Radiocarbon Dating Tutorial

Prepared in 2022 by David Killick

for the African Chronometric Dating Fund committee sponsored by the Partnership of the Society for Africanist Archaeologists, the PanAfrican Archaeological Association, and the British Institute in Eastern Africa

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Isotopes in Archaeology

Isotopes of any element have the same number of protons and electrons - and thus the same chemical properties - but different numbers of neutrons, so have different atomic masses

Hydrogen	^{1}H	^{2}H			
Carbon	^{12}C	^{13}C	^{14}C		
Nitrogen	^{14}N	^{15}N			
Oxygen	^{16}O	^{17}O	^{18}O		
Argon	^{36}Ar	^{38}Ar	^{39}Ar	^{40}Ar	
Potassium	^{39}K	^{40}K	^{41}K		
Strontium	^{84}Sr	^{86}Sr	^{87}Sr	^{88}Sr	
Lead	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb	^{210}Pb
Thorium	^{230}Th	^{232}Th	^{234}Th and 4 more		
Uranium	^{234}U	^{235}U	^{238}U and 3 more		

Isotopes of archaeological interest. Those in white are stable; those in red are unstable (radioactive); those in yellow are stable daughter products of radioactive decay.

Primordial radioactive isotopes were created before the formation of our solar system, and decay very slowly; cosmogenic isotopes are formed continually by interaction of cosmic rays with matter and are relatively short-lived.

Cosmogenic isotopes for archaeology and geomorphology

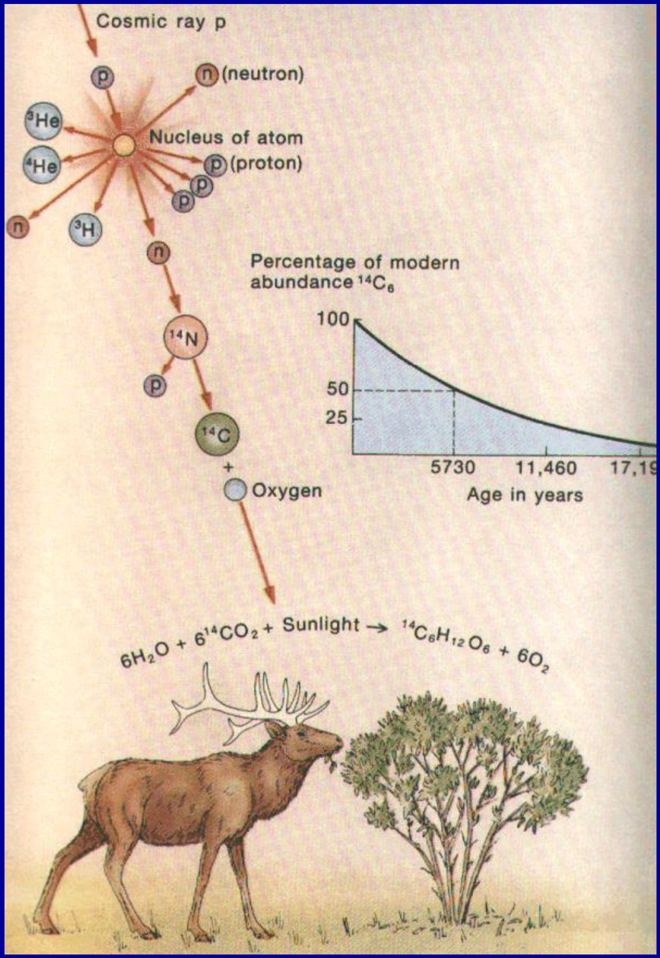
Isotope	*Half-life (yr)*	*Used to date*
^{14}C	5730 ± 40	biological tissues, soils, water, ice
^{36}Cl	300,000	ice, carved rock surfaces (max. age)
^{10}Be	1,500,000	flint mines, rock exposure, etc.

The half-life is the time it takes for half the initial number (N_o) of radioactive atoms to decay away. All radioactive decay obeys the following equation:

$$N = N_o\, e^{-\lambda t}$$

N is the number of atoms remaining; e is the exponential constant; λ is the decay constant (the reciprocal of the half-life) for the particular radioactive isotope; and t is time elapsed in years since new atoms stopped being added to the system. For radiocarbon this is when a biological organism dies, when a plant is harvested, or (in trees) at the end of each growing season. Each tree ring contains carbon captured in only one year.

Atmospheric production of ^{14}C



Nitrogen is converted to radiocarbon by neutrons

(14,7)N + (1,0)n ==> (14,6)C + (1,1)H

Total atmospheric production, per year, is only about 7 kg, so relative abundances of carbon isotopes in the atmosphere today, and in live vegetation are:

^{12}C : 99% ^{13}C <1% ^{14}C: 1 x 10^{-12}

Radiocarbon decays back to nitrogen

(14,6)C ==> (14,7) N + β (electron) + ű (neutrino) + Q (energy)

All measured ^{14}C ages are reported as radiocarbon years before 1950 – conventionally, years BP or years bp.

What does “years BP” mean ?

BP means ‘before present” which is an unfortunate choice of words. In radiocarbon dating, BP is ALWAYS ”radiocarbon years” before 1950.

Why 1950? From 1951 frequent testing of nuclear bombs (which produce massive numbers of neutrons) sent massive amounts of radiocarbon into the atmosphere – the “radiocarbon spike”. By convention, radiocarbon labs always compare the radiocarbon content of archaeological samples to the known radiocarbon content of the atmosphere in 1950.

The term “radiocarbon years before present” is also unfortunate and a source of much confusion because radiocarbon years are not necessarily calendar years - as shown in the section on calibration below. A much less confusing equivalent is pMC (percent modern carbon) which is the radiocarbon content of the sample compared to that of organic matter grown in 1950. Both radiocarbon years BP and pMC are reported by radiocarbon laboratories for every sample.

Age range for radiocarbon dating

There is very little radiocarbon in organic matter to begin with, and the amount reduces by half with every 5730 (± 40) years after death. Modern radiocarbon accelerators can in theory detect radiocarbon at 10 half-lives (ca. 57,300 BP) but in practice the range is limited by contamination from modern carbon to 35,000 – 40,000 BP. Some laboratories, especially in Australia, will attempt dating of carbon samples in the range 40,000 – 55,000 BP, but samples must be processed on dedicated lines reserved for very old samples. Most laboratories will ask for an estimated age when you submit the sample, and won't accept samples thought to be >35,000 BP.

There are also some ranges of age where it is a waste of money to attempt radiocarbon dating because conversion of radiocarbon (BP) dates to calendar ages (by calibration, discussed below) results in dates with such a wide range of possible calendar age as to be archaeologically useless. This is discussed in later slides.

Types of samples for radiocarbon dating

- WOOD CHARCOAL. Most abundant, but can potentially be tens to hundreds of years older than the archaeological event ("old wood")
- ANNUAL PLANT samples – leaves, seeds, grains, fruits, nuts, fibers (e.g., cotton, hair). Ideal if available. Plants that grow in water can pose special problems in hard (calcium-rich) waters.
- BONE and TEETH samples can be dated two ways. The better way is to date bone protein (collagen) if preserved. If the collagen is gone, then the bone mineral (apatite) can be dated, but this is often problematic.
- ROCK ART. Black pigments may be charcoal. Other pigments can't be dated, but sometimes were mixed with protein binders (e.g., egg) that contain radiocarbon.
- EGGSHELL (particularly ostrich eggshell, or OES) is attracting renewed attention as a suitable material for dating.
- CARBONATES such as flowstones over or under archaeological deposits in caves. These are not usually directly associated with archaeological events. Avoid pedogenic (soil) carbonates.
- STEEL if the carbon derives from smelting iron ore with charcoal.
- POTTERY if deliberately tempered with annual plant fibers.

Collection of radiocarbon samples

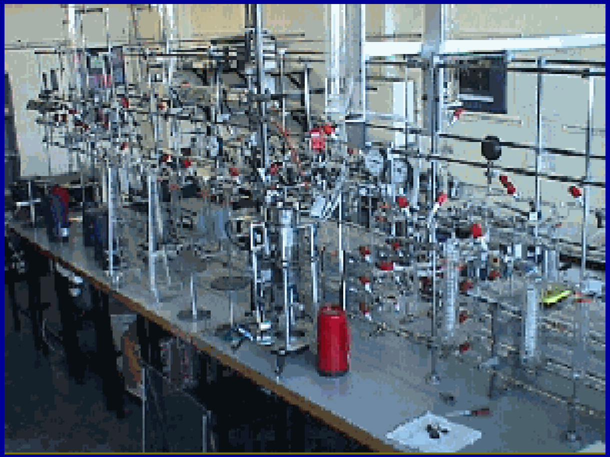
In the field Always take radiocarbon samples before any kind of glue or preservative is applied to stabilize fragile samples. Plastic bags are fine for any samples likely to be younger than 10,000 years. Older samples should be put in glass or unpainted metal containers, preferably after first rinsing the containers with pure alcohol or acetone. Make sure that samples are completely dry before sealing containers – any fungus that grows on damp samples will incorporate radiocarbon from the air. If you see any modern roots in the sample when excavating it, pick them out under magnification before they dry up and become invisible.

Stored samples in museums, etc. Always examine the samples closely for traces of preservatives, ink, etc. If you can't avoid taking treated samples, be sure to tell the radiocarbon laboratory so that they can try to remove these with organic solvents. Check the surfaces of all copper objects for preserved organic materials like cloth – copper ions kill bacteria and fungi. The green copper corrosion products are carbonates, but they are entirely removed by pretreatment with acid. We have had good results from dating the plant fiber cores of wound copper bangles.

Purification and extraction of carbon from samples

For carbonized plants (wood, leaves, fruits, nuts, grains, fibers)

1. Acid (HCl) to remove any soil carbonates
2. Base (NaOH) to remove any soil humic acids
3. Acid (HCl) to neutralize any base remaining
4. Wash and dry
5. Weigh and place in vacuum line with CuO
6. Pump to high vacuum; heat to make CO_2
7. Freeze out water and sulfur/nitrogen oxides
8. Remove purified CO_2
9. Convert to graphite for measurement of ^{14}C



ABA is the standard pretreatment for charcoal. Other materials (e.g., bones, teeth) require different pretreatment and extraction protocols. Contamination with tar, preservatives made from petrochemicals, etc. is removed with volatile organic solvents like acetone. Any solvent remaining in the sample after cleaning will evaporate completely, and thus will not affect the date.

Measurement of radiocarbon

Decay counting methods (now almost obsolete)

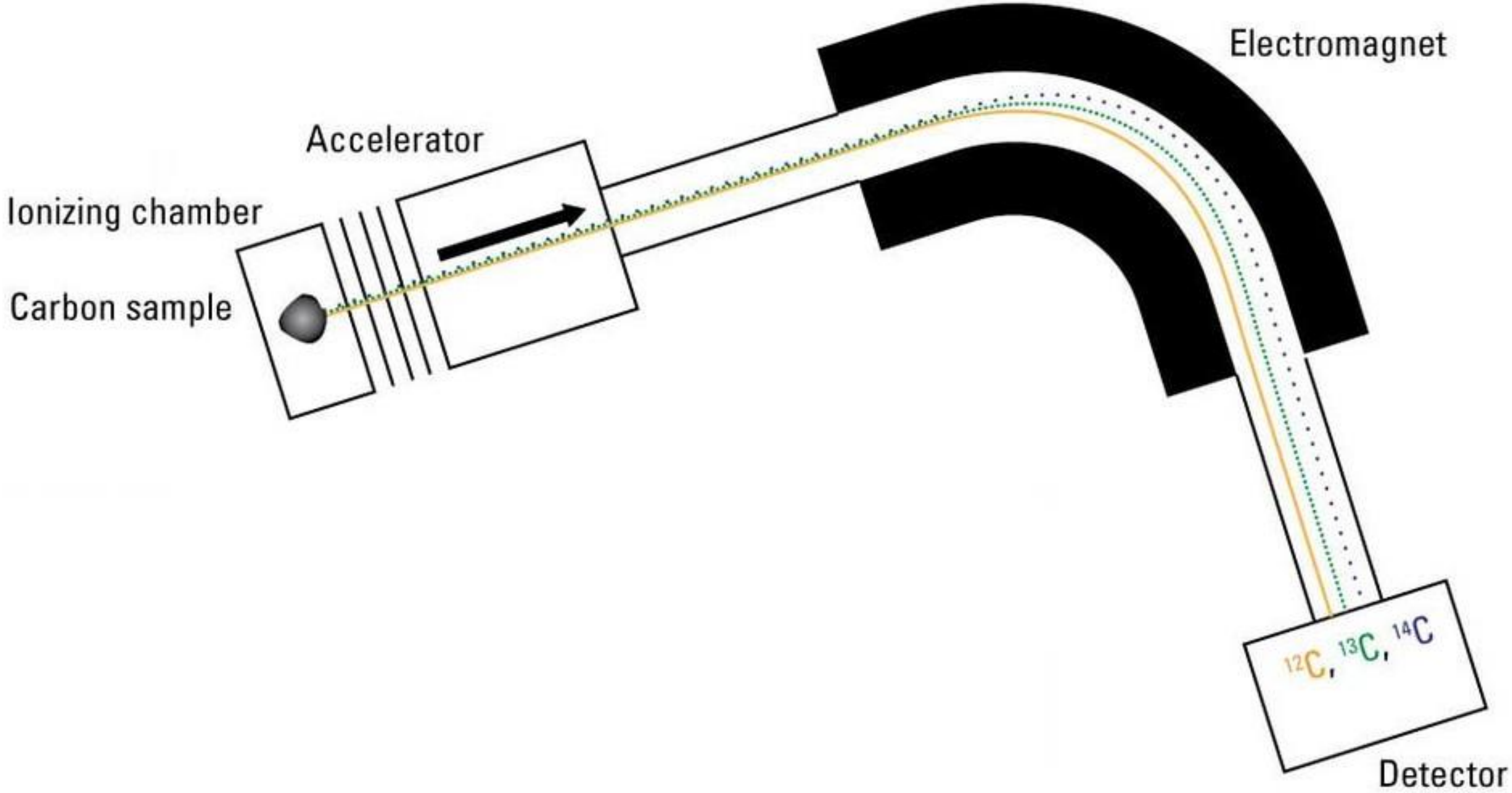
1. Gas proportional counting of CO_2 using a Geiger- Muller counter.
2. Liquid scintillation counting of benzene (C_6H_6)

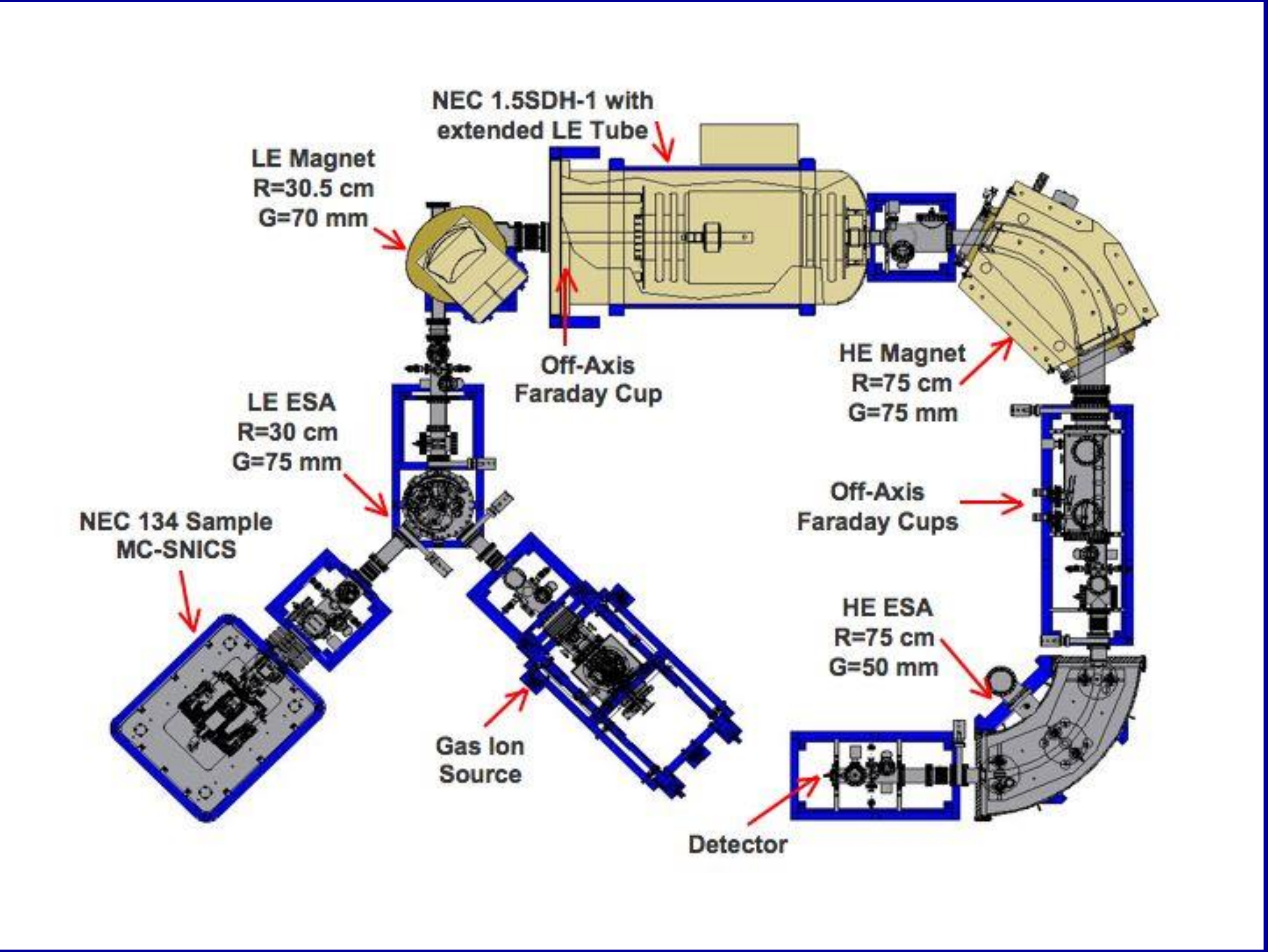
Both count decay of radiocarbon atoms back to nitrogen as these occur. Only a tiny fraction of radiocarbon atoms in a sample decays during measurement, so large samples (100-250 g charcoal) and long times (24-72) hours are required to get dates with reasonable precision.

Accelerator Mass Spectrometry (AMS)

These use tiny solid graphite targets. The graphite is ionized, and the ions are accelerated into a magnet, which bends the beam according to the mass/charge ratio. ^{12}C, ^{13}C and ^{14}C ions have the same charge but different masses, so are bent into different paths and can be counted separately. (See next slide). All radiocarbon atoms in the sample are counted, so much smaller samples (1- 10 mg pure carbon) are needed; counting times are typically around 20 minutes. AMS was introduced from the late 1980's and has gradually replaced decay counting methods.

How an Accelerator Mass Spectrometer Works



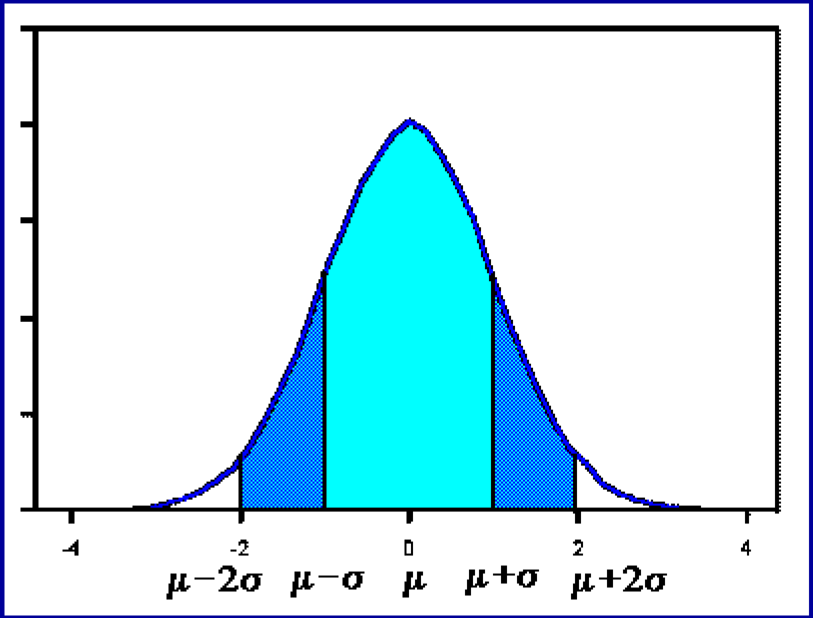


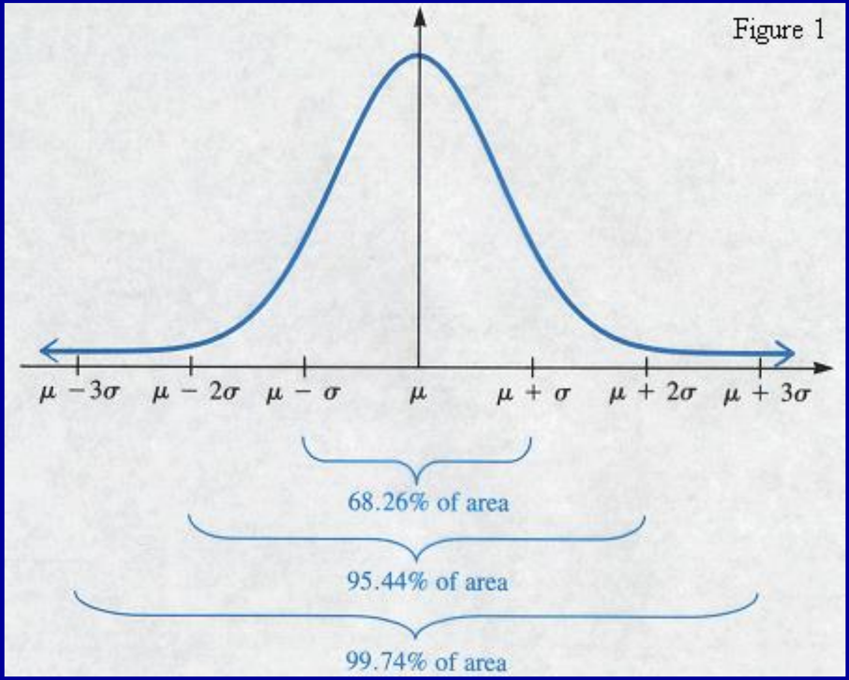
Plan of an actual AMS instrument. A wheel of 50 to 70 samples and standards placed in the LE ESA runs under computer control overnight.

Accuracy and precision in radiocarbon dating

All measurements of the abundance of isotopes are only estimates – repeat measurements will not provide the exact same number. It is therefore important to know the range within which the true value lies. This is the precision of the measurement, reported as the standard deviation (***σ***)

The electronics of the AMS instrument are not perfectly stable, so the number of counts per second (cps) varies. When all cps counts are plotted, they form a symmetrical Gaussian distribution, as seen below. In radiocarbon dating ***μ*** is the reported BP age and ***σ*** is the ± number after it





Radiocarbon measurements are reported in this form:

AA-12788 1250 ± 35 BP

AA - is the laboratory identifier (in this example the University of Arizona)

12788 is the unique sample number assigned by the laboratory

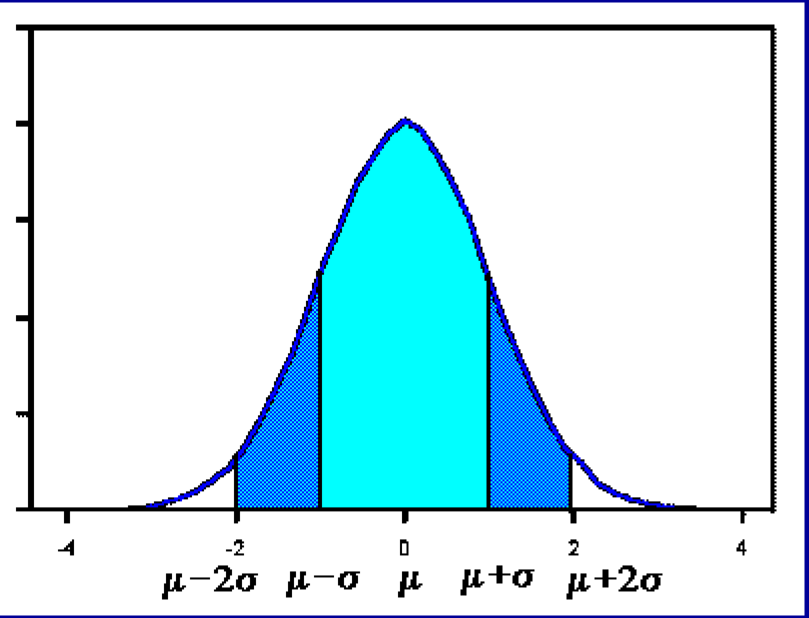
1250 is the peak (mean) age in radiocarbon years, usually rounded to nearest 10

35 is the 1σ standard deviation of the set of measurements of which 1250 BP is the mean (μ). As shown in the previous slide, there is a 68.26% probability that the true age lies in this range, and a 95.44% probability for 2σ (1250 ± 70 BP)

The smaller the standard deviation (σ), the more precise is the measurement.

$$\sigma(r) = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - r)^2}$$

Thus, 4x the number of counts (N) produces a ***σ*** half as large. The practical limit for AMS is about ± 20 years.



Where can I get radiocarbon dates done?

The journal *Radiocarbon* provides a list of radiocarbon laboratories on its home page: https://radiocarbon.webhost.uits.arizona.edu/node/11. This is a downloadable pdf that is updated annually.

For prices, sample size requirements, schedules and prices, contact the laboratories directly. We strongly advise using only accelerator mass spectrometry (AMS) laboratories. There is only one AMS lab in Africa in 2022, the iThemba laboratory in Pretoria.

Radiocarbon laboratories exist in more than 50 nations. They are in commercial businesses (e.g., Beta Analytic, DirectAMS), in government research facilities, and in universities. In mid-2022 prices for a single date, including delta-^{13}C measurement, ranged from \$330 to \$650. Laboratories may offer a discount for a block of ten or more dates. Commercial laboratories tend to deliver dates faster than government or university laboratories, but they are more expensive.

Adjustments to raw radiocarbon dates

In the late 1960s labs in the USA began noticing that radiocarbon dates on maize kernels and cobs were systematically younger than those on wood charcoal from the same archaeological contexts.

The explanation for this is that maize (and other tropical grasses, including sorghum and millets) use a different photosynthetic chemistry to turn atmospheric CO_2 into sugars than trees do. These are known as C3 and C4 photosynthesis. These both change the atmospheric ratios of ^{12}C, ^{13}C and ^{14}C when they produce sugars and wood, but do so differently. Radiocarbon dating was developed for wood (always C3) so radiocarbon ages on wood need little correction, but dates on C4 plants (grasses and grains from arid regions) must be corrected to yield accurate radiocarbon ages. Dates on human and animal bone will also need correcting because digestion and tissue building also change isotopic ratios.

The correction is made by measuring the ratio of the two abundant isotopes ^{12}C and ^{13}C and calculating delta ^{13}C, as defined in the next slide. The difference from the average for C3 plants is then doubled to correct the ^{14}C content. Delta ^{13}C should be measured on every radiocarbon sample.

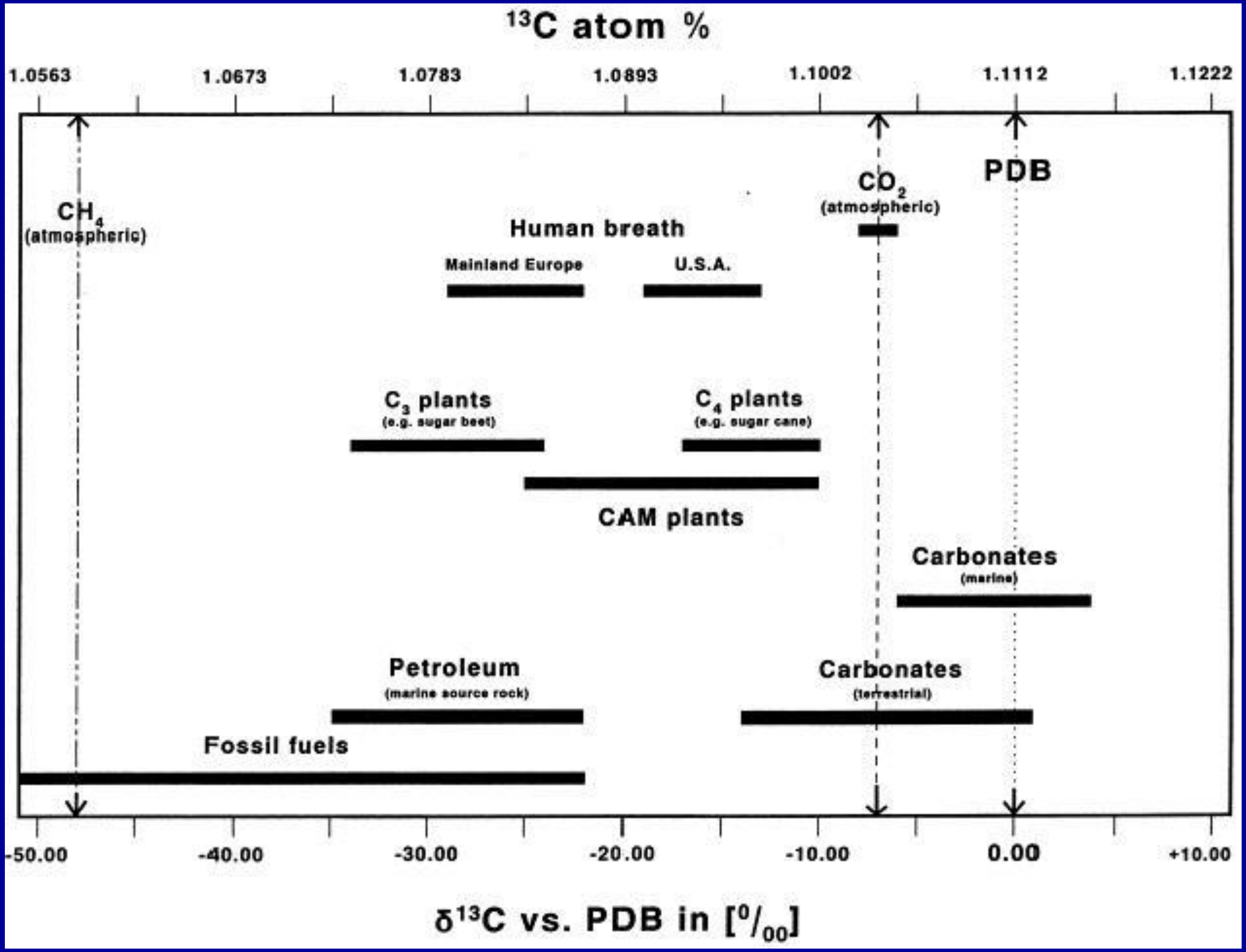
What are the C3 and C4 photosynthetic pathways?

The C3 (Calvin-Benson) photosynthetic pathway makes a 3-carbon compound as an intermediate step on the way to formation of a 12-carbon sugar (sucrose). All trees and almost all shrubs are C3, as are all plants growing in water. Grasses in cooler regions, in tropical rainforests, and at high altitudes are C3. C3 domesticates include wheat, barley, rye, buckwheat, rice, all root crops (potato, manioc, yam, taro), all tree crops (nuts, fruits), bananas and almost all green leafy vegetables.

The C4 (Hatch-Slack) photosynthetic pathway is more efficient in use of water than C3. It evolved during the Miocene, and was favored by natural selection in grasses in hot, arid regions. C4 plants include all African savanna grasses, maize, sorghum, African millets (*Pennisetum*, *Eleusine*), Asian millet (*Setaria*) and sugarcane.

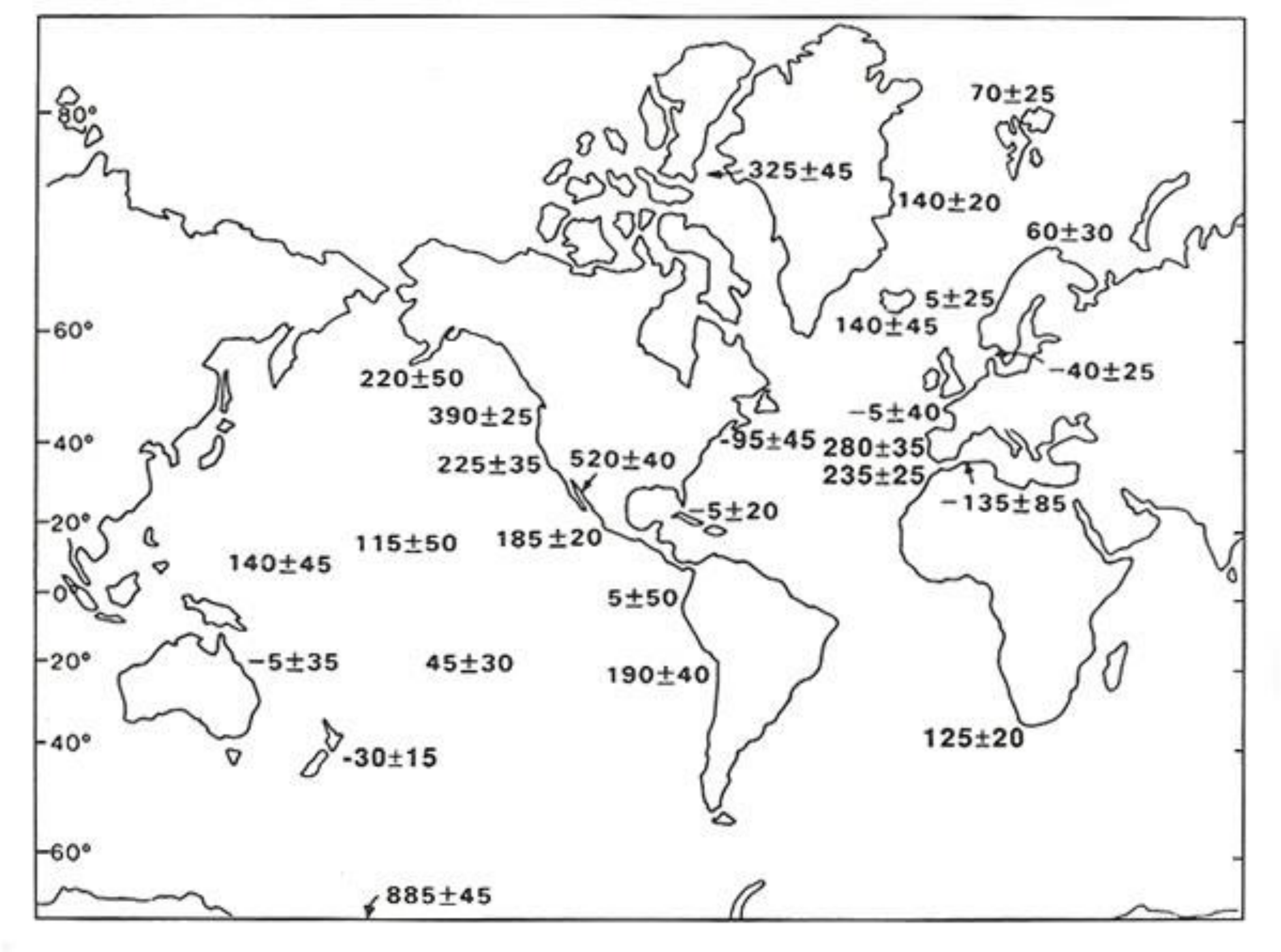
The CAM (Crassulacean Acid Metabolism) photosynthetic pathway (see next slide) is used only by succulent plants like cactus. If you have to date samples of succulents, be sure to tell the radiocarbon lab.

$$\delta^{13}C = \frac{(^{13}C/^{12}C)sample - (^{13}C/^{12}C)PDB}{(^{13}C/^{12}C)PDB} \times 1000$$



The lower scale is the relevant one for us. PDB is the standard (a marine limestone) used in all laboratories that measure delta^{13}C.

The marine reservoir correction, due to slow transport of CO_2 from mid-ocean by deep ocean currents. Living marine organisms in the labelled locations below will have these apparent radiocarbon ages! These ages should be subtracted from the BP age before calibrating. Marine correction factors around African coasts are poorly known, so date terrestrial samples instead if possible.



Dating freshwater organisms

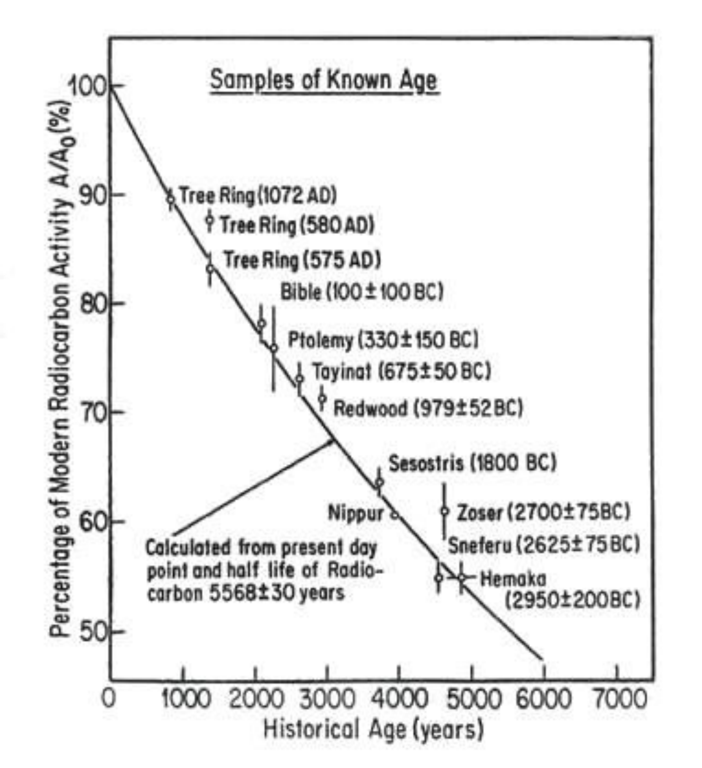
Plants that grow under water, and fish that eat these plants, can take up old carbon released from limestone rock. All of the radiocarbon in limestone has decayed away, so old CO_2 released from limestone mixes with CO_2 from the atmosphere in surface waters. This can make radiocarbon dates on some freshwater organisms appear too old. If a correction factor has been established for the lake from which your archaeological samples came, then you can subtract it from the BP age before calibration.

If the correction factor for the lake of interest is unknown, then it is best to avoid dating organisms that derive from the lake, and to date only terrestrial samples.

Calibration of radiocarbon dates using dendrochronology

Libby's curve of knowns (1952)

J. Willard Libby used dendro-dated tree ring samples provided by the University of Arizona, and wood from historically dated Egyptian and Mesopotamian sites to test the utility of radiocarbon as a dating method



Because his measurements were of low precision (typical σ was 150 - 350 radiocarbon years) systematic differences between radiocarbon and calendar years were not noticed. By the late 1960s greatly improved precision (σ 50-100 ^{14}C years) showed that for samples >2000 bp radiocarbon ages were too young when compared to known ages

Bristlecone pine (Pinus longaeva) and radiocarbon calibration

We now know that the amount of radiocarbon formed each year in the atmosphere is not constant. The oldest living trees are bristlecone pines in the White Mountains of California, which provide a continuous dendrochronological sequence for about 4500 years. By cross-dating fallen trunks to living trees, and working back, the tree-ring calibration now goes back to about 11700 bp. The rings are very narrow, so 10 rings at a time were used for radiocarbon measurements. The straight line below would apply if radiocarbon dates on tree rings were exactly equivalent to dendro ages; the jagged line shows that actual radiocarbon ages before 2000 BP are too young. This line is used to convert BP to calendar age.

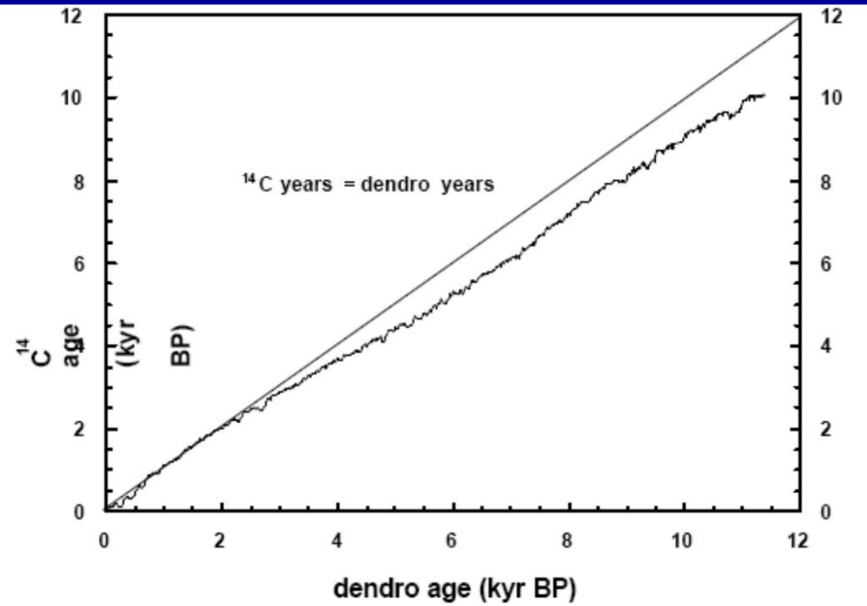
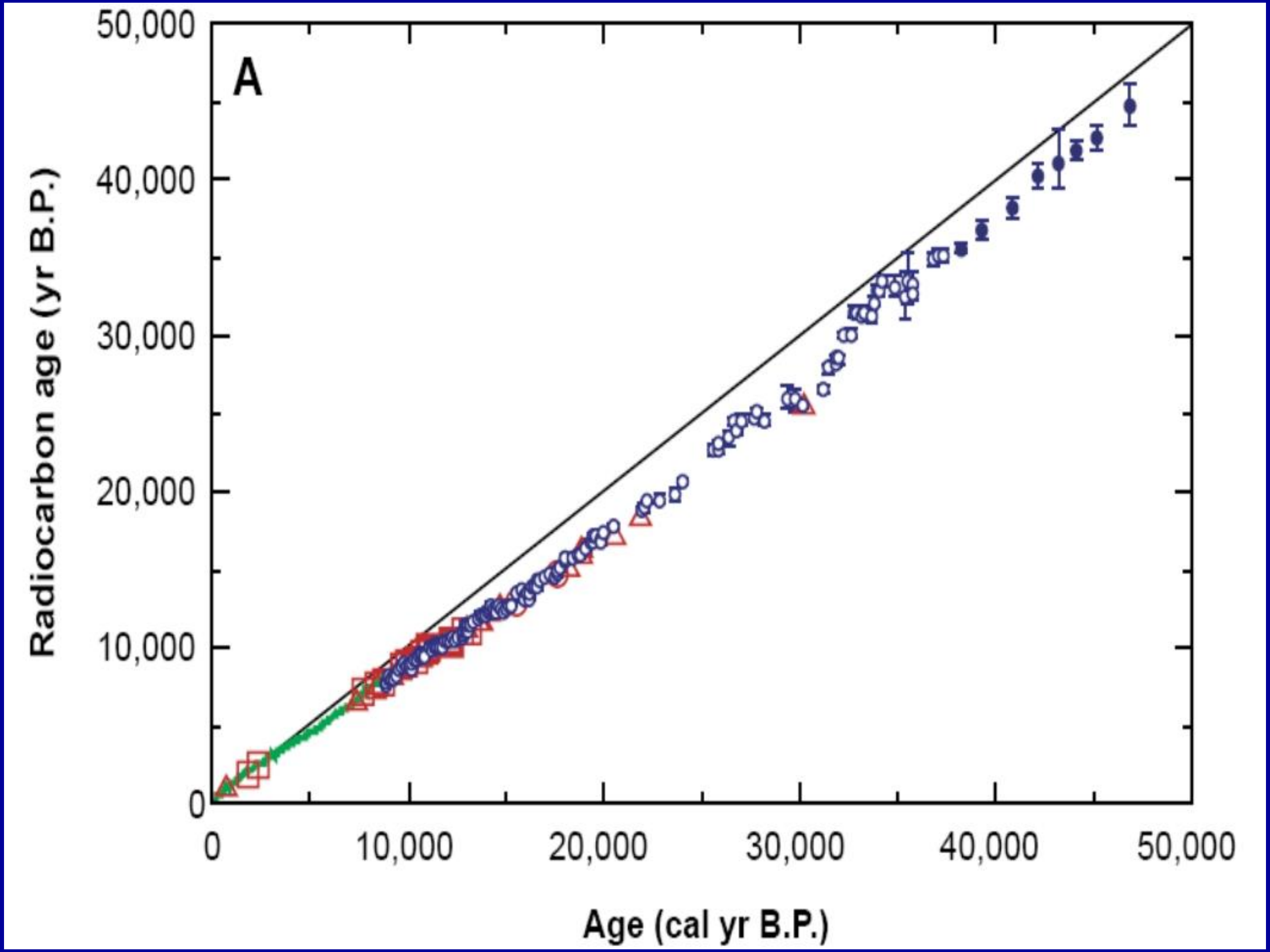


Figure 2. *Radiocarbon calibration curve obtained by dating tree rings (Stuiver and Kra 1986, Kromer and Becker 1993).*

Working independently, European researchers have exactly reproduced this record using oaks. The oldest living oaks are about 350 years; these were cross-dated with archaeological wood, and then with wood preserved by submersion in bogs.

Measurements made on tree rings in the southern hemisphere are slightly different and are compiled in a separate calibration file (SHCAL)

Extending calibration beyond the tree-ring record



Green symbols are tree rings; red symbols are dates on varves; blue are paired uranium series and radiocarbon on corals and speleothems (cave formations)

How to calibrate BP radiocarbon ages

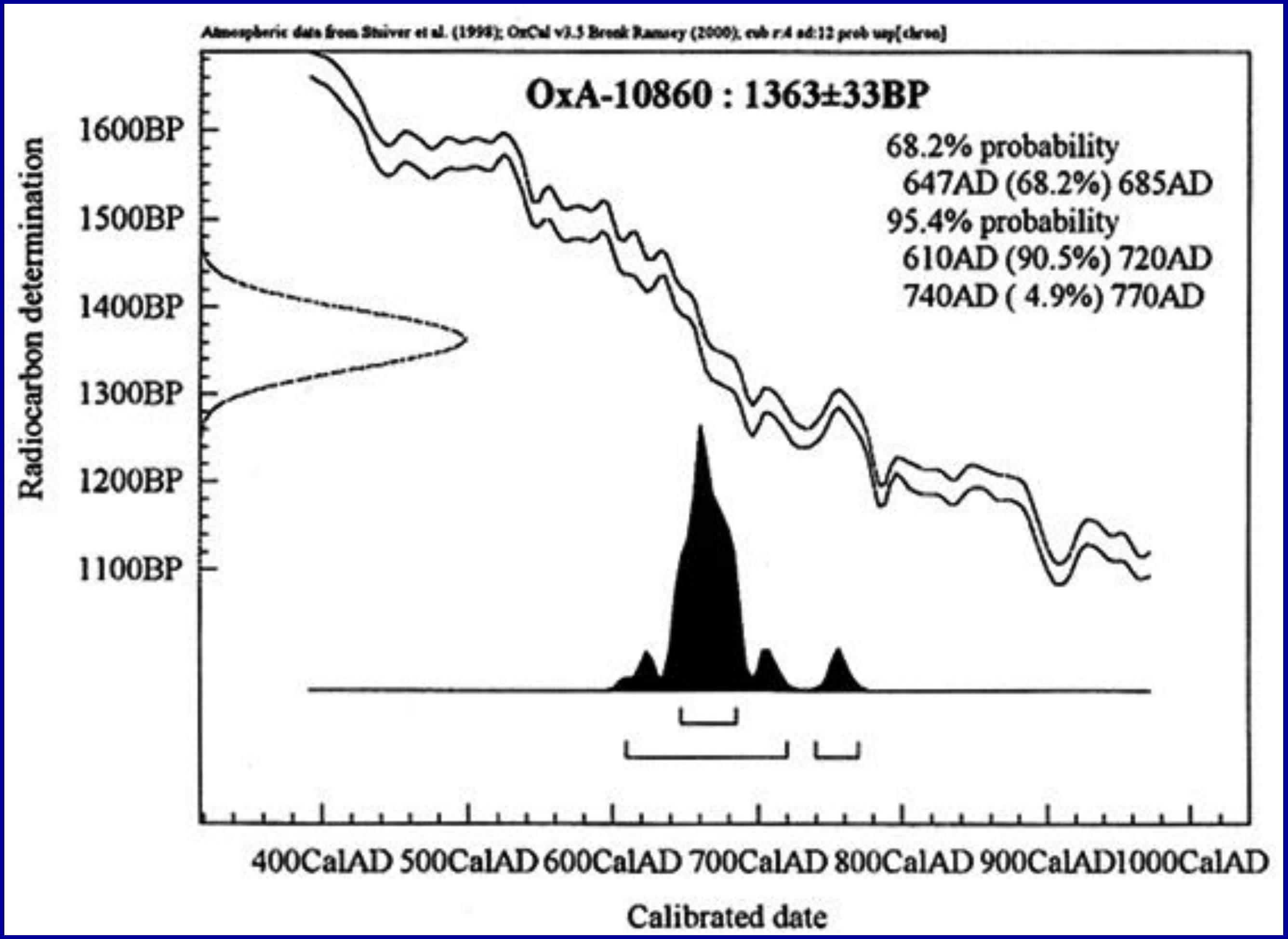
Most radiocarbon laboratories will calibrate dates for you in their report, but you should learn how to calibrate them yourself. The two leading computer programs for this can both be used online, or downloaded to your computer, for free. Both use the same databases of radiocarbon dates on tree rings to calibrate your dates. (Current versions: INTCAL 20 for northern hemisphere, SHCAL 20 for southern hemisphere). Both programs should therefore provide the same ranges of calendar years.

1. OXCAL (https://c14.arch.ox.ac.uk/oxcal.html). This is a powerful package with excellent graphics, but is not at all intuitive, and the online manual is poor.

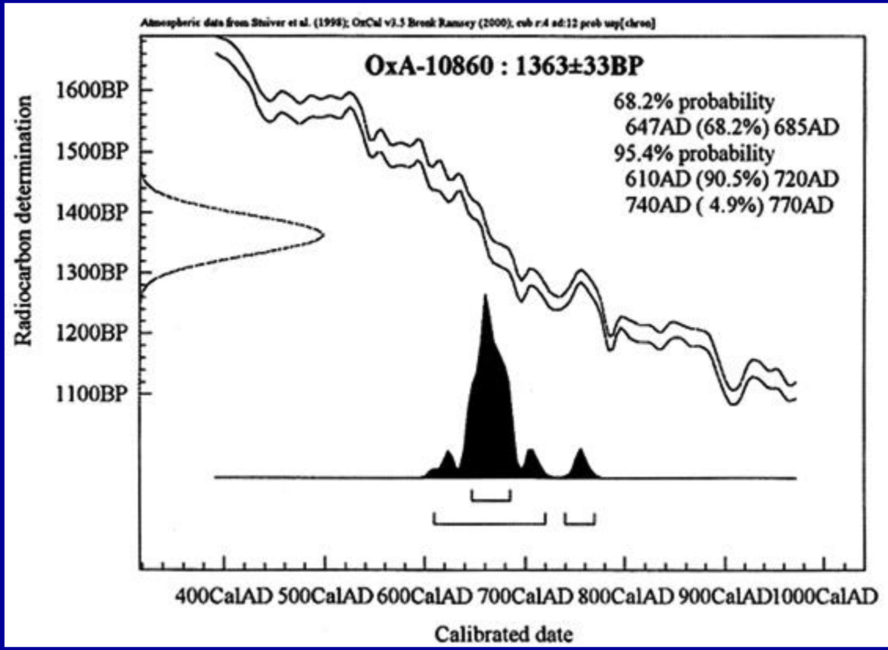
2. CALIB (http://calib.org/calib/). This has less impressive graphics but is easier to learn.

You should use one of these programs to recalibrate older dates from the literature. The tree-ring files (INTCAL/SHCAL) are updated every 5-10 years. Do not use uncalibrated (BP) ages for archaeological interpretation. In publishing, always give the BP age, the calibrated age range at 2 standard deviations (as cal BCE or cal CE) and the version of INTCAL/SHCAL used.

OXCAL calibration program – calibration of a single radiocarbon date



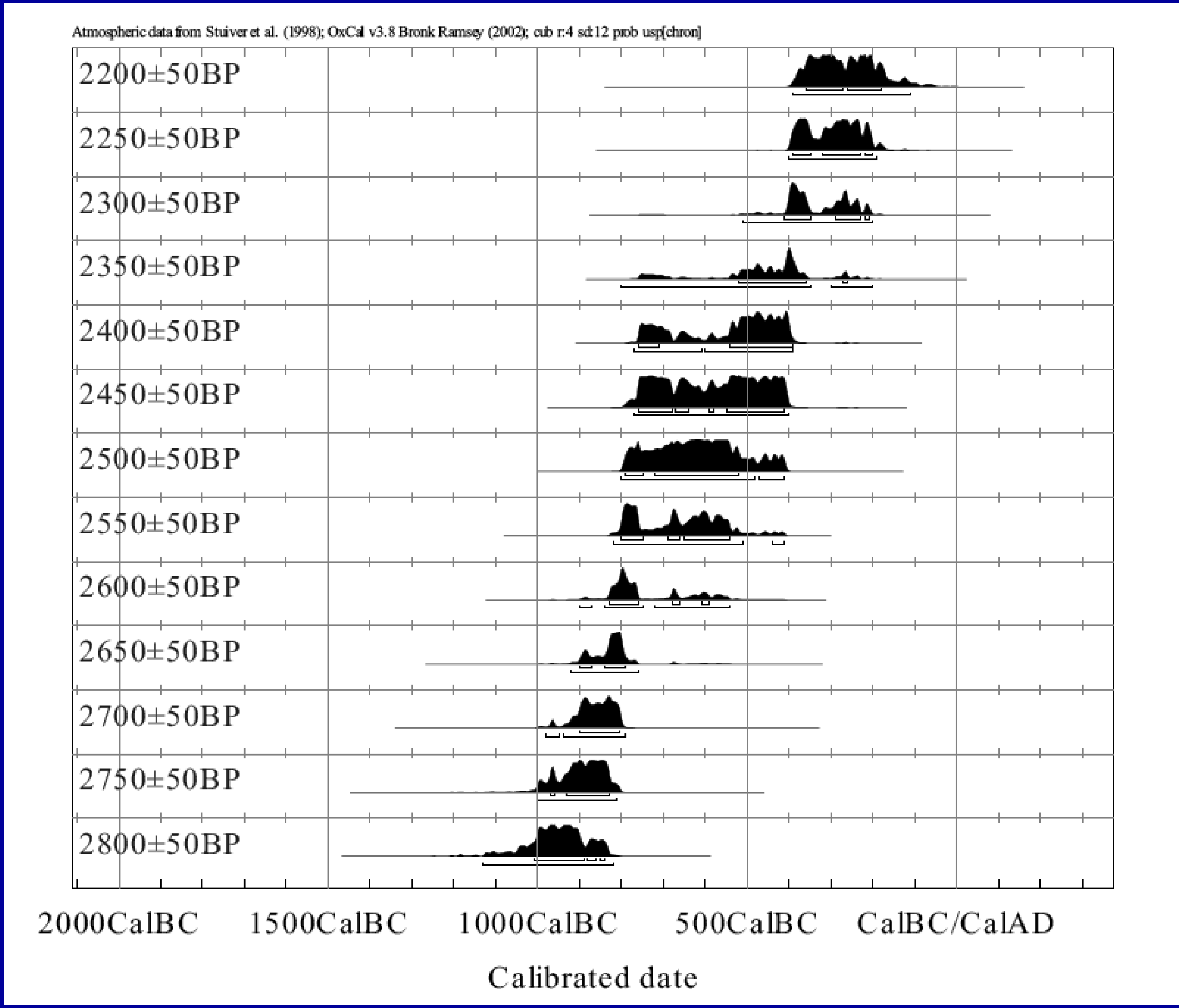
The double lines define the calibration curve (^{14}C dates on tree rings at 1σ). The solid black figure is the full probability distribution (calculated in ten-year vertical slices) for this BP age and precision. The taller the slice, the higher is the probability for that decade. The total 68.2% (1σ) and 95.4% (2σ) probability ranges of calendar ages correspond to the brackets under the black figure.



It is important to remember that the true age of the sample (a single year if it is an annual plant) can in theory be anywhere within the calibrated range, so always cite the calculated range (preferably at 2$\boldsymbol{\sigma}$) – NOT the age of the peak in the distribution. In this example the correct conclusion is that there is a 90.5% chance that the true age of the sample is between 610 and 720 AD/CE.

Some users mistakenly think that the calibrated age range is the span of occupation of the site. The span of occupation can only be estimated from multiple dates from different contexts.

OXCAL multiplot showing the problem with ^{14}C dates from 2350 -2550 BP



In calibrated (calendar) years this is from about 400 BCE to about 800 BCE. Dates in the range calibrate to ranges of 280-400 years – quite useless for archaeology

The problem of radiocarbon plateaus

The previous slide shows a severe radiocarbon plateau worldwide between about 800 cal BCE and 400 cal BCE. There is another one from 0 to 300 BP (ca. 1650 cal CE to 1950 cal CE). Radiocarbon is essentially useless in these age ranges. There is also a major plateau around 10,000 BP.

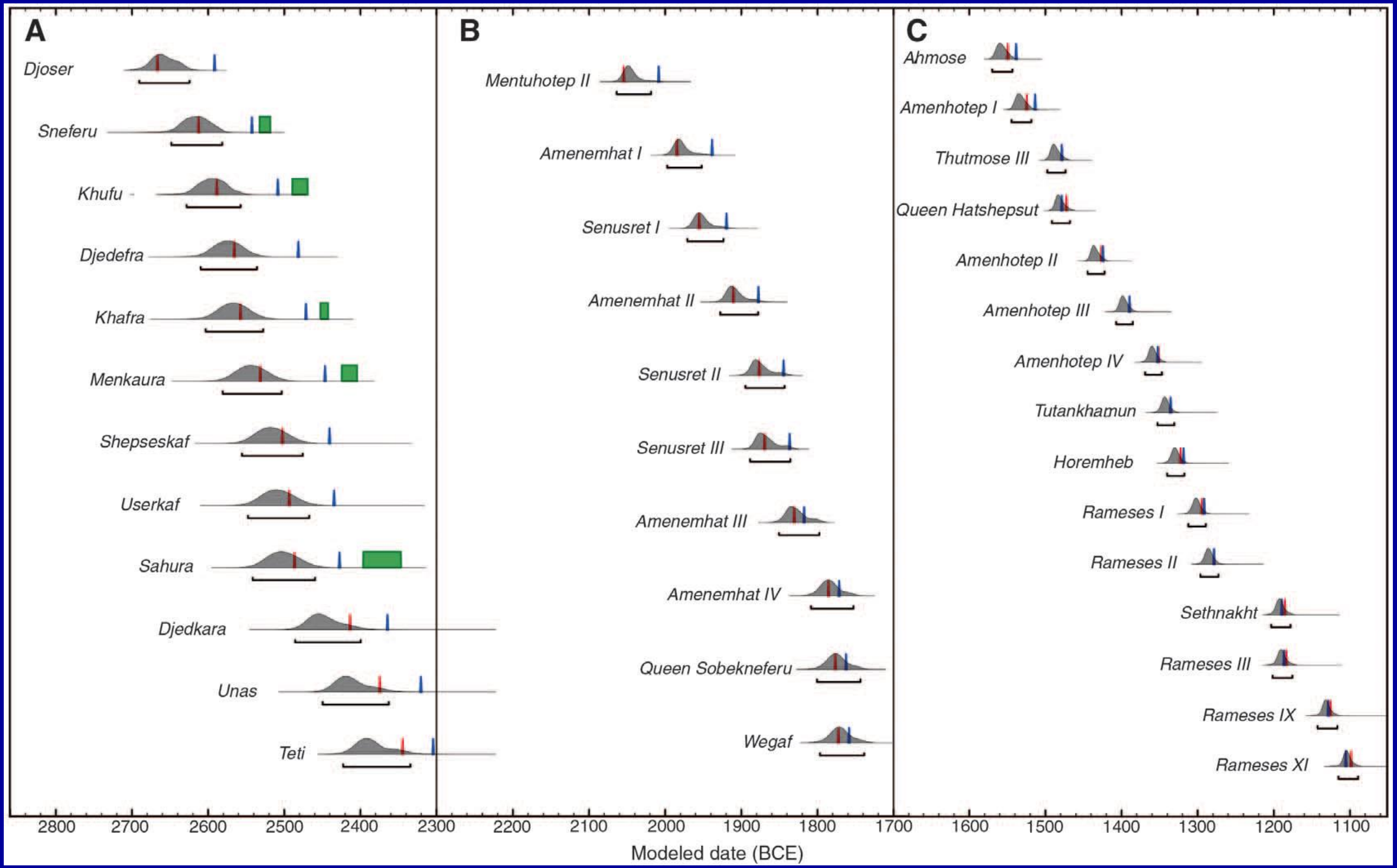
We recommend using OXCAL or CALIB to explore the shape of the calibration curve in the time range of interest to you, using hypothetical ages (as in the previous slide), and varying the precision of the date between ± 20 (the minimum using AMS) and ± 75 radiocarbon years. Note that the calibrated range is rarely less than 100 calendar years at 95.4% probability.

Alternative methods: If the likely range of age of your site is within a radiocarbon plateau, then Optically Stimulated Luminescence (OSL) dating of fired clay or fired stone may be a suitable alternative. OSL dates are considerably more expensive than radiocarbon dates (at minimum US $1000 per date), and field sampling should be done by an expert in the technique. This requires advance planning before excavation.

Bayesian radiocarbon calibration

Bayesian statistics can be used to reduce the calibrated ranges of radiocarbon dates using independent chronological information organized in a sequence. This could be historical, coins with dates on them, stratigraphic layers in a site, or a sequence of associated types of pottery, but all radiocarbon samples need to be reliably associated with these. The independent information is organized in a formal model, with Phases and Boundaries. The radiocarbon dates are then placed within Phases and Monte Carlo simulation is run on them. The Prior calibrated ranges are transformed into Posterior calibrated ranges. The more Phases, the narrower the Posterior ranges.

The next slide illustrates this with radiocarbon dates and (sometimes disputed) historical dates for rulers of the Egyptian Old Kingdom (A), Middle Kingdom (B) and New Kingdom (C). (Fig. 1 in C. Bronk Ramsey et al. (2010) Radiocarbon-based chronology for Dynastic Egypt *Science* 328:1554-1557.) The Bayesian model simply used the relative order of the Pharaohs. The grey humps are the Posterior calibrated ranges of 188 radiocarbon dates on annual plants associated with individual reigns of Pharaohs. The red, blue and green vertical bars are estimates by three different scholars of the historical dates for the reigns of pharaohs. The new ranges are mostly in good agreement with the red bars, except for the reigns of Unas and Teti (Old Kingdom).



Comparison of Bayesian calibrated radiocarbon dates with three estimates from historical records of the reign of Pharaohs of the Old (A), Middle (B) and New (C) Kingdoms

Are old radiocarbon dates usable?

The first international check on the accuracy of radiocarbon laboratories was published in 1982 and has been repeated at 10-years intervals. The first (1982) and second (1992) revealed an alarming lack of consistency in the analysis of samples of known age between laboratories, particularly in those doing decay counting by liquid scintillation. Results from tests since 2000 show much better agreement between laboratories. The agreement between AMS laboratories is very good.

Even if older dates were accurate, their precision (± 75 to 150 years) is often unacceptable for current archaeology when recalibrated. Dates run before 1975 often lack delta-^{13}C measurements and thus can't be adjusted. Many of the older labs have closed, and their sample records are often missing.

We suggest that radiocarbon dates run before 1980 – almost all of them on bulk wood charcoal - should not be used. Dates run between 1980 and 1995 can be used with caution. Dates obtained since 1995 should be reliable, but when constructing chronologies give priority to dates run on short-lived (annual) samples.

The “old wood” problem in radiocarbon dating

Each tree ring visible in a cross section contains carbon deposited in a single year. Some trees can live for more than a thousand years (e.g., California redwoods and bristlecone pines, New Zealand kauri). The life spans of most African trees are not well established, but in large trees likely exceed 300 years.

Once converted to charcoal, wood is potentially stable for many thousands of years. This creates three problems for the archaeologist:

1. We usually can’t tell whether a given piece of wood charcoal came from the outer rings or the inner rings of the tree. A radiocarbon date on wood charcoal can potentially be hundreds of years older than the archaeological feature with which it was associated.
2. Wood charcoal from ancient forest fires is commonly found throughout soil and sediment profiles and is brought to the surface by digging pits. This is discussed in detail in a separate Powerpoint by Bernard Clist.
3. Ancient charcoal is still usable, after drying, for making fires.

It is therefore much better to use carbonized annual plants (leaf, grass, nuts, fiber, etc.) for radiocarbon dating if these are available.