Radiocarbon (^{14}C)

Carbon has three naturally occurring isotopes: ^{12}C, ^{13}C and ^{14}C. ^{12}C and ^{13}C are stable, and occur in a natural proportion of about 99:1. ^{14}C, also called carbon-14 or radiocarbon, is a radioactive isotope of carbon with an atomic nucleus containing 6 protons and 8 neutrons. Radiocarbon occurs in trace amounts in nature: one out of a trillion atoms of carbon is ^{14}C.

Radiocarbon is formed when slow neutrons from cosmic rays strike nitrogen-14 (^{14}N) atoms in the atmosphere and cause them to turn into radioactive carbon-14 (^{14}C). After it has been produced in the atmosphere, ^{14}C is quickly oxidized by atmospheric oxygen to form carbon dioxide (CO_2). ^{14}C-tagged carbon dioxide is absorbed by plants, which is then consumed by animals, and distributed throughout the biosphere. Plants and animals assimilate ^{14}C throughout their lifetimes, and contain the same ratio of ^{14}C to ^{12}C that exists in the atmosphere: for every trillion atoms of ^{12}C in your body, there is one atom of ^{14}C.

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \rightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{p} \qquad ^{14}_{6}\text{C} \rightarrow ^{14}_{7}\text{N} + ^{0}_{-1}\text{e} + \bar{v}$$

Formation and decay of radiocarbon.

^{14}C decays to a stable nuclide, ^{14}N, by emitting a low-energy (156 keV) beta particle (an electron) and an antineutrino. The best estimate for the half-life ($T_{1/2}$) of ^{14}C is 5730 ± 40 years. When an organism dies it ceases to incorporate carbon into its tissues, and the concentration of ^{14}C in the tissues declines over time. After 5,730 years, only half of the initial amount of ^{14}C in the organism will remain; the other half will have decayed to ^{14}N. After approximately 60,000 years the amount of ^{14}C remaining falls below the detection limits of even the most advanced instruments, and the sample is considered "radiocarbon dead."

The known rate of decay of ^{14}C forms the basis of radiocarbon dating. ^{14}C declines as a function of time according to the equation:

$$N(t) = N_0 e^{-\lambda t}$$

where
N(t) = the quantity of parent atoms in the material at time (t);
N_0 = the initial quantity of parent atoms in a material;
λ = the decay constant = $\frac{0.693}{T_{1/2}}$;
t = time.

Using the so-called Libby half-life, the equation above can be re- arranged to solve for time (t), years since the sample was removed from equilibrium condition in the biosphere:

$$t = 8033 \ \ln(N_0/N)$$

The half-life of ^{14}C is known from empirical observations and has undergone revisions over the years. Libby and colleagues first estimated the half-life to be 5720 ± 47 years (Libby et al. 1949), and later offered an updated estimate of 5568 ± 30 years (Arnold and Libby 1951), which became known as the Libby half-life. Later measurements indicated that the Libby half-life was slightly low. The Cambridge half-life of 5730 ± 40 years is used in some fields of radiocarbon research, however the Libby half-life is used for calculating radiocarbon ages.

History of radiocarbon dating
In 1946 American chemist Willard Libby predicted that there should be a significant difference in ^{14}C activity between living organisms and fossil carbon due to the long half-life of ^{14}C. In the following years, Libby and his team of researchers at the University of Chicago conducted a series of experiments testing this prediction and its implications, which ultimately led to the publication of the first set of radiocarbon dates in 1949.

One of the greatest achievements of Libby and his team was that they devised a means of measuring the extremely low concentrations of ^{14}C that are found in nature. Instead of counting ^{14}C atoms directly, they used a Geiger-Müller counter to measure the radioactivity of solid carbon samples, inferring the concentration of ^{14}C from the number of decay events over time, in counts per minute (cpm). Libby and his team measured the ^{14}C activity of modern terrestrial organisms, and concluded that the concentration of ^{14}C in living things was constant across time and space. Thus, it would be possible to calculate the ^{14}C activity expected at a given time after the organic material was removed from the life cycle.

Libby and colleagues tested their method on geological and archaeological materials of known age. The first reported radiocarbon age was for a piece of wood taken from the tomb of Zoser, an Egyptian king who reigned from 2665 to 2650 BC. Radiocarbon age determinations from this and other historically dated Egyptian artifacts, as well as tree-ring dated wood samples—widely known as the 'Curve of Knowns'—demonstrated "satisfactory" agreement between the expected and measured ages. Libby was awarded the Nobel Prize in Chemistry for his research on ^{14}C dating in 1960.
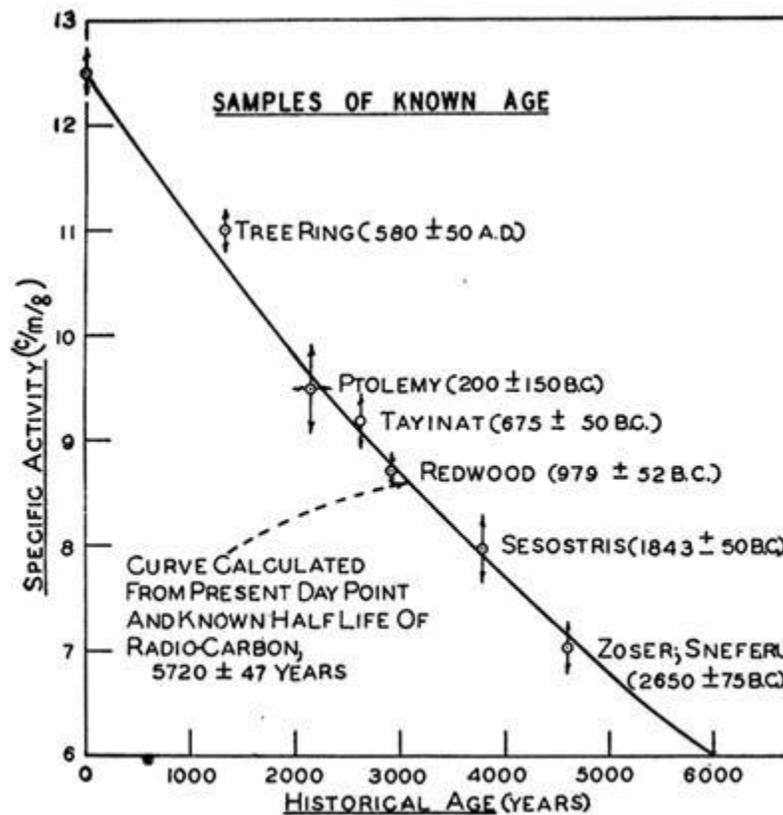
FIG. 1.   Specific activities for samples of known age.

First ever "Curve of Knowns" published in *Science* by Arnold and Libby (1949).

Advances in radiocarbon dating

Until the late 1970s all routine natural-level ^{14}C measurements were made radiometrically, by counting the number of decay events over a period of time in order to infer the concentration of ^{14}C in the sample. The first generation of screen-wall Geiger-Müller carbon counting instruments required several grams of solid elemental carbon. In order to generate this quantity of elemental carbon, you would need to begin with about 14 g of charcoal, or 100 g of shell! The precision and dating range of solid carbon counters were a function of the precision with which background levels of radiocarbon could be measured. Solid carbon counters were rendered obsolete by the mid-1950s due to problems with sample contamination from the fallout of thermonuclear weapons testing.

By the mid-1950s, gas proportional and liquid scintillation decay-counting systems were developed. This new generation of instruments increased counting efficiency, reduced the effects of background ^{14}C related to nuclear weapons testing, and required smaller amounts of carbon for analysis, as little as 1 g.

In the late 1970s radiocarbon researchers began experimenting with accelerator mass spectrometer (AMS) systems to directly measure the ratios of carbon isotopes. In an AMS instrument, a beam of charged carbon ions is accelerated through a magnetic field, which separates particles of mass 12, 13, and 14. The rates at which ^{12}C, ^{13}C, and ^{14}C reach the detectors can be translated into numbers of ions. AMS systems require far less carbon for analysis and obtain measurements of the same or even greater precision, compared to radiometric techniques. AMS systems allow us to analyze very small samples, ranging from 1 µg to 1 mg of carbon. This technology makes it possible to date individual seeds, single amino acids, pollen, and specific compounds isolated from bulk samples.

Calibration: radiocarbon dates versus calendar ages

In addition to technological advances in counting instruments, there also has been continuous improvement in the techniques used to correct and calibrate radiocarbon age determinations. By the mid-1960s, it became clear that major discrepancies existed between the measured and actual calendar ages of many materials because the assumptions underlying the radiocarbon dating method are only approximately true.

It was initially assumed that the natural ^{14}C concentrations in *living* organisms was globally uniform and constant over the ^{14}C time scale. Fortunately for Libby, the concentration of ^{14}C in the atmosphere has been approximately constant over the past few thousand years, therefore all of the samples used in the first Curve of Knowns were approximately correct. However, the rate of ^{14}C production in the atmosphere varies through time due to changes in solar activity and in the Earth's geomagnetic field. This variation is characterized by both major, long-term trends as well as short-

term perturbations of variable magnitude.

The process of calibration uses temporal proxy records, such as tree-ring data, to account for the variability in ^{14}C over time and to convert ^{14}C time into calendar years. Dendrochronologists and radiocarbon researchers obtained a detailed record of the offsets between the terrestrial ^{14}C timescale and calendar time over the range 0–13,900 cal BP by cross-matching ring patterns of progressively older trees. The calibration curve was extended to 50,000 cal BP based on ^{14}C measurements on terrestrial plant macrofossils extracted from varved sediments of Lake Suigetsu, Japan. The portion of the curve covering 14,000–26,000 cal BP is supplemented by ^{14}C measurements from 3 U-series-dated speleothems.
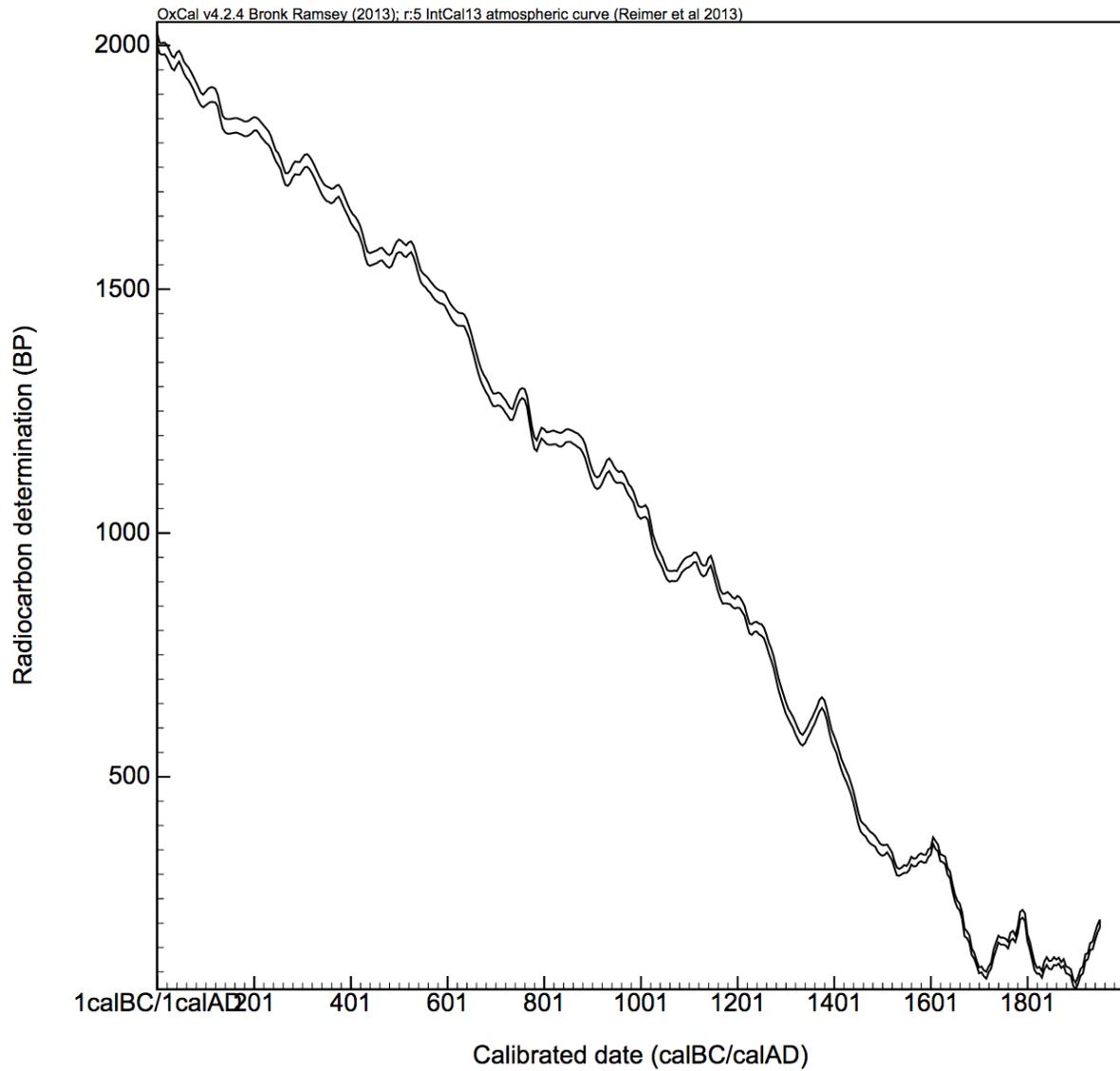
IntCal13 calibration curve covering the period 0–2,000 cal BP (Bronk Ramsey 2013; Reimer et al. 2013).
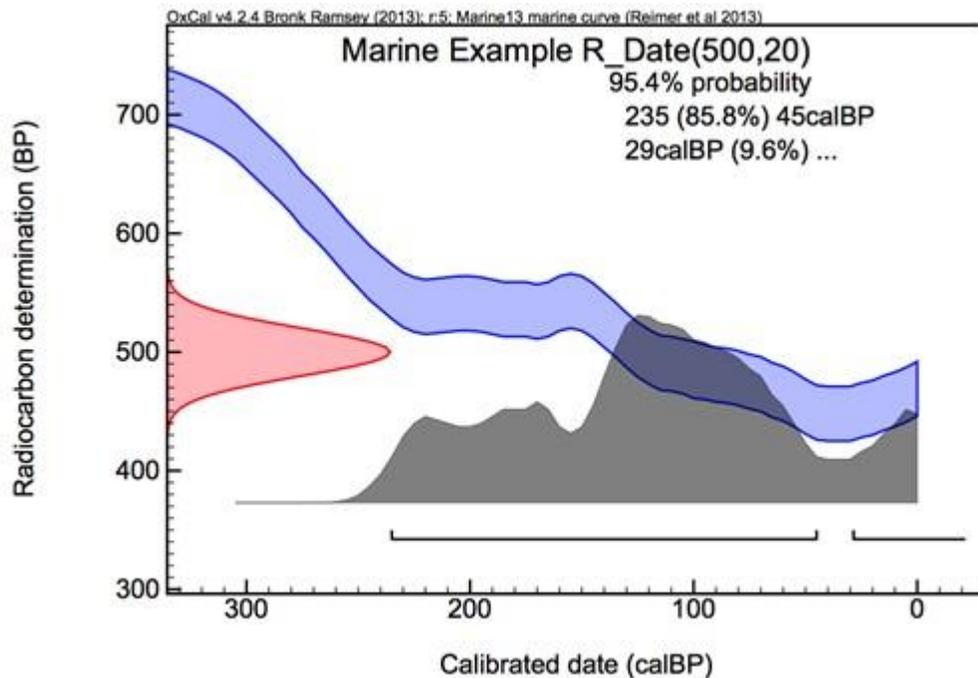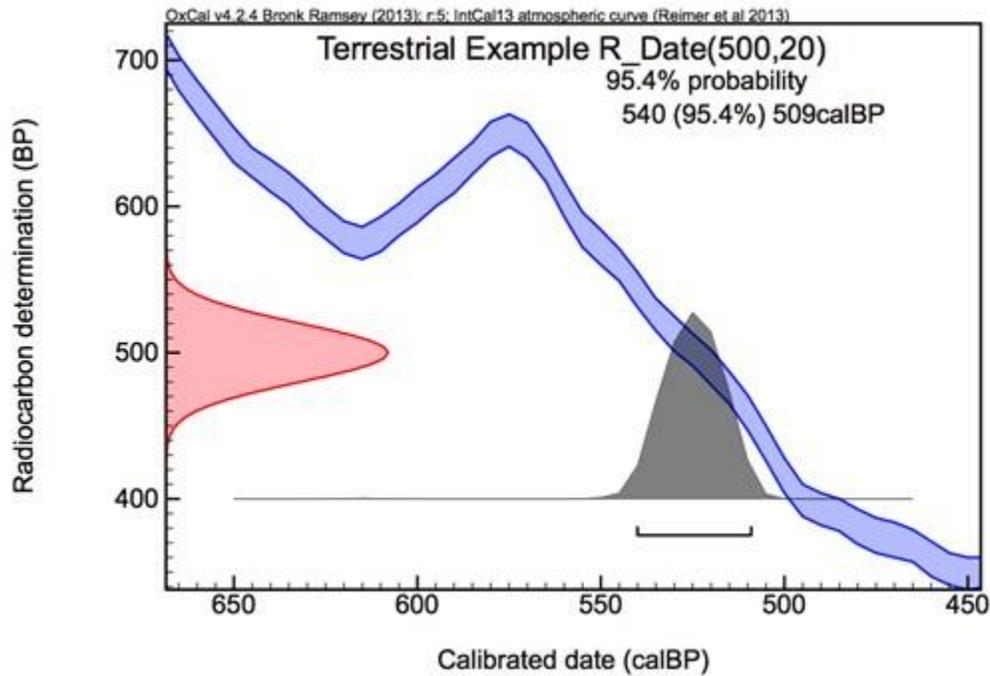
Example calibration of a conventional age of 500 ± 20 yr BP using different calibration curves. Top: IntCal13 for terrestrial samples. Bottom: Marine13 for marine samples. Implemented in OxCal v.4.2.4 (Bronk Ramsey 2013).

To complicate the issue further, mixing among carbon reservoirs may be slow or incomplete. Marine organisms derive carbon from the ocean, which is depleted in ^{14}C relative to the atmosphere. As a result, samples of marine origin yield radiocarbon ages older than contemporaneous samples of terrestrial origin. Separate curves are needed to calibrate radiocarbon ages on materials from different carbon reservoirs. The marine calibration curve covering the period from 0–10,500 cal BP is based on an ocean-atmosphere diffusion model. The portion of the marine curve from 10,500–13,900 cal BP is based on ^{14}C measurements on varved marine deposits and U-Th dated corals. The oldest portion of the marine curve combines all available data (marine, speleothem, and terrestrial), and is offset from the terrestrial curve by 405 ^{14}C years.

In the case of radiocarbon samples of marine origin, it is also necessary to account for local or regional deviations from the global marine curve caused by differences in coastal geomorphology, upwelling, and freshwater inputs. Reimer and Reimer (2001) maintain an online database of local marine reservoir corrections, termed ΔR values, accessed via mapping software.

It should be emphasized that conventional ^{14}C ages should always be reported, in addition to any calibrations or corrections applied to the conventional age. Conventional radiocarbon ages are calculated with respect to internationally recognized standards, such as OXI, OXII, and IAEA-C6, using the Libby half-life value of 5568 ± 30 years. They also are normalized to a common δ^{13}C value, to account for natural isotopic fractionation, and are presented in years BP where AD 1950 = 0 BP on the ^{14}C time scale.