

The ^{14}C Method. Its Possibilities and Some Pitfalls.

An Introduction

Abstract

The principle for radiocarbon dating is quite simple. ^{14}C is continuously produced by cosmic rays and oxidized to CO_2 , which is distributed over the whole world. It enters the carbon cycle and is then present in all living materia. In the first approximation we assumed the activity (in reality the $^{14}\text{C}/^{12}\text{C}$ ratio) to be the same over the whole world and to have been constant for thousands of years. There are yet several exceptions and complications making ^{14}C dating a science.

Some fractionation occurs when carbon dioxide is assimilated or dissolved in water. This means that radiocarbon is depleted or enriched compared with the stable isotope ^{12}C . By measuring the ratio $^{13}\text{C}/^{12}\text{C}$ it is possible to make a correction. This ratio, can also give further information — about the origin of the sample, for instance.

There have been secular variations. By high precision measurements we have a very good knowledge of the variations about 9 thousand years ago. Geomagnetic, solar and climatic variations are discussed as causes for the ^{14}C variations. A consequence of the secular ^{14}C variations is that samples 3,000 years old and above will be dated several hundred years too young. This difficulty can be resolved by calibration but only for Holocene samples. The period after A.D. 1500 is especially difficult. Samples about 10,000 years old should be difficult to date. Recent measurements indicated a drastic change in the CO_2 content 10,000 years ago. The calibration curve has such a shape that certain ^{14}C ages correspond to long intervals and others to short intervals.

Samples from seas and lakes are usually ascribed to too old radiocarbon ages since the $^{14}\text{C}/^{12}\text{C}$ ratio in water is lower than in the atmosphere. Sometimes hard groundwater may contribute to this but the exchange between the atmosphere and the surface water and between different water masses contributes also. Some plants even use the carbon dioxide in the bottom sediment. Fish, seals and whales naturally show a reservoir effect since they live in water and eat material from this water. As a consequence polar bears, some birds and fishermen may also have some reservoir age too.

Special problems may arise in certain areas. At volcanic eruptions and in areas with volcanic activity considerable amounts of carbon dioxide devoid of ^{14}C are released. Consequently some samples may be dated too old.

Some mixing of sediments may occur through the action of animals. It is called bioturbation. Also in the ground any transportation of, for instance, charcoal must be considered. Animals, frost cracks, penetrating roots or transport along cavities must be considered. A special problem arises at shore displacements with erosion and deposition of older material.

^{14}C is measured with the conventional technique or with the accelerator technique. In both cases a thorough analysis of possible uncertainties must be performed. The result is then given as a figure with a statistical uncertainty, which should be calculated from all uncertainties in the physical measurements. The contamination probability etc. should be discussed thereafter. Systematic errors such as the reservoir effect can now be estimated. Finally, calibration should be performed for samples $< 9,000$ years old. It is to be remembered that samples with a reservoir age should be calibrated using a smooth curve and that such a curve also suits samples with a long own age (part of a sediment core for instance).

INTRODUCTION

The radiocarbon dating method was devised by W.F. Libby in the late forties and in 1949 he published his first results. In 1960 he was awarded the Nobel Prize in chemistry for his revolutionary method. The first measurements were not very accurate but the technique for the measurement and treatment of the samples has been improved all the time during the four decades the method has been in use. There are many complications in nature and research is still going on to resolve the problems in order to improve the reliability of the datings.

The method

Radiocarbon is continuously produced in the atmosphere by cosmic rays, is oxidized to carbon dioxide and takes part in the carbon cycle. Thus plants and animals contain a certain amount of radioactive carbon, ^{14}C , when alive. The new uptake is balanced by the decay. When the exchange with the surroundings stops at death the radioactive decay is no longer compensated so that the organic remains gradually become less radioactive. By measuring the remaining activity one can determine the time passed since death (Libby, 1955).

Libby asked two important questions :

- a. is the concentration of ^{14}C the same all over the world and
- b. is the concentration of ^{14}C constant independent of time at least for several thousands of years ?

He also stated that we need to assume that we have closed systems for the samples so that the decrease of the $^{14}\text{C}/^{12}\text{C}$ ratio is solely dependent on the radioactive decay of the ^{14}C . Finally we must have a good value of the half-life of ^{14}C . Libby tested the constancy of the $^{14}\text{C}/^{12}\text{C}$ ratio by

measuring samples from different parts of the world and samples of different ages, and within the limits of errors he could state that the method would work. He improved the value of the half-life and also stated that treatment of the samples was very important in order to get a date of a product which really is representative for what should be dated.

When the method had been in use for some years it was discovered that the ¹⁴C/¹²C ratio had not been constant during the last 10,000 years. The improved measuring technique allowed such determinations. These variations have been studied and modern technique allows measurements with an accuracy of a few per mille whereas Libby could only reach an accuracy of a few per cent during the first years of the radiocarbon dating era. The measurements are made on dendrochronologically well dated samples. The value $5,568 \pm 30$ years was calculated by Libby (1955) from three independent measurements. It is still used for calculating results of datings since the value for the half-life was expected to be improved after 1962, when the radiocarbon community agreed on a new half-life of $5,730 \pm 40$ years to be used for physical measurements.

It must also be recalled that there are two stable carbon isotopes, ¹²C and ¹³C, with an abundance of 98.9 % and 1.1 % respectively in natural carbon. Radiocarbon has an abundance of 10^{-10} % in natural carbon still in exchange with atmospheric carbon dioxide.

Technique

¹⁴C measurements are made using either a conventional method or an accelerator. There are two basic conventional methods. One is based on proportional counters and one on scintillator counters. Both normally require one gram carbon or more, but recently small proportional counters have been developed for smaller samples. For accelerator measurements only about one mg is needed. It is, however, difficult to handle such small samples and the risk for contamination during handling very small samples is high. At least 10 mg carbon is to be preferred. It must be stressed that the dating method is the same independent of the measurement technique. Emphasis will be directed towards the complications in nature causing extra uncertainties in the results.

Age limit

Nowadays most laboratories can measure ¹⁴C in samples as old as 35,000 to 50,000 years using normal sample sizes. By enrichment or special techniques the range may be extended to about 60,000 years. Contamination risk also limits the range of ¹⁴C dating. Shells and bones have frequently proved to be contaminated and the age limit is usually regarded to be smaller for such samples than for charcoal and wood.

SOME OBVIOUS DIFFICULTIES IN INTERPRETATION OF RESULTS

Statistical uncertainty and presentation of ages

Nowadays all ^{14}C dates are given with the uncertainty $\pm \sigma$, for instance $3,000 \pm 80$ ^{14}C years B.P. Sometimes this is called the conventional radiocarbon age. This means that the age is calculated with the half-life 5,568 or 5,570 years and that no calibration is made (see below). B.P. stands for Before Present which should be understood as before A.D. 1950. The result should also have been normalized for the $\delta^{13}\text{C}$ deviation from -25 per mille on the PDB scale (see below). It must be recalled that in some literature results calculated with the physical half-life 5,730 years are presented and occasionally the \pm -values correspond to $\pm 2\sigma$. In many cases the results must also be corrected for the reservoir age and possible contamination (see below).

Radioactive decay is a spontaneous procedure and thus the events exhibit a statistical distribution (Fig. 1). If one laboratory dates portions of

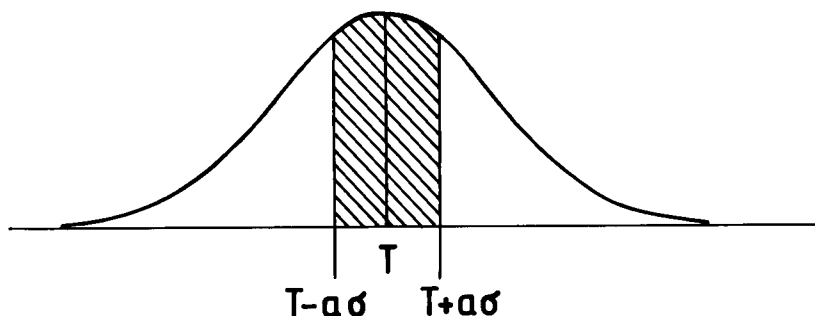


Fig. 1. A normal statistical distribution. The probability that a measurement will fall within a certain range (age $-\alpha\sigma$) to (age $+\alpha\sigma$) is 38 % for $\alpha = 1/2$, 68 % for $\alpha = 1$, 87 % for $\alpha = 1\frac{1}{2}$ and 95 % for $\alpha = 2\sigma$.

one homogeneous sample or if several laboratories date one sample a statistical spread of the results will be revealed. This means that 1/3 of the results will be outside the range (age $-\sigma$) to (age $+\sigma$). As a consequence there is no possibility of avoiding in a laboratory some dates being dated more than 1σ too old and some more than 1σ too young. The decay curve for ^{14}C is given in Fig. 2. If the activity of ^{14}C for the sample still is close to that for the modern standard (the sample is young) it is seen that the uncertainty in age is rather small and the \pm -values can be given equal figures. For a sample two half-lives older the absolute uncertainty in the activity measurements will be smaller, but translated into ages the uncertainty will be greater. In this case, but even more obvious for samples still two half-lives older, it is seen that the age should be given with unequal σ -

values, for instance $6,400^{+270}_{-250}$ ^{14}C years B.P. For very old samples close to the detection limit one should thus expect that the net activity, which should be close to zero (the measured activity – the detector background), can, within the limits of error, be negative in some cases. Table 1 gives the activity as a function of the age and it is seen that negative values for the activity or for the activity – 2σ (the -2σ limit corresponds to 2 % of the cases) must be obtained now and then even for samples with finite age. For samples older than the detection limit we can expect zero activity but in half of the cases the measured activity will appear slightly positive. To avoid most problems of interpretation there is a generally accepted special way to calculate ages when the net activity is measured as 2σ or less. For positive activities (less than 2σ) 2σ is added, the corresponding age is calculated and the result is given as older than this age. For negative activities the activity 2σ is used in the calculation. It is also advisable to give the measured activity in figures to allow mean values to be calculated when a single result should be used in special studies also using other results for statistical analysis.

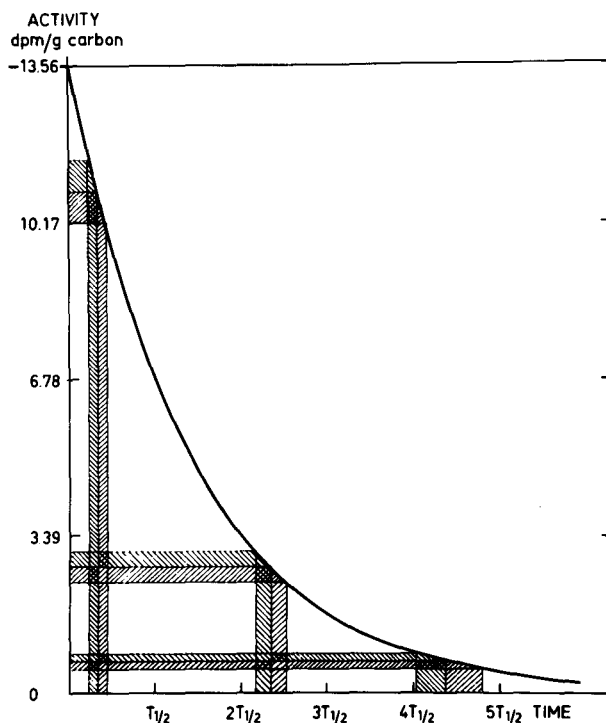


Fig. 2. The radioactive decay with 3 activities with uncertainties inserted. The relation between the activities is 16 : 4 : 1 and time for measurements is the same. Although the absolute errors are going down the relative errors are 1 : 2 : 4 and the uncertainties in years are increasing with decreasing activity (increasing age) and will be significantly asymmetric.

TABLE 1. — THE REMAINING ACTIVITY AFTER 1 TO 7 HALF-LIVES DEMONSTRATING THAT THE STATISTICAL UNCERTAINTY, $\pm\sigma$, CORRESPONDS TO UNEQUAL UNCERTAINTIES IN THE AGE. WHEN THE MEASURED ACTIVITY IS LESS THAN 2σ THE CALCULATIONS ARE MADE IN A SPECIAL WAY

The activity of a radioactive sample will decrease with time. For instance, if the activity is 10.00 cpm it will be reduced to 5.00 cpm after one half-life ($T_{1/2}$). (I will here use 5,570 as the half-life).

Elapsed time	Activity	Activity	Age
0	N_0	10.00	
$T_{1/2}$	$\frac{N_0}{2}$	5.00	
$2 \times T_{1/2}$	$\frac{N_0}{2^2} = \frac{N_0}{4}$	2.50	
$3 \times T_{1/2}$	$\frac{N_0}{2^3} = \frac{N_0}{8}$	1.25	
$4 \times T_{1/2}$	$\frac{N_0}{2^4} = \frac{N_0}{16}$	0.625	
$5 \times T_{1/2}$	$\frac{N_0}{2^5} = \frac{N_0}{32}$	0.3125	
$6 \times T_{1/2}$	$\frac{N_0}{2^6} = \frac{N_0}{64}$	0.156 (0.16)	33,400 yrs
$7 \times T_{1/2}$	$\frac{N_0}{2^7} = \frac{N_0}{128}$	0.078 (0.08)	39,000 yrs

If the statistical uncertainty in the determination is ± 0.040 and the measured activity is given as 0.077 ± 0.040 cpm, we get

$$0.077 + 0.040 = 0.117 \text{ corresponding to an age between } 6 \times T_{1/2} \text{ and } 7 \times T_{1/2} \text{ or } 35,750$$

and

$$0.077 - 0.040 = 0.037 \text{ corresponding to an age about } 8 \times T_{1/2} \text{ or } 45,000$$

and

$$0.077 \text{ corresponding to an age of } 39,100 \text{ years}$$

We do not write the result as

$$39,100^{+5900}_{-3350}$$

since activity -2σ ($0.077 - 0.080$) corresponds to a negative activity. We instead use activity $+2\sigma$ ($0.077 + 0.080 = 0.157$) to calculate a minimum age and the result given as

$$> 33,300 \text{ (older than } 33,300 \text{ years)}$$

For a negative activity as -0.030 ± 0.040 we instead use 2σ to calculate a minimum age and the result is given as

$$> 38,700 \text{ years (older than } 38,700)$$

It should be mentioned that most laboratories round-off the results to the nearest 5 years when the σ -values are small, to the nearest 10 years if the σ -values are greater up to a few hundred years, and to the nearest 50, 100 or 500 years if the σ -values are correspondingly higher.

If several values, $T_i \pm \Delta T_i$, are available and there is reason to assume that they should date the same event, a mean value can be calculated

$$T_{\text{mean}} = \frac{\left(\frac{1}{\Delta T_1}\right)^2 T_1 + \left(\frac{1}{\Delta T_2}\right)^2 T_2 + \dots + \left(\frac{1}{\Delta T_n}\right)^2 T_n}{\left(\frac{1}{\Delta T_1}\right)^2 + \left(\frac{1}{\Delta T_2}\right)^2 + \dots + \left(\frac{1}{\Delta T_n}\right)^2}$$

with the uncertainty in the mean value

$$\pm \left\{ \left(\frac{1}{\Delta T_1}\right)^2 + \left(\frac{1}{\Delta T_2}\right)^2 + \dots + \left(\frac{1}{\Delta T_n}\right)^2 \right\}^{-1/2}$$

It is, however, advisable to check that the distribution seems to be acceptable. This can be done by plotting the results as done in Fig. 7 for Bjurselet 11 and 14, but can also be done by plotting distribution curves and comparing the actual distribution with that derived from the quoted standard deviations (Stuiver, 1982). One example of several determinations made in Uppsala on an old sample finally given as older than 42,200 years is given in Fig. 3.

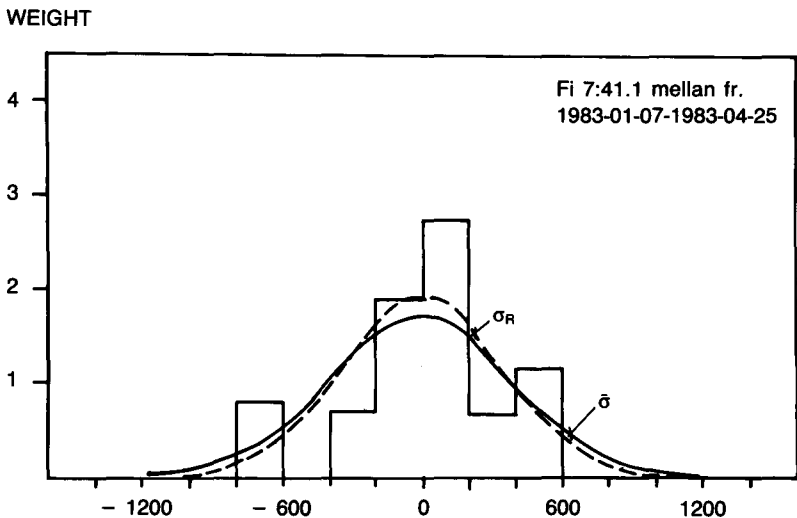


Fig. 3. The statistical distribution of activity measurements of a very old sample ($> 42,000$ ^{14}C years B.P.). The spread of the actual measurements with their σ -values is here slightly less than expected from the σ -values ascribed to each measurement ($\sigma_R/\sigma_{\text{expected}} = 0.88$).

¹³C fractionation and normalization

The chemical behaviour of the three carbon isotopes is essentially the same, although the small differences between their masses will affect the kinetic processes and the thermodynamic equilibrium of the reactions. The result is a fractionation, so that ¹³C is depleted in comparison with ¹²C on assimilation and enriched when dissolved in water. This behaviour was not known when the radiocarbon dating method was devised and the laboratories had used tree rings as recent standards. The thermodynamic laws say (Craig, 1954) that we can expect to double the enrichment for ¹⁴C than for ¹³C. Thus all values have to be normalized to one and the same value. It was then natural to choose that of wood. It is convenient to have a scale with the zero point for a normal ¹³C/¹²C ratio and express the deviations from the normal value as the differences ($\delta^{13}\text{C}$) in per mille from this standard ratio. The standard ratio used in radiocarbon dating is that of a carbonate, belemnite from the Pee Dee formation in South Carolina. We then get our values on the PDB scale where carbonates are close to zero and normal wood has a value of about -25 per mille.

Studies of photosynthetic pathways have revealed three main groups of terrestrial plants having the C₃ (Calvin), C₄ (Hatch-Slack) and the CAM (Crassulacean Acid Metabolism) metabolisms respectively. C₃ assimilation is typical for most plants in our area yielding $\delta^{13}\text{C}$ values close to -25 per mille, C₄ assimilation is typical for maize with $\delta^{13}\text{C}$ about -12 per mille and CAM assimilation for succulents with $\delta^{13}\text{C}$ about -17 per mille (Fig. 4). It must be recalled that there are considerable variations around the typical values. The spread is related to the species, the part chosen and environmental conditions. For instance, leaves, cellulose from the trunk and resin of a tree have different values. For submerged plants, fresh-water and marine animals we usually find $\delta^{13}\text{C}$ values different from and more spread than that of terrestrial samples (Fig. 4). Yet there is sometimes a possibility to discuss food as Tauber (1983) did and discovered that Mesolithic man in Denmark apparently had a very high intake of marine food. Even earlier Vogel and van der Merwe (1977) found that maize was an important part of the diet long ago. The $\delta^{13}\text{C}$ value of our food is reflected in the $\delta^{13}\text{C}$ value of collagen from the bones of man. There are, however, some problems in the interpretation of $\delta^{13}\text{C}$ values especially of bone material when the values derive from different dating laboratories. The collagen used can be extracted in different ways and is not a well defined product.

Since the food is a 4-component system (C₃-, C₄-plants, meat and fish) the conclusions are not straightforward. The $\delta^{13}\text{C}$ varies not only with the species and chosen tissue but also with age, sex and other factors. Dietary reconstructions should be based on multivariate studies (Bumsted, 1985).

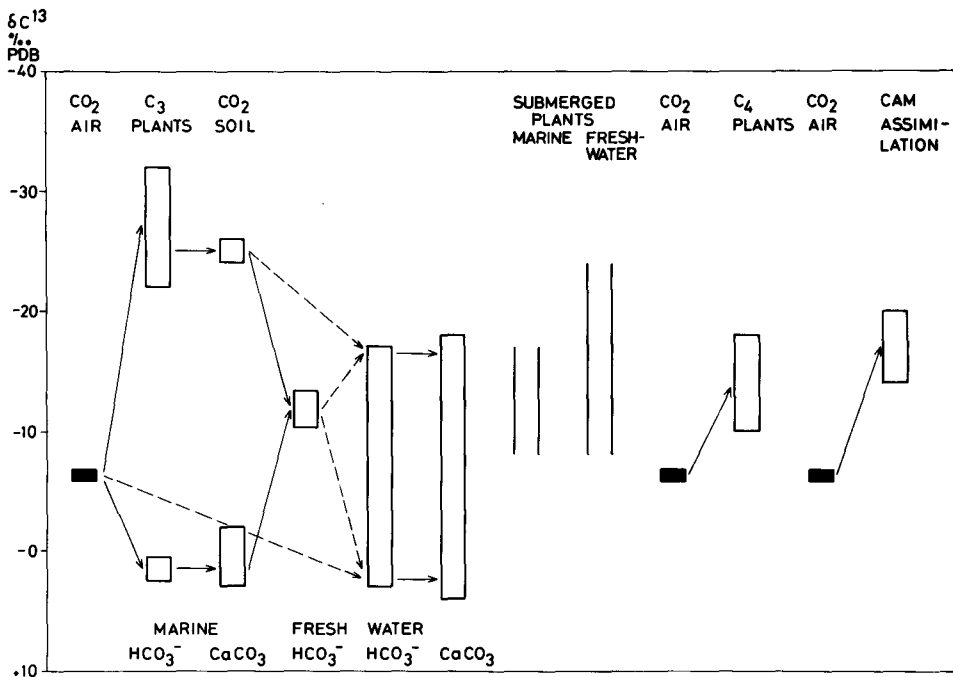


Fig. 4. Fractionation in nature of ^{13}C for different types of sample. The deviations from the chosen PDB standard are given in per mille. Early diagrams like this were plotted with depleted samples (neg. δ -values) towards the top of the diagram and that fashion is kept here although now abandoned by several authors.

Since marine carbonate has a $\delta^{13}\text{C}$ value close to 0 the age will be adjusted by about 410 years, when normalizing to -25 per mille, since $2 \times 25 \times 8$ is 400. Eight years is the change in age for a 1 per mille change in activity. Since the $\delta^{13}\text{C}$ value is 0 but the normalization means a reduction to -25 per mille in $\delta^{13}\text{C}$, the corresponding normalization for ^{14}C means a reduction of $2 \times 25 = 50$ per mille. 410 years have to be added to the age calculated without a $\delta^{13}\text{C}$ normalization.

Contamination and pretreatment of samples

Contamination of samples may obviously be a serious problem although sometimes of little harm. From the decay laws we know that 1% carbon without any ^{14}C activity (often called infinitely old) makes a sample appear 80 years too old irrespective of the age of the sample. Graphite can easily be released by weathering and deposited in sediments and affect the apparent age, especially in sediments poor in organic matter. Erosion and redeposition of older deposits often make lake sediments appear too old.

A typical contaminant making samples appear too young is roots. We often find roots and rootlets in the samples and try to remove them. A small

amount slightly younger than the sample itself will not be disastrous at all. It is often easy to mechanically remove most of the rootlets from charcoal samples. Sediments can often be sieved to remove roots before being submitted to the laboratory. If ten percent of a sample are roots 2,000 years younger than the sample the error will be c. 225 years. A warning against explaining much too young results by root effects is often justified (Fig. 5). It must, however, be recalled that atmospheric ^{14}C activity in 1963 and 1964 was double the normal because of the nuclear-bomb tests. This corresponds to an age of one half-life. It might be very difficult to distinguish root remains from the plant remains which really can date a stratigraphic level in a bog or in a lake sediment. Plants act as pumps transporting ^{14}C from the atmosphere down into the ground where CO_2 may be released and various humus products will contribute to the sample. Humus may be dissolved, transported and precipitated causing a sample to appear too old or too young. It should always be removed from charcoal by chemical treatment. Any calcium carbonate is removed by hot HCl and water washings. Then the humus is dissolved by hot NaOH treatment for several hours or over night, followed by water washings. This step may be repeated once or twice when necessary. A final treatment with acid will ascertain that no CO_2 absorbed from the air will be left. In the case of sediments such as silt, clay and even gyttja the NaOH -soluble fraction may be more reliable than the insoluble fraction. This is especially the case when the sample is contaminated with graphite. Wood is generally treated

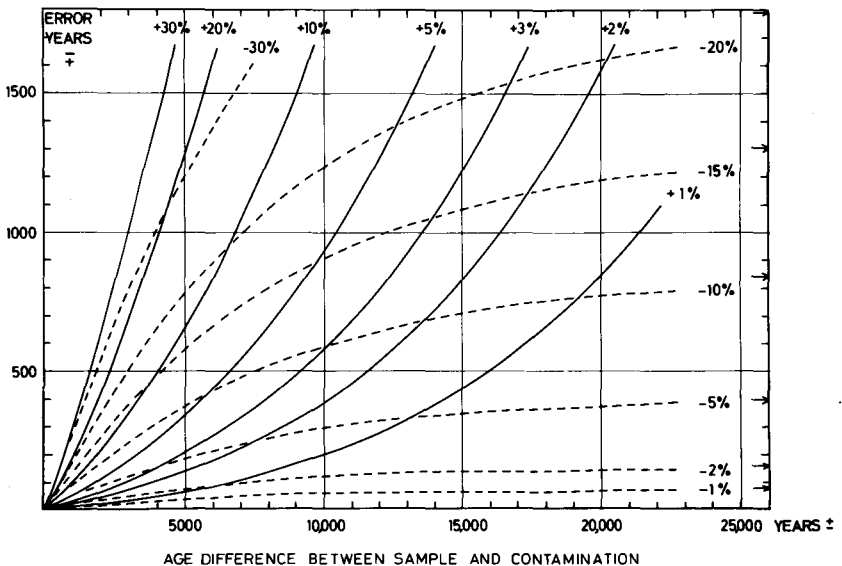


Fig. 5. Error in years as a consequence of a contaminant replacing some percentage of a sample. If the contaminant is older the dashed curves are valid. If the contaminant is younger the continuous curves are valid.

as charcoal. A thorough NaOH treatment removes the resin which can be transported radially across the tree rings within the soft wood. The cellulose or well-treated wood will reflect the atmospheric activity of the corresponding year. This is very essential when ¹⁴C measuring soft wood from trees growing as late as or later than about 1960, when the nuclear-bomb effect was already appreciable. Charcoal cannot be chemically pretreated to remove foreign charred particles of other age. Sometimes a fractionation based on the size of the pieces can be rewarding. Uncharred roots can be removed by treatment which converts the roots to cellulose.

When collecting samples the possibility of mechanical displacement must be considered. Thus poles are pressed down into the ground, and charcoal may, for instance, be displaced in frost cracks, along cavities from roots and by worms. Wood may be reused and old wood may be collected for fires or simply burned for clearing an area. In certain areas drift-wood is a severe problem. Selecting wood which cannot be transported is then a must. Sediments may be disturbed by bioturbation, erosion and redeposition (Olsson, 1983).

Shells may be contaminated when stored in the atmosphere, for instance in a museum for a very long time. The laboratory in Uppsala has some examples of infinitely old shells being contaminated to appear about 33,700 years old, corresponding to contamination by 1½ % modern carbon dioxide. Such contamination proceeds quicker in a moist atmosphere than in a dry atmosphere. Similarly there are many examples of contamination in the ground affected by ground water. For 30 years the Uppsala laboratory has used a pretreatment aiming to remove the outer parts of the shells since these should be more easily contaminated than the inner parts. The inner parts are then separated in similar fractions to provide the possibility to compare the innermost parts with intermediate layers of the shells. Old shells and small shells should be stored sealed from the atmosphere.

Bone, being a complex material, may easily be contaminated by ground water, rootlets etc. Fortunately the collagen and the amino acids are not contaminated in a manner such that any carbon is exchanged. A chemical treatment, following a mechanical treatment, should thus be chosen to yield a chemically pure product, free from contaminants. In the Uppsala laboratory we prefer a treatment with EDTA and HCl and final dissolution in water (Olsson *et al.*, 1974 ; El-Daoushy *et al.*, 1978). Since the EDTA solution is slightly basic the humus will be removed. Sometimes a HCl and NaOH treatment is sufficient. Preparation of amino acids, which is to be preferred, is often possible nowadays when we can use accelerators for the ¹⁴C determination. A review of different treatments of bones is given by Taylor (1980). Research on the use of hydroxyproline to be dated using accelerators is on-going.

Reservoir effects

Since ^{14}C takes part in the carbon cycle and is thus assimilated by plants, released under ground by decaying plants and from roots, and dissolved in water and since the mixing of waters takes some time it is rather natural that different reservoirs may have somewhat different $^{14}\text{C}/^{12}\text{C}$ ratios.

Most parts of the oceans have a well-mixed surface layer and well-mixed deep water. The volume ratio of these two water masses is of the order of 1 : 10^2 . Then it is easily understood that a smaller percentage of the deep water mixes with the surface water than the percentage of the surface water which mixes with the deep water at equilibrium or conditions not much different from equilibrium. The residence time for carbon dioxide is thus longer in the deep water than in the surface water. More ^{14}C can thus decay in the deep water than in the surface water before the carbon dioxide is exchanged between the reservoirs. The exchange over the boundary is rather slow and so is the exchange between the atmosphere and the surface water. The deep water will thus normally have a lower ^{14}C activity than the surface water and the surface water will have a lower activity than the atmosphere. We say that the water has a reservoir age, larger for the deep water than for the surface water. Any organic matter and carbonates from the seas will reflect the ^{14}C activity of the water. Land animals such as polar bears will also have a reservoir age as well as fishermen and many birds. Lakes also have reservoir ages. The conditions may be rather varying from lake to lake. The slow exchange over the surface water seems to be of great importance but sometimes a supply of hard ground water or aged water is as important or even worse. Decaying organic matter on the bottom of the lake will yield carbon dioxide with less ^{14}C than in the atmosphere. Some plants take their carbon mainly from the bicarbonate, others from the dissolved carbon dioxide and still others through their roots from the carbon dioxide in the sediment. Emergent plants use carbon dioxide from the atmosphere and for plants with floating leaves the uptake may vary during the season. Fresh-water shells are thus less reliable than salt-water shells. Some reservoir age should be regarded as normal for material deriving from lakes. Local reservoir ages are to be expected in volcanic areas because of the release of inactive carbon dioxide.

Secular variations of the ^{14}C activity

Since ^{14}C is produced as a consequence of cosmic-ray interaction with the atmosphere, and charged particles such as those in the cosmic rays will be deviated in magnetic fields and in electrical fields, it is quite natural to assume that the relative ^{14}C activity has varied. There is some correlation between sunspot variation and short-term variation of ^{14}C . The long-term variations have been correlated with the variations in the geomagnetic field (Bucha, 1970). Comparisons with the ^{10}Be variations (Beer *et al.*, 1984) have resulted in some doubts. The ^{14}C dependence on climate has been discussed for a long

time. It is a complicated question with variables such as temperature, changing ocean-water volume, solubility of carbon dioxide and changing vegetation. Recently we have learned that the carbon dioxide content has varied appreciably and was indeed very low about 10,000 years ago. So if production is constant the relative amount of ^{14}C has decreased when the partial pressure of carbon dioxide has increased.

Man is responsible for the recent decrease of the activity by about 2 % due to combustion of fossil fuel. Part of the carbon dioxide has stayed in the atmosphere so that there is a steady increase of the carbon dioxide content. Man is also responsible for the very recent increase of the activity because of tests of nuclear weapons. The artificial excess of ^{14}C amounted to about 100 % in 1963 and 1964 in the northern hemisphere except for low latitudes. The excess has now decreased to about 20 % for normal air free from excessive pollution. The pattern for secular ^{14}C variation is normally a rapid change, an increase, followed by a rather stable or even decreasing ^{14}C concentration on the short-term scale. There was an excess of ^{14}C corresponding to about 800 years six thousand years ago. This excess decreased to be close to zero about 2,000 years ago.

One pitfall in connection with the variation is that there are periods for which the ^{14}C ages will be essentially the same and others for which one ^{14}C year will be longer or shorter than one calendar year. An uneven distribution with clustering of the results around a certain ^{14}C age may easily be misinterpreted as a short period with comparably many finds. The calibrated value should normally have different plus and minus values of σ expressed in years. In some cases the ^{14}C values are such that more than one possibility for the age is valid. The old most accurate calibration curves are now reprinted in *Radiocarbon*, 1986, 28, N^o 2B. Some new approaches are also found there. A calibration programme is also commercially available and is described in the mentioned volume of *Radiocarbon*.

There is another pitfall connected with the calibration. Samples covering long periods such as peat sections and long-lived lichens should not be calibrated using curves based on one year samples (Olsson, 1974 ; Mook, 1983). Similarly one year samples should preferably not be calibrated using curves based on long-lived samples. Submerged samples from lakes and the sea having a delay in response to the atmospheric variations of ^{14}C must also be calibrated in a special way (Olsson, 1980 ; Olsson and Florin, 1980).

The fate of samples

In Fig. 6 the fate of the samples is depicted from collection to interpretation of the results. It is seen that the exchange of information between the submitter of a sample and the dating laboratory is very essential in many cases until the archaeologist and the dating scientist have acquired experience beyond the normal situation. The fact that the ^{14}C method is not a

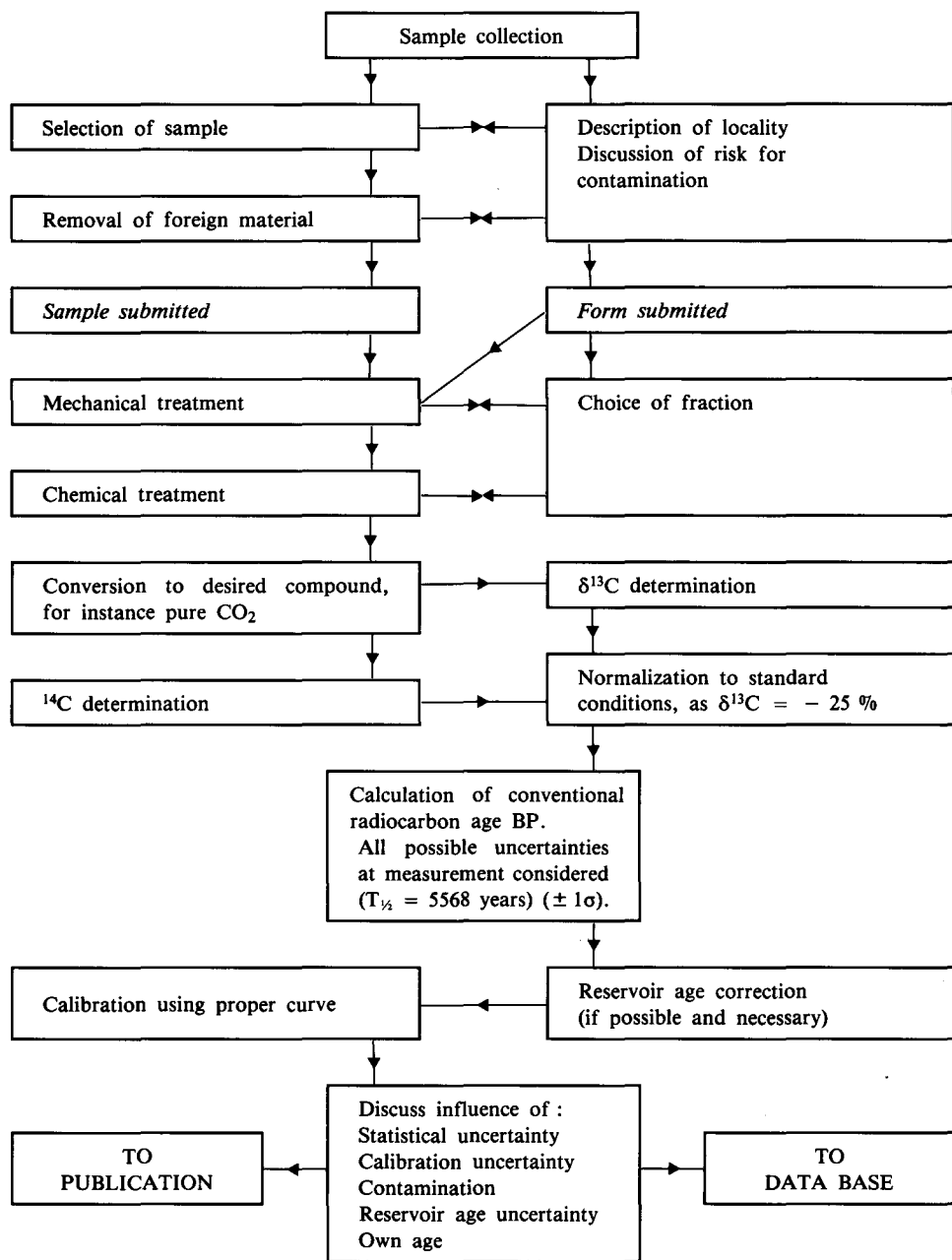


Fig. 6. A chart illustrating the most important steps in the dating procedure from collection of sample until a result can be given. The scheme will be slightly changed for other detector systems than gas-filled proportional counters. Long-term stability tests may contribute to a realistic estimate of the statistical uncertainty. Some exchange of information is normally of great value at the final discussion before storage in the data base or released in a publication.

routine method is seen from the proceedings from the ^{14}C conferences. Reference is given in the reference list to such proceedings and a review book is also included for further readings.

Sometimes it is difficult to find ^{14}C results, for instance dated to elucidate a certain archaeological period over large areas or the development at a certain locality. Many results are published in date lists in Radiocarbon but others are unpublished or published in various journals or books. Most probably there will be a data base for ^{14}C dates allowing searching by personal computers (see *Radiocarbon*, 28, N° 2A). For the communication between the archaeologists (and many other scientists) and the scientists in the ^{14}C laboratories it is useful to use forms from the laboratories with space for some standardized information.

A case study

Some datings made about 20 years ago are selected to illustrate how the scientists in a ^{14}C laboratory may look at the samples and the results (Fig. 7).

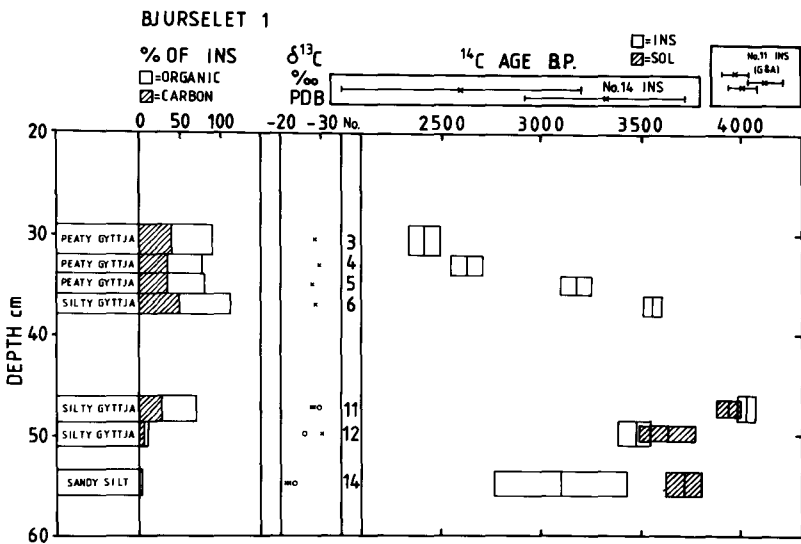


Fig. 7. A case study of datings made in 1966 to 1971 on samples from Bjurselet. The stratigraphy and pollen analysis is given by Königsson (1970). The interpretation is somewhat difficult. Most probably there is a disturbance due to some erosion at level 11. The first suggestion that there was graphite causing this old age seems not very justified since the latest measurement in this series — on the NaOH-soluble fraction at level 11 — yielded within the limits of error the same age as the mean of three measurements on the insoluble fraction. The material is such that allocthonous carbon is to be expected in the samples. In most cases it was possible to give a realistic estimate of the carbon content. The low content of carbon in the deepest samples should be a warning that the results may be too old.

The combustion of sample 5G was interrupted when enough gas was received. The uncertainty of the organic content of this sample is about 20 % whereas that for the other samples from 11G upwards is about 10 %, for sample 12G about 2 % and for 14G less than 1 %.

The samples derive from Bjurselet in Sweden. The geological description including pollen diagrams is given by Königsson (1970). It is seen that the samples have different composition. Peat is generally more reliable than gyttja. Often the NaOH-soluble fraction is more reliable than the insoluble fraction when dating lake sediments. If the insoluble fraction yields older ages it is often an indication of contamination by graphite. In this case 3 pairs were dated and the difference between the two fractions in each pair is not significant. In one case (sample 11) the soluble fraction was younger and that sample appears older than others above and below. This may be due to contamination by erosion but hardly by graphite, or only to a minor extent by graphite, since graphite is not soluble in NaOH and even the soluble fraction seems to be too old. Varying conditions yielding varying reservoir ages could also result in jumps in the general trend. Such a case can sometimes be traced by diatoms.

The insoluble fraction of sample 11 was dated three times. the third time a completely new sample was used. The three results are plotted in the upper part of the diagram with the bars indicating $\pm \sigma$. It is seen that the datings agree very well so that a weighted mean value could be calculated to be used in the main diagram with rather small σ -values. The statistical uncertainty of the insoluble fraction of sample 14 was rather high. Two independent measurements (see the upper part of the diagram), agree with each other so that a weighted mean value was calculated and used in the main diagram. If the three differences between the insoluble and soluble fractions are used for a weighted mean value it is seen that the differences insoluble fraction minus soluble fraction yield a positive value, although far from significantly positive.

The ash after the combustion and the CO₂ yield are normally registered to yield two independent semi-quantitative results of the carbon content. Twenty years ago the notes about this were less reliable in the laboratory than now and thus the corresponding columns in Fig. 7 are not complete. Sometimes, as is the case here, an incomplete combustion makes it difficult to give any figure: The combustion was interrupted when enough gas was received. Generally the risk for contamination is increasing when the carbon content is decreasing. A few percent carbon is to be regarded as a severe warning.

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