

4.4 Radiocarbon dating of the Iceman Ötzi with accelerator mass spectrometry

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The discovery of the Iceman

On 19 September 1991 an extraordinary archaeological discovery was made at a high-altitude mountain pass (Tisenjoch, 3210 m) of the Ötztal Alps near the Austrian-Italian border. Two mountain hikers from Nürnberg, Erika and Helmut Simon, after having scaled the Finail Peak (3516 m) that day were on their way back to the Similaun mountain hut (3019 m) located at the lowest part of a mountain ridge connecting the Finail Peak with the Similaun (3607). This ridge forms the border between Austria (to the north) and Italy (to the south). As the hikers approached a shallow ice-filled depression along the ridge, they were startled by seeing the body of a man sticking half-way out from the ice. Unusual climatic conditions in the summer of 1991 (including dust from Sahara resulting in enhanced melting of snow) had partly freed the body from his icy grave. The Iceman was later nicknamed “Ötzi”, after the mountain range where he was found. Two days after the first discovery, Hans Kammerlander and Reinhold Messner, two famous mountain climbers from South Tyrol happened to arrive at the site, and the photo of figure 1 shows them watching the Iceman. Messner made a first guess at the age of the man and thought he might have died some 500 years ago. Another two days later (on 23 September 1991) the body was recovered from the ice by Rainer Henn from the Institute of Forensic Medicine at the University of Innsbruck, and was flown to his institute by helicopter. Next day, when Konrad Spindler from the Institute of Pre- and Protohistory of the University of Innsbruck saw the unusual pieces of equipment found together with the body (in particular an ax with a bronze-like blade), he estimated a very old age (~4000 years) of the find. This immediately created great excitement for both scientists and the public, resulting in many “colorful” events in the ensuing weeks.

One of the more serious events was the determination of the exact location of the finding place as it was very close to the Austrian-Italian border. According to the Treaty of Saint Germain from 1919, the border was supposed to run along the water divide between the river Inn to the north and the river Etsch (Adige) to the south. After an official remeasuring of the border line it was established that the Iceman had been found 92 m inside Italian territory. According to international regulations, the Iceman therefore belonged to Italy, even though the meltwater from the discovery site was now draining towards the Inn. When the border was fixed originally, the site was filled with ice and snow, and it was not possible to determine the exact location of the water divide. However, the Iceman remained more than 6 years at the University of Innsbruck, from where most of the scientific investigations were organized. In January 1998, Ötzi was brought to his final home at the newly established Archaeological Museum in Bolzano, South Tyrol, Italy, where he is on display for the public. There he is safely stored in a glass vitrine with controlled temperature (-6°C) and humidity (98%) at glacier-like conditions. In addition, an impressive display of his clothing and equipment can be visited. Popular write-ups of the Iceman story are available in German [1] and in English [2]. Scientific investigations of the Iceman are published in a series of monographs, with the latest one concentrating on paleobotanical results [3].



Fig. 1. The partly freed body of the Iceman as watched by two famous mountain climbers from South Tyrol, Hans Kammerlander (left) and Reinhold Messner (right). The picture was taken by K. Fritz (Photo Paul Hanny). Kammerlander holds part of a wooden structure later identified as a carrying support of Ötzi. In the right upper corner the bow can be seen, its lower part stuck in the ice and the upper one leaning against the rocks. Just below the tip of the ski pole held by Messner one can see the smashed remains of a container made of bark from a birch-tree, probably used to carry equipment for making fire.

¹⁴C dating of the Iceman

The AMS laboratories in Zürich and Oxford performed the first ¹⁴C measurements on milligram amounts of bone and tissue from the Iceman [4, 5]. In Figure 2 the determination of the calibrated date from the measured radiocarbon age is depicted. Although this procedure looks complicated, it is well established among the international radiocarbon community. It is apparent that the calibrated date covers a much larger time range than the uncalibrated radiocarbon age, which is obtained directly from the results of the AMS measurements. This is due to the “wiggles” in the calibration curve, which results in a 95.4% (2σ) confidence range of 3370 to 3100 BC (For more details on the calibration issue see the section on ‘The radiocarbon dating method’ below). Nevertheless, the ¹⁴C dating result unambiguously established that the Iceman lived before the Bronze Age (2400 – 800 BC), at the end of the Neolithic period. Besides the body of the Iceman itself, a lot of equipment and other material was recovered from the finding place, apparently belonging to the Iceman as evidenced from ¹⁴C dating at the AMS facilities of Uppsala, Gif-sur-Yvette, and Vienna [6]. In addition, some 500 kg of sediments were collected from the discovery site, and botanical and other remains were extracted by the Institute of Botany of the University of Innsbruck for ¹⁴C dating at the Vienna Environmental Research Accelerator (VERA).

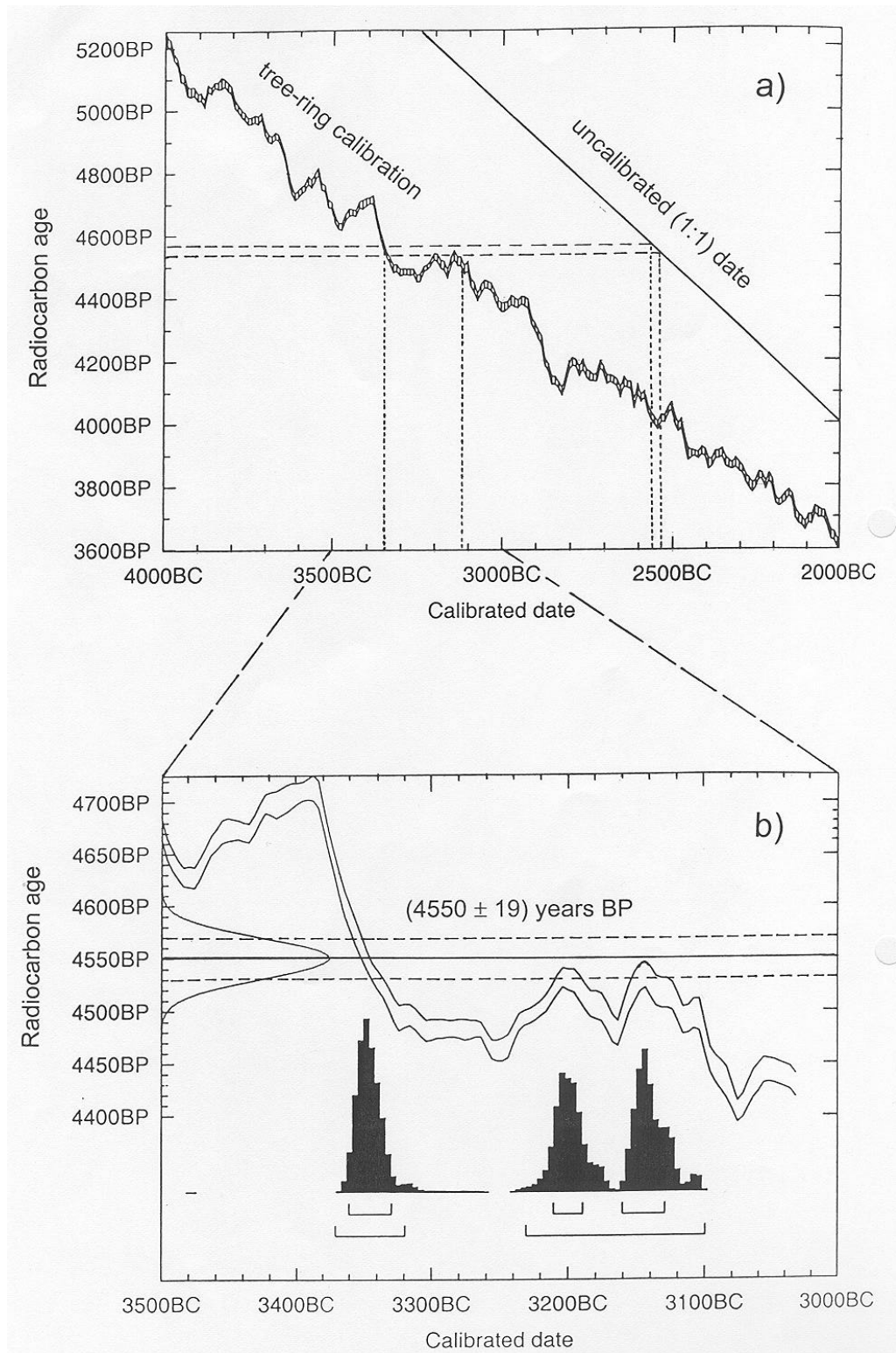


Fig. 2. The determination of the age of the Iceman from ^{14}C measurements at the AMS laboratories of Zürich [4] and Oxford [5]. The combined radiocarbon age from these measurements is 4550 ± 19 years BP (Before Present = 1950 AD). The error is the 68.2% (1σ) confidence value. The uncalibrated age is translated into a calibrated age with the help of the computer program OxCal using the INTCAL98 tree-ring calibration curve [12]. (a) Calibration curve from 4000 to 2000 BC (Before Christ). The straight line at 45° indicates a 1:1 transformation of the radiocarbon age into an uncalibrated calendar date. The intersection of the radiocarbon age with this line and the tree-ring calibration curve shows that the calibrated date is approximately 650 years older. (b) The enlarged “wiggly” section of the calibration curve leads to three different solutions for the calendar date spanning 250 years. The small rectangular brackets beneath the peaks indicate the distribution of the 68.2% (1σ) confidence ranges into three sections of 3360-3300 BC (29.3%), 3210-3190 BC (19.8%), and 3160-3130 BC (19.1%). The large brackets indicate the 95.4% (2σ) confidence ranges of 3370-3320 BC (34.3%), and 3230-3100 BC (61.1%).

¹⁴C dating of various materials from the Ötzi finding place

There exist strong evidence that early in the Holocene (which covers the last 10,000 years since the end of the last ice age) there were periods considerably warmer than today. Such changes in temperature can be most sensitively traced at high altitudes, where the vegetation reaches its limit of existence. For example, tree logs set free by the rapidly receding Pasterze Glacier of the Grossglockner, the highest mountain in the Austrian Alps, have been ¹⁴C-dated to the period between 8000 and 6900 BC [7]. These finds indicate that trees must have grown during that time at locations still covered by glaciers today. Similarly, one might expect that the high-altitude pass where Ötzi was found may have enjoyed ice-free periods also at other times. Figure 3 summarizes the results of 64 ¹⁴C measurements, most of them performed at VERA [8].

¹⁴C-dating of material from the finding place of the Iceman
(all dates are calibrated 2-σ ranges)

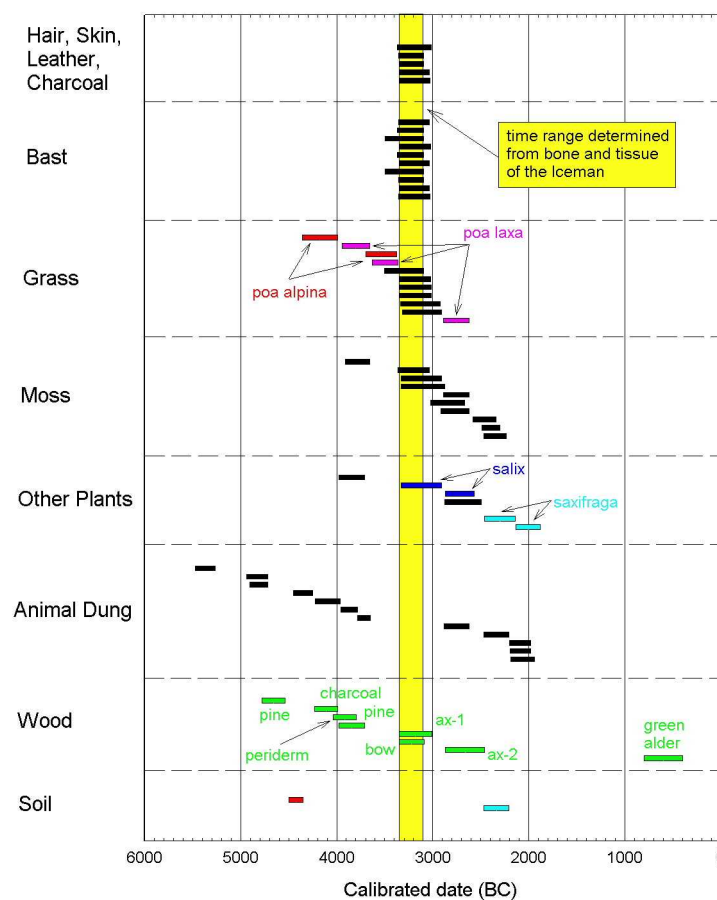


Fig. 3. Comparison of the ages for various materials collected at the discovery site of the Iceman, determined from ¹⁴C measurements at the AMS facility VERA in Vienna [10]. These results indicate that the site of the Iceman was probably ice-free also at considerably earlier and later times, and used as a high-altitude pathway across the Alps. See text for a more detailed discussion of the results.

The materials are grouped into different species. It is apparent that they are spread over a large time range from approximately 5000 to 2000 BC. The upper two groups in figure 3 fall within the time period determined from body samples of the Iceman himself [4,5], and are thus most likely part of his belongings. The group labeled “grass” includes several different species. Those falling within the Ötzi period are species which cannot grow at these altitudes and must have been brought to the place, probably by Ötzi himself. The grasses labeled *poa alpina* and *poa laxa* presently grow up to altitudes of 3000 and 3100 m, respectively. Since they apparently grew also at 3210 m (the Ötzi finding place) indicates that a warmer period than today may have existed at the respective time period. Mosses are less sensitive indicators of temperature changes, since they grow at these altitudes at a variety of climatic conditions. The group labeled “other plants” include *salix herbacea*, which grows in shallow depressions filled with snow for most of the year, whereas *saxifraga moschata* can be found today up to 50 to 120 m below the Ötzi finding place. The other two samples are needles from trees which do not grow at these altitudes, probably blown up by winds across the surface of the glacier. Dates from animal dung of caprine origin (capricorn, goat, sheep, etc.) spread over a large time range. It is perhaps not surprising that those remains are found there, as these are typical mountain animals. The lack of samples from this group during the Ötzi period looks curious,

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but may be explained by the observation that animals actually prefer to lie down on snow to cool off in summer time, and do not like bare rock as was probably present during Ötzi's time. The group labeled "wood" are samples which must have been brought up by man. The two samples, ax-1 and bow, clearly belong to the Iceman. Among the older samples, the most significant find is a piece of charcoal, which indicates that thousand years before the Iceman a human being may have visited the place making fire right there or having brought remains of it to the site. The youngest sample, green alder, falls into the Iron Age (Hallstatt period), and shows signs of being cut and worked on by man. It is the first sample of this period found in this particular region of the Alps. Finally, two samples of soil have been collected in a spot close to the Ötzi site by two Italian scientists, and the total organic content of this material was ^{14}C dated [9]. The older sample came from a somewhat thicker layer of soil, indicating a possibly warmer climate as compared to the younger one.

The new ^{14}C dates raise hopes that climate indicators are present at this unique site. Combined with information from other regions in the Alps about climatic changes during the Holocene, this may allow one to link the presence of the Iceman to some climatic condition which favored his appearance at this high altitude. Although, at this time, we can only hint at such a connection, it may be another stone in the puzzle to solve the mystery of the Iceman's origin, and his perishing at this lonely site high up in the mountains.

The radiocarbon dating method

Carbon forms the basic building blocks of organic compounds and therefore is an essential part of all life on Earth. As a consequence, the human body with an average weight of 70 kg contains approximately 16 kg of carbon. Almost all of this carbon is formed by the two stable isotopes, ^{12}C (98.9%) and ^{13}C (1.1%). However, a minute fraction of the carbon consists of the long-lived radioisotope ^{14}C ($1.2 \cdot 10^{-12}$), originating from cosmic-ray interaction in the atmosphere (see below). Since the half-life of ^{14}C is 5730 years, the total ^{14}C activity of our body is 3700 Becquerel (1 Bq = 1 decay per second). This follows from the basic law of radioactivity

$$d(^{14}\text{C}_t)/dt = -\lambda \cdot ^{14}\text{C}_t = -(\ln 2)/(t_{1/2}) \cdot ^{14}\text{C}_t \quad (1)$$

Here, $^{14}\text{C}_t$ denotes the number of radiocarbon atoms present at time t , λ is the decay constant, $\ln 2$ the natural logarithm of 2 ($\ln 2 = 0.693$), and $t_{1/2}$ the half-life. In our example $^{14}\text{C}_t = 9.6 \cdot 10^{14}$ ^{14}C atoms.

When we die, the supply of fresh carbon from the environment stops, and the radioactivity of the body decreases exponentially with time.

$$^{14}\text{C}_t = ^{14}\text{C}_o \cdot e^{-\lambda t} \quad (2)$$

By knowing the initial ^{14}C content, $^{14}\text{C}_o$, and measuring $^{14}\text{C}_t$, we can determine the time t from

$$t = -1/\lambda \cdot \ln(^{14}\text{C}_t / ^{14}\text{C}_o) = -(t_{1/2}) / (\ln 2) \cdot \ln(^{14}\text{C}_t / ^{14}\text{C}_o) \quad (3)$$

Equation (3) is the basis for the age determination by the radiocarbon method developed by Willard Libby in the late 1940s [10, 11]. This earned him the 1960 Noble Prize in Chemistry

“for his method to use carbon-14 for age determination in archaeology, geology, geophysics, and other branches of science”.

Accelerator mass spectrometry (AMS) measurements of $^{14}\text{C}_t$ in bone and tissue of the Iceman Ötzi revealed that the original ^{14}C content ($^{14}\text{C}_o$) had decreased to 53% [4, 5]. From equation (3) one then calculates that the Iceman has lived 5200 years ago, i.e. at the end of the stone age. However, a correct determination of the age requires to know the actual atmospheric $^{14}\text{C}_o$ value at the time when Ötzi lived. In contrast to Libby’s original assumption, the ^{14}C content of the atmosphere was not constant in time, and thus cannot be inferred for the past by measuring present-day ^{14}C . We now know that both the earth and the solar magnetic field change with time. This has a varying shielding effect on the cosmic rays impinging on the atmosphere, and thus on the ^{14}C production rate. In addition, climatic effects can also change the atmospheric ^{14}C content by variations in the exchange of ^{14}C between the global reservoirs of ^{14}C (see below). For the past 12,000 years, a $^{14}\text{C}_o$ calibration was obtained by measuring $^{14}\text{C}_t$ in tree rings whose absolute age (calendar year) was determined from dendrochronology (tree-ring dating) [12]. For earlier times, other objects such as corals, stalagmites, and lake sediments can be used [12, 13]. It is important to note that the uncalibrated “radiocarbon age” must not be confused with the calibrated “calendar date”, since there can be considerable time differences between the two (see figure 2).

The production of ^{14}C through cosmic rays

High-energy protons originating from the sun and from outside the solar system continuously bombard our atmosphere and produce secondary neutrons by smashing atomic nuclei of nitrogen, oxygen, and argon, the main constituents of the air. The neutrons are slowed down by elastic collisions with other air nuclei, and are eventually captured by nitrogen producing ^{14}C through the nuclear reaction $^{14}\text{N} + n \rightarrow ^{14}\text{C} + p$. The freshly produced ^{14}C atoms are chemically very reactive and immediately form carbon monoxide through the reaction $^{14}\text{C} + \text{O}_2 \rightarrow ^{14}\text{CO} + \text{O}$. After an atmospheric residence time of 2 to 6 months, ^{14}CO molecules react with the extremely aggressive OH radical to form carbon dioxide through the reaction $^{14}\text{CO} + \text{OH} \rightarrow ^{14}\text{CO}_2 + \text{H}$. After a mean atmospheric residence time of several years, where $^{14}\text{CO}_2$ is thoroughly mixed with the stable CO_2 content of the atmosphere, it exchanges with the biosphere (through photosynthesis), and with the hydrosphere (dissolution in oceans and other water systems). It is interesting to note that approximately one fifth of the total atmospheric CO_2 inventory is cycled through these reservoirs per year. As a consequence of these processes, a well equilibrated distribution of the global ^{14}C inventory is reached, with ~93% of ^{14}C residing in the ocean, ~5% in the biosphere, and ~2% in the atmosphere.

Measurement of ^{14}C with accelerator mass spectrometry

The ^{14}C content of a sample can be measured through decay counting (radioactivity, see eq. 1) or through atom counting ($^{14}\text{C}/^{12}\text{C}$ isotope ratio). In the latter measurement one doesn’t have to wait for the infrequent decays of ^{14}C . Since the archaeologist in general wants to preserve as much material as possible from a precious find, it is important to use only little material for the age determination. In this respect, accelerator mass spectrometry (AMS) has an enormous advantage compared to decay counting. From the example above, one can calculate that one milligram (10^{-3} g) of carbon from our body still contains 60 million ^{14}C atoms. However, because of the long half-life of ^{14}C , the radioactivity of this material is only 2.3×10^{-4} Bq, or

about one decay per hour. On the other hand, with AMS it is possible to measure about 2% of all ^{14}C atoms in one hour, i.e. 1.2 million. One thus gains a factor of one million in the detection sensitivity of ^{14}C ! This is comparable with the gain in light collecting power of a 5-m telescope (e.g. on Mount Palomar) as compared to the naked eye which has an aperture of about 5 mm (the light collecting power is proportional to the square of the diameter). For ^{14}C measurements this means that instead of using several grams of carbon in several days of beta counting, an AMS measurement can be performed with 1 milligram of carbon in about one hour, reaching the same statistical accuracy.

AMS determines the isotopic composition of a sample material by first producing a negatively-charged ion beam, which is then subjected to a series of extremely selective filtering procedures in order to find ^{14}C , “the needle in the hay stack”. $^{14}\text{C}/^{12}\text{C}$ ratios in the range of 10^{-12} to 10^{-15} can be measured in this way. Details of the measuring procedures, which at essentially all AMS facilities involves a tandem accelerator, can be found in references [14, 15, 16].

An important part of ^{14}C dating is the sample preparation, i.e. the extraction of genuine carbon from the raw sample material. For AMS measurements there are four distinct steps involved: i) a precleaning procedure aiming at removing all non-indigenous carbon, ii) the complete combustion of carbon to CO_2 , iii) the reduction of CO_2 to elemental carbon with H_2 using Fe or Co as a catalyst (graphitisation), and iv) the pressing of small pellets containing typically 1 mg of carbon for the use in the Cs-beam sputter source to produce negative ions. At the AMS facility in Vienna, the Vienna Environmental Research Accelerator (VERA), 40 carbon samples can be loaded into the ion source, usually 30 unknowns together with 8 calibration samples of known $^{14}\text{C}/^{12}\text{C}$ ratios, and 2 background samples.

With careful consideration of all steps in sample preparation and isotope ratio measurements, overall uncertainties around ± 35 years are achieved at VERA for uncalibrated radiocarbon ages less than about 10,000 years BP. However this uncertainty can increase considerably through the “wiggleness” of the tree-ring calibration curve (see figure 2). The ^{14}C dating limit lies at about 50,000 years BP. This limit is not determined by the counting statistics, but by the finite background correction, which lies in the same time range. It means that the unavoidable contamination with modern carbon in the sample preparation procedures must be kept below 1‰ (i.e. 1 μg out of 1 mg). There are many other factors which have to be taken into account (isotope fractionation, reservoir effects, the ‘old wood’ problem, etc.) in order to arrive at a reliable date. Altogether it is wise to follow the Libby rule: “Radiocarbon dating is something like the discipline of surgery – cleanliness, care, seriousness, and practice”.

Conclusion

AMS measurements of ^{14}C in small samples with AMS has grown into an extremely useful method in a variety of different fields [16]. Besides numerous applications in archaeology, such diverse fields as oceanography, ground water dating, atmospheric science, forensic medicine, biomedical science, glaciology, sedimentology, meteoritics, all benefit from the extreme sensitivity of the method and the smallness of the required sample size. Although other cosmogenic radionuclides are being measured with AMS, ^{14}C is by far the most used one. More than 90% of all AMS measurements world-wide are devoted to ^{14}C . The variation of the atmospheric ^{14}C content with time is a serious problem limiting the achievable precision of ^{14}C dating, as shown by the example of dating the Iceman. One is well advised

not to push the precision beyond the limits set by these natural variations, even though under certain circumstances one can improve the precision of the age determination by performing so-called “wiggle matching” calibrations. This is possible if a series of samples is available, where a relative chronology of the samples can be deduced from other considerations (e.g. stratigraphy in an archaeological find). Notwithstanding this *caveat*, ^{14}C is a true gift of nature to man, allowing us to look at our world in a way not possible by any other means.

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