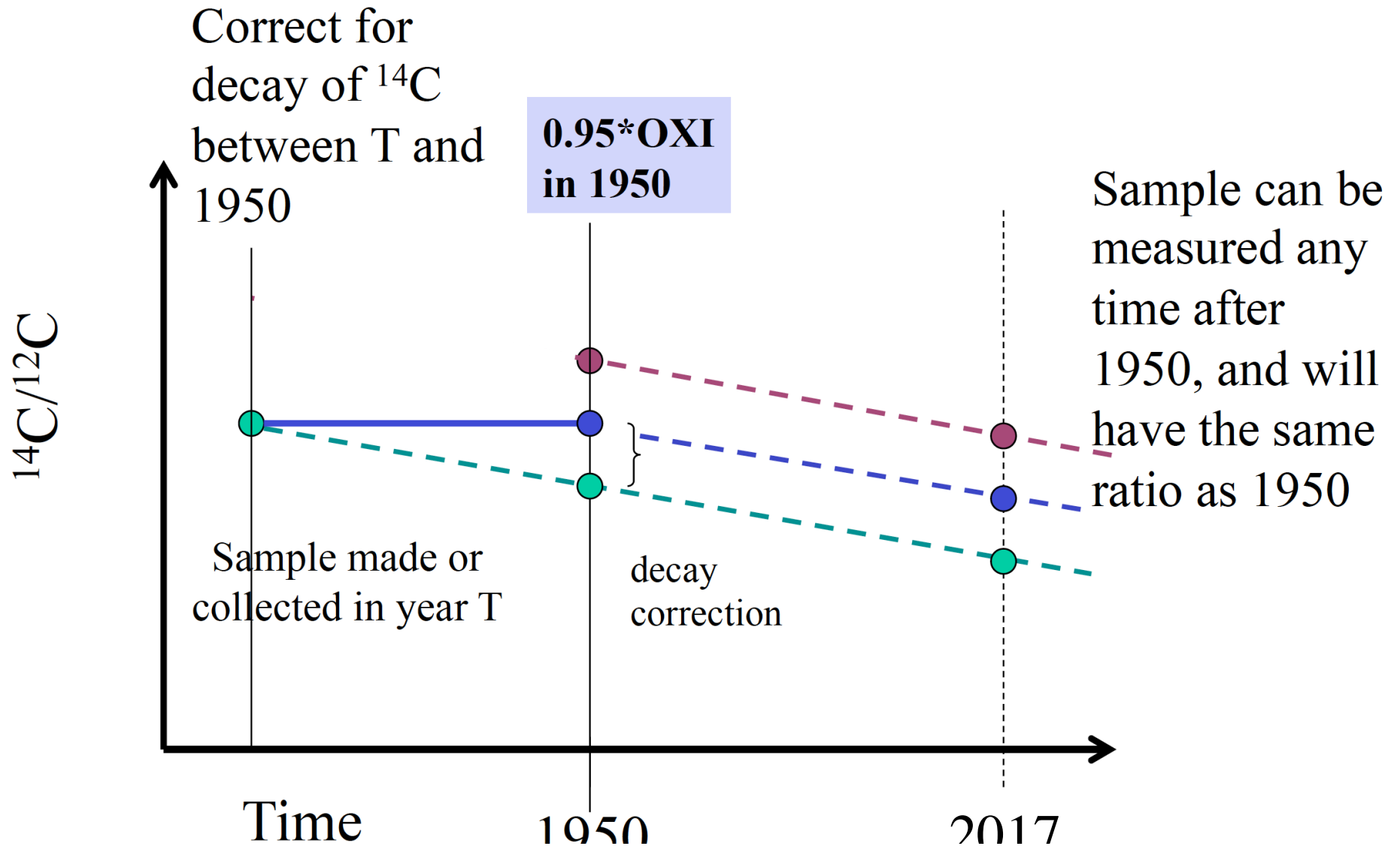
Corrects for decay of  $^{14}\text{C}$  in the sample from the year of growth (x) to 1950)

$$\Delta = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25} \exp\left(\frac{(1950-x)}{8267}\right)}{\left[ 0.95 \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19}} - 1 \right] 1000$$

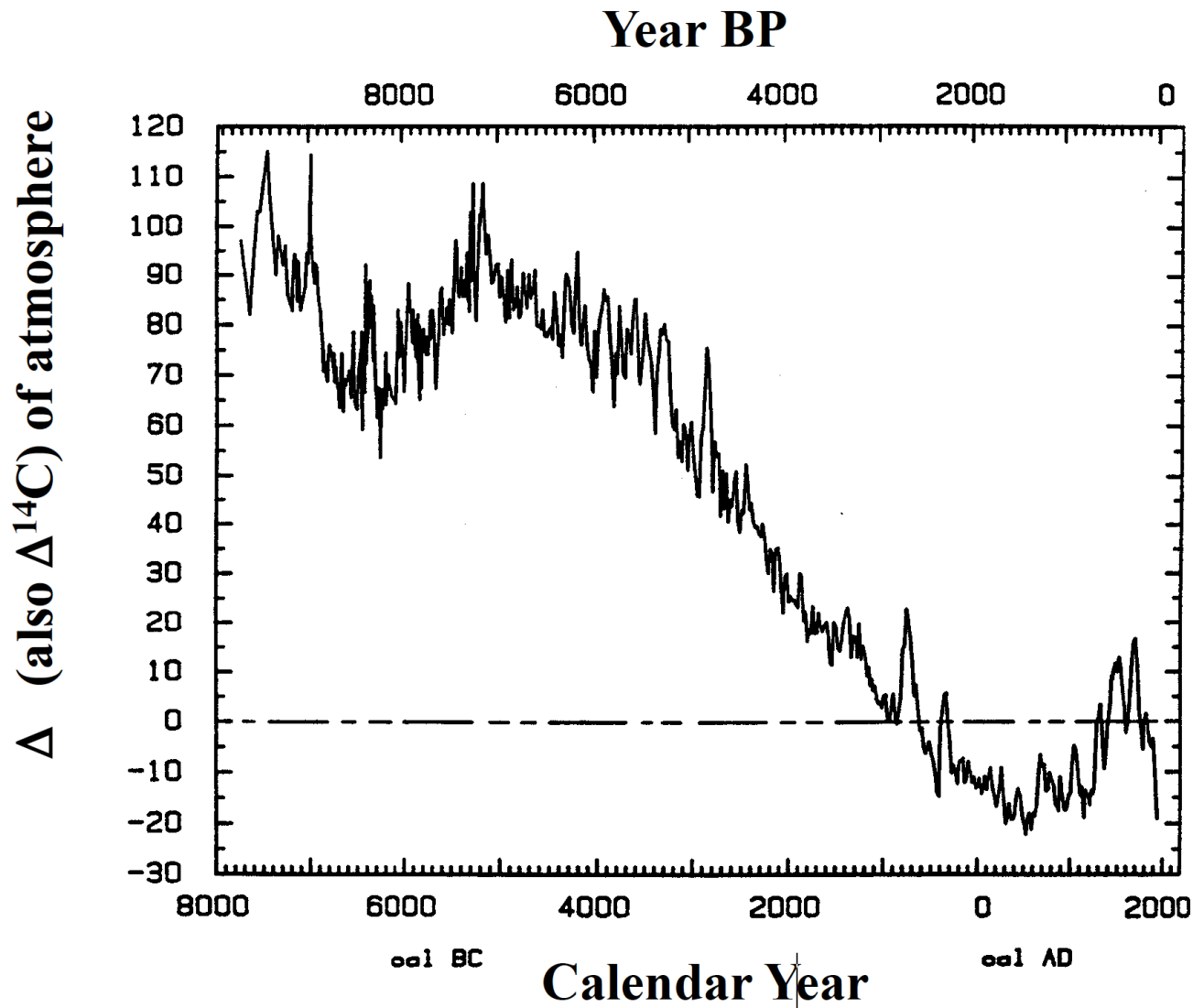
$\Delta$  expresses the radiocarbon signature relative to “Modern” had the sample been measured in 1950. This is useful for studies attempting to show how the radiocarbon signature of air (tree rings) and water (corals) changes with time. It is the basis for creating the calibration curves used to calculate calendar age from radiocarbon age



One of the applications of  $\Delta$  – to get past changes of atmospheric  $^{14}\text{C}/^{12}\text{C}$  using known-age samples



# Past Changes in Atmospheric $\Delta$ (pre-1950, $\Delta = \Delta^{14}\text{C}$ ) recorded in tree rings

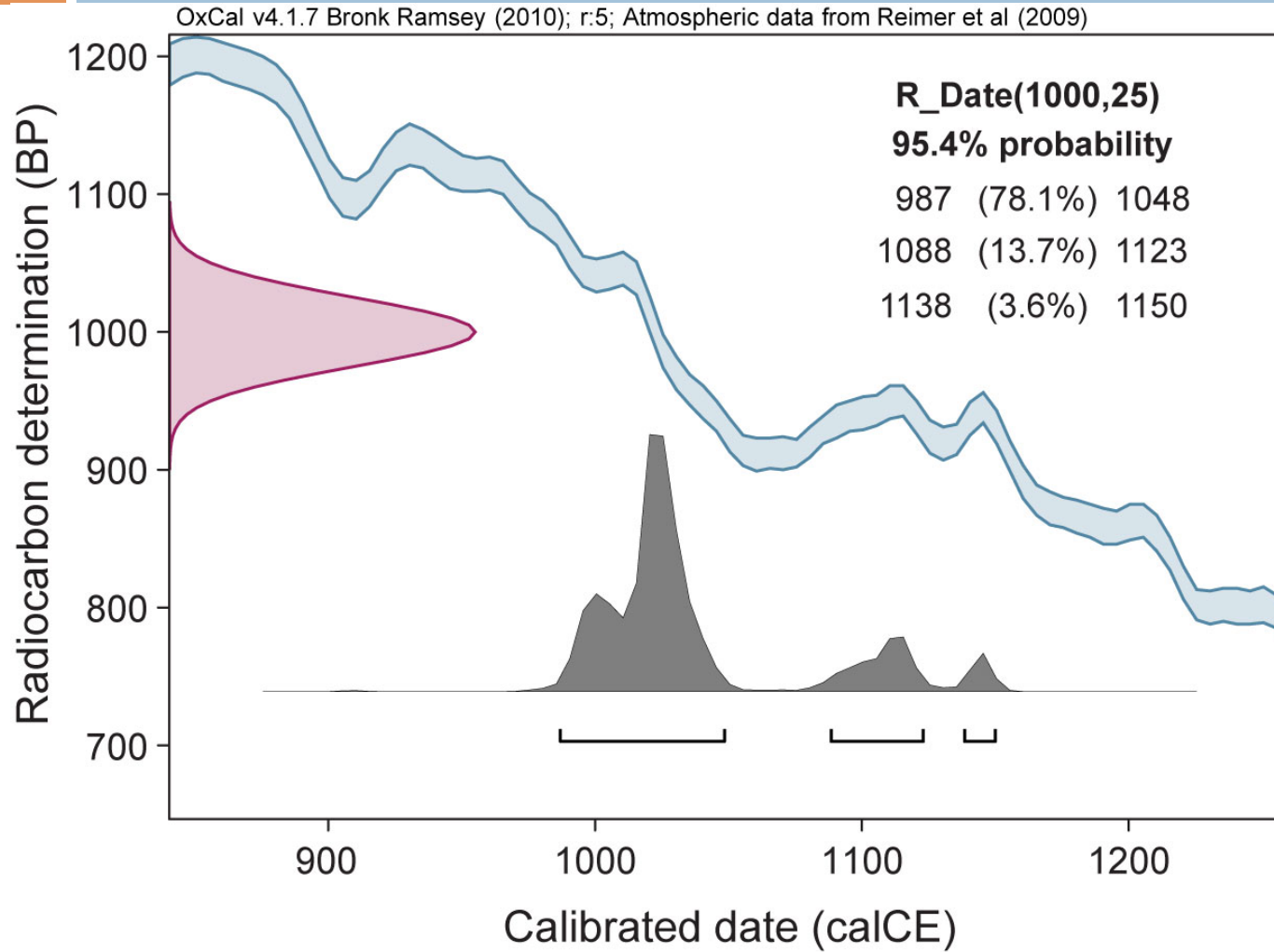


If we know the year the sample was formed, we can correct for radiodecay from that year to 1950 to determine what the  $^{14}\text{C}$  of the atmosphere was in the past.

Note that 8000 yrs ago,  $^{14}\text{C}$  was about 10% higher than in 1950;

Higher production rates or different distribution of Radiocarbon among atmosphere, ocean and land?

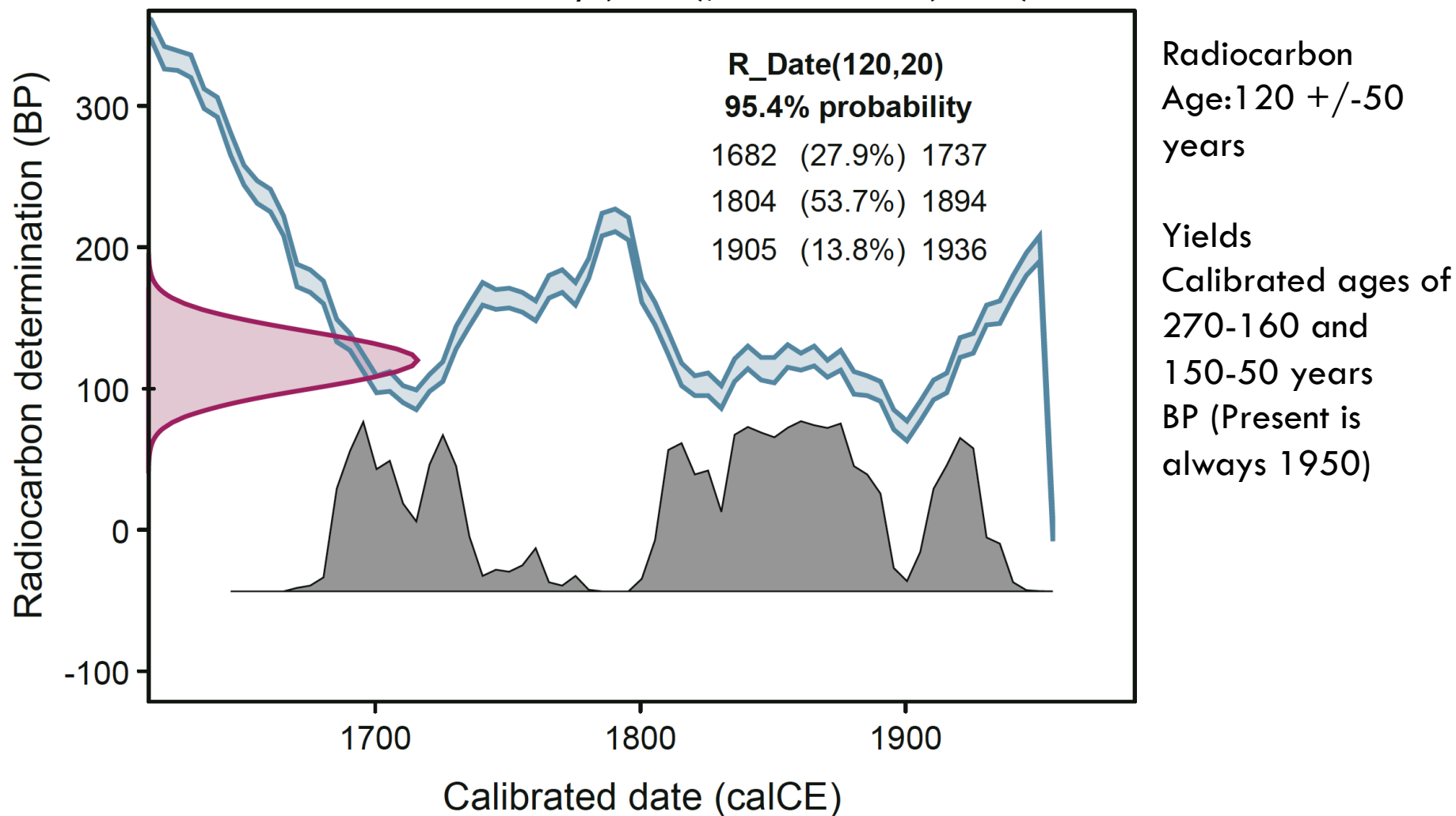
# Tree-ring calibration curve



The  $^{14}\text{C}$  value measured in tree rings of known age is used to determine the  $^{14}\text{C}$  value of the atmosphere for the year of tree growth

# The special problem of $^{14}\text{C}$ calibration for the calendar time period 1650–1950

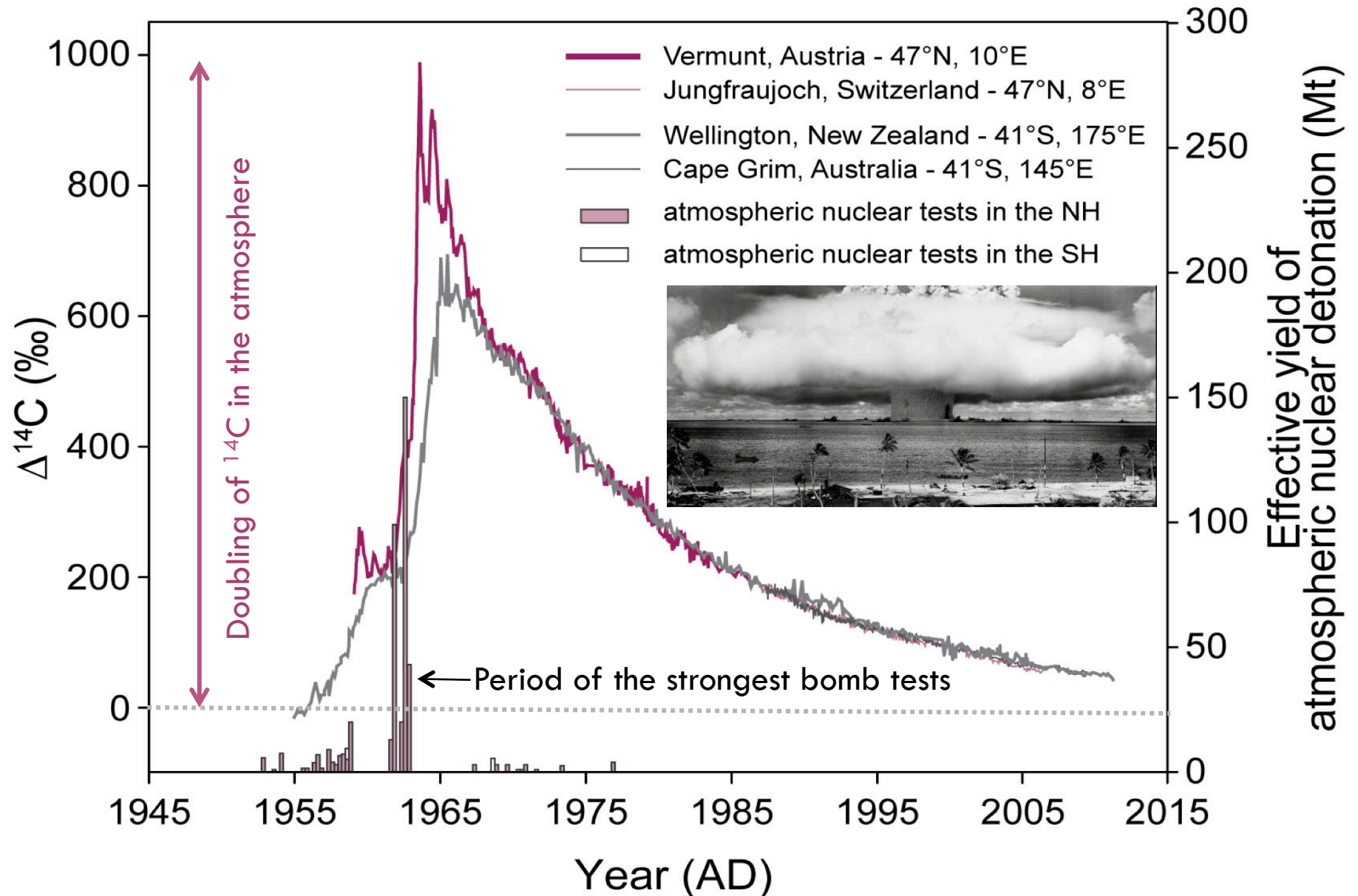
OxCal v4.1.7 Bronk Ramsey (2010), Reimer et al. (2009)



# Where is my Calibration Curve?

- The most up-to-date calibration curves can be found in the journal Radiocarbon ([www.radiocarbon.org/Info/index.html](http://www.radiocarbon.org/Info/index.html)). The latest is **INTCAL13** (Reimer 2013) and are used in the various calibration programs posted on the Web by different labs.
- Considerations: Sample type (note reservoir age R for marine samples), Sample time period, Sample origin (hemisphere/region), Standardized and internationally accepted?
- Calibrated dates are expressed in terms of cal BC, cal AD or cal BP.
- $^{14}\text{C}$  calibration data evolves: every version is different. **NEVER quote calibrated ages without also giving the original  $^{14}\text{C}$  data (i.e. F, pMC,  $^{14}\text{C}$  age).**

# $\Delta^{14}\text{CO}_2$ and the magnitude of nuclear explosions



For geochemical modeling, especially involving the distribution of bomb  $^{14}\text{C}$ , we need a way to report the absolute amount of  $^{14}\text{C}$  in the sample:

### Absolute percent Modern or $\Delta^{14}\text{C}$

- Requires defining a standard that does not change with time: decay-correct the oxalic acid standard to what it would have been in 1950 (i.e. add back radiocarbon that decayed in the standard since 1950)
- The value will therefore depend on the year in which the measurement was made (as long as the measurement was made after 1950)
- For known age samples after 1950, if the sample was not measured in the same year of the growth, but after, then decay correction for OX1 is from 1950 to the **year of sample growth**

# Expressing the Absolute Amount of Radiocarbon

Deviation in parts per thousand (per mil, ‰) from the isotopic ratio of an absolute standard (like stable isotope notation)

$$\Delta^{14}\text{C} = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample, -25}}}{0.95 \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1, -19}} e^{\left( \frac{y-1950}{8267} \right)}} - 1 \right] 1000$$

$y$  = year of sample growth or collection = year of measurement

Corrects for decay of OX1 standard since 1950

**This gives an absolute value of radiocarbon that does not change with time**



# The Absolute Fraction Modern

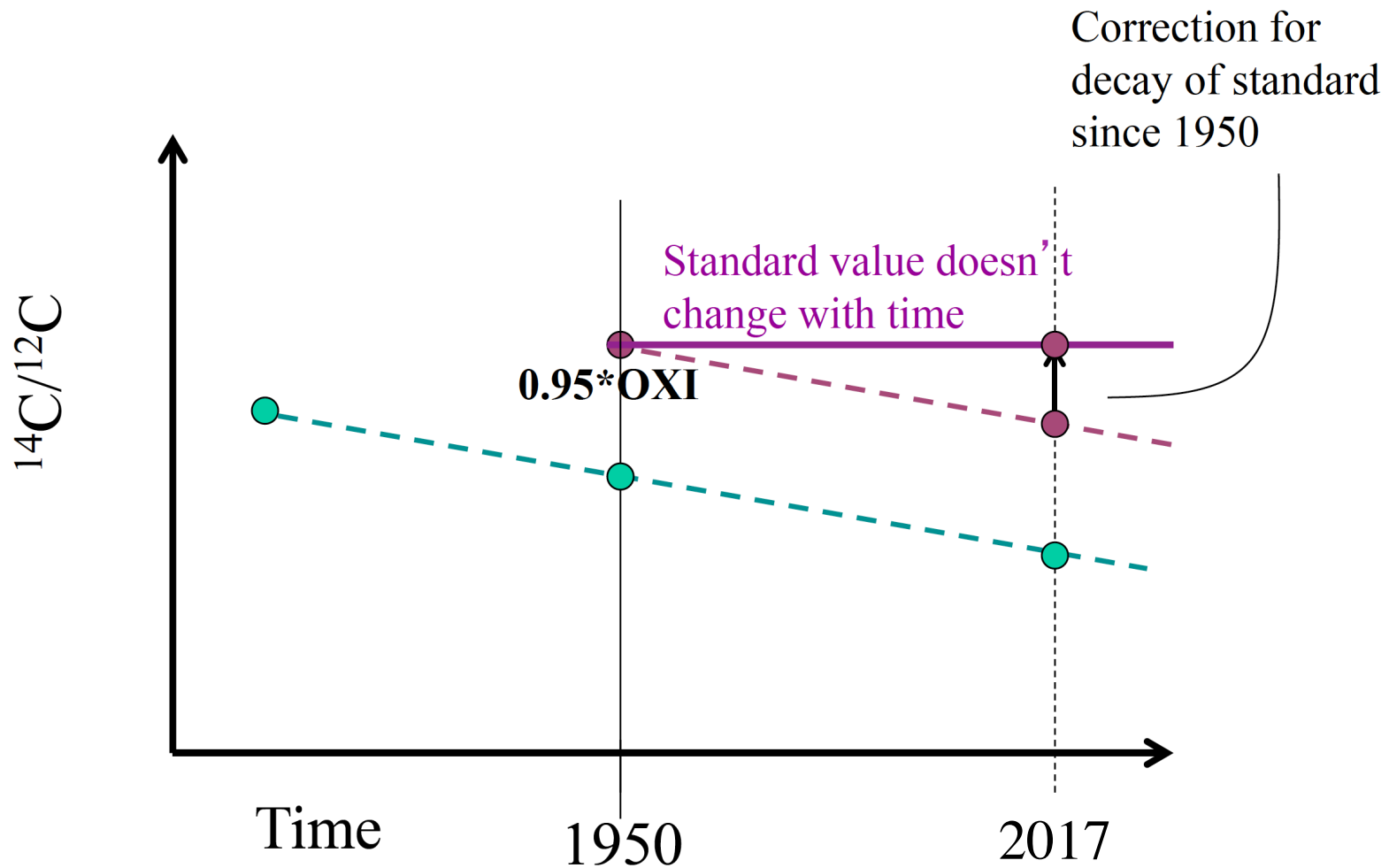
$$F' = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25}}{0.95 \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19} \exp((y-1950)/8267)} \right] = F \exp((1950-y)/8267)$$

$$\Delta^{14}\text{C} = (F' - 1) \times 1000$$

$y$  = year of sample growth or collection = year of measurement

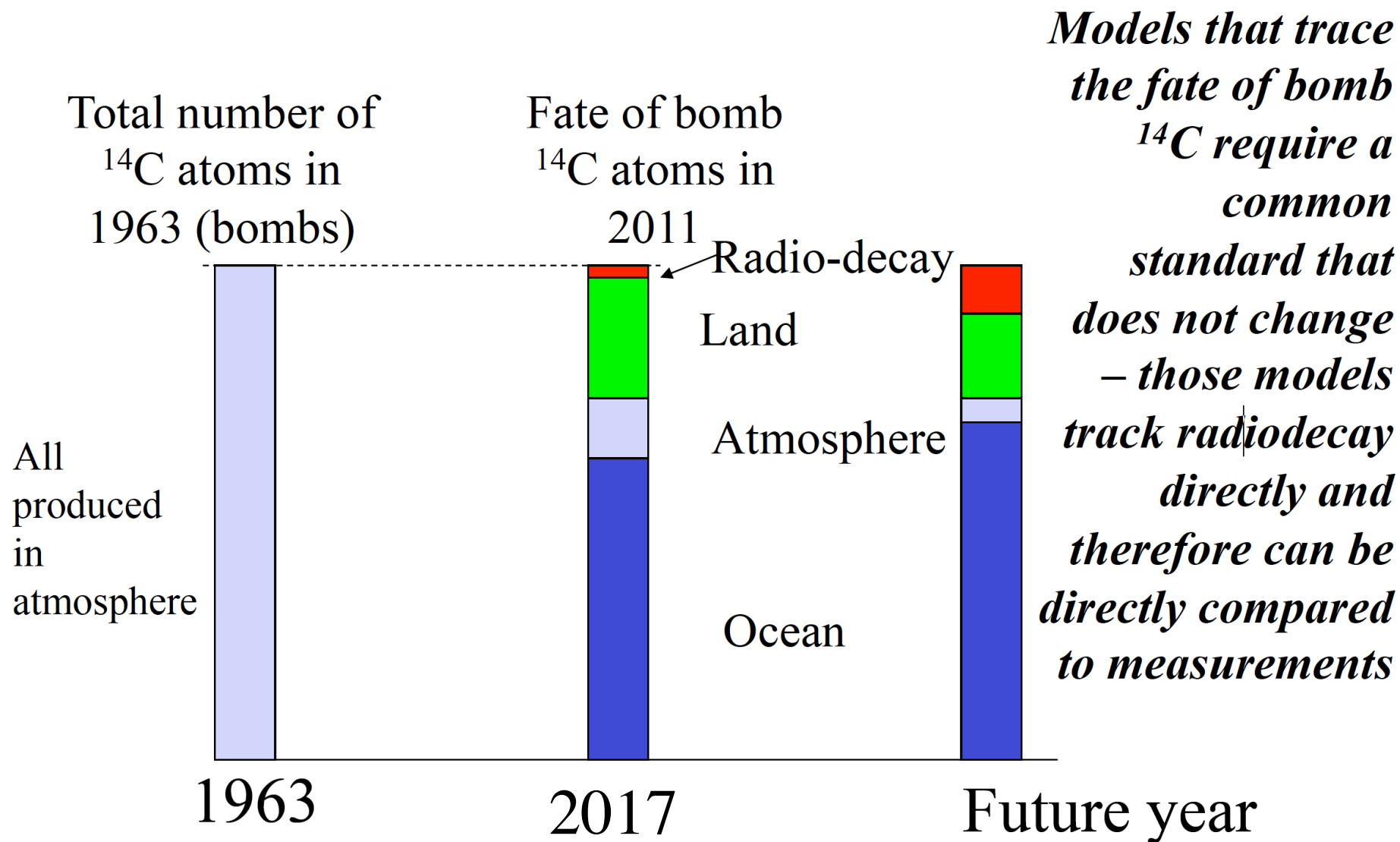
$\Delta^{14}\text{C}$  reports the  $^{14}\text{C}/^{12}\text{C}$  ratio in the year of measurement compared to the standard measured in 1950

- $\Delta^{14}\text{C}$  will change for the same sample measured in different years

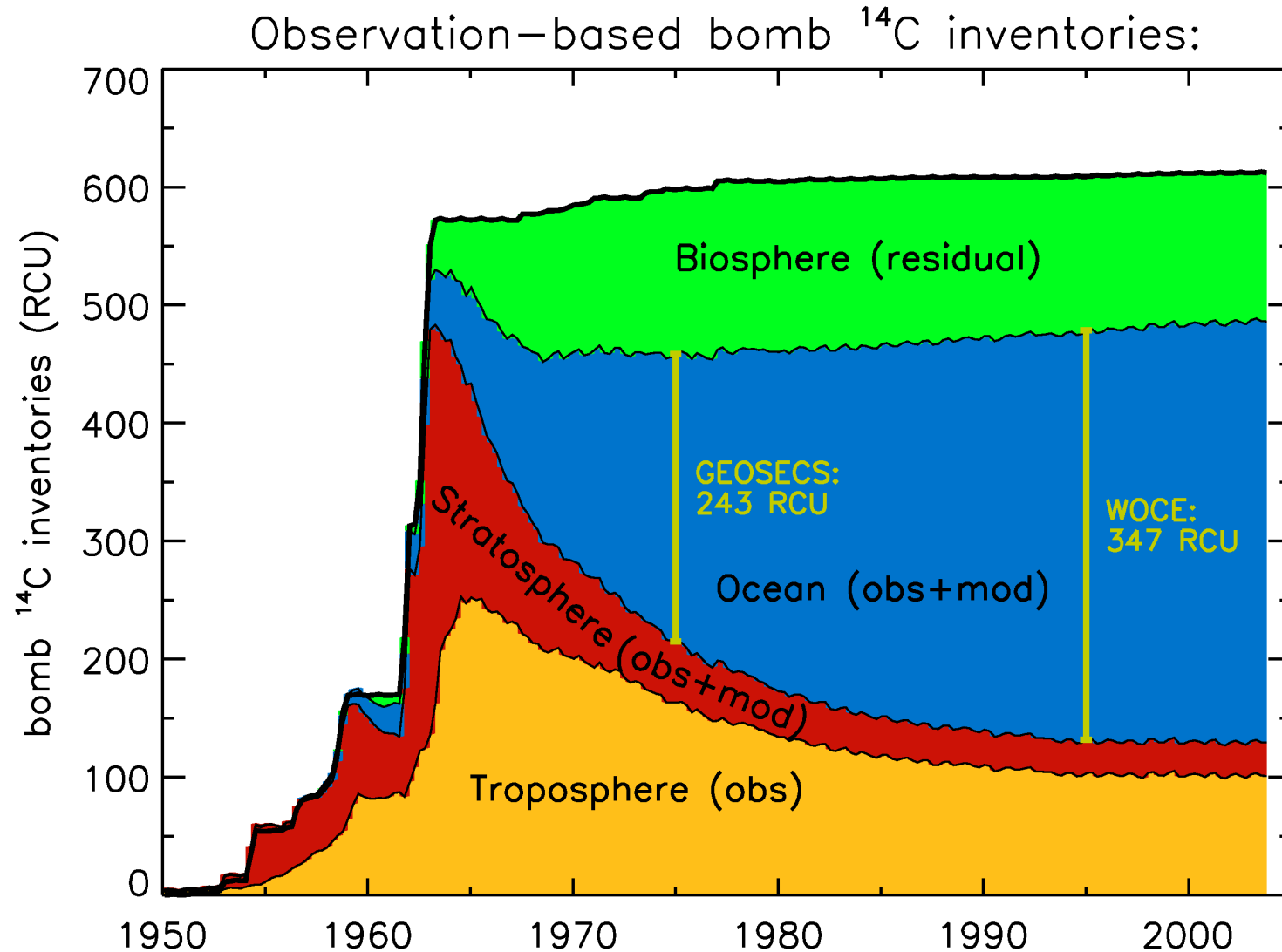


# Why on earth would you want to use $\Delta^{14}\text{C}$ ?

To perform mass balance – called the “geochemical” notation



# Observation-based bomb $^{14}\text{C}$ inventories (T. Naegler/I. Levin)



# Review Question

- Compared to the pre-industrial atmosphere, aboveground nuclear bomb-testing had doubled the amount of radiocarbon atoms in the northern hemisphere by 1965. What was the  $\Delta^{14}\text{C}$  [‰] of the northern hemisphere in 1965? (Assume that the NH is well mixed)

$$\Delta^{14}\text{C} = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25}}{0.95 \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19}} e^{\left( \frac{y-1950}{8267} \right)} - 1 \right] 1000$$

# The various ways to express $^{14}\text{C}$ information. Where given, $y$ indicates the year of measurement

Notification	Name	Definition	$^{13}\text{C}$ normalized	Decay-corrected	
				Standard since 1950	Known-age sample
F	Fraction Modern	(See text)	Yes	No	
pM	percent Modern	$100 \times F$	Yes	No	
$^{14}\text{C}$ age	Conventional radiocarbon age	$-8033\ln(F)$	Yes	No	
D	Delta	$1000 \times (F - 1)$	Yes	No	
<i>Absolute expressions</i>					
$\text{pM}_{\text{abs}}$	Absolute percent Modern	$(F \times \exp(((1950 - y)/8267)) \times 100$	Yes	Yes on OX1	
$\Delta^{14}\text{C}$	Delta $^{14}\text{C}$	(See text)	Yes	Yes on OX1	
$\Delta$	Delta	(See text)	Yes	Yes on sample	Yes

$\Delta^{14}\text{C}$ : Decay correction on OX1 from 1950 to yr of sample collection/growth (meas. in the same yr, post 1950)

$\Delta$ : Decay correction on Sample from yr of growth to 1950 (prior 1950 samples)

# Review Question

Tree-ring sample grown in 1970, but  $^{14}\text{C}$  was measured in 2017, what year should you use for  $y$ ?

$$\Delta^{14}\text{C} = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25}}{0.95 \left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19} e^{\left( \frac{(y-1950)}{8267} \right)}} - 1 \right] 1000$$

# Review Question

Tree-ring sample grown in 1970, but  $^{14}\text{C}$  was measured in 2017, what year should you use for  $y$ ?

$$\Delta^{14}\text{C} = \left[ \frac{\left[ \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{sample}, -25}}{\left[ 0.95 \frac{^{14}\text{C}}{^{12}\text{C}} \right]_{\text{OX1}, -19} e^{\left( \frac{y-1950}{8267} \right)}} - 1 \right] 1000$$

Answer: **1970** (also called known age correction)

Sample collection year = growth year, and sample **should be measured in the same year of collection**; Post 1950 collections



# Measurement of $^{14}\text{C}$

Two methods for C-14 measurements:

(1) **Beta-decay counting** ( $^{14}\text{C} \rightarrow ^{14}\text{N} + \text{b}^-$ ); measure radioactivity (decay constant x no. of  $^{14}\text{C}$  atoms)

(2) **Accelerator mass spectrometry (AMS)**

Count individual  $^{14}\text{C}$  atoms to get  $^{14}\text{C}/^{12}\text{C}$  ratio (some labs measure  $^{14}\text{C}/^{13}\text{C}$  ratio and use  $^{13}\text{C}/^{12}\text{C}$  to calculate  $^{14}\text{C}/^{12}\text{C}$ )

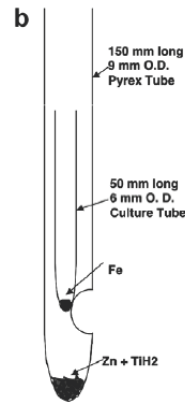
One gram of "modern" carbon produces about 14 beta-decay events per minute. To measure the age of a 1g sample to a precision of +/- 20 years one needs 160,000 counts, or about 8 days of beta-counting.

**AMS allows you to do the same measurement on a 1 milligram sample in a few minutes.**

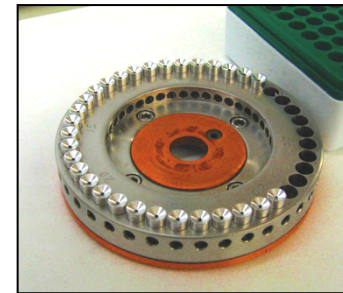
# Sample preparation (AMS)

**Solid ion source:** 1) purification/convert C to  $\text{CO}_2$ ; 2) reduce catalytically to **graphite** using catalyst (Fe). At UCI, we use two methods for reduction ( $\text{H}_2$  reduction vs. sealed tube zinc reduction)

$\text{H}_2$  on Fe @ 550 °C

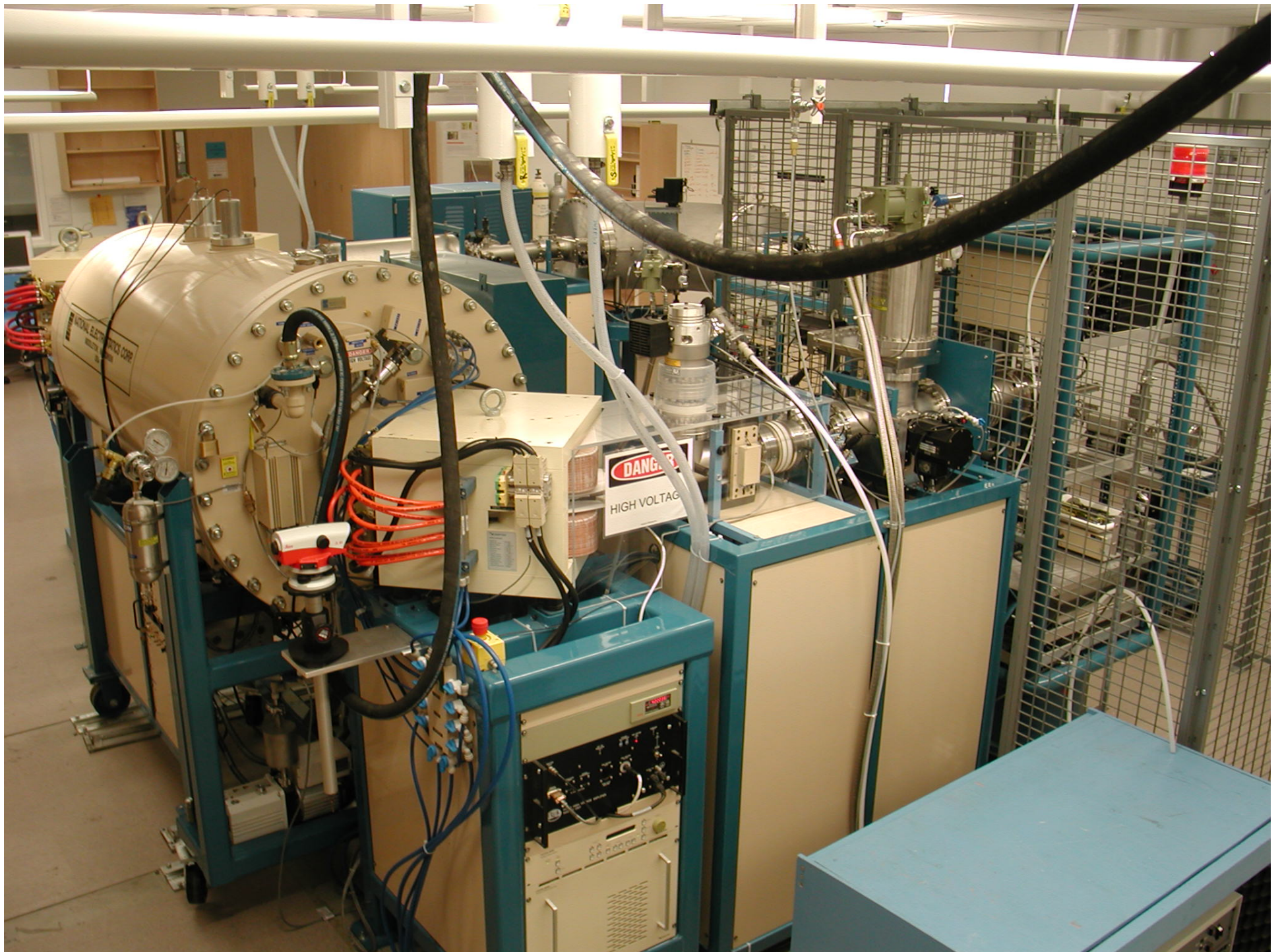


Graphite targets in a wheel



Sealed tube Zn @ 550 °C

**Gas ion sources ( $\text{CO}_2$ ):** e.g. MICADAS (ETH, Ionplus)



# Processes determining the error in a $^{14}\text{C}$ measurement

## **Sample heterogeneity**

*Random error estimated by measuring replicate samples.*

## **Contamination with C during pretreatment/purification**

*Systematic errors assessed by processing standards and blanks of known radiocarbon content that are appropriate for the type of sample being measured.*

## **Precision of radiocarbon measurement with AMS**

*Error when the same sample is measured multiple times.*

## **Accuracy of radiocarbon measurement with AMS**

*Error for a standard of known age measured as an unknown over a long period of time.*

Responsibility of the  
sample submitter

Reported by  
AMS lab

# How do we obtain accurate $^{14}\text{C}$ measurements?

- **Background** – how much  $^{14}\text{C}$  do you add to a sample during processing? Needs to be subtracted from a sample
  - 1) Sample collection
  - 2) Pretreatment
  - 3) Combustion/graphitization
  - 4) Machine (ion source)
  
- **Primary standards** for normalization (OX1 or OX2) – 6-8 in each wheel; plus 3-5 different **secondary stds** for quality control
  
- **Precision & Accuracy** – long term reproducibility of secondary standards and comparison to their consensus values (IAEA stds of different ages and different type of materials);  $^{14}\text{C}$  calibration program

# Background and sample size effect on $^{14}\text{C}$ errors

$m_s$ ( $\mu\text{g}$ )	$m_{\text{bg}}$ ( $\mu\text{g}$ )	$m_{\text{mix}}$ $\mu\text{g}$	$F_s$	$F_{\text{bg}}$	$F_{\text{mix}}$	$F_{\text{mix}} - F_s$	Error 100* ( $F_{\text{mix}} - F_s$ )/ $F_s$
990	10	1000	0.100	0.100	0.100	0	0
990	10	1000	0.100	1.100	0.110	-0.010	-10
90	10	100	0.100	1.100	0.200	-0.100	-100
90	10	100	0.100	0.200	0.110	0.010	-10
990	10	1000	1.100	0.100	1.089	0.011	1.0
90	10	100	1.100	0.100	1.000	0.100	9.1

$$m_{\text{mix}} = m_{\text{bg}} + m_s$$

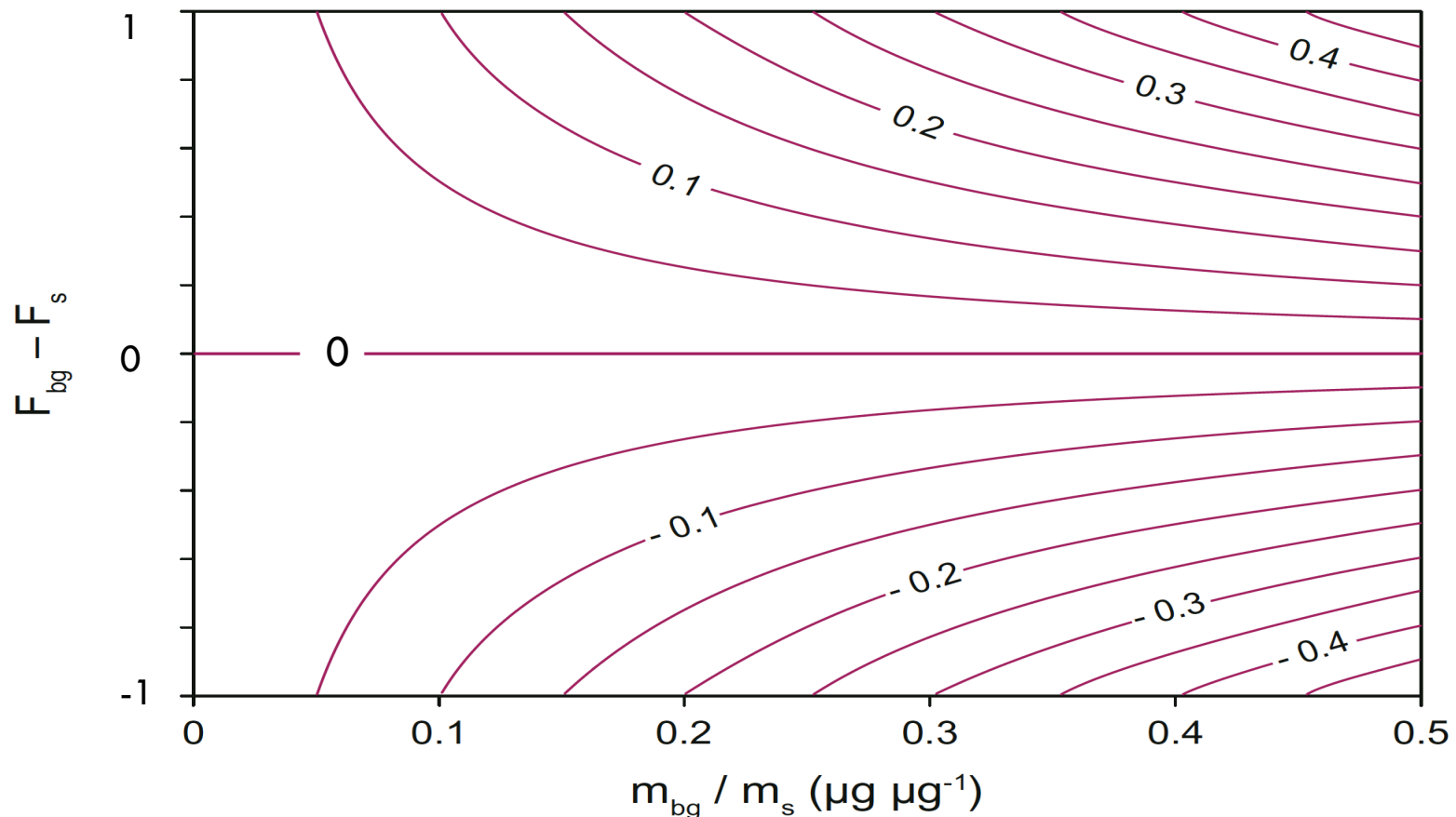
$$F_{\text{mix}} = (F_{\text{bg}}m_{\text{bg}} + F_s m_s) / m_{\text{mix}}$$

$$F_{\text{mix}} - F_s = (F_{\text{bg}} - F_s) \times (m_{\text{bg}} / m_{\text{mix}})$$

s = pure sample; bg = background; mix = sample + background

# Background and sample size effect on $^{14}\text{C}$ errors

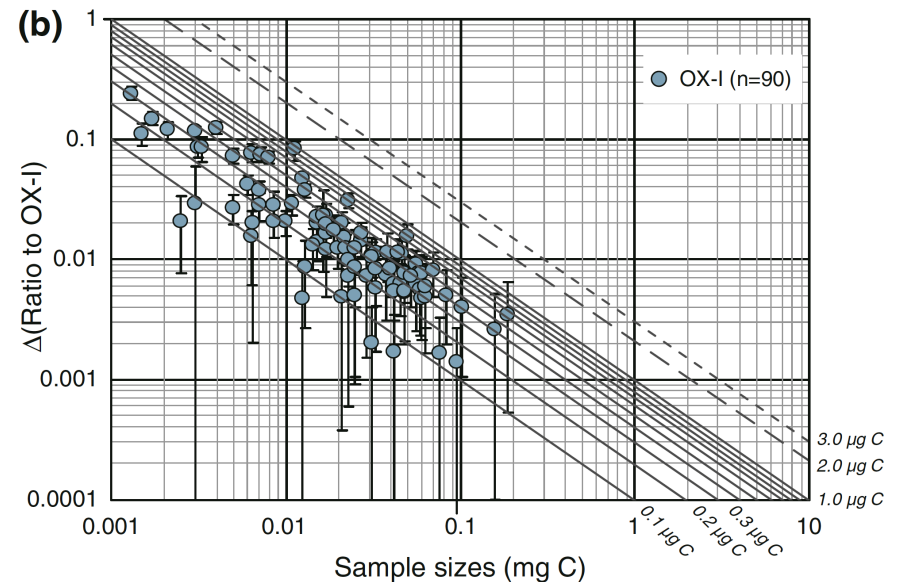
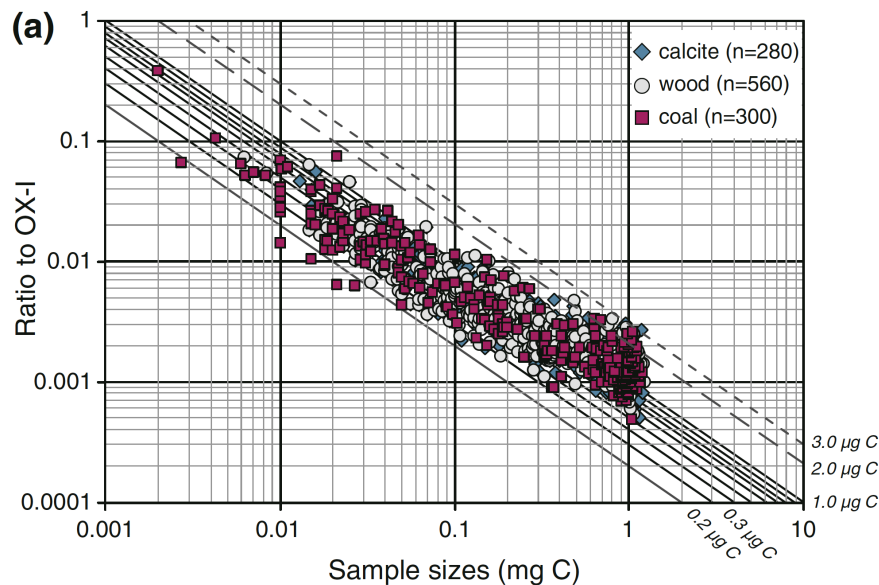
$$F_{\text{mix}} - F_s = (F_{\text{bg}} - F_s) \times (m_{\text{bg}}/m_{\text{mix}})$$



Contour lines are  $^{14}\text{C}$  errors ( $F_{\text{mix}} - F_s$ ); Minimizing the proportion of contamination ( $m_{\text{bg}}/m_{\text{mix}}$ ) is one of the most promising means for improving the accuracy of  $^{14}\text{C}$  measurements

# How to determine backgrounds

- Direct measurement: “blank blank” – running nothing through a procedure, get  $m_{bg}$  and  $F_{bg}$ . Challenge:  $F_{bg}$  is difficult to obtain because it's often too small
- Indirect measurement: (a) run a series of matching sizes  $^{14}\text{C}$  free materials => modern C contribution; (b) A series of matching sizes modern standards => dead C contribution (Santos et al., 2007)





# Summary: $^{14}\text{C}$ data reported

- As isotope ratios
- Relative to an universal standard (OxI) that has to be measured alongside the unknown sample
- Corrected for mass-dependent isotope fractionation to  $\delta^{13}\text{C} = -25\text{‰}$
- By convention 1950 is year 0
- Data may be corrected for  $^{14}\text{C}$ -decay of the standard or the sample
- With uncertainties related to processing (processing blanks) and measurement uncertainties (secondary standards)

F or pMC	All samples; Always appropriate	Not change with year of measurement
$\Delta^{14}\text{C}$	All samples Collected & measured in the same year, otherwise do known age correction for samples After 1950	Also report F & year of measurement; Changes with the year of sample collection/or measurement
$\Delta$	Known age samples Before 1950	Also report F & known age Not change with year of measurement
Conventional radiocarbon age	Unknown Aged samples Before 1950 (closed system)	$\neq$ calendar year Not a linear scale!

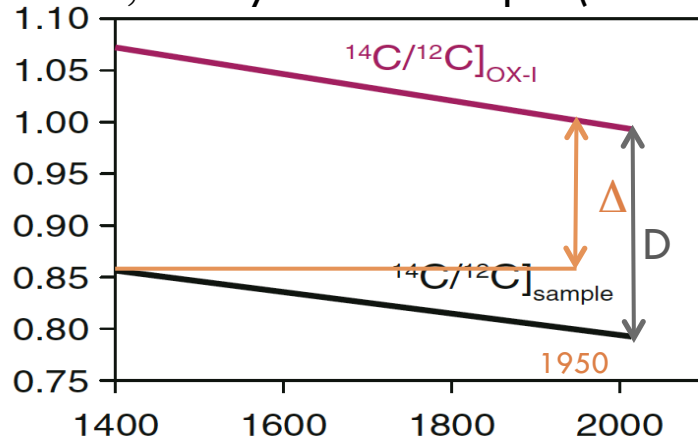
# Warning

$\Delta$ ,  $\Delta^{14}\text{C}$  and D are often mixed-up in publications. Therefore, for data comparison, or for combining different data sets (for global models), you need to know what the notations (and data) in the papers really mean before any actions.

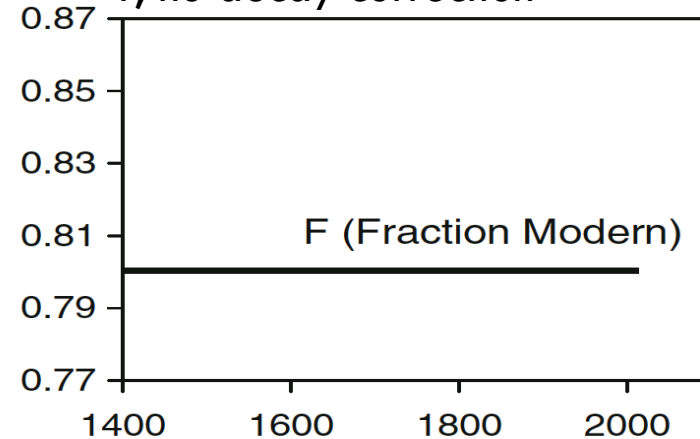
# Different ways of reporting $^{14}\text{C}$

The more accurate half-life **5730 years** is used in decay correction

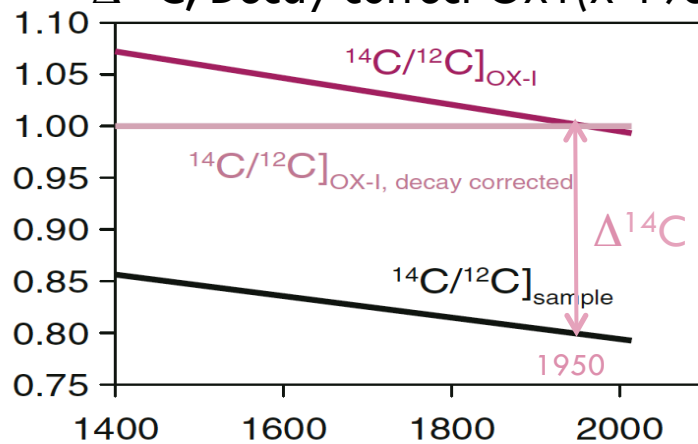
**(a)**  $\Delta$ , Decay correct sample (1950-X)



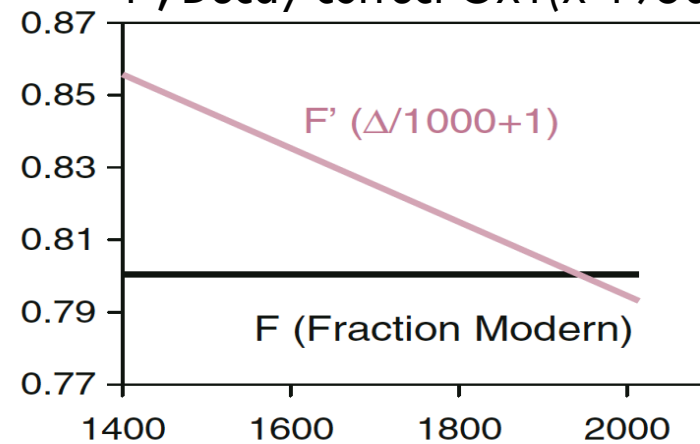
**(b)**  $F$ , no decay correction



**(c)**  $\Delta^{14}\text{C}$ , Decay correct OX1(X-1950)



**(d)**  $F'$ , Decay correct OX1(X-1950)



Year

Year

# Resources

- <http://www.c14dating.com/agecalc.html>
- <http://www.who.edu/nosams/radiocarbon-data-calculations>
- <http://www.hic.ch.ntu.edu.tw/AMS/A%20guide%20to%20radiocarbon%20units%20and%20calculations.pdf>
- Donahue, D. J., Linick, T. W., & Jull, A.T. (1990) Isotope-ratio and background corrections for accelerator mass spectrometry radiocarbon measurements. *Radiocarbon*, 32(2), 135-142.
- Stuiver, M., and H.A. Polach. 1977. Reporting of C-14 data—discussion. *Radiocarbon* 19: 355–363.
- Trumbore S.E., Sierra, C.A., & Hicks Pries, C.E. (2016) Radiocarbon Nomenclature, Theory, Models, and Interpretation: Measuring Age, Determining Cycling Rates, and Tracing Source Pools. In Schuur, E. A., Druffel, E., & Trumbore, S. E. (Eds.). (2016). *Radiocarbon and Climate Change: Mechanisms, Applications and Laboratory Techniques*. Springer.

# $^{14}\text{C}$ Standards

## International Atomic Energy Agency (IAEA)

ID	Material	$\delta^{13}\text{C}$ (‰)	Standard deviation	$^{14}\text{C}$ (Fraction Modern)	1 sigma error
IAEA-C1	Marble	2.42	0.33	0.0000	0.0002
IAEA-C2	Travertine	-8.25	0.31	0.4114	0.0003
IAEA-C3	Cellulose	-24.91	0.49	1.2941	0.0006
IAEA-C4	Wood	-23.96	0.62	0.002–0.0044	Range
IAEA-C5	Wood	-25.49	0.72	0.2305	0.0002
IAEA-C6	Sucrose	-10.80	0.47	1.506	0.0011
IAEA-C7	Oxalic acid	-14.48	0.20	0.4953	0.0012
IAEA-C8	Oxalic acid	-18.31	0.20	0.1503	0.0017

## U.S. National Institute of Standards and Technology (NIST)

ID (NIST)	Material	$\delta^{13}\text{C}$ (‰)	$^{14}\text{C}$ FM
OX-I (SRM 4990 B)	Oxalic acid	-19.1	1.0397
OX-II (SRM 4990C)	Oxalic acid	-17.8	1.3407

OX-I is not commercially available anymore;  $0.95R_{\text{OXI}_{19}} = 0.7459R_{\text{OXII}_{25}}$

# $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$

## isotopic fractionation ratio (b = 2?)

$$\alpha_{14} = \alpha_{13}^b \text{ or } b = \frac{\ln \alpha_{14}}{\ln \alpha_{13}} = \frac{\ln(1 + \varepsilon_{14})}{\ln(1 + \varepsilon_{13})} \approx \frac{\varepsilon_{14}}{\varepsilon_{13}}$$

Where  $\alpha$  is the fractionation factor,  $\varepsilon$  the enrichment factor, and b the fractionation ratio (b=2).

$$\left(\frac{\frac{^{13}\text{C}}{^{12}\text{C}}_{-25}}{\frac{^{13}\text{C}}{^{12}\text{C}}_{\delta}}}\right)^2 = \left(\frac{\left(1 - \frac{25}{1000}\right) \frac{^{13}\text{C}}{^{12}\text{C}}_{VPDB}}{\left(1 - \frac{\delta}{1000}\right) \frac{^{13}\text{C}}{^{12}\text{C}}_{VPDB}}\right)^2 = \left(\frac{\left(1 - \frac{25}{1000}\right)}{\left(1 - \frac{\delta}{1000}\right)}\right)^2$$

Fahrni et al., *Geochimica et Cosmochimica Acta* 213 (2017) 330–345

- $b = 1.882 \pm 0.019$  for reduction of  $\text{CO}_2$  to graphite
- $b = 1.953 \pm 0.025$  for C3 and C4 photosynthesis pathways
- Roughly 1 radiocarbon year offset for every 1‰ of  $\delta^{13}\text{C}$  apart from 25‰ with  $b = 1.882$

Thank you!

