PROCEEDINGS OF SCIENCE

Radiocarbon Dating Coming of Age

Walter Kutschera[1]
University of Vienna, Faculty of Physics – Isotope Research, VERA Laboratory
Währingerstrasse 17, A-1090 Vienna, Austria
E-mail: walter.kutschera@univie.ac.at

Radiocarbon dating was invented some 60 years ago by Willard Libby at the University of Chicago, and has since developed into an extraordinary versatile tool in many fields of science. The biggest technical advance came in the late 1970s with accelerator mass spectrometry (AMS), which allowed one to move from ^{14}C beta-decay counting to direct ^{14}C atom counting. This allowed a reduction of sample size by a factor of 1000 and more (grams to milligrams of carbon), and also reduced the measuring time per sample from days to half an hour. Developments in recent years allowed a further reduction in sample size down to about 10 µg C. Over the years, the size of accelerators required for ^{14}C AMS measurements was also drastically reduced, eventually reaching table-top dimensions. The accuracy of absolute age determination has been greatly improved through frequent updates of the ^{14}C calibration curve by a large group of experts. The calibration now reaches back to 50,000 years covering the entire range of radiocarbon dating. For the last 12,000 years a very reliable calibration is provided by dendrochronology, i.e. a continuous year-by-year record of tree rings. Beyond 12,000 years the calibration awaits further improvements. Another important development was the introduction of Bayesian analysis into the calibration process, which allows a considerable reduction of uncertainty in absolute age determination. Man-made ^{14}C introduced into the atmosphere by the nuclear weapons testing program in the late 1950s and early 1960s created the so called ^{14}C bomb peak, which can be used as a unique tracer and a fast running clock during the past 50 years. The current paper attempts to highlight some of these developments, necessarily limited to representative examples. A rather extensive list of references is provided for readers who would like to get deeper insights into the various aspects of radiocarbon dating touched upon in this paper.

50th International Winter Meeting on Nuclear Physics,
Bormio, Italy
23-27 January 2012

[1] Speaker

1. Introduction

This year we are celebrating the centenary of the discovery of cosmic rays by Victor Franz Hess. Measuring the ionization of air in a closed chamber equipped with a charged-up electrometer, he undertook balloon flights up to 5300 m where he registered an increase of the ionization which he interpreted as the result of a penetrating radiation "from above" [1, 2]. Although his discovery was confirmed shortly thereafter by Werner Kolhörster with balloon flights up to 9300 m [3, 4], some prominent physicists remained skeptical (e.g. Robert Millikan [5]). Eventually, they all recognized the existence of cosmic rays, and in 1936 Hess received the Nobel Prize in Physics together with Carl David Anderson who in 1932 had discovered the positron in cloud chamber measurements [6, 7]. Also in 1936, the first hint of a particle intermediate in mass between the electron and the proton was observed [8-10], later recognized as the Muon. In 1937, the complete disintegration of a heavy nucleus by high-energy cosmic rays was observed by Blau and Wambacher [11] in photographic plates exposed for several months at Hess' cosmic ray observational station at Hafelekar (2300 m a.s.l.) near Innsbruck.

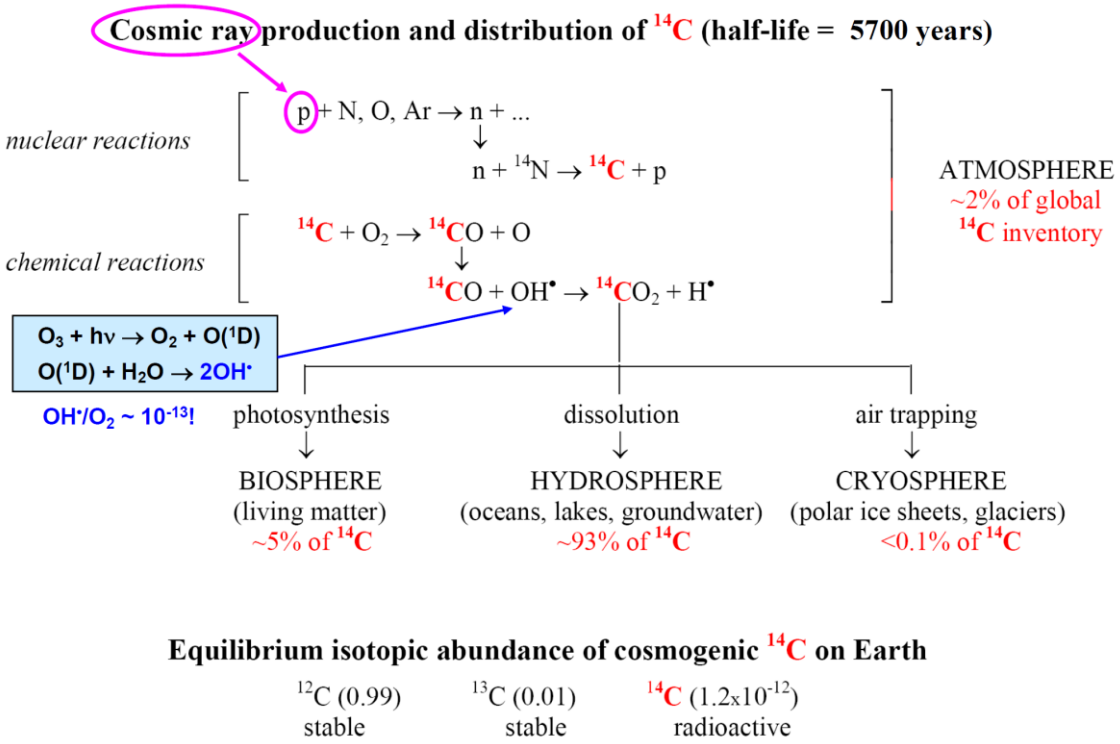


Fig. 1. Schematic presentation of the cosmic-ray production of ^{14}C in the atmosphere, its two-step conversion to $^{14}CO_2$, and its distribution into the biosphere and the ocean. The inventory of ^{14}C in the various archives is given in percent. Note that the minute, but extremely reactive OH radical plays an important role in the oxidation of ^{14}CO to $^{14}CO_2$ [17]. It is an important oxidant of trace gases in the atmosphere [18].

After the Second World War, the year 1947 turned out to be another rich year for discoveries of new cosmic-ray products. In photographic emulsions exposed at the Pic du Midi observatory (2870 m a.s.l.) in the French Pyrenees the Pion was discovered by Occhialini and Powell [12], leading to the 1950 Nobelprize in Physics for Cecil F. Powell. In counter-controlled cloud chamber photographs at Manchester hints of new unstable elementary particles were observed by Rochester and Butler [13], eventually identified as the Kaon and Lambda particles. Meanwhile Willard F. Libby at the University of Chicago had figured out that radiocarbon (^{14}C) should be produced by cosmic ray secondary neutrons in the atmosphere through the $^{14}N(n,p)^{14}C$ reaction [14], eventually entering the biosphere through the uptake of $^{14}CO_2$ by plants (Fig. 1).

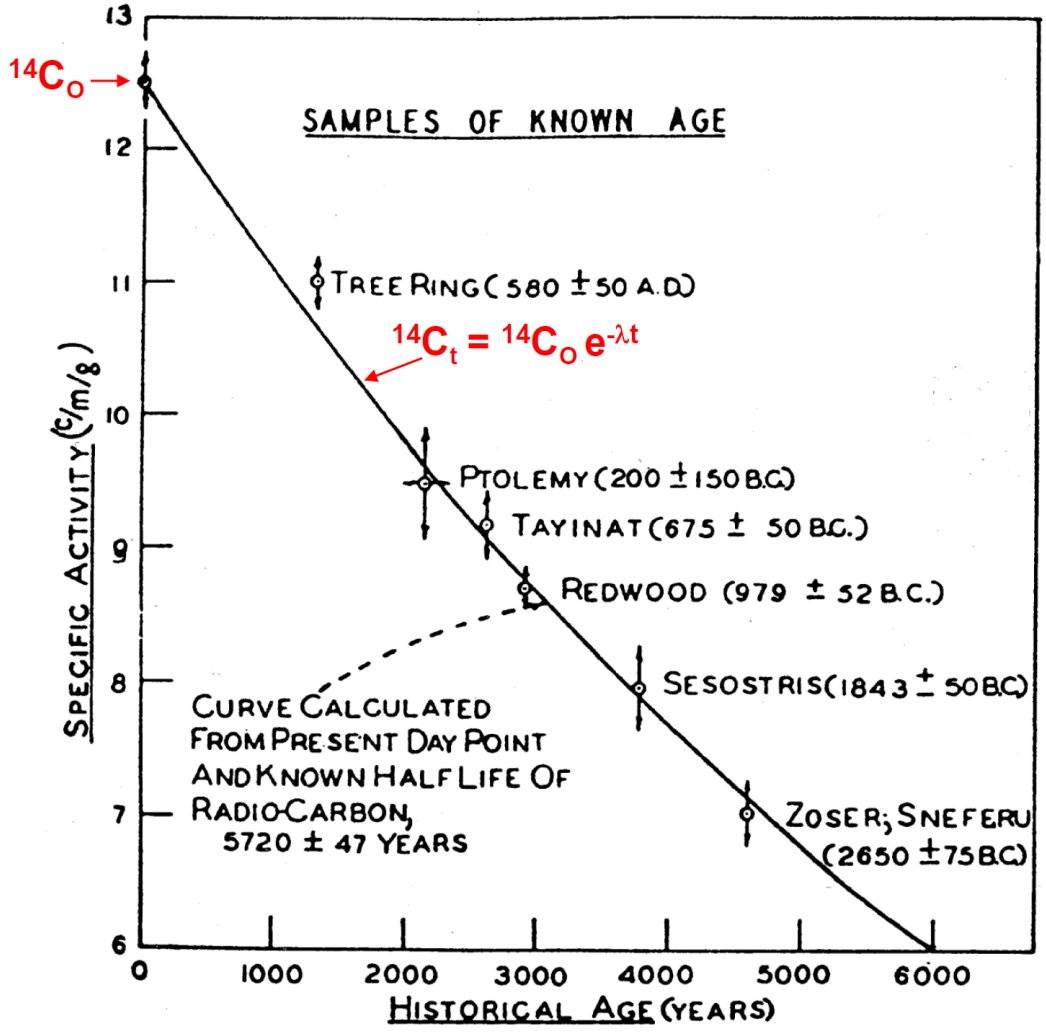


Fig. 2. Reproduction of the original figure from Arnold and Libby [16], where samples of known age were compared with their ^{14}C content measured through the specific activity. Since the age was reasonably well described by the radioactive decay curve (labeled in red), it presented the proof that ^{14}C can be used for dating.

A first measurement of natural ^{14}C in organic matter was performed in methane (CH_4) emerging from a sewage disposal plant in Baltimore, using isotope enrichment to make the expected feeble beta decay from ^{14}C measurable in large methane-filled Geiger-Müller counters [15]. The proof that ^{14}C can be used for dating was performed by measuring ^{14}C in samples of known age (Fig. 2) [16]. This, then, was the starting point of radiocarbon dating, and earned Willard Libby the 1960 Nobelprize in Chemistry "for his method to use carbon-14 for age determination in archaeology, geology, geophysics, and other branches of sciences".

For about 30 years the ^{14}C content in carbon samples was measured through the beta-decay requiring a few grams of carbon (~13.8 ^{14}C decays per minute per gram of carbon), which limited the method to samples which contained that much carbon. Considering that there are $6x10^{10}$ ^{14}C atoms in one gram of carbon ($^{14}C/^{12}C = 1.2x10^{-12}$), the long half-life of ^{14}C (5700 yr) clearly makes a detection by decay counting very inefficient. Although it was recognized that direct atom counting would be much more efficient [19], attempts to perform $^{14}C/^{12}C$ isotopic ratio measurements with low-energy mass spectrometry fell short by one order of magnitude [20]. The advantage of atom counting over decay counting grows with increasing half-life. In fact, atom counting is not dependent on the half-life, and therefore allows one to measure long-lived radioisotopes which could not be detected at natural abundances with decay counting. An example is cosmogenic ^{41}Ca ($t_{1/2}$ = 104,000 yr), which was studied with AMS in a variety of applications [21,22].

2. The Advent of Accelerator mass spectrometry

In 1977, a big step forward in atom counting of ^{14}C was made at several accelerator laboratories in the USA [23, 24] and Canada [25]. Although at the beginning a cyclotron operating with positive ions was used at Berkeley [23], the use of negative ions with tandem accelerators [24, 25] turned out to be far superior for a ^{14}C detection. The main reason was the discovery that ^{14}N does not form stable negative ions [26], thus removing the otherwise strong interference from this stable isobar already in the ion source. In addition, the terminal stripping process inherent to a tandem accelerator dissociates mass-14 molecular interferences from $^{12}CH_2^-$ and $^{13}CH^-$. It is interesting to note that for about 20 years one believed that it is necessary to strip to the 3+ charge state of ^{14}C to be sure that the molecules break apart (see below). To obtain sufficient yield for this charge state, AMS tandem accelerator systems with a terminal voltage of ~3 MV were considered to be the best choice.

With accelerator mass spectrometry (AMS), the required sample mass for a $^{14}C/^{12}C$ ratio measurement was reduced from grams to milligrams of carbon, opening up a wide range of applications. One milligram of organic carbon still contains 60 million ^{14}C atoms at a present-day $^{14}C/^{12}C$ ratio of $1.2x10^{-12}$. On average, only one of these ^{14}C atoms decays in one hour, whereas about one million can be counted with AMS in the same time. This is clearly an enormous gain in detection sensitivity. For example, in the field of oceanography it was now possible to perform high-precision $^{14}C/^{12}C$ measurements from dissolved inorganic carbon extracted from just 0.5 liter of ocean water [27]. With the beta counting method, CO_2 from 250 litres of ocean water had to be extracted. The atom-counting advantage led to establishing the National Oceanographic AMS (NOSAMS) facility at Woods Hole Oceanographic Institution

[28]. More than 13,000 AMS measurements provided information on the ^{14}C content of dissolved inorganic carbon throughout the world oceans within the World Ocean Circulation Experiment (WOCE) [29, 30]. This leads to a better understanding of the dynamics of ocean currents, which transport heat around the globe and therefore have a great impact on the climate.

3. Technical advances of AMS

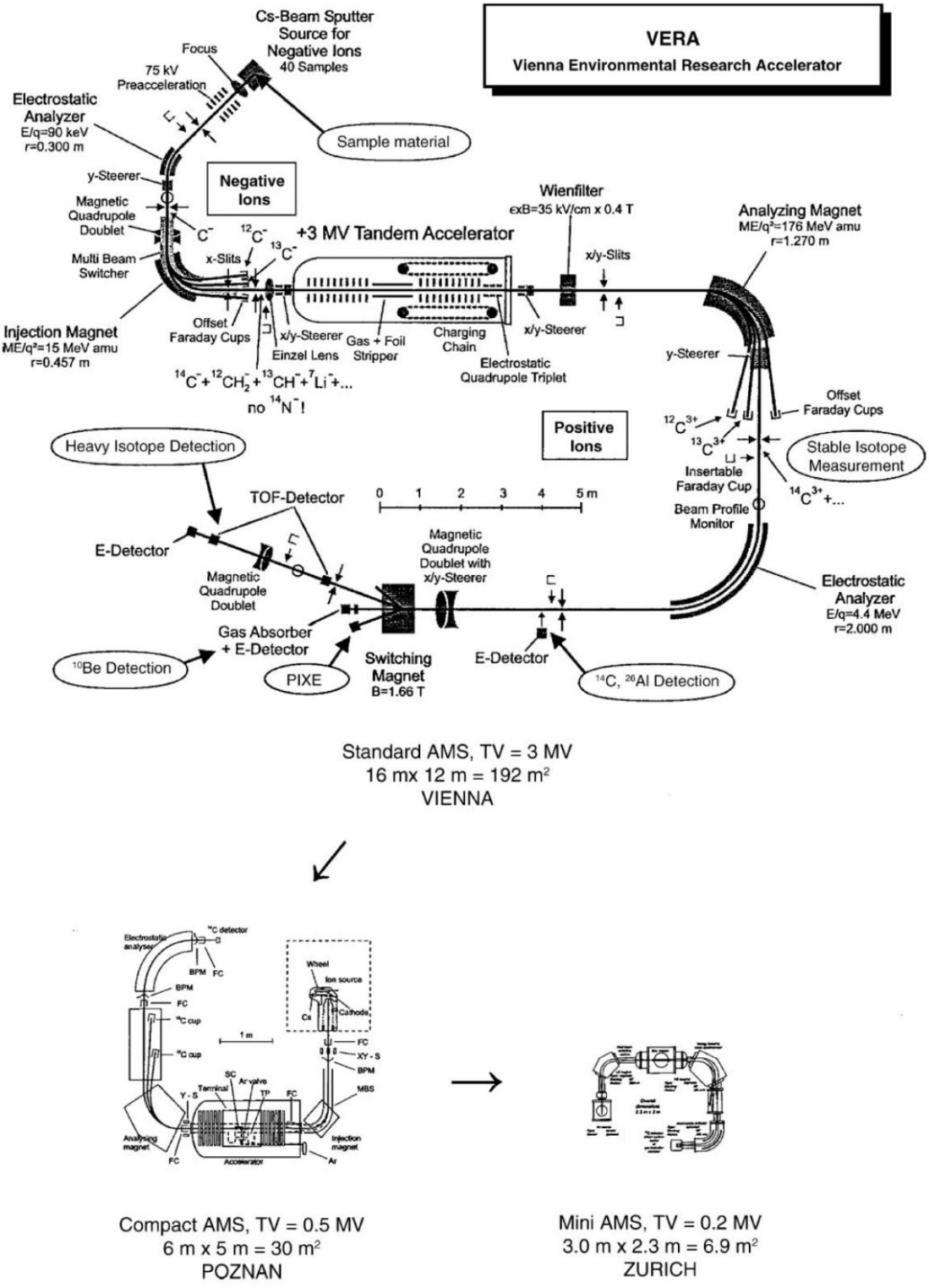
AMS was first developed at accelerators originally used for nuclear physics experiments. It was soon realized that AMS can be performed much better at accelerators dedicated to AMS, particularly for high-precision ^{14}C measurements [31, 32]. Although AMS is being used to measure long-lived radioisotopes throughout the entire mass range of nuclides [33], more than 90 percent of all AMS measurements are devoted to ^{14}C. In fact, out of the approximately one hundred AMS facilities world-wide, about half of them perform ^{14}C measurements only. This emphasizes ^{14}C as the most important natural radioisotope to be used in almost any field of science [33].

3.1. The miniaturization of AMS facilities

One of the most significant advances in AMS technology since its invention came about by breaking the paradigm of stripping $^{14}C^-$ ions at the tandem terminal to $^{14}C^{3+}$ in order to dissociate for sure the otherwise overwhelming interference from the mass-14 molecules, $^{12}CH_2^-$ and $^{13}CH^-$. Although early experiments at Toronto indicated a molecule dissociation at lower energies [34], the break-through came from systematic investigations at the AMS facility of the ETH Zürich [36]. They proved that the molecules can be dissociated even in the 1+ charge state, provided that the gas-stripper thickness is sufficiently large. It turns out that besides the Coulomb break-up at the 3+ charge state, there is also a collisional break-up of molecules possible at lower energy and lower charge states. This then allowed one to lower the terminal voltage from 3 MV to eventually 0.2 MV, leading to a dramatic reduction in overall size of the corresponding AMS facilities (Fig. 3). Such small facilities have foot prints of only ~30 m^2 (Compact AMS [37] and Single Stage AMS [38]), and ~7 m^2 (MICADAS [39]), respectively. One thus came down to essentially table-top machines comparable in size to stable-isotope mass spectrometers.

3.2. The miniaturization of sample size

As mentioned above, 1 mg C contains $6x10^7$ ^{14}C atoms. With AMS about 5 % of these atoms can be detected. A reduction of the sample size by a factor of hundred down to 10 µg C still leaves $6x10^5$ ^{14}C atoms in the sample, of which about $3x10^4$ ^{14}C atoms can be counted. In practical terms, the limit to perform AMS measurements with such ultra-small samples is not the number of ^{14}C atoms – even 1 µg C may be feasible -, it is the problem of avoiding contamination in sample preparation procedures. At VERA we have pushed the 'Vogel' method



Standard AMS, TV = 3 MV
16 mx 12 m = 192 m²
VIENNA

Compact AMS, TV = 0.5 MV
6 m x 5 m = 30 m²
POZNAN

Mini AMS, TV = 0.2 MV
3.0 m x 2.3 m = 6.9 m²
ZURICH

Fig. 3. Comparison of the size of modern AMS facilities. The figure is reproduced from a review article on AMS [33], showing the development from the relatively large VERA facility via a compact AMS facility [35] to the 'table-top' Mini AMS facility [40].

of graphitization [41] down to the level of a few µg C for dating human brain cells with the ^{14}C bomb peak [42] (see below). ^{14}C AMS measurements of carbon samples in the µg range were also performed in ice cores from the Monte Rosa mountains in Switzerland [43]. The need for small samples also arises in biomedical investigations with ^{14}C-labelled materials, e.g compound-specific, metabolic studies [44]. Another future use of small samples is continuous-flow AMS [45].

4. The calibration for ^{14}C dating

Libby assumed in his original assessment of radiocarbon dating [16], that the ^{14}C content in the atmosphere was constant in time. A lowering of the atmospheric $^{14}C/^{12}C$ ratio by the addition of ^{14}C-free CO_2 from fossil fuel burning was first observed by Hans Suess in modern wood [46] ('Suess effect'). A few years later, Hessel de Vries found deviations from a constant $^{14}C/^{12}C$ ratio also in older wood of known age (tree rings), concluding that Libby's assumption had to be revised [47]. After de Vries' discovery it was clear that one needed a calibration of ^{14}C as a function of time, in order to determine absolute dates correctly. With the help of dendrochronology (tree-ring dating), it was possible to measure the deviations of ^{14}C from a constant reference value for the last 12,000 years [48] (Fig. 4). During the ice age, i.e. before 12,000 years ago, trees were not abundant and other archives such as corals and sediments had to be employed for calibration, albeit with less precision [50]. Sometimes called the 'final frontier' of radiocarbon dating [51], an updated calibration curve was published in 2009, reaching now back to 50,000 years [52]. Establishing a precise calibration for this full range of radiocarbon dating is still a challenging task.

4.1. On the global validity of the ^{14}C calibration curve

The fact that ^{14}C forms CO_2 in the atmosphere (See Fig. 1), and that the troposphere gets mixed within weeks over large distances is a prerequisite of using a master calibration curve for determining absolute dates everywhere on Earth for land-based material. On the other hand, it is well known that there exist 'reservoir effects', i.e. in the ocean the $^{14}C/^{12}C$ ratio is lower as compared to the atmosphere due to admixtures of deep ocean water depleted in ^{14}C [53]. This leads to a time shift of about 400 years to older ages. Subtle deviations occur even in land plants due to different growing seasons as compared to trees used for the master calibration curve. For example it was found that plants of know age from Egypt show an offset of 19 ± 5 radiocarbon years to older ages [54], because the seasonal low of ^{14}C falls into the growing season late in the year determined by the yearly flooding of the nile.

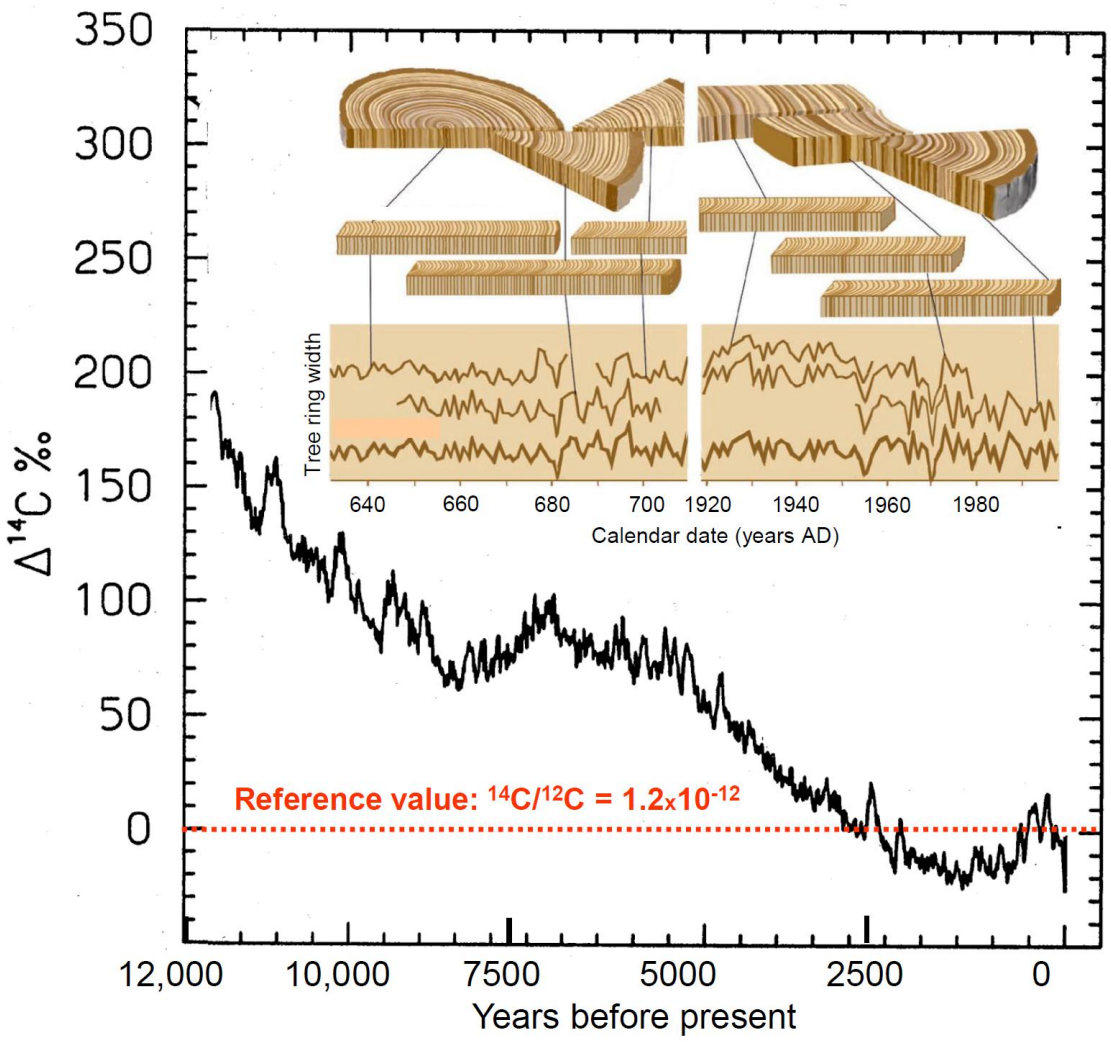


Fig. 4. Deviation of the atmospheric ^{14}C content from a constant reference value for the last 12,000 years [48]. The $\Delta^{14}C$ values were determined by measuring today the ^{14}C content in tree rings, whose absolute date was determined by dendrochronology, and then calculating the ^{14}C content for the time the tree ring was grown by applying the radioactive decay law. As shown by two examples in the figure, continuous tree-ring sequences can be established by matching overlapping tree-ring widths for wood from different time periods [49].

4.2. Radiocarbon dating of ancient human remains

4.2.1 The Iceman Ötzi

The varying ^{14}C content of the atmosphere including relatively fast fluctuations (see Fig. 4) leads to a limit of precision for absolute ^{14}C dating [55]. An example is shown in Figure 5 for the age determination of the famous Iceman Ötzi, a human body which was locked up in ice at high altitude (3210 m a.s.l.) for approximately 5000 years in the Ötztal Alps near the Austrian-Italian border [56]. The relatively precise value for the uncalibrated radiocarbon age of

(4550 ± 19) years BP (BP = before present, i.e. 1950 AD) translates into a calibrated age range of 5300 to 5050 years BP. This is caused by the "wiggles" of the calibration curve. Even though the absolute age cannot be determined with high precision, the result is highly relevant because it clearly puts the Iceman into the end of the Neolithic period making him the oldest, well preserved human body from ancient times.

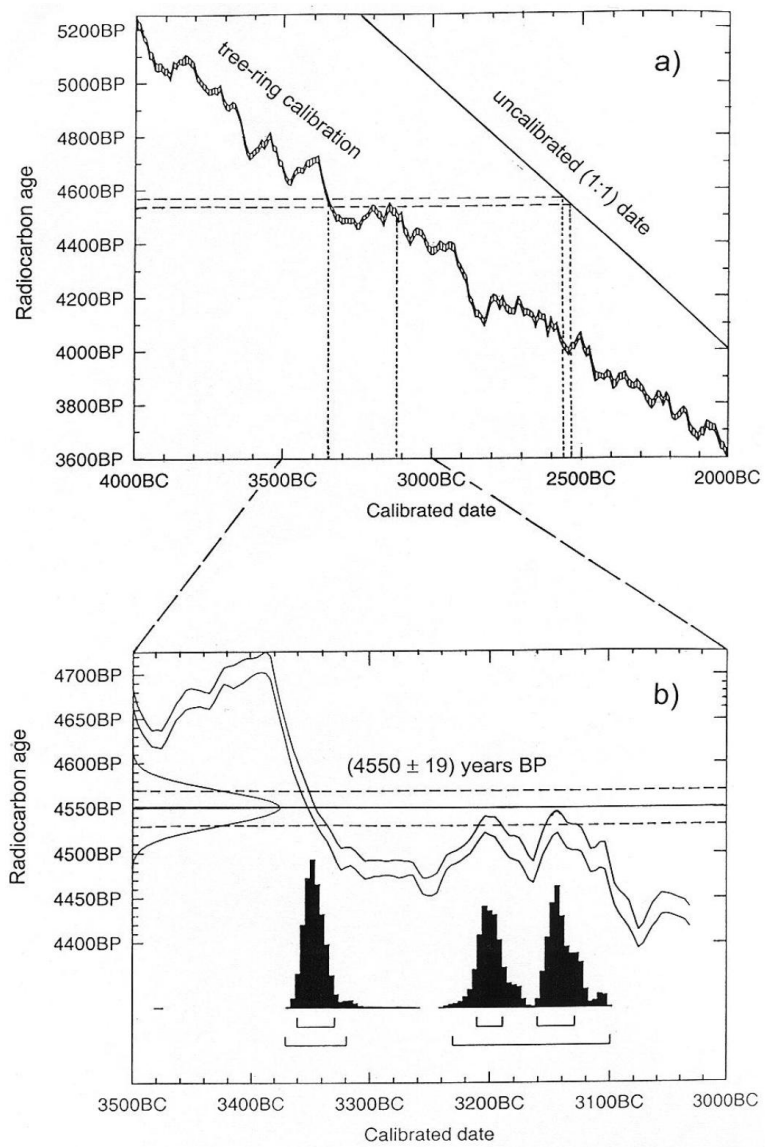


Fig. 5 Calibration of radiocarbon measurements in bone and tissue samples from the Iceman Ötzi [56]. The ^{14}C measurements were performed at the AMS laboratories of the ETH Zürich and the University of Oxford, resulting in a rather precise mean value for the radiocarbon age of 4550 ± 19 years BP. However, due to the wiggles in the calibration curve this translates into three possible time regions (black shaded areas, 95.4 % probability above the large brackets), covering a total calibrated time of range from 3350 to 3100 BC. Note that a BC date (Before Christ) can be converted to calibrated years BP by adding 1950 years.

4.2.2. Early appearance of anatomically modern humans in Europe

Due to the 'out-of-Africa' hypothesis, anatomically modern humans moved into Central Europe some 30 to 40 thousand years ago [57, 58]. Human remains from this period are rare, and some had never been dated by radiocarbon before the advent of AMS, because the beta counting method required too much material. An example of this is a beautiful female skull (Fig 6), which had been found in the Mladec cave in Moravia (Czech Republic) some hundred years ago, and had been preserved at the Museum of Natural History in Vienna in its original state.

Recently, we were allowed to extract small samples from teeth and bone material which were radiocarbon dated at VERA [59]. The result from Table 1 reveals radiocarbon ages of ~31,000 years BP. Note that these are uncalibrated radiocarbon years. A recent calibration with INTCAL09 [52], shifts the absolute age by 4000 to 5000 years further back in time. Similar ages – but about 1000 years older – were recently reported for early presence of humans in a rockshelter of southwestern France [60]. In this case Bayesian analysis (see below) could be employed to reduce the calibrated uncertainty and to narrow down the occupation range. The two lower ^{14}C ages in Table 1 (~26 kyr and ~27 kyr) are likely due to *in situ* degradation of the collagen, and residual contamination which could not be completely removed in the sample preparation, respectively.

Fig. 6. Human fossil specimens from the Mladec cave, which were dated with ^{14}C AMS measurements at VERA [59]. In (a) an upper jaw fragment, Mladec 8, is displayed, exhibiting human features and some 'archaic' features. In (b) a female cranium, Mladec 1, is displayed, exhibiting modern human features. The division on the scales is in centimeters. The ^{14}C dating results from these objects are summarized in Table 1.

Table 1. Radiocarbon ages (uncalibrated) determined for human remains from the Mladeč site in Moravia [59]

Lab Number	Sample Name	Sample material	^{14}C-age (years BP)
VERA-2736	Mladeč 25c	Ulna	26,330 ± 170
VERA-3073	Mladeč 1	Right molar M2 distal half of the crown	31,190 ± 400 (36,500 – 35,000) [a]
VERA-3074	Mladeč 2	Left molar M3 distal half of crown	31,320 ± 400
VERA-3075	Mladeč 8	Left molar M2 mesial-buccal root	30,680 ± 380
VERA-3076A	Mladeč 9a	Right maxillary canine, Lingual half of the root (white-coloured collagen)	31,500 ± 410
VERA-3076B	Mladeč 9a	Right maxillary canine, Lingual half of the root (brown-coulored collagen)	27,370 ± 230

[a] Resulting age range (95.4 % probability) after calibration with INTCAL09 [52].

4.3. Bayesian sequencing

In order to reduce the uncertainty in the calibration process, the method of Bayesian sequencing has been developed in recent years [61-63]. This well-defined mathematical procedure is applicable for a sequence of samples, which allows reasonable assumption about their relative chronological order. This so called *prior* information can then be combined with the uncalibrated radiocarbon dates and used in the calibration process. The result is a *posterior* probability distribution of the calibrated ages, with a considerably reduced uncertainty. Cases where such conditions exist are: (i) Tree ring sequences (every year a new ring is formed); (ii) archaeological excavation, where a sequence of separate phases and/or layers can be identified (deeper layers are older); (iii) a historical ordering of events (e.g. sequence of pharaos). In the following, we will give examples for these three cases.

4.3.1. Dating the Minoan eruption of Santorini

The cataclysmic eruption of the Aegean Island of Santorini in the middle of the second millennium BC is an important time marker for the synchronization of civilizations in the late Bronze Age in the East Mediterranean. Numerous efforts have been undertaken to pin down the exact age of this eruption [64]. So far, the most precise radiocarbon date was obtained from an olive tree branch buried by tephra from the eruption [65]. After identifying 72 tree rings in the

branch and ‘wiggle-matching’ 4 consecutive groups of tree rings, a calibrated date range of 1627 – 1600 years BC (95.4 % confidence level) could be determined for the outermost tree ring. In another investigation [66], a large set of radiocarbon dates from the destruction layer of the volcanic eruption was combined with dates from other islands surrounding Santorini, resulting in a date range of 1659 to 1612 BC (95.4 % confidence level) for the eruption . However, these two dates are disputed by some Egyptologists linking archaeological evidence with the Egyptian historical chronology, who claim that the eruption must have happened approximately 100 years later, i.e. after the beginning of the New Kingdom [67, 68]. Currently, this disagreement has not been resolved.

4.3.2. Radiocarbon dating of the Dynastic Period in Egypt

Since discrepancies such as the one described in the previous section seem to persist, radiocarbon dating of short-lived material directly linked to Kings from the Old, Middle and New Kingdom in Egypt were performed [69]. The full tools of Bayesian sequencing [62, 63] were employed with *a priori* conditions from the chronological order of kings and their respective reign periods based on the Egyptian historical chronology. The result of this extensive investigation is displayed in Figure 7.

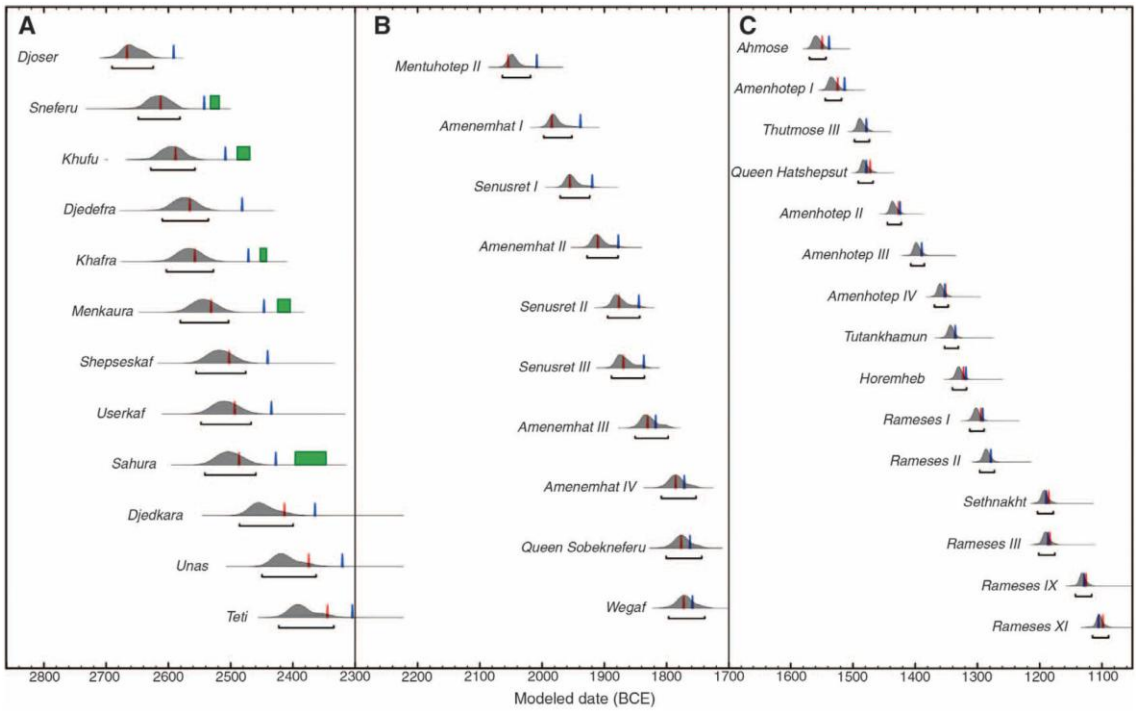


Fig. 7. Result of the Oxford project to radiocarbon date the dynastic periods in Egypt [69]. This figure from Ref. [69] shows a comparison of the Bayesian-modeled ^{14}C dates (gray shaded areas) with various historical chronologies for the accession dates of specific kings in the Old Kingdom (A), Middle Kingdom (B), and New Kingdom (C). Good agreement is reached with the consensus chronology of Shaw [70] (red bars).

The radiocarbon results are compared with different historical chronologies. While the latter agree within each other and with the radiocarbon results for the New Kingdom, there are deviations in the Middle Kingdom, and even more so in the Old Kingdom. Overall, the so called consensus chronology of Shaw [70] shows the best agreement with radiocarbon dating. This result is considered a milestone in the debate whether the absolute time scales of radiocarbon dating and historical chronology of Ancient Egypt are compatible with each other. However, for some critics of radiocarbon dating an uneasiness remains due to the fact that the high precision of the calibrated radiocarbon dates could only be achieved by including the *a priori* assumptions mentioned above.

5. Dating the birth of human cells with the ^{14}C bomb peak

When atmospheric nuclear weapons testing started after the Second World War it was soon noticed that the ^{14}C content in the atmosphere was increasing [71]. Since the natural production happens through the $^{14}N(n,p)^{14}C$ reaction (see Fig. 1), neutrons from nuclear explosions added ^{14}C through the same reaction. In 1963 the atmospheric ^{14}C content was doubled, when the superpowers (USA and USSR) decided to stop the atmospheric nuclear weapons testing. Figure 8a shows the ^{14}C variations during the past 4000 years, and in Figure 8b the $\Delta^{14}C$ values measured in CO_2 of the troposphere during the second half of the 20^{th} century [72, 73] are displayed. The rapid decrease of this excess after the limited Nuclear Test Ban Treaty (NTBT) in 1963 is due to the exchange of CO_2 with the biosphere and the ocean. For this short period of time the radioactive decay of ^{14}C is negligible as indicated by the almost horizontal decay curve. Assuming that the varying atmospheric ^{14}C content is also reflected in biological material, it can be used to date such material with an uncertainty of only one to two years. This condition triggered a very interesting project by the Department of Cell and Molecular Biology of the Karolinska Institute in Stockholm [74]. The basic assumption was formulated in the following way [74]:

> "Most molecules in a cell are in constant flux, with the unique exception of genomic DNA, which is not exchanged after a cell has gone through its last division. The level of ^{14}C integrated into genomic DNA should thus reflect the level in the atmosphere at any given point, and we hypothesized that determination of ^{14}C levels in genomic DNA could be used to retrospectively establish the birth date of cells in the human body."

Table 2 summarizes the composition of human DNA, which shows that DNA from 10 cell nuclei must be collected to obtain 1 ^{14}C atom. In order to make meaningful measurements, DNA from millions of cells must be extracted. Such a task can be achieved with modern methods of molecular biology, distinguishing also neurons from non-neuronal cells in the extraction procedure. Depending on the subjects to be studied, the total amount of carbon available for AMS measurements is sometimes quite low (<100 µg C).

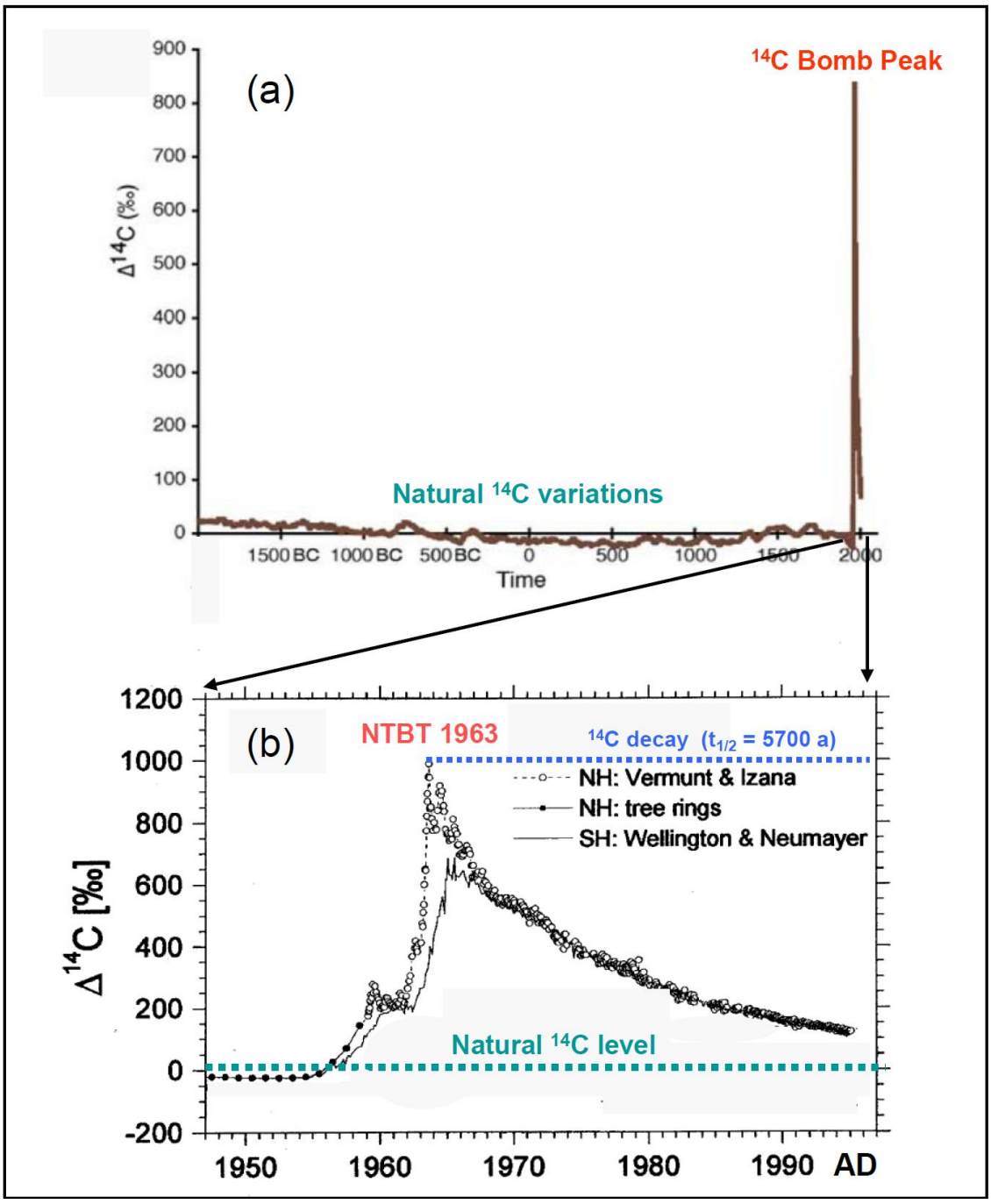


Fig. 8. The ^{14}C bomb peak. In (a) the variation of the ^{14}C content in tropospheric CO_2 during the last 4000 years including the ^{14}C bomb peak are shown [74]. In (b) a detailed display of the Δ^{14}C values measured for the last 50 years in tropospheric CO_2 at stations in the northern hemisphere (NH) and the southern hemisphere (SH) is shown [72, 73]. The tree ring measurements (filled symbols) around 1950 AD show a ^{14}C depletion due to the fossil fuel effect [46].

Table 2. Composition of the DNA molecule and its ^{14}C content (a physicist's view)

Basic composition of DNA:	Macromolecule with $3x10^9$ base pairs (bp)
Chemical sum formula per bp:	$C_{20}H_{23}N_7O_{13}P_2$ and $C_{19}H_{22}N_8O_{13}P_2$
Molecular weight:.	~630 Daltons (Da) per base pair, total ~$1.9x10^{12}$ Da
Mass of DNA per cell:	2 DNA per cell = 2 x 3 pg = 6 pg
Mass of carbon (40 wt% C):	2.4 pg
Total length of DNA per cell:	2 x $3x10^9$ x (0.34 nm, distance between bp) = 2 m
C atoms of DNA per cell:	2 x $3x10^9$ x (20 C) = $1.2x10^{11}$ C atoms
$^{14}C/^{12}C$:	$1.2x10^{-12}$
DNA of 10 cells:	~1 ^{14}C atom
15 million cells:	1.5 million ^{14}C atoms
C from DNA of 15 million cells:	~36 µg C
Total ^{14}C AMS detection efficiency:	~2% → ~30,000 ^{14}C atoms detected

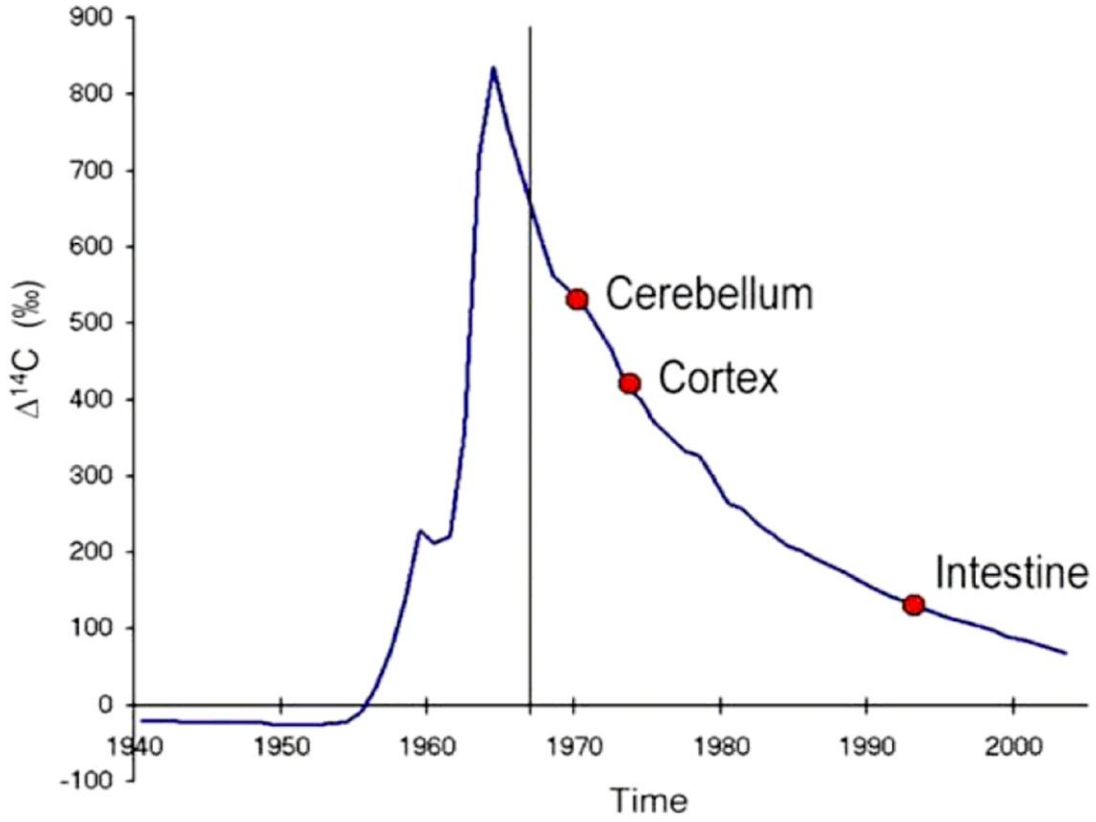


Fig. 9. ^{14}C bomb peak dating. The $\Delta^{14}C$ values measured for different human cells of an individual whose birth date (vertical line) is known indicate when the respective organ forms new cells [74].

Figure 9 demonstrates how the measured $\Delta^{14}C$ can be used to assign an average birth date of cells for the respective organs of an individual whose life span is known. It is of

particular interest to find out from such measurements whether new cells are formed after the birth of the individual.

Within a collaboration between VERA and the Karolinska Institute we have investigated the human olfactory bulb, which required the reduction of the carbon sample material down to the few-microgram level [75]. Since a long chain of procedures is necessary to prepare the final graphite sample for the ^{14}C AMS measurements from the original human material (olfactory bulb), a very careful protocol had to be developed to avoid any contamination with foreign carbon material. Fig. 10 displays the $\Delta^{14}C$ results measured in human olfactory bulbs of several individuals for non-neuronal cells and for neurons, respectively [42]. Whereas there is some turnover after birth apparent for non-neuronal cells, there is essentially no neurogenesis after birth for olfactory bulb neurons. This is in contrast to the finding for rodents, which form 50% new neurons after birth [76].

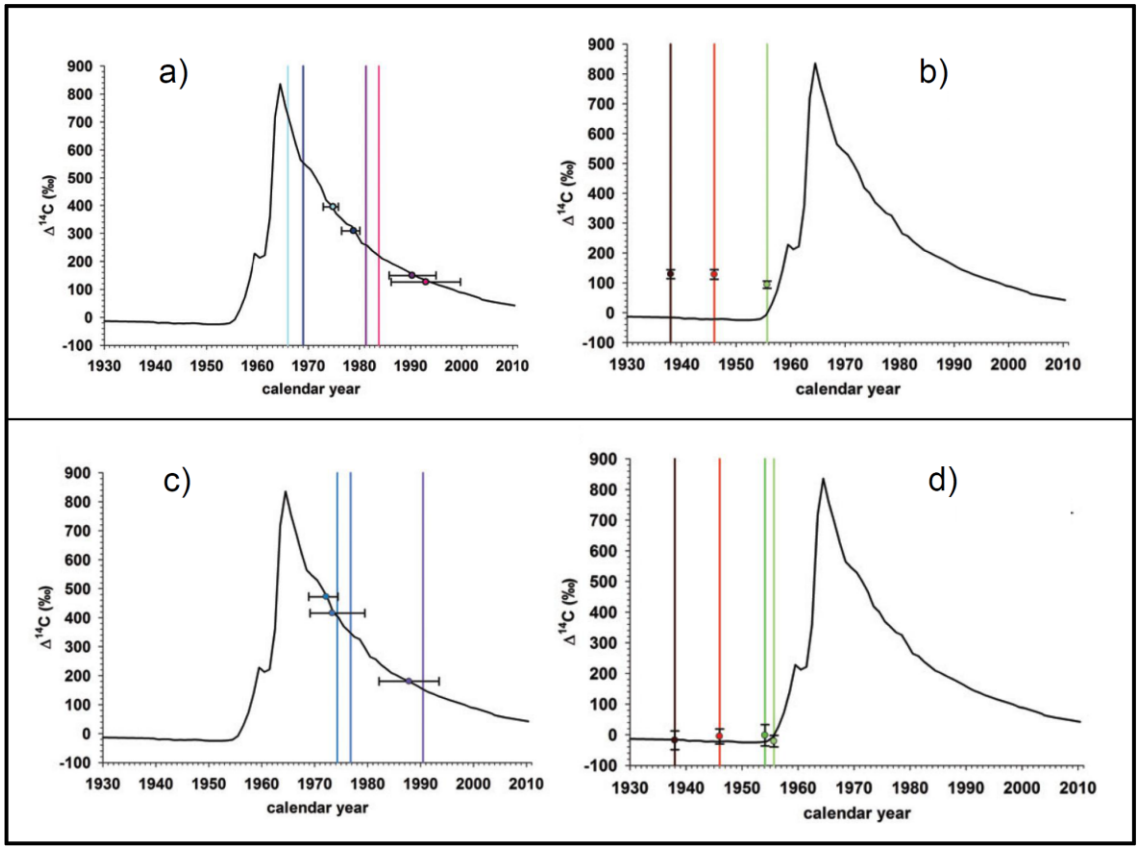


Fig. 10. Results of $\Delta^{14}C$ measurements in DNA extracted from non-neuronal cells (a and b) and neurons (c and d) for the human olfactory bulb of individuals born before and after the bomb peak (vertical lines) [42]. In (a) and (b) a clear indication of post-birth production for non-neuronal cells is observed, whereas in (c) and (d) neurogenesis after birth is essentially absent [42].

6. Conclusion

In the 60 years after its invention, radiocarbon dating has developed into a versatile tool to help solving problems in many branches of science and the humanities. As such it has fulfilled the promise which was expressed in the quotation of Libby's 1960 Nobel Prize in Chemistry (see above). Radiocarbon is used most successfully when it is not pushed beyond the inherent limitation of the precision due to the necessity to use the 'wiggly' calibration curve. Although Bayesian sequencing helps to overcome this limitation, it has to be exercised with great care in order not to introduce unwanted effects of the method [77].

In principle, a calibration could be avoided if $^{14}C/^{14}N^*$ ratios rather than ^{14}C alone are measured. A first attempt at such an absolute ^{14}C dating has been reported [78], where the possibility was discussed that the low energy of the recoiling, radiogenic $^{14}N^*$ atoms (< 7eV) after the beta decay of ^{14}C would lead to a considerable retention probability of $^{14}N^*$ at the site of the parent ^{14}C atom in an organic molecule. Currently, it is still an open question whether the ensuing minute changes of the molecular properties in a sample material can be traced with the required sensitivity. Nevertheless, it poses a challenging problem for the future, particularly also for other, potentially interesting radioisotopes such as ^{41}Ca ($t_{1/2}$ = 104,000 yr), where no calibration is possible [79].

References

[1] V. F. Hess, *Über die Absorption der γ-Strahlen in der Atmosphäre, Physik. Zeitschr*. **12** (1911) 998.

[2] V. F. Hess, *Über Beobachtungen der durchdringenden Strahlung bei sieben Freiballonfahrten, Physik. Zeitschr.* **13** (1912) 1084.

[3] W. Kolhörster, *Messungen der durchdringenden Strahlung im Freiballon in größeren Höhen, Physik. Zeitschr.* **14** (1913) 1153.

[4] W. Kolhörster, *Messungen der durchdringenden Strahlung bis in Höhen von 9300 m, Verh. d. Deutschen Phys. Ges*. **15** (1914) 719.

[5] R. A. Millikan, I. S. Bowen, *High frequency rays of cosmic origin I. Sounding balloon observations at extreme altitudes, Phys. Rev*. **27** (1926) 353.

[6] C. D. Anderson, *The apparent existence of easily deflectable positives, Science* **76** (1932) 238.

[7] C. D. Anderson, *The positive electron, Phys. Rev*. **43** (1933) 491.

[8] C. D. Anderson, S. H. Neddermeyer, *Cloud chamber observations of cosmic rays at 4300 meters elevation and near sea-level, Phys. Rev*. **50** (1936) 263.

[9] S. H. Neddermeyer, C. D. Anderson, *Note on the nature of cosmic-ray particles*, *Phys. Rev*. **51** (1937) 884.

[10] J. C. Street, E. C. Stevenson, *New evidence for the existence of a particle of mass intermediate between the proton and electron*, *Phys. Rev*. **52** (1937) 1003.

[11] M. Blau, H. Wambacher, *Disintegration process by cosmic rays with the simultaneous emission of several heavy particles*, *Nature* **140** (1937) 585.

[12] G. P. S. Occhialini, C. F. Powell, *Nuclear disintegrations produced by slow charged particles of small mass*, *Nature* **159** (1947)186.

[13] G. D. Rochester, C. C. Butler, *Evidence for the existence of new unstable elementary particles*, *Nature* **160** (1947) 855.

[14] W. F. Libby, *Atmospheric helium three and radiocarbon from cosmic radiation*, *Phys. Rev*. **69** (1946) 671.

[15] E. C. Anderson, W. F. Libby, S. Weinhouse, A. F. Reid, A. D. Kirshenbaum, A. V. Grosse, *Natural radiocarbon from cosmic radiation*, *Phys. Rev*. **72** (1947) 931.

[16] J. R. Arnold, W. F. Libby, *Age determination by radiocarbon content: checks with samples of known age*, *Science* **110** (1949) 678.

[17] C. A. M. Brenninkmeijer, M. R. Manning, D. C. Lowe, G. Wallace, R. J. Sparks, A. Volz-Thomas, *Interhemispheric asymmetry in OH abundance inferred from measurements of atmospheric ^{14}CO*, *Nature* **356** (1992) 50.

[18] P. J. Crutzen, *My life with O_3, NO_x, and other YZO_x compounds (Nobel Lecture)*, *Angew. Chem. Int. Ed. Engl.* **35** (1996) 1758.

[19] H. Oeschger, J. Houtermans, H. Loosli, M. Wahlen, *The constancy of cosmic radiation from isotope studies in meteorites and on Earth*, in: *12th Nobel Symposium on Radiocarbon Variations and Absolute Chronology*, I. U. Olssen, ed., John Wiley & Sons, New York (1970) p. 471.

[20] M. Anbar, *The limitations of mass spectrometric radiocarbon dating using CN^- ions*, in: H. E. Gove, ed., *Proceedings of the First Conference on Radiocarbon Dating with Accelerators*, University of Rochester (1978) 152.

[21] W. Henning, W. A. Bell, P. J. Billquist, B. G. Glagola, W. Kutschera, Z. Liu, H. F. Lucas, M. Paul, K. E. Rehm, J. L. Yntema, *Calcium-41 concentration in terrestrial materials - prospects for dating of Pleistocene samples*, *Science* **236** (1987) 725.

[22] D. Fink, J. Klein, R. Middleton, *^{41}Ca: past, present and future*, *Nucl. Instrum. Meth. B* **52** (1990) 572.

[23] R. A. Muller, *Radioisotope dating with a cyclotron*, *Science* **196** (1977) 489.

[24] C. L. Bennet, R. P. Beukens, M. R. Clover, H. E. Gove, R. B. Liebert, A. E. Litherland, K. H. Purser, W. E. Sondheim, *Radiocarbon dating using electrostatic accelerators: negative ions provide the key*, *Science* **198** (1977) 508.

[25] D. E. Nelson, R. G. Korteling, W. R. Stott, Carbon-14: direct detection at natural concentrations, *Science* **198** (1977) 507.

[26] K. H. Purser, R. B. Liebert, A. E. Litherland, R. P. Beukens, H. E. Gove, C. L. Bennet, H. R. Clover, W. E. Sondheim, *An attempt to detect stable N- ions from a sputter ion source and some*

implications of the results fort he design of tandems for ultrasensitive carbon analysis, Revue de Physique Applicée **12** (1977) 1487.

[27] A. P. McNichol, E. A. Osborne, A. R. Gargon, B. Fry, G. A. Jones, *TIC, TOC, DIC, PIC, POC – unique aspects in the preparation of oceanographic samples for ^{14}C-AMS, Nucl. Instrum. Meth. B* **92** (1994) 162.

[28] G. A. Jones, A. P. McNichol, K. F. von Reden, R. J. Schneider, *The National Ocean Sciences AMS Facility at Woods Hole Oceanographic Institution, Nucl. Instrum. Meth. B* **52** (1990) 278.

[29] A. P. McNichol, R. J. Schneider, K. F. von Reden, A. R. Gagnon, K. L. Elder, R. M. Key, P. D. Quay, *Ten years after – The WOCE AMS radiocarbon program, Nucl. Instrum. Meth. B* **172** (2000) 479.

[30] R. M. Key, A. Kozyr, C. L. Sabine, K. Lee, R. Wannikhof, J. L. Bullister, R. A. Feely, F. J., Millero, C. Mordy, T.-H. Peng, *A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochemical Journal* **18** (2004) GB 4031, pp. 23.

[31] K. H. Purser, R. J. Schneider, J. McG. Dobbs, R. Post, *A preliminary description of a dedicated commercial ultra-sensitive mass spectrometer for direct atom counting of ^{14}C*, in: W. Henning, W. Kutschera, R.k. Smither, J. L. Yntema, eds., *Proceedings of the Symposium on Accelerator Mass Spectrometry*, Argonne National Laboratory, Physics Division Report **ANL/PHY-81-1** (1981) p. 431.

[32] K. H. Purser, T. H. Smick, R. K. Purser, *A precision ^{14}C accelerator mass spectrometer, Nucl. Instrum. Meth. B* **52** (1990) 263.

[33] W. Kutschera, *Progress in isotope analysis at ultra-trace level by AMS, International Journal of Mass Spectrometry* **242** (2005) 145.

[34] H. W. Lee, A. Galindo-Uribarri, K. H. Chang, L. R. Kilius, A. E. Litherland, *The $(^{12}CH_2)^{2+}$ molecule and radiocarbon dating by accelerator mass spectrometry, Nucl. Instrum. Meth. B* **5** (1984) 208.

[35] T. Goslar, J. Czernik, E. Goslar, *Low-energy ^{14}C AMS in Poznan Radiocarbon Laboratory, Poland, Nucl. Instrum. Meth. B* **223-224** (2004) 5.

[36] M. Suter, S. Jacob, H. A. Synal, *AMS of ^{14}C at low energies, Nucl. Instrum. Meth. B* **123** (1997) 148.

[37] H.-A. Synal, S. Jacob, M. Suter, *The PSI/ETH small radiocarbon dating system, Nucl. Instrum. Meth. B* **172** (2000) 1.

[38] G. M. Klody, J. B. Schroeder, G. A. Norton, R. L. Loger, R. L. Kitchen, M. L. Sundquist, *New results for single stage low energy carbon AMS, Nucl. Instrum. Meth. B* **240** (2005) 464.

[39] H.-A. Synal, M. Döbeli, S. Jacob, M. Stocker, M. Suter, *Radiocarbon AMS towards its low-energy limits, Nucl. Instrum. Meth. B* **223-224** (2004) 339.

[40] H.-A. Synal, M. Stocker, M. Suter, MICADAS: *A new compact radiocarbon AMS system, Nucl. Instrum. Meth. B* **259** (2007) 7.

[41] J. S. Vogel, J. R. Southon, D. E. Nelson, T. A. Brown, *Performance of catalytically condensed carbon for use in accelerator mass spectrometry, Nucl. Instrum. Meth. B* **5** (1984) 289.

[42] O. Bergmann, J. Liebl, S. Bernards, K. Alkass, M. S. Y. Yeung, P. Steier, W. Kutschera, L. Johnson, M. Landén, H. Druid, K. L. Spalding, J. Frisén, *The age of olfactory bulb neurons in humans, Neuron* **74** (2012) 634.

[43] T. M. Jenk, S. Szidat, D. Bolius, M. Sigl, H. W. Gäggeler, L. Wacker, M. Ruff, C. Barbante, C. F. Boutron, M. Schwikowski, *A novel radiocarbon dating technique applied to an ice core from the Alps indicating late Pleistocene ages*, *J. Geophys. Res*. **114** (2009) D14305.

[44] S. R. Dueker, Le Thuy Vuong, B. Faulkner, B. A. Buchholz, J. S. Vogel, *Disposition of ^{14}C-ß-carotene following delivery with autologous triacyclglyceride-rich lipoproteins*, *Nucl. Instrum. Meth. B* **259** (2007) 767.

[45] K. F. von Reden, M. L. Roberts, C. P. McIntyre, J. R. Burton, *Design and reality: Continuous-flow accelerator mass spectrometry (CFAMS*), *Nucl. Instrum. Meth. B* **269** (2011) 3176.

[46] H. E. Suess, *Radiocarbon concentration in modern wood*, *Science* **122** (1955) 415.

[47] H. De Vries: *Variation in concentration of radiocarbon with time and location on earth*. In: *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen*, North-Holland Publishing Company, Amsterdam, Vol. **61** (1958) p. 1.

[48] M. Stuiver et al.,*INTCAL98 radiocarbon age calibration, 24,000 – 0 cal BP*, *Radiocarbon* **40/3** (1998) 1041.

[49] E. M. Wild, W. Kutschera, *^{14}C und die Chronologie Ägyptens*, *Spektrum der Wissenschaft*, Heidelberg (Dez. 2011) 48.

[50] E. Bard, F. Rostek, G. Ménot-Combes, *A better radiocarbon clock*, *Science* **303** (2004) 178.

[51] M. Balter, *Radiocarbon dating's final frontier*, *Science* **313** (2006) 1560.

[52] P. J. Reimer et al.: *INTCAL09 and MARINE09 radiocarbon age calibration curves, 0–50,000 years cal BP*. *Radiocarbon* **51** (2009) 1111.

[53] S. Bowman, *Radiocarbon Dating (Interpreting the Past)*, *British Museums Publications*, London (1990) p. 24.

[54] M.W. Dee, F. Brock, S. A. Harris, C. Bronk Ramsey, A. J. Shortland, T. F. G. Higham, J. M. Rowland, *Investigating the likelihood of a reservoir offset in the radiocarbon record for ancient Egypt*, *Journal of Archaeological Science* **37** (2010) 687.

[55] T. P. Guilderson, P. J. Reimer, T. A. Brown, *The boon and bane of radiocarbon dating*, *Science* **307** (2005) 362.

[56] W. Kutschera, W. Müller, *"Isotope language" of the Alpine Iceman investigated with AMS and MS*, *Nucl. Instrum. Meth. B* **204** (2003) 705.

[57] P. Mellars, *A new radiocarbon revolution and the dispersal of modern humans in Eurasia*, *Nature* **439** (2006) 931.

[58] J. R. Stewart, C. B. Stringer, *Human evolution out of Africa: the role of refugia and climate change*, *Science* **335** (2012) 1318.

[59] E. M. Wild, M. Teschler-Nicola, W. Kutschera, P. Steier, E. Trinkhaus, W. Wanek, *Direct dating of Early Upper Paleolithic human remains from Mladec*, *Nature* **435** (2005) 332.

[60] R. White et al., *Context and dating of Aurignacian vulvar representations from Abri Castanet*, France, *Proc. Nat'l. Acad. Sci*. Early Edition (2012), www.pnas.org/cgi/doi/10.1073/pnas.1119663109

[61] C. E. Buck, J. B. Kenworth, C. D. Litton, A. F. M. Smith, *Combining archaeological and radiocarbon information: a Bayesian approach to calibration*, *Antiquity* **65** (1991) 808.

[62] C. Bronk Ramsey, *Bayesian analysis of radiocarbon dates*, *Radiocarbon* **51/1** (2009) 337.

[63] C. Bronk Ramsey, *dealing with outliers and offsets in radiocarbon dating*, *Radiocarbon* **51/3** (2009) 1023.

[64] D. A. Warburton, ed., *Time's Up! Dating the Minoan Eruption of Santorini*, *Proceedings of the Minoan Eruption Workshop*, Sandbjerg 2007, Monographs of the Danish Institute at Athens, Vol. **10** (2009) pp. 298.

[65] W. L. Friedrich, B. Kromer, M. Friedrich, J. Heinemeier, T. Pfeiffer, S. Talamo, *Santorini eruption dated to 1627 – 1600 B.C.*, *Science* **312** (2006) 548.

[66] S. W. Manning, C. Bronk Ramsey, W. Kutschera, T. Higham, B. Kromer, P. Steier, E. M. Wild, *Chronology for the Aegean Late Bronze Age 1700 – 1400 B.C.*, *Science* **312** (2006) 565.

[67] M. Balter, *New carbon dates support revised history of ancient Mediterranean*, *Science* **312** (2006) 508.

[68] M. Bietak, F. Höflmayer, *Introduction: high and low chronology*, In: M. Bietak, E. Czerny, eds., *The Synchronisation of civilisations in the Eastern Mediterranean in the Second Millenium BC – III*. Austrian Academy of Sciences, Vienna (2007) p. 13.

[69] C. Bronk Ramsey, M. W. Dee, J. M. Rowland, T. F. G. Higham, S. A. Harris, F. Brock, A. Quiles, E. M. Wild, E. S. Marcus, A. J. Shortland, *Radiocarbon-based chronology for Dynastic Egypt*, *Science* **328** (2010) 1554.

[70] I. Shaw, *The Oxford History of Ancient Egypt*, Oxford University Press, Oxford (2003).

[71] H. de Vries, *Atomic bomb effect: Variation of radiocarbon in plants, shells, and snails in the past 4 years*, *Science* **128** (1958) 250.

[72] I. Levin, V. Hesshaimer, *Radiocarbon – a unique tracer of global carbon cycle dynamics*, *Radiocarbon* **42/1** (2000) 69.

[73] I. Levin, T. Naegler, B. Kromer, M. Diehl, R. J. Francey, A. J. Gomez-Pelaez, L. P. Steele, D. Wagenbach, R. Weller, D. E. Worthy, *Observations and modeling of the global distribution and long-term trend of atmospheric $^{14}CO_2$*, *Tellus* **62B** (2010) 26.

[74] K. L. Spalding, R. D. Bhardwaj, B. A. Buchholz, H. Druid, J. Frisén, *Retrospective birth dating of cells in humans*, *Cell* **122** (2005) 133.

[75] J. Liebl, *C-14 bomb peak dating of human DNA samples at the microgram level*, PhD thesis, University of Vienna (2011).

[76] I. Imayoshi, M. Sakamoto, T. Ohtska, K. Takao, T. Miyakawa, M. Yamaguchi, K. Mori, T. Ikeda, S. Itohara, R. Kageyama, *Roles of continuous neurogenesis in the structural and functional integrity of the adult forebrain*, *Nature Neuroscience* **11** (2008) 1153.

[77] F. Weninger, P. Steier, W. Kutschera, E. M. Wild, *Robust Bayesian analysis, an attempt to improve Bayesian sequencing*, *Radiocarbon* **52/2-3** (2010) 962.

[78] J. Szabo, I. Carmi, D. Segal, E. U. Mintz, *An attempt at absolute ^{14}C dating*, *Radiocarbon* **40** (1998) 77.

[79] W. Kutschera, *Accelerator mass spectrometry, analyzing our world atom by atom*, *Amer. Inst. Phys. Conf. Series* **495** (1999) 407.