Radiocarbon dating

All carbon atoms have 6 protons in the nucleus,
but the nucleus may also contain 6, 7, or 8 neutrons.

carbon-12

Carbon with 6 protons and 6 neutrons is called carbon-12 (^{12}C).
This is a stable nucleus.   99% of all natural carbon is ^{12}C .
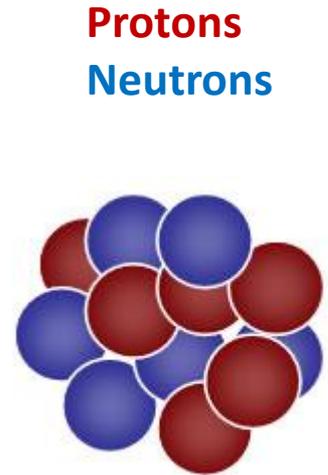
carbon-13

Carbon with 6 protons and 7 neutrons is called carbon-13 (^{13}C).
This is also a stable nucleus.   1% of all natural carbon is ^{13}C .
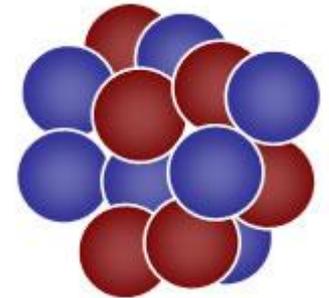
carbon-14

Carbon with 6 protons and 8 neutrons is called carbon-14 (^{14}C).
This is an unstable radioactive isotope. About 1 in 10^{12} carbon atoms
in the atmosphere is ^{14}C.
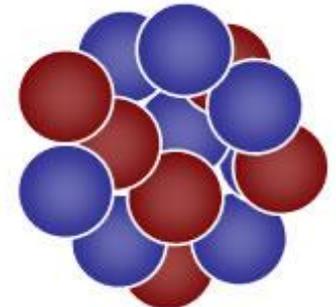
Radioactive carbon (^{14}C) is generated in the upper troposphere when a cosmic ray (typically a proton) hits the nucleus of an atom and produces a neutron (among other things) that is then captured by a nitrogen atom (^{14}N)

$$^{14}_{7}N + {}^{1}_{0}n \Rightarrow {}^{14}_{6}C + {}^{1}_{1}H^{+}$$

cosmic ray proton

^{14}N

p

Radioactive carbon-14 is present in all living organisms. ^{14}C

Carbon dioxide takes it into the food cycle. $^{14}CO_2$

O_2
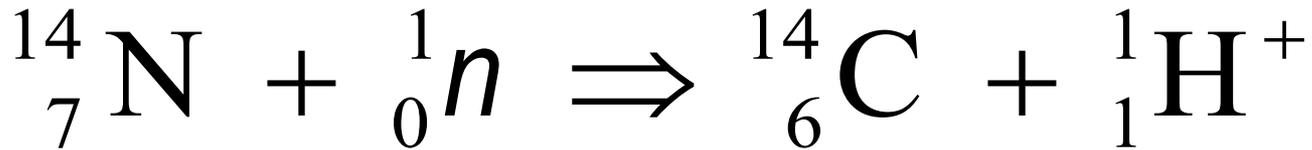
In the process the ^{14}N becomes ^{14}C, and a H$^+$ ion (a proton) is released.
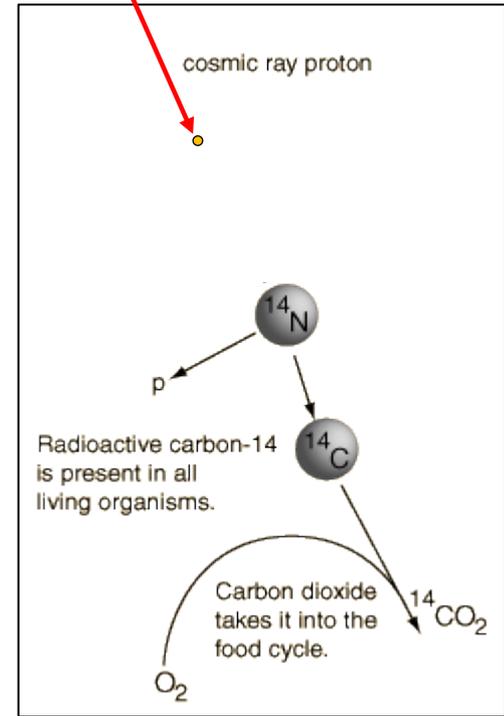
by convention:
upper numbers indicate the number of protons + neutrons in the atom or particle
        (proton = +1, neutron = +1); these numbers must balance (15 each side)

lower numbers indicate the electric charge of the atom or particle
        (proton = +1, neutron =0); ; these numbers must balance (7 each side)

Generation of radioactive ^{14}C occurs primarily in the upper troposphere, but C (mostly as CO_2) mixes thoroughly in the atmosphere, and is incorporated into living organisms.

The proportion of ^{14}C to ^{12}C in living tissue is comparable with the proportion in the atmosphere (for terrestrial organisms), or to a water body for aquatic organisms.

Animals get their ^{14}C dose from the food that they consume.

When the organism (or a tissue) dies absorption of ^{14}C ceases, and the amount of ^{14}C gradually decays.

Radioactive carbon (^{14}C) decays back to nitrogen (^{14}N) emitting an electron (e^-) and an antineutrino ($\bar{\nu}$) with no mass or charge.

$$^{14}_{6}\text{C} \Rightarrow \ ^{14}_{7}\text{N} + \ ^{0}_{-1}e^- + \ ^{0}_{0}\bar{\nu}$$
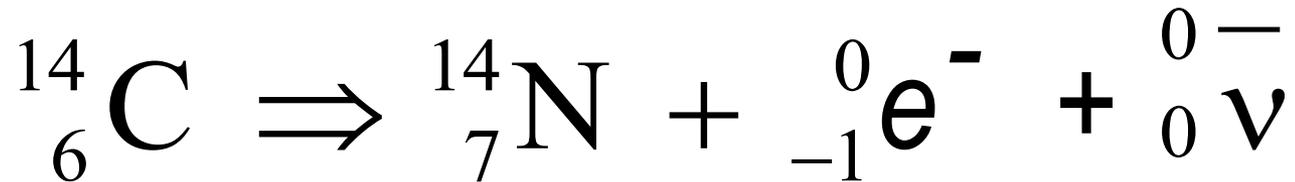
This radioactivity in living tissue is very weak; about 2.5% of that due to the decay of naturally occurring potassium-40 (^{40}K).

No, you can't tell if somebody is alive or not using a Geiger counter; flesh is practically opaque to the radiation. The path length in air is about 22 cm.

After about ten ^{14}C to ^{14}N half-lives (~57 ka) there is almost no more ^{14}C left in the tissue.

By measuring ^{14}C content, you can estimate how long ago the tissue died (providing that it isn't so old that the ^{14}C level is too low to measure accurately)

The half-life of the decay of ^{14}C to nitrogen is 5730 years so the concentration halves every 5730 years.

A practical limit for accurate dating is 26,000 years (in other words material that is younger than the Last Glacial Maximum), but you can get less accurate dates up to 43,500 years and, some facilities provide rough dates to ~60,000 years.
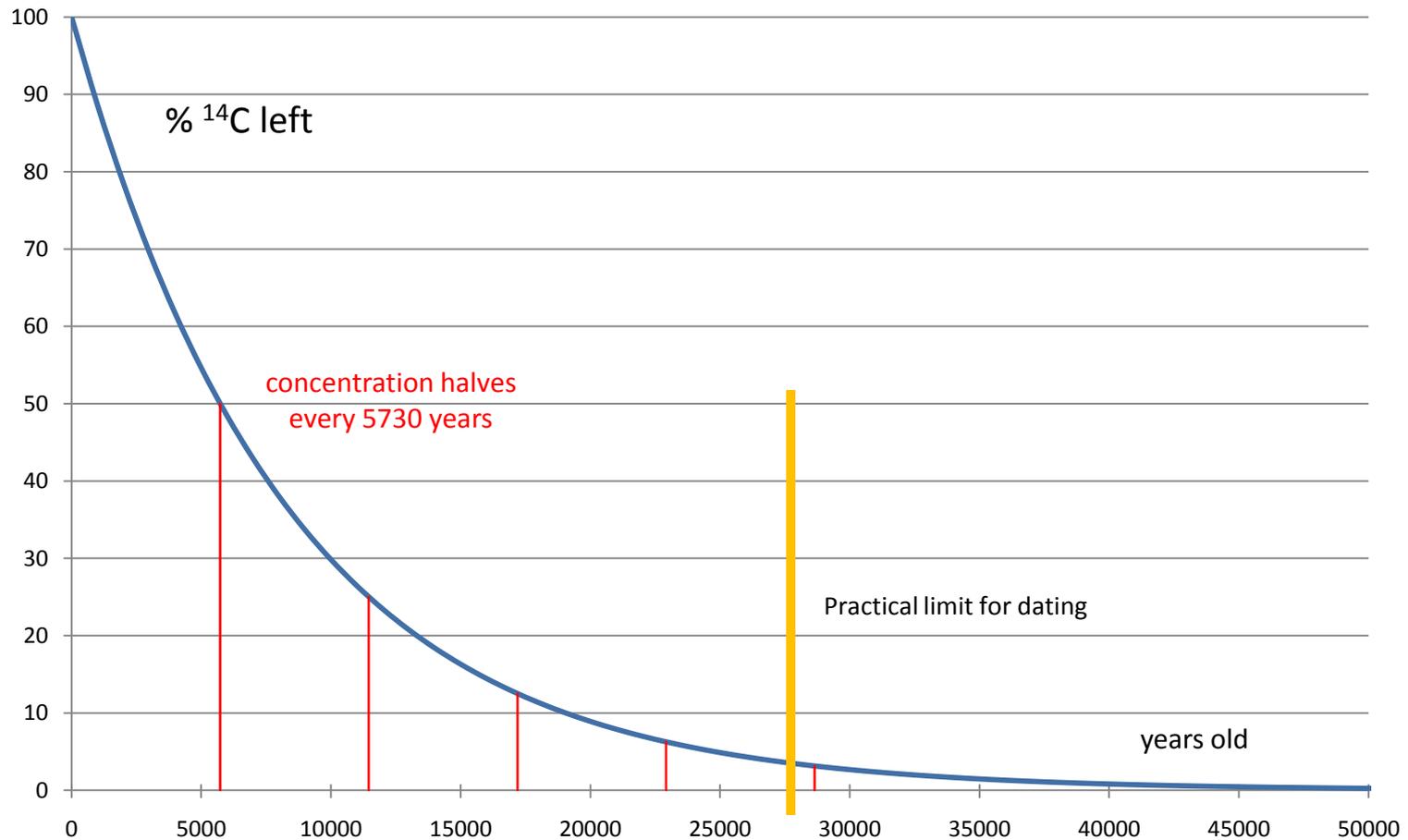
Measuring ^{14}C concentrations

Two basic methods:

Radiometric: you count the decay rate of individual atoms in a sample using a gas proportional counter (a form of Geiger counter) or a liquid scintillation counter;

AMS: you do a complete isotopic analysis in an accelerator mass spectrometer (AMS).

Radiometric dating is relatively cheap (about $300/sample), takes about a month to achieve satisfactory statistics, requires about a 100 grams. It is a good method for averaging material composed of material of various ages (lake sediments etc.).

AMS dating is relatively expensive (about $600/sample or more depending on prep. time needed), takes about a week, requires only about a gram. It is a good method for dating specific samples, a pine needle for example, when the sample may contain younger extraneous material.

Accelerator mass spectrometers are expensive, millions of dollars, and only a few facilities are equipped with them, but these have managed to keep prices low by having high throughput. Nowadays, very few universities or companies do their own dating.
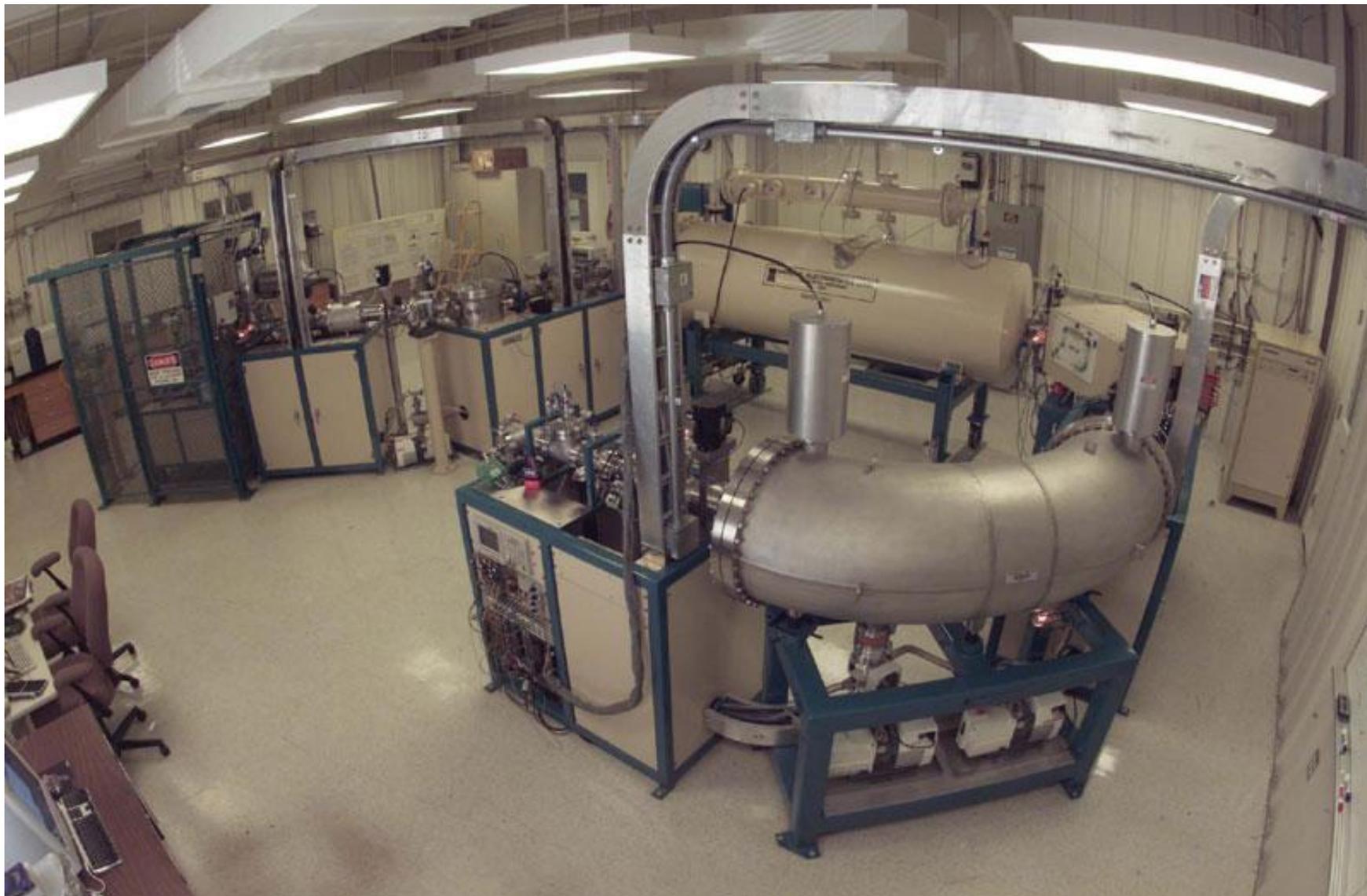
Accelerator mass spectrometer at Lawrence Livermore National Laboratory, California

Low-energy Mass Spectrometry

magnet

A2

F1

A1

magnet box

L3

electrostatic analyzer

L2

cesium gun

L1

C$^-$ ion source

sample holder

Tandem Accelerator

insulating gas

voltmeter

acceleration tube

10^6-volt electrode

stripping canal

L4

High-energy Mass Spectrometry

A3

electrostatic analyzer

F2

magnet

C-12

C-13

ion currents

A4

electrostatic analyzer

C-14 ion detector

Various calibration standard s are used for radioactivity measurements. A common one currently in use is <u>Oxalic Acid II</u>, which was derived from a crop of 1977 French beet molasses. Facilities date this to make sure they all get the same answer.

Sample preparation (which is a skilled and labour-intensive process) involves extracting the carbon as CO_2, purifying it, and then converting it to an organic compound such as benzene or toluene that's easy to handle.*

* Methods differ from lab to lab.

Materials that have been radiocarbon dated since the inception of the method include:

- charcoal, wood, twigs, seeds, peat, pollen, resins
- bones, shells, corals
- hair, leather, blood residues
- lake mud, soil, water
- pottery, wall paintings, fabrics, paper, and parchment.

All must have at least some carbon of organic origin.

Published articles on glaciation in the Strait of Georgia and Fraser Valley report using: twigs, wood fragments, stumps, lake sediments, shells, forams, and others.

Unfortunately, not everything is easy to date.

This woolly mammoth leg bone found on Gabriola does not contain enough collagen for ^{14}C analysis.

Bone is mostly *hydroxy-apatite* a form of calcium phosphate:
$Ca_{10}(PO_4)_6(OH)_2$
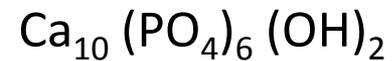
The bone probably dates back to the Port Moody Interstade *ca.* 18,000 BP , but that's a guess.

Carbon-13 isotope fractionation

Many biochemical processes alter the ratios of ^{12}C, ^{13}C, and ^{14}C. Photo-synthesis, for example, depletes the amount of ^{13}C compared to ^{12}C by -18‰. The carbon in seawater is the reverse. It is enhanced by +7‰.
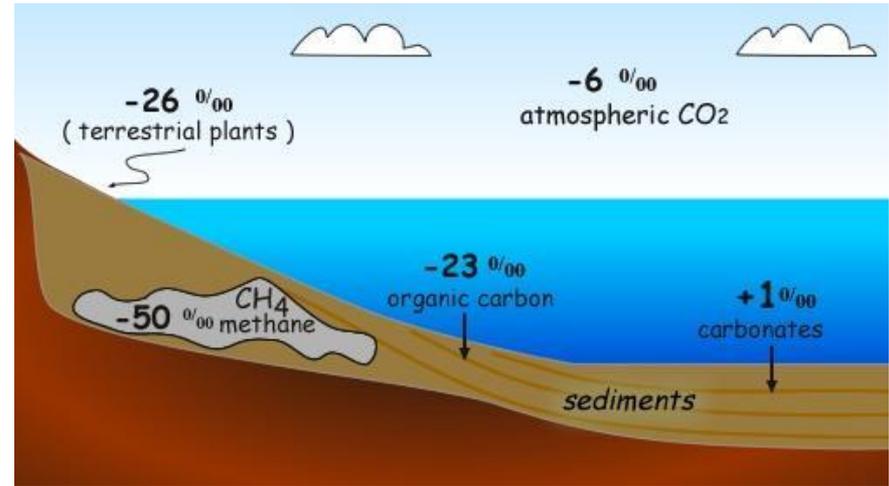
If a sample shows a lower ratio of ^{13}C to ^{12}C than exists in the atmosphere, it is reasonable to expect that the amount of ^{14}C to ^{12}C has also been reduced, making the sample appear older than it actually is.

It is standard practice to correct for deviations of ^{13}C to ^{12}C from the norm. These will be reported as a "delta 13 C" correction ($\delta^{13}C$). The $\delta^{14}C$ fractionation is commonly taken in calculations to be 3 times greater. The norm for $\delta^{13}C$ is -25‰.

It is sometimes important to note that measurements published in articles before *ca.* 1990 either did NOT make this adjustment, or used a different standard such as 0.0‰. These have to be re-evaluated before being compared with more recent measurements.

Radiocarbon years

Radiocarbon years are reckoned as "before present", present being defined as 1950 AD which was when the method was first developed.

It is important to understand that for various reasons radiocarbon years are <u>not the same as calendar years</u>.

If a geologist said in 2000 AD, the last ice age ended *ca*. 11000 "years ago" what he or she probably meant is 11000 ^{14}C BP (11000 radiocarbon years before 1950 AD). This happens to be 10964 BC (≈13000 calendar years before 2000 AD). <u>It is not 9,000 BC</u>.

Among geologists this difference scarcely matters so long as they are all on the same page, but it is obviously important to historians and archaeologists who have access to other dating methods.

Radiocarbon years – variations in ^{14}C generation rates

There are several reasons why <u>conventional radiocarbon years BP</u> correspond only approximately to calendar years BP. The most important is that the rate of generation of ^{14}C in the upper atmosphere has not been and is not constant, but varies slightly from year-to- year, primarily because of variations in cosmic ray intensities from the sun.

Because the information needed to convert radiocarbon ages to calendar ages is constantly being improved, it was decided to make it a standard that <u>radiocarbon ages and not calendar ages be the prime method of recording results</u>. This has the advantage that thousands of dates published in articles previous to any update do not have to be re-calculated. <u>It is primarily up to the user of the data to make the conversion using the best data available</u> and in whatever way seems appropriate.
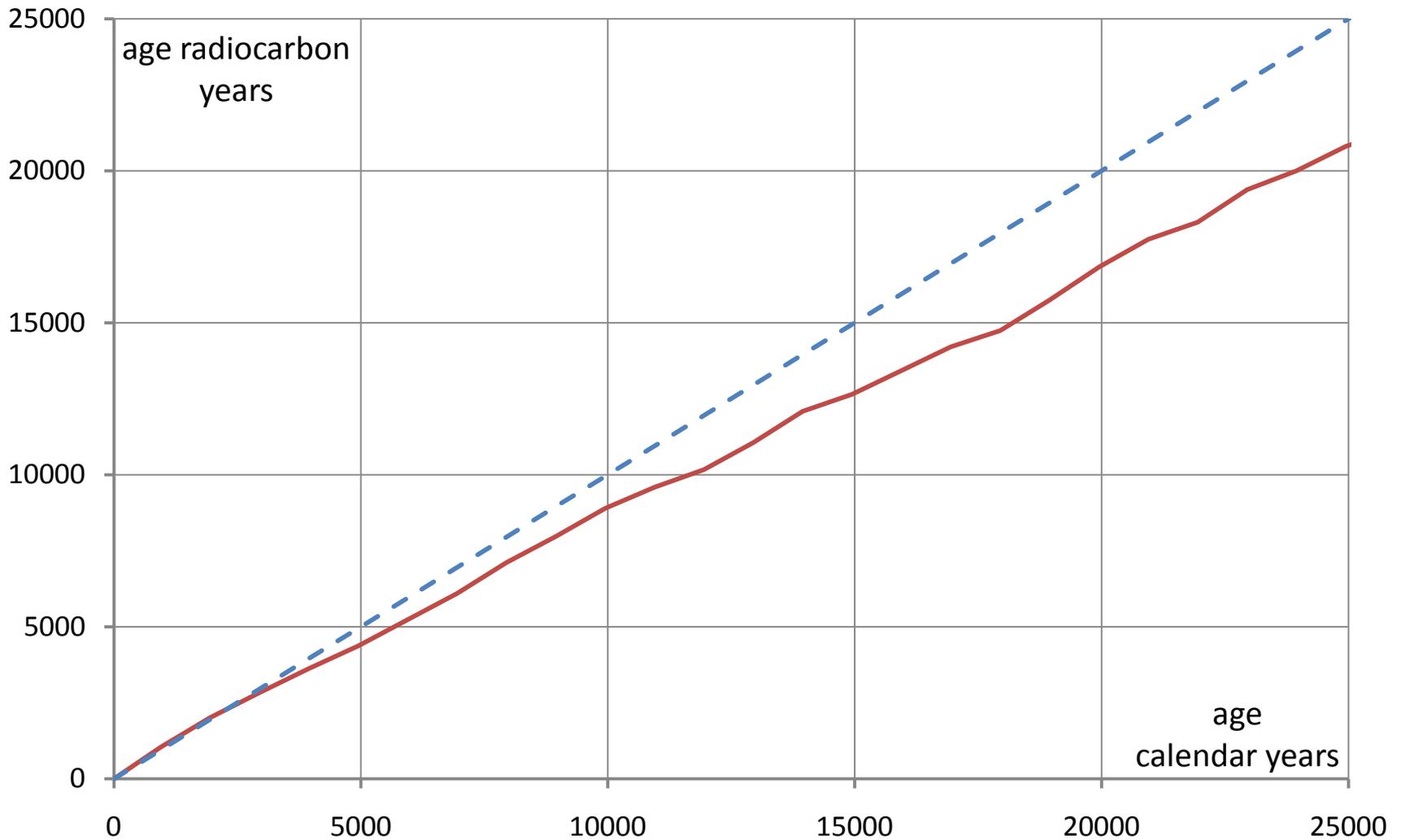
The general trend is for conventional radiocarbon ages to be about 22% less than calendar ages. Something that is measured to be say ten thousand years old, is actually about twelve thousand years old.

At a few locations on the calibration curve the results are ambiguous. One ^{14}C value could be equivalent to more than one calibrated age.
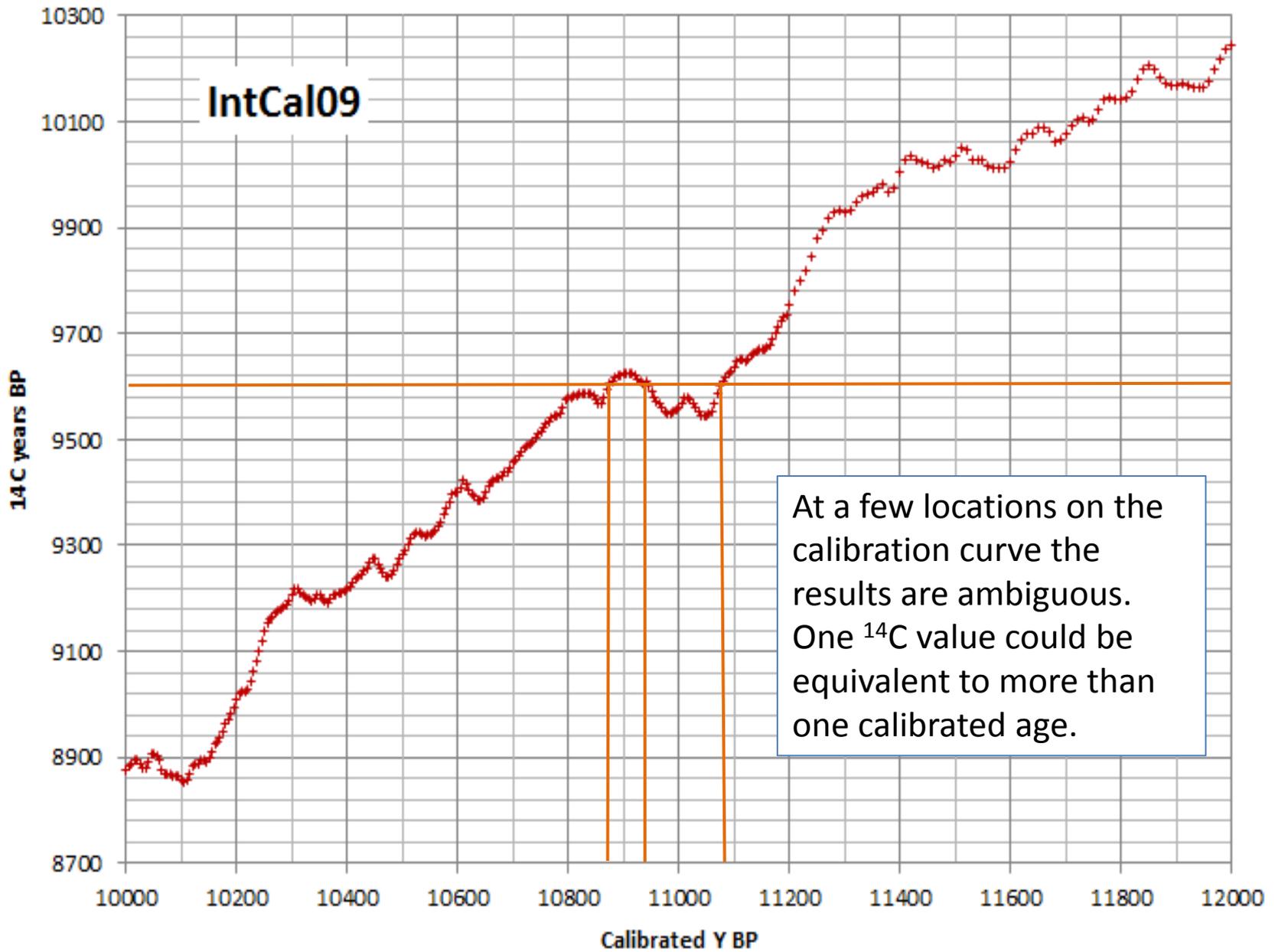
Radiocarbon years – the actual half-life of ^{14}C

Another reason for the <u>conventional radiocarbon years BP</u> (RC) age not being the same as the calendar age is that:

When Willard Libby and his team invented the method in 1949 they estimated that the half-life of ^{14}C was <u>5568</u> years. When it was later discovered that the half-life is closer to <u>5730</u> years, it was decided to continue to use the "Libby standard" so that the thousands of dates published in articles previously could still be compared to dates going forward.

The half-life correction is now made when the conventional radiocarbon ages are converted to calendar or calibrated ages.

"Present" in "before present" (BP) continues to be defined as 1950 AD for the same reason, but also because atomic bomb testing in the 1960s and 1970s artificially raised levels of ^{14}C in the atmosphere.

Radiocarbon nomenclature

The <u>conventional radiocarbon age</u> (^{14}C years BP) is a report that conforms to International Standards using:

- a half-life of 5568 years (the Libby standard);
- Oxalic Acid I or II as the modern radiocarbon standard;
- correction for sample isotopic fractionation (δ^{13}C) to -25 ‰ relative to the ratio of ^{13}C/^{12}C in the carbonate standard VPDB (Vienna Peedee Belemnite);
- 1950 AD as 0 BP;
- the assumption that ^{14}C reservoirs have remained constant through time.

Older data often has to be re-interpreted to conform to this standard.

Radiocarbon nomenclature

The <u>calibrated age</u> (cal. years BP) is the calendar year equivalent of the conventional radiocarbon age.

Because of the constant improvements to calibration data, there is no guarantee that one person's cal. BP will be the same as another's.

Some authors use 2000 AD as a base, some use 1950 AD.

The databases currently used for conversion of ^{14}C years BP ages to cal. years BP are IntCal09 and Marine09. These are maintained by an international committee and published in the journal RADIOCARBON. They are up-dated about once every 5 years.

Information needed for constructing the database comes from analysis of samples that can be independently dated (e.g., counting tree rings, and uranium-thorium analysis of corals and foraminifera).

Radiocarbon nomenclature

The corrected radiocarbon age is an intermediate figure, not usually included in final reports.

It usually means the measured radiocarbon age after correction for $\delta^{13}C$ fractionation.

Some authors use the term to mean the conventional radiocarbon age after correction for carbon storage in reservoirs. This applies only to marine or lacustrine samples.

Radiocarbon years – variations in reservoirs (global)

Lakes and oceans act as reservoirs of carbon.

The carbon content of a small lake may be only 20 years older than the carbon on the atmosphere, but in the ocean, the carbon may be many hundreds of years older. This will result in marine shells and foraminifera appearing to be older than they actually are.

The average age of carbon in the surface water of the world's oceans is about 400 radiocarbon years, and this is quite constant in places like the eastern Atlantic Ocean.

Prior to 2004, it used to be standard practice to subtract 400 years from the conventional radiocarbon age of marine samples. This is called R(t), the pre-industrial "<u>global reservoir correction</u>".

Radiocarbon years – variations in reservoirs (local)

Since 2004, marine samples have been calibrated using a separate database from that used for terrestrial samples. This database includes the global reservoir correction, which does vary slightly from year-to-year from the previous standard of 400 radiocarbon years.

You do not need to subtract the global reservoir age R(t) from the conventional radiocarbon age before using Marine04 or Marine09 to calibrate it.

HOWEVER, we in the northwest Pacific area and a few other places in the world have a problem with this. Because the surface ocean water off our coast contains both surface water and deep water brought to the surface in upwellings, the carbon in our water is much older than the global norm.

We do have to make an additional "local reservoir correction" ΔR to the radiocarbon age even if we use Marine04 or Marine09 to calibrate it. Archaeologists and geologists in the Salish Sea area commonly subtract ΔR = 390 radiocarbon years from the radiocarbon age of shell samples (it varies slightly from location to location).

Radiocarbon years – more variations in reservoirs (local)

While having a "local reservoir correction" that is approximately constant
at 390 radiocarbon years is convenient for archaeologists, geologists,
and others, working on events in the Holocene, there is a further problem.

Research has shown that this "constant" was far from constant during the
late-Pleistocene/early-Holocene transition. This is undoubtedly because
because the age of the carbon in the ocean here on the west coast depends on deep-
water circulation patterns in the Pacific, and these were different during the ice age.

Comparisons between the radiocarbon ages of wood and shell found at the same
location in ice-age deposits have shown differences in excess of 1000 years. One
paper records a total reservoir correction (R(t) + ΔR) that for younger samples would
be 790 radiocarbon years, as 1250 years at the time of de-glaciation.

This requires further research. Apart from improving the accuracy of
the dates for late-Pleistocene/early-Holocene samples, it might provide interesting
data on changes in ocean circulation in the north Pacific at that time.

Dating hazards: roots of horsetails extending down several metres in glaciofluvial sand on Gabriola. BTW you should not touch samples destined to be dated with bare hands. Plastic zip-lock bags are OK.

Dating hazards: the log recovered from 2-metres down in a glaciomarine deposit was dated to 11590 C^{14} BP; but shells, lying on the surface of the same deposit dated to 11632 C^{14} BP using R(t) + ΔR = 1250 years. Are the shells are older than the log? The reservoir correction is too low, or perhaps the copious meltwater added "old" carbon to the ocean locally.

Radiocarbon dating is an extremely useful technique for determining the ages of geological materials (<u>that have some organic-derived carbon in them</u>), and it is highly applicable to the study of Quaternary materials (that are younger than 50 ka).

But, interpretation of radiocarbon data can be quite complex, and several factors need to be taken into account to understand what the results actually mean.

An application of radiocarbon dating on the west coast of Vancouver Island

125° 56' W   125° 52' W

N

Metres

1000   0   2000

49° 15' N

CYPRESS BAY

MEARES
ISLAND

Lemmens Inlet

49° 12' N

M E A

Kakawis Lake

I S L

Legend to symbols

open water area

aquatic vegetation cover

clear-cut / low vegetation zone

supra-tidal / accreted land zone

inter-tidal zone lower limit

shallow waters contour

7   core number
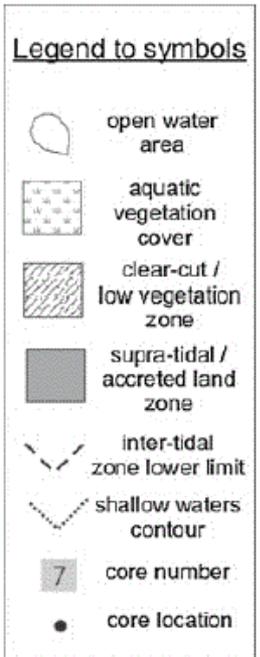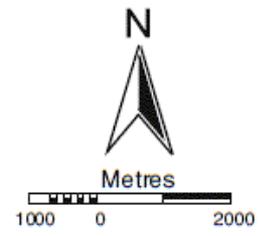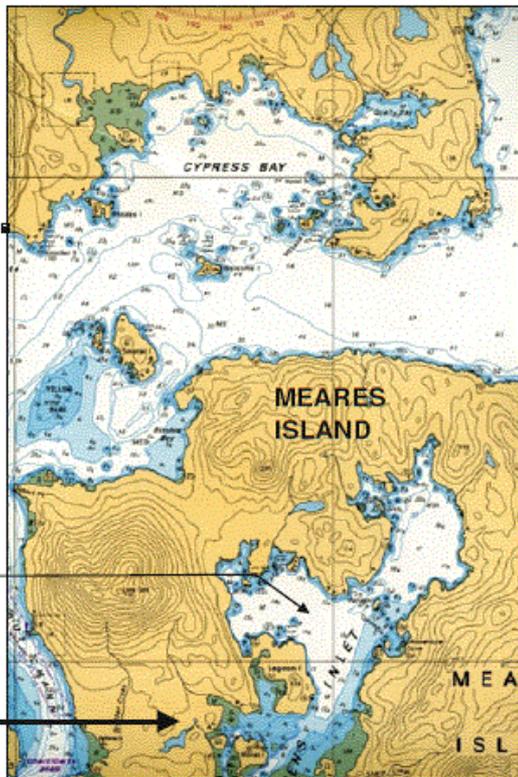
•   core location

Kakawis Lake
Southwest & Northeast basins

125° 54.2' N   125° 53.5' N

49° 11.6' N

Meares Island - W Peninsula

outlet stream

Lemmens Inlet

Island

0   100   200 m

49° 11.4' N

0   100 m

7
3
6
1
5
2
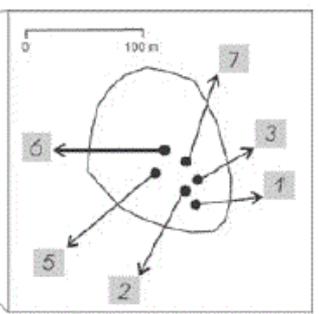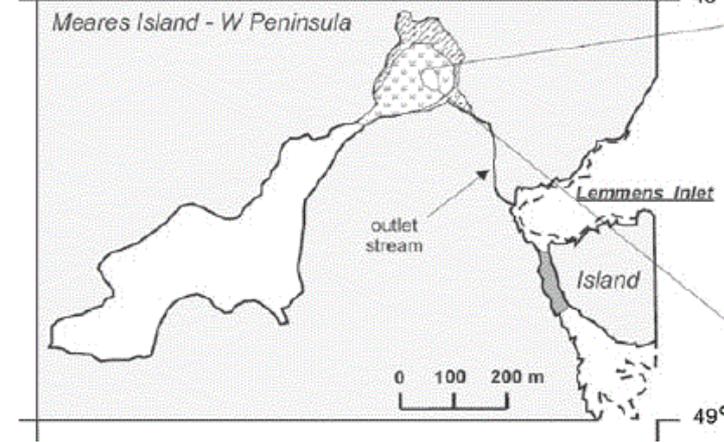
Location of cores in the open water area of the NE basin

Lopez, 2012

During coseismic event

Tsunami Surge

gyttja & glaciomarine clays

?

Run-up limit →

erosion

Tsunami influx (pulse)

erosion

erosion

TIME (minutes to hours)

(several tsunami wave pulses may surge onto the lake)

deposition (in lake)

erosion

erosion

Tsunami outflow (inter-pulse)

erosion

settling by density differentials

End of tsunami event (different facies deposited by multiple tsunami pulses and inter-pulses)

m.s.l.

Lopez, 2012

Lopez, 2012

Core K6

Lopez, 2012

Core	Depth (cm)	Material	^{14}C yr BP	Calibrated age (before 2000)
5	147	Twigs	2,510	
5	169–171	Twigs	2,340	
5	169–171	Needles	2,470	
5	203–205	Cone	3,220	
5	224–225	Bark	3,540	
5	229–230	Twig	3,410	
5	320	Twig	3,450	
5	331–332	Twig	3,580	
5	335	Twig	3,300	
5	335	Twig	4,120	
5	340	Twig	7,160	
5	341–342	Wood	7,430	
5	361	Twig	7,560	
5	458–460	Wood	11,620	
5	500	Shell	13,260	
5	530	Shell	13,810	
1	193	Cone	7,870	
1	193	Twig	6,990	
1	193	Wood	9,690	

Lopez, 2012