

The absolute age of events in Earth and human history on the basis of radiocarbon dating

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ABSTRACT

Radiocarbon chronometry holds a special place among the many discoveries made in the field of applied nuclear research. Few discoveries in fact, even among those being honored with the Nobel Prize, have had such a powerful and lasting impact on the further development of science. This method, as well as many other complex research methods, which appear to constitute an independent scientific discipline, arose as a result of many years of work by a team of several scientists. However, the actual founder of radiocarbon chronometry was one man, Willard Frank Libby, honored for his contribution with the Nobel Prize in Chemistry in 1960. In Poland, the creative activity in this area was begun in the late 1940s by Włodzimierz Mościcki, who continued it in the last 10 years of his life in the Silesian University of Technology in Gliwice, where he founded the Gliwice Radiocarbon Laboratory.

1. INTRODUCTION

Application of physical methods is required to place in time various events from the Earth's history, which resulted in landscape formation, or climatic conditions favorable for specific plants and animals. Studies on the

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origin and time and space expansion of human cultures, strongly connected with changes of environment, frequently make use of physical methods. Archaeologists and Earth scientists in every case are interested in knowledge about the absolute (calendar) age of a given event. For this purposes physicists have applied phenomena of known rate in time, in particular radioactive decay of nucleus of various isotopes of elements contained in rocks and minerals of the Earth's crust. Content of some of the isotopes decreases in time, while others accumulate. Some of the minerals subjected to natural ionizing radiation gain an ability of luminescence, whose intensity depends on the age of this material. These phenomena are used for construction of isotope and luminescence clocks for measurement of time in the past. The most commonly used isotope clocks apply the radioactive isotope of carbon of mass number 14, so-called radiocarbon, which is contained in organic and carbonate sediments, as well as similar properties of uranium and thorium, which are found in continental and oceanic carbonate rocks. The luminescence properties are attributed to quartz and feldspar, which accumulate mainly in loess and sand. Physicists, who determine ages of various objects like sediments, rocks and minerals, archaeological findings, are challenged to construct the clocks of identified and the highest possible precision for creation of an ordered in time sequence of events, called chronology. This challenge requires a close interdisciplinary cooperation with Earth scientists (geologists, geomorphologists, geographers, palaeobotanists) and archaeologists, and the methods applied are called methods of absolute chronology. A measurement of particular physical properties aimed at determination of the age is called dating, and the result of measurement – a date. Therefore, there may be radiocarbon, uranium-thorium, luminescence dates, all provided with corresponding laboratory uncertainty.

The isotope methods mentioned above allow construction of absolute time scales covering a range of the last 50 thousand years in the case of radiocarbon method, 300 thousand for uranium-thorium and 500 thousand for luminescence method. Other techniques of absolute chronology include methods using annual rhythmicity of sedimentation in water reservoirs, called also a method of varve chronology, and annual tree-rings of trees like oak, pine, redwood, called dendrochronology. Calendar time scales constructed on the basis of varve chronology and dendrochronology are employed for calibration of isotope clocks.

Table 1. Some important dating methods for Quaternary and archeological research. OSL/TL – Optically Stimulated Luminescence/Thermoluminescence methods, ESR – Electron Spin Resonance method, BP - Before Present

Dating method	Application	Range of dating (years BP)
^{14}C	Remains and organic sediments, Carbonate sediments	up to 50 000
OSL/TL	Mineral sediments, ceramics	up to 500 000
ESR	Carbonate sediments, bones	up to 1 000 000
$^{234}\text{U}/^{230}\text{Th}$	Carbonate sediments, bones, peat	up to 300 000
$^{40}\text{K}/^{40}\text{Ar}$	Volcanic deposits	more then 50 000
^{210}Pb	Sediments in water reservoirs, peat	up to 150
^{137}Cs	Lake sediments, soils	up to 60
Dendrochronology	Wood construction, fossil wood	up to 12 000
Varve chronology	Annually laminated marine and lake sediments	up to 120 000

Additional investigations of stable carbon and oxygen isotope ratios in carbonate sediments, like carbonate tufas, cave speleothems, lake sediments and in tree-rings, analysis of probability distributions of radiocarbon and luminescence dates on the time scale enable reconstruction of climate change in the period covering the range of dating methods. Combining these information with obtained archaeological chronologies allows a much wider view on the background of human activity.

2. RADIOCARBON METHOD

Radiocarbon chronometry occupies special place among many discoveries made in applied nuclear physics, for few discoveries, even among those honored by Nobel price, exerted such a broad and long-lasting influence on further science development. This method, like many other compound re-

search methods, which bear marks of independent scientific discipline, arose as a result of long-term research of group of scientists. However, the actual founder of the radiocarbon chronometry was one man – Willard Frank Libby [1], who was honored for his contribution in project by Nobel price in chemistry in 1960.

For the first time ^{14}C isotope was found in nuclear reaction between thermal neutrons and nitrogen nucleus (reaction $^{14}\text{N} (n,p) ^{14}\text{C}$) in the mid-1930-s. Libby's publication, in which he estimated neutron flux in upper atmosphere, then by using simple equilibrium assumptions and information about carbon total content in its upper reservoirs (atmosphere, biosphere, hydrosphere and lithosphere), he estimated the relative activity of ^{14}C isotope in atmospheric CO_2 and in modern vegetation to 10 disintegrations per minute in 1 gram of carbon ($10 \text{ dpmg}^{-1} \text{ C}$), was an important step towards the emergence of radiocarbon chronometry. Libby's estimate is close to $13.56 \text{ dpmg}^{-1} \text{ C}$ value, calculated later, on the basis of precise measurements. To verify his hypothesis about existing ^{14}C isotope with natural origin and its relative activity, Libby used methane produced in the decay of modern vegetation. The last step towards founding radiocarbon chronometry was to prove that ^{14}C isotope occurs evenly in Earth's biosphere. It was in this publication, where it appeared for the first time, changed in relation to Engelkemeir's publication [2], value of ^{14}C isotope β decay half-life, amounted to 5568 years. This value is still used in calculating radiocarbon dates and comprise a base for conventional radiocarbon time scale definition, although the correct value of ^{14}C isotope half-life is 5720 ± 30 years [3]. At present, natural speed of radiocarbon production in upper atmosphere, is estimated to be around $2 \text{ atoms}/(\text{cm}^2\text{sec})$ in relation to Earth's surface. It means that the amount of ^{14}C in Earth's atmosphere (as a part of CO_2 particles), is around 60 kg. This value drastically increased in the period of nuclear weapon tests, in which radiocarbon was artificially produced. The content of ^{14}C in atmospheric CO_2 can also be lower, depending on the region because of CO_2 emission as a result of fossil fuel burning (so-called Suess effect).

Basic limitation of range and accuracy in radiocarbon dating is the low, natural concentration of ^{14}C isotope. This concentration decreases in time according to the abovementioned half-life, from the moment of death of living organism, which assimilated CO_2 from atmosphere, or sedimentation of mineral deposits, especially crystallisation of calcite. Other important limitations in applying techniques of radiocarbon concentration measurement through measurement of β (beta) radioactivity are small value of ^{14}C decay

constant ($\lambda = 2,368 \cdot 10^{-10} \text{ min}^{-1}$) and the low value of maximum β radiation energy, which is 156 keV.

Conventional radiocarbon age of a sample is usually represented by: years BP, yrs BP, conv BP, BP. Conventional age represents time, which has passed from the moment when exchange of carbon between the matter, from which the sample was taken, and environment stopped, until the arbitrary given so-called present, which means 1950 AD. This year is an approximate calendar year, which closes the period of the last 50000 years in which no significant human interference with radiocarbon concentration in atmosphere was found. The established, constant value of ^{14}C concentration in modern biosphere (S_0), in the range of radiocarbon method, along with a knowledge of radiocarbon concentration in sample at present (S), allow to calculate conventional radiocarbon age (T), according to formula:

$$T = 8033 \ln \frac{S_0}{S} \quad (1)$$

Carbon isotope fractionation occurs in processes of carbon assimilation by living organisms, in geochemical cycle of carbon in its different reservoirs and during inter-reservoir exchange. Because of that, it is required to add $\delta^{13}\text{C}$ value as a correction to already measured ^{14}C concentration value in the sample and in standard as well. Radiocarbon concentration including isotope fractionation correction is calculated according to the following formula:

$$S = S_m \left[1 - \frac{2(\delta^{13}\text{C} + 25)}{1000} \right] \quad (2)$$

where S_m is the radiocarbon concentration in sample.

Mass spectrometry is used to measure $\delta^{13}\text{C}$ and its value is -25‰ for standard and vary in a few dozen brackets from positive values for some carbonate sediments, till around -40‰ in samples of plants assimilating carbon in C3 photosynthesis cycle.

METHODS OF RADIOCARBON MEASUREMENTS

Gas proportional counting technique (GPC)

This technique, in short GPC, was initiated by Suess, who applied acetylene-filled counters. Acetylene was obtained directly from sample, by using appropriate chemical preparation. Number of electrons from ^{14}C isotope decay, estimated from the number of electrical impulses from detector (counter), is proportional to concentration of this isotope in sample. Methane-filled counters were a next generation of counters. The most numerous and the widest currently applied generation of counters are carbon dioxide-filled counters. This kind of counters require a CO_2 of high purity [4].

Crucial development in the gas proportional counting technique were: pursuit to increase measurements accuracy and to extend period in which dating was possible. Works on achieving the first goal were mainly stimulated because of radiocarbon time-scale calibration research, and demands made along with dating of archeological sites. Extending range of radiocarbon method beyond typical of the most laboratories, i.e. 40000 years, was caused by needs of Earth and environmental sciences. The possibility of getting absolute time-scale for whole period of last glaciation, which embrace approximately the last 100000 years, is very important for chronostratigraphy of early Quaternary.

Liquid scintillation counting technique (LSC)

For effective use of liquid scintillation counting technique for radiocarbon dating, it was crucial to develop technique of acetylene synthesis in reaction with melted lithium [5]; but the real breakthrough was made by Noakes *et al.* [6], who applied benzene synthesis by acetylene trimerisation in the presence of vanadium catalyst. G.W. Pearson has created a system, using a commercial PACKARD spectrometers, which was able to obtain accuracy comparable with GPC technique. It was very convincing proof of large abilities of LSC method. In the 1980s LSC technique visibly enriched, because of the new version of commercial scintillation spectrometer called QUANTULUS manufactured by WALLAC company [7].

Like in GPC method, much effort has been taken into measuring ^{14}C in small samples and extending dating range. It is necessary to notice that commercial scintillation spectrometers mentioned above, allow us to receive similar results in radiocarbon dating, in terms of precision and measuring abilities, as laboratories equipped with proportional counters [8].

Accelerator mass spectrometry technique (AMS)

Unlike the two previous methods, AMS technique works by direct counting of ^{14}C atoms instead of counting beta particles from ^{14}C decay. This idea, derived from Oeschger *et al.*, (1970), was realized for the first time by Müller in Berkeley [9], who by the way of tests with cyclotron, made an attempt of acceleration of ^{14}C ions.

Purser's [10] discovery consists in elimination of influence of ions with the same mass through recharge of negative ions with charge -1, to multiple charged positive ions. The first radiocarbon dating of wood samples (previously dated by conventional technique), using AMS method, was carried out at Rochester University [11]. Dating gave a positive results, proving its usefulness for dating small samples containing only milligram of carbon.

At present, there are approximately 40 accelerators in different science facilities around the world, which are used for AMS radiocarbon dating. Results of international intercomparison program, in which majority of "classic" laboratories participated, proved that results of AMS and classical techniques are comparable. AMS technique has a serious advantage over the radiometric methods, because of sample size (sample can be less than 1mg of carbon). It allows us to date many objects, which were impossible to date with conventional techniques. Another important advantage of AMS method is very high efficiency of accelerators laboratory, which is determined by the amount of analyzed samples. Typical time needed to determine ^{14}C relative concentration with 1% accuracy (which in radiocarbon age measurement is equivalent to standard error of ± 80 years), is 30-50 min. Theoretically, it allows to carry out from 3 to 5 thousands analyses a year. The main limitation in AMS technique spreading around the world are the price of measuring equipment and operating costs, which reach millions of euros.

4. RADIOCARBON TIME-SCALE CALIBRATION

In radiocarbon dating method, it is assumed that ^{14}C isotope concentration is constant and decreases after organism's death, according to radioactive decay law. To determine the time, which has passed from the moment of the death, it is necessary to compare ^{14}C isotope concentration in unknown sample and in organism at the time of death. In radiocarbon dating a sample called "standard of modern biosphere" is used as a standard of ^{14}C concentration at the time of death. Because ^{14}C standard was made from an organism, which assimilated carbon from atmosphere, the most accurate is the radi-

ocarbon age of land organisms remains, which assimilated carbon from atmospheric CO₂. However, even for such samples, the radiocarbon age differ from the real age (from now on called a calendar or absolute age), mainly because radiocarbon concentration in atmospheric CO₂ has been changing in the past and differs from concentration in standard of modern carbon. Discrepancy between radiocarbon age and calendar age in dated samples was noticed for the first time in late '50s. From then, this issue became crucial to radiocarbon chronometry and investigations on that issue are still carried on. Determining a relationship between radiocarbon and calendar age is the subject of so-called calibration of radiocarbon time-scale. Knowledge of this relationship (calibration curve) allows us to calibrate radiocarbon age of any sample. Obtained in this way, so-called calibrated age is the best approximation of sample calendar age. It is possible to reconstruct calibration curve by ¹⁴C dating of known-age sample. Calibration pertains directly to remains of organisms, which assimilated carbon from atmospheric CO₂. In order to use this calibration curve in calibration of radiocarbon age of other remains, it is required to include a correction for assimilation of carbon from the environment, in which radiocarbon concentration was different (always lower) than in atmosphere. This correction is well-known for organisms living in surface oceans water on latitudes lower than 50°, but for various sample types (lake sediments, speleothems and other carbonate sediments, organisms from deep of oceans), is usually poorly-known.

In radiocarbon time-scale calibration the following archives are used: dendrochronologically dated wood, corals dated by U/Th method and specific organic remains, found in sediments dated by counting of annual layers (varve chronology).

The most accurate calibration dataset was obtained by using wood. Characteristic changeability of tree-rings thickness in every trunk allow to perform dendrochronological dating with one-year accuracy. Radiocarbon time-scale calibration curve uses well preserved oaks and pines trunks from swamps and river beds from Western and Central Europe, dead pine trunks from American Cordillera, which were not decomposed in dry, high-mountain climate and tree trunks of long-living species from western coast of North America. It is necessary to say that absolute dating of every *subfossil tree* with dendrochronologic method, requires a dendrochronological scale received from many analyses of tree trunks, whose growing periods cover the continuing period of time till the present.

The earliest calibration measurements, published in 1970, used trunks of long-living trees (*Pinus aristata* and *Sequoia gigantea*) from USA. Mea-

Measurements have shown that in almost the whole period of last couple of thousand years, radiocarbon age is younger than the calendar age and for samples of age 6000 years difference can be as big as 700 years. Measurements also suggested existence of many small bends (non-monotone) in calibrating curve, but their significance was questioned for many years. Universality of the curve i.e. its chance for being used to reliably determine calibrating age of other samples, was also challenged [15]. Calibration, as an absolute dating tool, gains trust after 1985, when the high-precision results of ^{14}C dating of tree trunks from different parts of Earth were announced. Perfect conformity of tree-rings dating results from trees from western coast of USA, Ireland and FDR, carried out in radiocarbon laboratories in Seattle (USA) and Belfast (Northern Ireland), allowed us to create calibration curve, which was officially approved by XII International Radiocarbon Conference in Trondheim. Calibration curve can be used in dating samples from any place on northern hemisphere. A slightly lower radiocarbon concentration in atmosphere on the southern hemisphere causes, that before calibration it is necessary to include appropriate correction. The best developed part of calibration curve embraced period from 2490 BC (Before Christ) to 1940 AD. Older part was using only trees from Ireland (up to 5210 BC) or USA (6654 – 5350 BC).

In the next couple of years, progress was mainly made because of lengthening absolute chronology of oaks from Germany. Thanks to using many trunks in constructing the chronology, its correctness is beyond any doubt. Results of their dating in radiocarbon laboratory in Heidelberg (Germany), were used to extend calibration curve up to 7875 BC. Calibration data for 1940AD - 7875 BC period was collected in the special issue of *Radiocarbon* in 1993.

In this special calibration issue, alongside with calibration curve results of pine trunks radiocarbon dating can be found. German pine chronology from glacial and Holocene breakthrough, embraced 1768 years and potentially can be used to lengthen precise calibration curve beyond reach of oak chronology. Pine chronology does not reach present times, so this is not absolute dating. This chronology was dated (period 9439 – 7981 BC) by comparing tree-rings thickness in oak and pine chronologies. If this dating is correct, then pine and oak interfere in 212 years period. This relatively short period of interference and fact, that two different species (with slightly different reactions of yearly increases on climatic condition changes) were compared, causes the sanctioning of pine dendrochronological dating as temporary.

Calibration curve (see Fig. 1) unequivocally shows that the difference between radiocarbon age and calendar age is growing alongside with samples age, up to more than 1000 years for samples from early Holocene. Characteristic of calibration curve is appearance of plateau – period of several hundred years, in which radiocarbon age was near constant. Plateaus longer than 300 years embrace periods: 2350 – 2700 BP, 4550 – 4850 BP, 5000 – 5300 BP, 8650 – 9000 BP, 9050 – 9400 BP, 9600 – 9950 BP and two periods from pine chronology for radiocarbon age around 10000 ^{14}C BP and 9550 ^{14}C BP. Particular consequences for chronology of Earth's natural environment changes, are caused by plateau of radiocarbon age 10000 ^{14}C BC, which is commonly accepted radiocarbon date for border between younger Dryas and Holocene. The plateaus cause the fact that radiocarbon dating of sample from that period of time, does not allow us to specify the calendar age with an error smaller than a couple of hundred years.

It seems that further extension of German dendrochronological scales will run into serious difficulties. In cool period of younger Dryas, followed by Holocene, and also at the beginning of Holocene oaks did not grow in this area. Cool climate was well tolerated by pines, but deficiency of precipitation in this period and the accompanying meagre transport force of rivers, probably caused pine trunks to fail to accumulate in favorable conditions and they did not survive until today.

Calibration data for periods, which were not embraced by oaks and pines chronologies, is possible thanks to dating of corals and annually laminated marine and lake sediments. Absolute ages of annually laminated sediments are obtained by counting layers, while calendar age of coral samples was measured using U/Th method. Samples of corals, which were living in oceans surface, and now are lying several dozens below the ocean surface, originally were used to determine the rate of growing level of global ocean as a result of inland ice melting. Living corals absorb carbon from the ocean (not from atmosphere!), but it can be shown that the relationship between the radiocarbon age of organisms, which used to live in ocean surface water on low latitudes and the age of remains of organisms, which assimilated carbon from atmosphere is well specified. Data obtained from corals show that difference between calendar age and radiocarbon age is growing even more for older samples (Fig. 1). A large scatter of available datasets and difficulties in their absolute chronologies make calibration of radiocarbon dates older than 25000 ^{14}C BP imprecise.

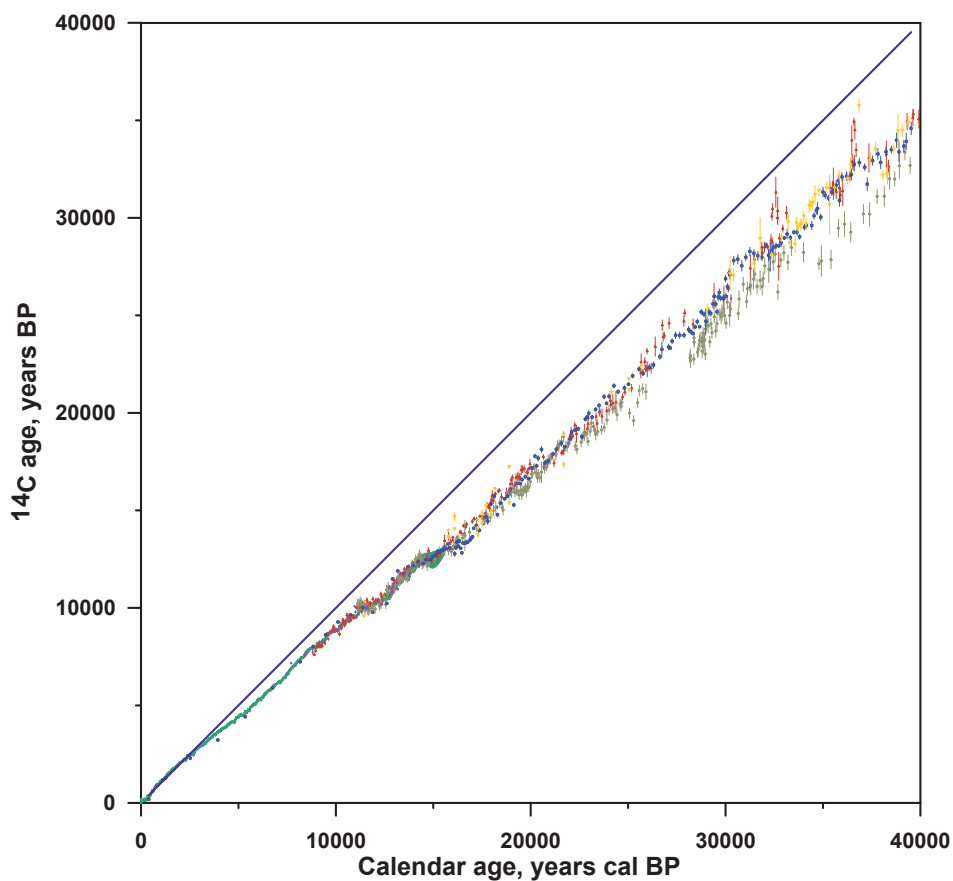


Fig. 1. Datasets used for calibration of radiocarbon ages. Straight line indicates on equal ^{14}C and calendar ages. Green line is calibration curve [16], points represent results of measurements obtained for various records mentioned in the text. After N. Piotrowska, PhD thesis (2005).

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