Chronometric Dating in Archaeology

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CASE STUDY: ARCHAEOLOGICAL APPLICATIONS OF AMS TECHNOLOGY

Over the last decade, the expanding utilization of AMS-based ^{14}C analysis has continued to open up new and expanded areas of research where ^{14}C data have yielded important new understandings that would have not been possible or practical with decay counting. In archaeology, there have been a variety of issues and topics which have been significantly impacted by the new capability to obtain ^{14}C measurements on milligram amounts of sample.

Table 3.3. AMS [14]C Dating of the Shroud of Turin*

Laboratory	Known age Egyptian linen AMS ^{14}C age (yrs. BP)	Shroud AMS [14]C (yrs. BP)
	2,010±80 110 BC-AD 75	
Arizona AMS	1,838±47 2,041±43 1,960±55 1,983±37 2,137±46	591±30 690±35 606±41 701±33
	Mean = 1,995±46	Mean = 646±31
Oxford AMS	1,955±70 1,975±55 1,990±50	795±65 730±45 745±55
	Mean = 1,980±35	Mean = 750±30
Zurich AMS	1,984±50 1,886±48 1,954±50	733±61 722±56 635±57 639±45 679±51
	Mean = 1,940±30	Mean = 676±24
Combined	Mean ^{14}C age = 1,964±20	Mean ^{14}C age = 689±16
	Calibrated age = 10 BC-AD 80[b]	Calibrated age = AD 1260-1390[b]

* Based on data from Damon et al. 1989.
[b] 95% confidence interval.

Some AMS-based ^{14}C values have been obtained in situations where larger amounts of sample were available. However, those having responsibility for an unique archaeological or historic object would consent to the removal of only a small portion of the larger sample. Such was the case with the AMS ^{14}C dating of the Shroud of Turin. This 4.3 by 1 meter rectangular-shaped linen cloth housed in the Cathedral of St. John the Baptist in Turin, Italy has been characterized, since 1353 when its existence is first documented, as the "True Burial Sheet of Christ." Table 3.3 presents the results of an analysis by three AMS laboratories of a known-age Egyptian linen approximately 2,000 years old and the Shroud. The calibrated ^{14}C age indicates that the flax from which the linen was fabricated was most probably growing sometime during the later part of the 13th or in the 14th century, exactly the period during which the shroud first appeared (Damon et al. 1989).

An excellent illustration of the ability of AMS technology to obtain ^{14}C measurements on microsamples is illustrated by a study of maize specimens excavated from two rockshelters in the Tehuacan Valley, Mexico. Samples of Zea mays from these sites had been regarded as the earliest example of cultivated maize in the New World. In the early 1970s, their age had been determined on the basis of conventional ^{14}C determinations obtained on charcoal assumed to be stratigraphically associated with the maize samples in the Tehuacan Valley sites. Table 3.4 compares the ^{14}C values previously obtained on associated charcoal with the AMS ^{14}C values obtained directly on the maize samples. In contrast to the 5350 to 7000 BP values on the charcoal, the range in ^{14}C values directly obtained on maize is 1560 to 4700 BP for the samples from San Marcos Cave and 450 to 4090 BP for the specimens from Coxcatlan Cave (Long et al. 1989). The significantly later occurrence of maize at Tehuacan raises questions concerning assumptions about where the center(s) of maize domestication in Mesoamerica may have been.

A further example of usefulness of AMS technology in ^{14}C studies is the use of such data as part of efforts to address one of most acrimonious debates in New World archaeology—the nature and timing of the peopling of the Western Hemisphere. Historically, this debate has centered on two issues: the scientific validity of data offered as evidence for human presence and the accuracy of the age estimates associated with these data (Dillehay and Meltzer 1991).

A number of discussions have centered on questions concerning the validity of purported Paleoindian materials with assigned ages purportedly in excess of the well-documented Clovis period occupation of North America (Haynes 1992). Of the more than 100 sites in North America that have been reported to contain evidence of "pre-Clovis" occupation, only a relatively small number currently remain under active consideration. Of these remaining alleged pre-Clovis sites in North (Payen 1982) or South (Lynch 1990; Meltzer 1994) America, either the cultural nature of the material or the adequacy of

Table 3.4. Comparison of ^{14}C Determination on Samples of Charcoal and Maize from Tehuacan Valley, Mexico

Decay counting on associated charcoal[a]		AMS on maize specimens[b]	
^{14}C age BP (range)	calibrated AD/BC (range)	^{14}C age BP	calibrated range AD/BC
		San Marcos Cave	
5350-7000	4150-5800 BC	1560±45	AD 440-620
		4150±50	2880-2660 BC
		4600±60	3380-3360 BC
		4680±50	3500-3380 BC
		4700±60	3500-3380 BC
		4700±110	3640-3360 BC
		Coxcatlan Cave	
		450±40	AD 1400-1460
		1860±45	AD 80-220
		1900±60	AD 20-220
		3740±60	2280-2040 BC
		4040±100	2580-2500 BC
		4090±50	2870-2580 BC

[a] Taken from Johnson and Willis 1970 and Johnson and MacNeish 1972.
[b] Taken from Long et al. 1989.

the geochronological data associated with the remains—or both—have been, and continues to be, questioned.

It is generally accepted that debates concerning the validity of dating frameworks associated with Paleoindian materials—and particularly purported pre-Clovis materials—were substantively transformed with the introduction of the ^{14}C method. For almost all archaeologists, the ^{14}C method has acquired the status of the final arbiter of the accuracy of chronological inferences for materials associated with actual or apparent Paleoindian contexts. There is, however, the recognition that the validity of ^{14}C-inferred ages can depend on the type of sample material being dated. One of these problematical sample types is bone.

There are numerous examples in the history of ^{14}C applications in archaeology of misassociation of a ^{14}C-dated sample with the item or context for which a date had been sought. When ^{14}C age determinations are obtained directly on a bone sample clearly identified on widely-accepted morphological criteria as being genus *Homo*, any question of human involvement or instrumentality is, by definition, rendered moot. One is thus able to evaluate the

validity of a ^{14}C-based age determination on physiochemical grounds alone. This highlights one of the great advantages of AMS technology for ^{14}C analysis—the ability to obtain a ^{14}C value directly on a specific fraction of a target organic, in this case mammalian bone, and more specifically in this discussion, human bone.

From the very inception of ^{14}C studies, bone acquired a reputation as an unreliable sample type. Rather quickly, a major problem was recognized. Early bone ^{14}C determinations had most often been carried out employing the whole-bone matrix which is composed largely of inorganic constituents. Inorganic carbonates can be derived either from the apatite structure in the bone itself or from secondary, diagenetic carbonates which had been transported into the bone matrix from groundwater and soil constituents by chemical exchange and/or through dissolution and reprecipitation processes. Therefore, the ^{14}C contained in a total inorganic carbonate fraction may reflect the environmental source(s) of the carbonates contained in the soils to which the bone has been exposed and the degree of isotopic exchange between the bone and ground water carbonates rather than the age of the bone sample itself. Radiocarbon measurements on a carbonate component of bone can be older, younger, or of essentially the same age as an organic fraction from the same bone.

In contrast to the carbonate fraction, bone contains a relatively stable organic product, the protein collagen, representing between 60-70% of the organics in fresh, fat-free bone. Collagen in modern bone can be distinguished by several types of biogeochemical "fingerprints" including characteristic amounts of nitrogen, a distinctive nitrogen/carbon ratio, and a pattern in the relative concentration of the approximately 20 amino acids which make up mammalian collagen.

By the early 1960s, collagen—in some cases characterized as gelatin—became the target of much of the chemical pretreatment of bone for ^{14}C analysis. Initially, most often "collagen" was the label given to an acid insoluble product isolated by a treatment of the bone with dilute acid, which destroyed the carbonates, leaving, it was assumed, the collagen fraction. In some cases, this product was heated at a constant temperature and pH to form gelatin. An early application of this approach to the ^{14}C dating of human bone was that of the Galley Hill skeleton in England. When discovered in the 19th century, the Galley Hill skeleton was thought to be Pleistocene in age. However, bone fluorine values suggested that it was a post-Pleistocene burial that had intruded into Pleistocene sediments. The ^{14}C age of the acid-insoluble fraction ("collagen") of a humerus of this skeleton yielded a date of 3310±150 BP (Barker and Mackey 1961: 41).

The ability of AMS technology to permit ^{14}C values to be measured routinely using milligram amounts of carbon provided the technical capability to undertake a direct examination of a series of human skeletons from North American sites that, on various grounds, had been declared to date to a period

before 11,000–12,000 BP; i.e., these human skeletons were alleged to be pre-Clovis in age. AMS technology permitted a detailed analysis of the validity of ^{14}C age estimates on a range of extracts from bone including individual amino acids and other highly specific organic constituents contained in bone. Table 3.5 is a summary of ^{14}C values obtained on various organic fractions extracted from human skeletal samples and, in one case, an artifact fabricated from a

Table 3.5. Revisions in Age Estimates on Human Bone (Except Old Crow) from North America Sites of Purported Pleistocene Age Based on AMS ^{14}C Determinations and Related Data[k]

Skeleton(s)/ artifact	[A] Original estimate Basis	[A] Original estimate Age	[B] Revised estimate ^{14}C Age	Laboratories
Sunnyvale	AAR U-series	70,000 8300/9000	3600-4850 6300[a]	UCR/Arizona AMS UCSD(Scripps)/ Oxford AMS
Haverty [Angeles Mesa]	AAR	>50,000	4050-5350[d] 5200[d] 7900-10,500[d] 2730-4630[e] 4600-13,500[f] 5250[e] 15,900[f]	UCR GX (Geochron) UCLA UCR/LLNL-CAMS AMS UCR/LLNL-CAMS AMS DSIR, New Zealand AMS DSIR, New Zealand AMS
Del Mar	AAR U-series	41,000-48,000 11,000/11,300	4900[a] 4830 1150-5060[a]	UCSD(Scripps)/ Oxford AMS Arizona AMS Arizona AMS
Los Angeles [Baldwin Hills]	^{14}C AAR	>23,000[a] 26,000	3560	UCR/Arizona AMS
Taber	geologic	22,000-60,000	3550	Chalk River AMS
Yuha	^{14}C AAR U-series	22,000[b] 23,000 19,000	1650-3850	Arizona AMS
Old Crow[c]	^{14}C	23,000	1350	Simon Frazer/ McMaster AMS
Laguna	^{14}C	7100[g] 17,150[h] >14,800[i]	5100[a]	UCSD(Scripps)/ Oxford AMS
Natchez	geologic	"Pleistocene"	5580	Arizona AMS
Anzick	Clovis	10,000-11,000	8610-10,680[j]	Arizona AMS
Tepexpan	geologic	"Pleistocene"	920-1980[j]	Arizona AMS
Calaveras	geologic	"Pliocene"	740	UCR/Arizona AMS

[a] Amino acid fraction. [b] Diagenetic carbonate. [c] Artifact fabricated from bone. [d] Acid insoluble fraction, decay counting. [e] collagen (gelatin) fraction. [f] Osteocalcin fraction. [g] skull, "first run" (Berger 1992). [h] Skull, "second run" (Berger 1992). [i] long-bone. [j] multiple analysis of different fractions (Stafford et al. 1991). [k] References for all values except Calaveras are cited in the caption for Table 25.5 in Taylor 1992. Yuha U-series value listed in Taylor (1992) has been corrected. Calaveras data from Taylor et al. 1992.

non-human bone from North America sites, all of which had been assigned a pre-Clovis age. The basis of the initial age assignment of these samples included other Quaternary dating methods such as amino acid racemization and uranium-series and, in a small number of cases, prior ^{14}C determinations.

The AMS-based ^{14}C values on these human skeletal samples indicate that, with two exceptions, all are younger than 11,000 BP. These data are the basis of the conclusion that all currently-known, ^{14}C-dated human skeletons from the Western Hemisphere are of Clovis age or younger. The only exceptions are two ^{14}C values obtained in connection with experiments to determine the validity of ^{14}C determinations on a non-collagen component of bone, osteocalcin (Ajie et al. 1992). These two values are interpreted to represent fractions which have been contaminated in the process of being chemically extracted since a significant corpus of ^{14}C dates, along with other evidence, points to the age of the Haverty (Angeles Mesa) skeletons as being in the range of 4000 to 5000 years BP (Brooks et al. 1991).

The experimental osteocalcin ^{14}C determinations reflect current efforts to deal with the problem of bones containing only trace amounts of residual collagen. The assumption that an acid insoluble fraction is primarily composed of intact collagen would be a reasonable inference for relatively young bone or bone from environments where diagenetic effects would be less severe, i.e., very cold and/or very arid climates; but such an assumption would not be necessarily valid for bone subject to elevated temperatures and high humidity environments and/or for Pleistocene-age bone.

The collagen contained in post mortem bones deposited in temperate and tropical environments would be expected to undergo diagenetic chemical reactions which degrades them into their constituent peptides and amino acids which can then be removed from the bone matrix by ground-water action. In this process, the bone loses its collagen-like amino acid pattern biochemical "fingerprint" while, at the same time, the total amount of residual organics—primarily derived from the collagen—in the bone may be significantly reduced to the point where it is extremely difficult, if not impossible, to distinguish trace amounts of collagen-derived products from exogenous contamination in the form of various organic compounds such as soil bacteria and humic or fulvic acids.

An example of the capabilities of AMS technology is provided by Stafford and his collaborators (Stafford et al. 1987; 1990; 1991) who examined the range of ^{14}C ages exhibited in different chemical fractions of collagen-profile and non-collagen-profile bones. Using a relatively well-preserved bone—i.e., a bone exhibiting a collagen-like amino acid profile—associated with a wood sample dated at 11,490±450 BP, these researchers obtained ^{14}C measurements on a wide spectrum of organic fractions prepared by a variety of chemical separation methods. These fractions ranged from untreated gelatin, HCl-insoluble residues with and without gelatinization, ion exchange purified com-
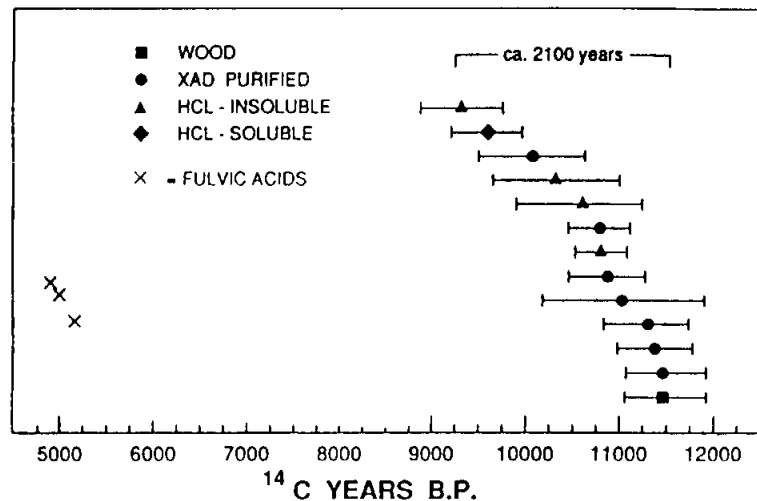
■ WOOD
● XAD PURIFIED
▲ HCL - INSOLUBLE
◆ HCL - SOLUBLE

✕ - FULVIC ACIDS

┌── ca. 2100 years ──┐

5000   6000   7000   8000   9000   10000   11000   12000

^{14}C YEARS B.P.

Figure 3.6. Distribution of AMS-based ^{14}C values on wood and various organic extracts from mammoth bone. Data taken from Stafford *et al.* (1987).

ponents, individual and combined amino acids, and humic/fulvic acids. As illustrated in Figure 3.6, nine fractions yielded ^{14}C ages within two sigma of the wood value, whereas five fractions exhibited still younger ages. With the exception of one organic fraction which was prepared using a solvent extraction technique and humic acids, the youngest organic fraction was about 2000 (±500) years younger than the actual age of the bone. The principal contaminant in the bone was identified as humic compounds with ages of about 5000 BP.

AMS ^{14}C measurements were also obtained on a comparable series of fractions (25 analyses on 14 different chemical fractions) from another mammoth bone exhibiting a non-collagen amino acid composition pattern. The actual age of the mammoth was inferred to be approximately 11,000 BP on several lines of evidence. The ^{14}C age of individual amino acids extracted from this mammoth ranged from about 3000 to 4500 BP. The youngest ^{14}C value (2270±360 BP) was obtained on a combined aliquot containing four amino acids: aspartic acid, glutamic acid, serine and threonine. Extracted fulvic acid yielded ages ranging from about 7200 to 8800 BP. The oldest ^{14}C value obtained (12,280±110 BP) was obtained on a fraction described as "nonhydrolyzable organic matter (humins)."

There now appears to be a general consensus among investigators concerning the reliability of bone ^{14}C values: that where appropriate biochemical

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purification procedures are employed, accurate ^{14}C age estimates can be obtained on bones retaining significant amounts of intact collagen. However, bones seriously depleted in protein (mostly collagen) content (< 5% of the original amount) can yield seriously anomalous ^{14}C values. Various studies have examined other organic components in bone that might resist the effects of contamination. Initial experiments with osteocalcin, a non-collagen protein, has been previously noted. Experiments that examined the ^{14}C ages exhibited by the characteristic amino acid of osteocalcin, gamma-carboxylglutamic acid (Gla), indicated that, in some cases, the isotopic integrity of Gla can be compromised (Burky 1996).

CONCLUSION

The impact of ^{14}C dating on the conduct of archaeological research has been, in some aspects, clear and explicit and in others, subtle. In addition to providing a common chronometric time scale for the entire late Quaternary, an important contribution of the ^{14}C method for archaeology is that the technique provides a means of deriving relatively precise chronometric relationships completely independent of any assumptions about cultural processes and totally unrelated to any type of manipulation of artifact data. It has also been suggested that ^{14}C dating led to a noticeable improvement in archaeological field methods (Johnson 1965: 764) and was, at least in part, responsible for the increasing attention given to statistical approaches in the evaluation of archaeological data (Thomas 1978:323).

Radiocarbon data provide the foundation on which most of the prehistoric archaeological time scales in most areas of the world for the last 40,000 years are, directly or indirectly, constructed. While currently not often stressed, the influence of ^{14}C data continue to be profound and pervasive.

ACKNOWLEDGMENTS

M. J. Aitken

Science-based dating in archaeology

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Impact on archaeology

As mentioned at the beginning of the chapter the reduction in the amount of carbon required – of the order of 1 mg instead of 1 g or more (except for mini- and microcounters) gives access to a new range of samples, allowing the archaeologist to select the more significant finds on a site without regard to size, but with full regard to suitability for the technique. It also allows the chemist in the laboratory to select the organic components from a sample that, from experience, are most reliable. The initial impact of this greater selectivity, and other aspects, have been reviewed by Harris (1987), among others, and there are various collated accounts of applications such as that edited by Gowlett and Hedges (1986). Another advantage is the ease with which a measurement can be repeated. For technical discussion the reader may refer to publications such as those by Litherland (1987) and by Hedges (1987).

4.1.6. *LIMITS OF MEANINGFUL AGE: TERMINOLOGY*

Whatever type of installation is employed for measurement there is a limit at which the sample-plus-background count rate is not distinguishable from background. The recommended practice (Stuiver and Polach 1977) is that a sample for which the *net* count rate is within 1σ of zero should be reported as *sample activity not distinguishable from background*; on the other hand, some laboratories report an age such as $(45,000^{+\infty}_{-3000})$ if the net count rate is positive, or as *infinite* if negative.

If the net count rate is between 1σ and 2σ of zero the recommended practice is to report a *minimum age* corresponding to net count rate *plus* 2σ, though some laboratories report such a sample in the usual way.

At the other end of the time-scale the recommendation is that samples for which the radiocarbon age (after reservoir correction – see section 4.4.2) is less than 200 years should be reported as *modern* and that samples having an apparent age in the future (e.g. due to contamination with bomb carbon) should be reported as > *modern*.

4.2 EFFECT OF CONTAMINATION

Because the concentration ratio of carbon-14 to carbon-12 is lower in old samples, contamination with a small amount of modern carbon causes a disproportionately large shift in apparent age, the effect becoming more serious with increasing age of sample. Thus in a sample which is 17,000 years old the addition of 1% of new carbon will cause the age to be too recent by 600 years, for a 34,000-year-old sample the same percentage causes an error of 4000 years and for a 50,000-year-old sample the apparent age

will be 36,000 years. For an infinitely old sample, the addition of 1% of modern carbon will give an apparent age of 38,000 years.

Contamination by 'dead' carbon, i.e. carbon in which the carbon-14 has long since decayed as in carboniferous material beyond the age of 100,000 years (e.g. coal and oil), does not have such a dramatic effect though it can still be serious. An addition of 1% increases the age by about 80 years, irrespective of age.

Besides the extrinsic contamination acquired, for instance in the laboratory (within the measurement system or during sample preparation), there is the question of contamination which is intrinsic to the sample itself, as now discussed.

4.3 SAMPLES AND SAMPLING

4.3.1 SAMPLE INTEGRITY; CONTAMINATION

An essential characteristic of a sample is that over the centuries of burial it has not acquired any fresh carbon from the atmosphere (e.g. by fungal growth) or other components of the exchange reservoir (e.g. in the case of shell, by later incorporation of ocean carbonate). The requirement must be fulfilled stringently, since as we have seen above, only a minute amount of modern carbon can cause a significant error in the age. As noted in section 3.4.2 there was a sharp increase in atmospheric carbon-14 activity due to nuclear weapons testing; hence one indication of high integrity for a type of sample material is that there should be no excess carbon-14 in samples of this material that were grown before commencement of testing. The various components of wood (cellulose, lignin, etc.) have been investigated in this way.

In respect of dead carbon it is not a matter of later incorporation but of the possibility of incorporation at formation, e.g. aquatic plants growing in a limestone region where the carbonate in the ground water may be 'old' because derived from the limestone.

Although the sample material itself may have high integrity there may be intrusive contamination acquired during burial. The humic acids carried in percolating ground water are an example, likewise carbonates; both of these are likely to have an age different to that of the sample.

4.3.2 SAMPLE TYPES AND LABORATORY PRE-TREATMENT

It follows that the extent to which a sample is reliable is bound up with the stringency of the laboratory pre-treatment that can be applied. At minimum there must be removal of humic acids by washing in alkali, and removal of carbonates by washing in acid. The severity that the laboratory can afford to use is dependent both on the size of the initial sample and on the amount of carbon required by the measurement facility; the severity needed depends also on the age. Obviously the use of AMS with the requirement of only

a few milligrams of carbon is highly advantageous in this context. The following notes, intended only as indicative of the sort of samples being dated and of the procedures being applied, are based mainly on the useful and concise handbook by Gillespie (1984); the reader is also referred to the European Science Foundation handbook (Mook and Waterbolk 1985), and to the comprehensive text by Taylor (1987).

Wood. The most reliable component of wood is cellulose and extraction of this component avoids lignin, which is less reliable, and humic acids from the soil; however, this is a drastic procedure and the amount of cellulose obtained may be as low as one-fifth of the initial sample. As far as humic acids are concerned these can be extracted and discarded. The more serious problem with wood and charcoal is estimation of the extent to which its formation pre-dated the archaeological event of interest, and in the case of charcoal certainty of archaeological association is often questionable.

Bone. For reliable dates from bone it is necessary to extract the protein fraction (collagen, gelatin); the carbonate fraction is not usually reliable because of the difficulty of removing secondary carbonates that have washed in from the soil. The difficulty over protein is that the amount remaining decreases with age, to a degree depending on burial environment, and there may not be much left; there is then greater risk that what is measured is dominated by contamination acquired during burial. A check on this can be made by amino acid analysis thereby determining the extent to which the amino acid 'signature' corresponds to that for collagen. With AMS dating a refinement in special cases (but too time-consuming routinely) is to obtain dates for individual amino acids (see Fig. 4.4); one of these – hydroxyproline – is particularly advantageous since it is almost unique to bone (though it has also been detected in natural water).

Shell. This material – composed almost entirely of calcium carbonate – is difficult because of continued exchange of carbon with the environment, particularly in the case of land shells; a powdery appearance indicates that substantial exchange has taken place. One approach is to subject the sample to increasing severity of acid and to date a portion after each treatment. Layers in which exchange has occurred are on the outside and more vulnerable; when these have been removed there is a levelling off of the dates obtained – this may require removal of up to 50% of the starting weight.

This does not deal with the problem of carbon exchange through recrystallization; in respect of this, shells for which the calcium carbonate is in the form of argonite are safer than those for which it is in the form of calcite. This is because on recrystallization argonite forms calcite; thus if the shell is free from calcite there is built-in evidence that no exchange has occurred. The presence of calcite can be detected by X-ray diffraction or thin section microscopy. Another possibility with shell is to use the
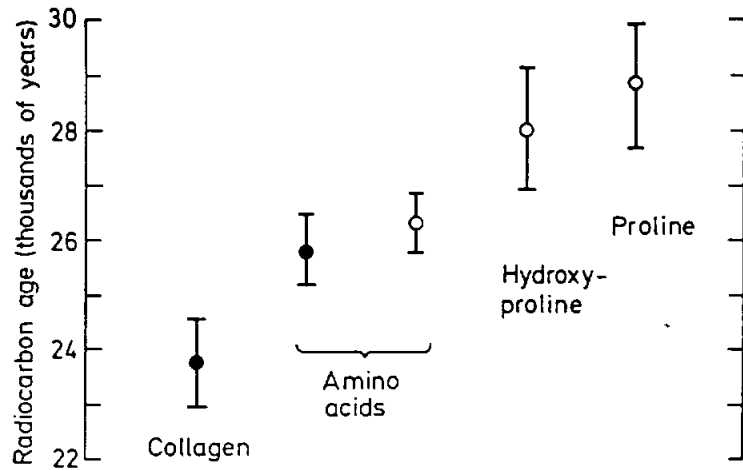
Fig. 4.4   Radiocarbon ages for different fractions extracted from a rhinoceros bone. Open symbols indicate AMS dating (at Oxford) and closed symbols conventional beta-decay counting (at the British Museum). The older ages given by the proline and hydroxyproline, which are amino acids generally specific to bone, suggest contamination by intrusive amino acids in the other fractions.

organic protein constituent, conchiolin; however, even in modern shell this is present only to 1 or 2%.

With marine shells a dominant uncertainty is the extent of the reservoir correction (see section 3.2.3) – the present-day value does not necessarily have validity in the past.

Sediments and soils. The usual approach is to date the bulk organic carbon but success is variable, the dates often being too young due to the presence of modern humic acids. Conversely, small particles of shale or coal may lead to dates which are too ancient. Although in arid regions the dating of soil carbonates may be meaningful, remains of plants and lower organisms, separable by sieving, are a preferable component and particularly applicable if the minicounter or AMS technique is being used. These techniques also give the possibility of dating specific chemical compounds, e.g. fatty acids and other lipids.

Peat. The remains of the original vegetation from which the peat was formed are represented by *humins*, which are insoluble in alkali; hence this fraction is more reliable than the alkali-soluble humic and fulvic acids, which may or may not be intrusive.

Mortar. As mortar sets, carbon dioxide is absorbed from the atmosphere to form calcium carbonate; hence in principle mortar should be datable, likewise lime burials (e.g. Stuiver and Waldren 1975). In practice the dates obtained for mortar are liable to be too old by several thousand years;

possible causes include admixture of carbonate rock chips (of infinite age) and incomplete heating of the limestone (also of infinite age) used to make the quicklime. Encouraging results have been obtained in some cases by removal of chips and also by monitoring with stable oxygen-isotope measurements (e.g. Dauchot-Dehon *et al.* 1983; Van Strydonck *et al.* 1986; Zouridakis *et al.* 1987).

Other materials. There are also procedures for seeds, grain, ivory, paper and textiles; with all of these the small sample aspect of AMS dating is advantageous. The same is true for charred organic matter within pottery, straw within mudbricks and traces of charcoal in iron objects originating in the fabrication process. Dating of stalagmites (e.g. Gascogne and Nelson 1983; Bastin and Gewelt 1986; Geyh and Hennig 1986) and other carbonate deposits (e.g. Muzzolini 1982) is also attempted, but there is uncertainty because some of the carbon incorporated is 'old', originating from limestone.

4.3.3 COLLECTION (ALSO BASED MAINLY ON GILLESPIE 1984)

Of more immediate concern to the archaeologist than the extent to which pre-treatment can remove intrinsic contamination is the possibility of external contamination during collection and storage. Cigarette ash and food scraps are well known in this context, but it is sometimes forgotten that paper, cloth and cotton wool, etc. are rich in carbon too. Polythene (polyethylene) bags (i.e. ordinary plastic bags, though they should be strong ones) are acceptable as containers, but other plastics such as PVC or PVA must be avoided since they may contain plasticizers which can be absorbed by the sample material. Aluminium foil and glass bottles are excellent, as long as the latter are carefully packed for transit. For padding within the container glass wool should be used, not cotton wool or paper tissues. Obviously labelling is of paramount importance but cards should not be put inside the same immediate container as the sample.

Sampling strategy

The expense and effort involved in obtaining a date is substantial, warranting careful thought in advance about objectives and the means to achieve them. There are two types of consideration here. First there is the archaeological one of the directness of association with the occupational phase under consideration. However reliable the laboratory's dating, sending a sample of reused timber is not usually relevant, likewise a ritual or inherited object from a grave. Similarly, there is a need to distinguish between long-lived and short-lived samples. Even if not reused the date obtained for the timber in a building will relate not to its construction nor to the felling of the tree, but to the formation of the wood as the tree grew; of course it is sometimes possible to relate

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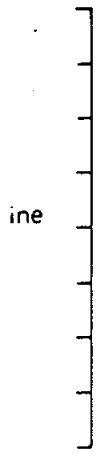
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the latter event to the date of felling by counting the annual rings – as long as there is sapwood remaining on the timber.

A second consideration is the laboratory one that different types of samples are subject to different problems. Burial conditions on a particular site may alter the usual hierarchy of reliabilities and if several types of sample are available it is prudent to collect them; if all types give the same date then confidence in the answer is substantial. Another point here is that a laboratory may be interested in having different types of sample from the same horizon in order to test the efficacy of pre-treatment procedures. Obviously this involves collaboration, but in any case, even for routine dating the more liaison between archaeologist and laboratory the better.

Archaeological association

Returning to the question of certainty of association the following categorization is derived from Waterbolk (1971, 1983):

A. Full certainty: the measured sample comes from the archaeological object itself. Examples: human bone from grave, tree-trunk canoe, wagon wheel, post from house, organic backing material in pottery.
B. High probability: there is a direct functional relationship between the organic material which is measured and the diagnostic archaeological finds. Examples: carbonized coffin in a grave with finds, carbonized grain in rubbish pit with sherds, charcoal in an urn, hearth in floor of house.
C. Probability: there is not a demonstrable functional relation between measured sample and archaeological material, but the quantity of organic material and the size of the fragments argue in favour of a relationship. Example: charcoal concentration in a rubbish pit or occupation layer.
D. Reasonable probability: as C, but the fragments are small and scattered. Examples: 'dark earth' in occupation layer, particles of charcoal in a grave.

Waterbolk also notes the lower reliability that should be assigned to samples from test excavations in which the interpretation is tentative compared with those from prolonged systematic excavations. In addition he categorizes samples in respect of the delay that there may have been between sample formation and archaeological association.

A. The difference in date is so small as to be negligible (< 20 years). Examples: twigs, grain, leather, bone, outermost tree-rings.
B. The time difference can amount to several decades (between 20 and 100 years). Examples: charcoal from wood species with a short life span; outermost tree-rings from durable wood species when there is no reason to expect a long period of use.

Table 4.1 Optimum sample weights (in grams)

Material	Beta counting		Accelerator
	Conventional	Minicounter	
Charcoal	5–10	0.1–0.5	0.01–0.1
Wood, dry	10–20	0.5–1	0.05–0.1
Wood, wet	40–80	1–2	0.1–0.2
Bone	100–500	10–50	0.5–5
Shell	50–100	0.5–2	0.05–0.1
Carbonates	100–200	2–10	0.1–0.2
Peat, dry	50–100	1–3	0.1–0.2
Peat, wet	100–200	3–5	0.2–0.5
Sediment, dry	100–200	3–5	0.5–5
Sediment, wet	200–500	10–50	1–10

Note: This table is from Gillespie (1984) who adds that these are approximate weights and for samples free of soil, sand and artefacts, etc.; also that in some cases smaller samples will be acceptable but with possible increase in cost and poorer precision. If the sample is likely to be contaminated and/or more than 20,000 years old then the amounts given above should be doubled.

C. The time difference may amount to centuries (> 100 years). Example: charcoal from wood species with a long life span possibly subject to re-use).

D. The nature of the dated organic material is not precisely known. Examples: samples consisting of 'dark earth', 'ash', 'soil'.

Amount of sample

Table 4.1 shows optimum sample amounts for the three types of measurement facility. This is a guide only, and if a greater amount is available, it should be collected; the laboratory can then intensify its pre-treatment procedures. Another prudent policy in the case of plenty is for the archaeologist to retain a reserve sample against various contingencies, e.g. the need to check an unexpected result, the development of improved pre-treatment procedures or other aspects of technique, or simply the loss of the first sample due to equipment failure or other causes.

The minimum amounts from which an age can be obtained in special circumstances are substantially less than those given in Table 4.1, particularly if the sample is not more than a few thousand years old. As has been mentioned, using AMS a single seed can be dated, or a few threads of linen (as with the Shroud of Turin); pushing the technique to the limit it has been demonstrated that it is feasible to date the order of 0.1 mg of blood residue from a prehistoric stone tool (Nelson *et al.* 1986).

Documentation

To an archaeologist each radiocarbon sample is one of a few, but in the laboratory it is one in an annual throughput of several hundreds or even a thousand. Therefore efficient labelling is essential, together with all the information about archaeological context that the particular laboratory requests and needs for publication; the standardized form proposed by Kra (1986) is a guide to what is required. Indication of expected age is useful because it guides the laboratory in its pre-treatment procedures and the measurement time that will be needed. For an old sample the emphasis is on removal of modern contamination and the measurement time is long. For a young sample it is 'old' contamination that matters most and the measurement time is shorter. In general, inadequate pre-treatment causes an old sample to have an apparent age that is too recent and a young sample to have one that is too ancient. It should be recognized that pre-treatment procedures are continually being improved and that a date obtained a decade or so ago cannot have the same reliability as one recently performed, unless the sample was a straightforward one.

Pre-cleaning

It is worth while for the archaeologist to take a critical look at his material before dispatch, picking out all obvious foreign matter such as stones, artefacts, plant roots and leaves, loose soil or sand. Each material type, e.g. charcoal, bone, wood, marine shells, non-marine shells, etc. should be packaged on its own. Indication of contaminants known to be likely is helpful so that the laboratory can be prepared in its pre-treatment approach.

Before the laboratory starts on the pre-treatment proper there is further removal of foreign matter using a low-power microscope, and flotation techniques where appropriate. It is not only a matter of avoiding a wrong answer but also of avoiding overload in the subsequent processing procedures.

4.4 STEPS TOWARDS A CALENDAR DATE

4.4.1 THE NEED FOR CALIBRATION

Laboratory measurements on a sample yield an age – the *age in conventional radiocarbon years* – based on the premiss that the atmospheric ratio of (carbon-14/carbon-12) has been constant. As discussed in section 3.3.1 this premiss is only approximately true and the age so obtained is not the same as the age in calendar years; the latter is derived by means of calibration curves based on known-age samples, mostly wood dated by dendrochronology – hence the terms *dendrodates* and *dendrochronological calibration* (alternatively *tree-ring calibration, bristlecone pine calibration*.

There are two reasons for needing to convert to calendar years:

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first, to permit comparisons with dates obtained by other methods, and second, to make a correct assessment of speed of development – there are periods when only a small difference in radiocarbon years corresponds to a substantial change in calendar date, and vice versa. For example, in the first millennium BC the difference between radiocarbon ages corresponding to samples having calendar dates of 800 BC and 400 BC is only about 250 years. Obviously it is important for an archaeologist to know of this, and other less extreme distortions of the radiocarbon time-scale.

Conversion to calendar date is confusing because of the irregular form of the calibration curve; the difficulty of translating error limits from one time-scale to the other is particularly acute and here we are inevitably in the hands of the statisticians. First, however, we deal with the derivation of an age in radiocarbon years.

4.4.2 CONVENTIONAL RADIOCARBON YEARS

The basic principle has been illustrated in Figs 3.2 and 3.3. For the latter the curve was drawn using the revised half-life of 5730 years which was determined, by laboratory measurement, in the early 1960s. This value is 3% greater than the Libby half-life of 5568 years used for Fig. 3.2, and it is this latter value that is used for calculation of conventional radiocarbon years. The reason for retaining it is to avoid confusion and risk of multiple correction. The consequence is that even if there was no distortion of the time-scale the age in calendar years would be 3% greater than the age in conventional radiocarbon years, e.g. 1000 radiocarbon years correspond to 1030 calendar years; however, in general the half-life correction is dwarfed by the correction for distortion. In practice the correction made by the calibration curve subsumes the half-life correction; it is only beyond the limit of the calibration that separate attention needs to be given to the latter.

Years before present (BP)

Because samples get older as the years go by all radiocarbon ages are referred to AD 1950 as 'present'. Of course it is only for very precise dates that this is more than a trivial consideration, but the situation will gradually change in the future. It is less confusing to regard BP as meaning 'before physics' – AD 1950 being the year in which radiocarbon dates began to be published. In radiocarbon terminology 'BP' means an uncalibrated age, with 'cal BP' indicating calibration.

Reference to modern standard

Rather than to attempt a direct evaluation of a sample's carbon-14 activity it is more convenient and more precise to make comparison with a reference standard measured in the same installation just before or just after the sample. The basic reference material is the oxalic acid

specially prepared by the US National Bureau of Standards from a crop of sugar-beet. Standard 'modern' activity, A_m, is defined as 0.95 times the activity of this standard[6] when measured[7] in the same installation as the sample at about the same time. Other standards, which have been related to A_m, are used in addition; it is common practice to use one of the same material as the sample being measured.

Isotopic fractionation

Before the age is calculated it is necessary to make correction for any isotopic fractionation that occurred during uptake of carbon by the sample while forming[8] (see section 3.2.2). The standard modern activity refers to wood having the average carbon-13/carbon-12 concentration ratio for wood. In order to allow for the different degree of fractionation occurring in other types of sample, one approach would be to define a standard modern activity for each type. Instead of this the measured sample activity, A', is adjusted so as to correspond to wood, the fractionation-corrected value being denoted by A.

The adjustment is made on the basis that the fractionation effect for carbon-14 is twice that for carbon-13. As an example consider bone collagen, for which the average carbon-13/carbon-12 ratio is 0.5% higher than that for wood, i.e. during formation collagen takes in the heavier isotopes more readily than does wood. Hence the starting carbon-14 activity for a collagen sample would have been higher than for a wood sample formed at the same time, by 1%. To allow for this the measured activity of a collagen sample is reduced by 1%, i.e. $A = 0.99A'$. Failure to make the adjustment would give an age erroneously too recent by 80 years.

High-precision, and some other laboratories, measure the carbon-13/carbon-12 ratio, for each group of samples being processed, by means of an ordinary mass spectrometer. Otherwise the standard value for the sample type concerned is used (see Table 3.1); there is then a small increase in the uncertainty of the date obtained arising from the spread of values for a given sample type.

The age equation

Having adjusted the measured activity A' to the fractionation-corrected activity A, the age[9] in conventional radiocarbon years before AD 1950 is given by

$$\text{Age} = 8033 \ln\left(\frac{A}{A_m}\right) \tag{4.1}$$

$$= 18,497 \log\left(\frac{A}{A_m}\right)$$

where, as indicated above, A_m is the standard modern activity.

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The numerical factors, 3% lower than those in equation (3.3), correspond to the Libby half-life of 5568 years instead of the revised half-life of 5730 years.

For further discussion of the basis on which conventional radiocarbon ages are derived, and the symbols used,[10] the reader should refer to Stuiver and Polach (1977); these authors also give recommendations in respect of rounding-off of reported ages, e.g. if the error limits are below ±50 the age should be rounded off to the nearest multiple of 5, and if between ±50 and ±100 to the nearest multiple of 10. However, with the advent of high-precision calibration curves there is a tendency to delay the rounding-off of high-precision results until quoting the calendar date.

Reservoir-corrected age

As discussed in section 3.2.3 present-day carbonate in deep ocean water may have an apparent age of several thousand years because of its long residence time there. Because there is some admixture of deep water into the surface ocean shells grown there have some apparent age too – around 400 years for mid-latitudes, rising to the order of 1000 years in regions of upwelling. The reservoir correction is determined by measurements on historically dated samples of the same material and origin as the sample being dated; samples prior to the Industrial Revolution need to be used in order to avoid interference by fossil-fuel effect. It is also necessary to consider the way in which the ocean responds to the atmospheric fluctuations in carbon-14 activity (see Fig. 3.5), and appropriate calibration curves for marine samples have been given by Stuiver *et al.* (1986); these are substantially smoother than for atmospheric samples. The same authors give corrections appropriate to various marine regions, based on reported values.

There are also other types of sample which are affected by abnormalities in the carbon-14 activity of carbon taken in during formation, e.g. shells and aquatic plants in limestone regions; other examples were mentioned in section 3.2.3. Reliable correction is only possible in some cases.

The conventional radiocarbon age of a sample refers to the age *before* correction; if the reservoir-corrected age is reported the former is usually given also. It should also be remembered that there is a slight overall reservoir effect between Northern and Southern Hemispheres; late-nineteenth-century dendrochronologically dated wood from southern mid-latitudes gives an apparent radiocarbon age that is about 35 years less recent than contemporary wood from northern mid-latitudes.

4.4.3 COMBINING DATES

'One date is no date' for several reasons – contamination, intrusive material, mistaken attribution, laboratory error, etc. A second determination for the same archaeological phase is many times more useful than a single one:

if the ±1σ spans (68% level of confidence) overlap then confidence in both is enormously strengthened, but if there is no overlap even at the 95% level of confidence (±2σ spans) then both are in doubt.[11] It may be, in the latter case, that the separation is indicative of the duration of the phase, but it is also possible that one of the dates is a 'rogue' – through an interference such as mentioned above. More determinations will throw light on these and comparable questions though in the end there are no hard-and-fast answers, only assessments of probabilities – as indeed is the case with nearly all the techniques of this book; of course in some circumstances there may be confidence in a given interpretation at, say, the 99.7% level or higher, qualifying as 'hard-and-fast', but unfortunately this is not often so.

Reliable assessment of probabilities can be made through rather daunting statistical procedures (e.g. Long and Rippeteau 1974; Ward and Wilson 1978; Wilson and Ward 1981) and increasingly these are becoming accessible through availability as computer programs. Discussion of these is somewhat outside the scope of this book, but some basic considerations relevant to preliminary assessment of a group of dates will be given. Among the aspects involved are (i) whether it is justified to average the dates, (ii) whether it is justifiable to discard some of the outliers as 'rogues' and (iii) the error limits appropriate to the average. In general, averaging is best done before conversion to calendar dates, i.e. the average age in conventional radiocarbon years should be obtained and then calibrated as indicated in section 4.4.4. An exception is when the samples being combined are not coeval but have a known spacing in calendar years, i.e. they form part of a 'floating' tree-ring sequence. *Wiggle-matching* and special statistical treatment are then possible, as discussed at the end of section 4.4.4. When the spacing in calendar years is not known but the samples all relate to a well-defined archaeological period, a useful way of expressing them *in toto* is by means of quoting the interquartile range (Ottaway 1973); the dates are arranged in order and the limits of this range are set so as to exclude the upper quarter and the lower quarter.

The expected spread

The curve of Fig. 4.1 indicated the probability that the true age differed by a given amount from a single measured age. The same curve can be used to express the expected spread in the measured ages obtained from a number of coeval samples. The average for these will be close to the true age and the scatter of individual ages should be such that for 68% of the samples the average is encompassed by the error limits for the sample concerned; of course the 68% is rather approximate unless the number of samples is large and Fig 4.5 illustrates two cases where small numbers are involved. In case (a) the ±1σ error limits of four of the seven

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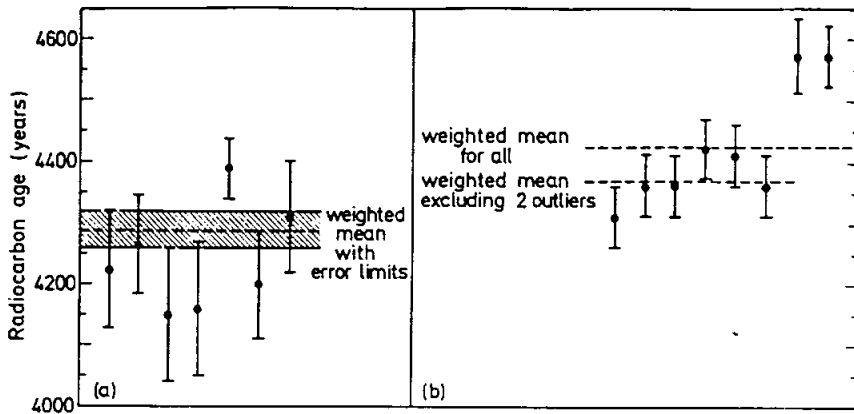'up even at the
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Fig. 4.5 The scatter of individual ages shown in (a) is consistent with the samples being coeval, the weighted mean being 4290 ± 30 years. The samples in (b) cannot be accepted as a group and it is not justifiable to use the weighted mean for all of them; after exclusion of the two outliers the remaining six samples form an acceptable group with a weighted mean of 4370 ± 20 years. The data are discussed further in the text and in notes 12 and 13.

samples encompass the average value, whereas in case (b) only two out of eight do so.

Statistical assessment[12] confirms acceptance of the samples of case (a) as being coeval and without rogues; hence it is justifiable to use the average value as the best estimate of the true radiocarbon age and to quote somewhat tighter error limits than the individual error limits – see below. For case (b) statistical assessment confirms that averaging is not justified for all eight samples but that it is justified for the six that remain after discarding the two outliers; we may note that four out of these six encompass the new average.

In rejecting the two outliers the supposition is either that those two samples were not coeval with the rest, or that they were specially subject to some measurement interference (contamination, etc.). Rejection of outliers is of course a thorny subject liable to stimulate accusations that the data are being manipulated to fit preconceived ideas. Hence it is highly desirable to use soundly based statistics in this context (see above p. 96 for references); the dating of the Bronze Age eruption of the volcano of Thera in the Aegean is a case where different rejection procedures lead to different final dates (Aitken *et al.* 1988; Manning 1988; also Fig. 4.12).

Weighted mean and its error limits
A result with small error limits carries more weight than one with wider limits and this needs to be taken into account in calculating[13] the

weighted mean age (or *pooled mean*) for a group of coeval samples. Thus for the samples of Fig. 4.5(a) the weighted mean is 4290 years, whereas the unweighted mean (or *arithmetic mean*) is 4240 years; the former is older because of the extra weight given to the sample having an age of 4390 years; the quoted error limits for this one are ±50 years, whereas for the others the limits are ±80 years or greater.

An average is likely to be nearer to the true value than any individual age and this is reflected in the error limits calculated[13] for the mean. In the simple case of individual ages all with the same individual error limits, σ_i, the error limits for the mean age are $(\pm\sigma_i/n^{1/2})$, where n is the number of samples; thus the error limits for the mean in the case of n = 4 and σ = 80 are ±40 years and for n = 16 they are ±20 years.

It is sometimes asked whether there is advantage in measuring, say, four samples compared to counting one sample only for at least four times as long. The answer is emphatically in favour of the former as long as four samples of high suitability (in terms of archaeological association and type of material) are available. There are two reasons: first, the coherence of multiple ages allows assessment of reliability, as indicated above; second, the uncertainty arising from statistical fluctuations in count rate is not the only contribution to the error limits but there is also the rather intangible contribution from minor variations in the sample preparation process. This latter is evaluated by intermittent test runs involving replicate preparations of the same sample, and in the discussion above it is taken for granted that the quoted error limits for an individual age include that contribution (sometimes introduced as the 'error multiplier' – see section 4.1.3).

4.4.4 CALIBRATION

In using calibration curves there are three main aspects. The first is the appreciable divergence between radiocarbon age and calendar age as one goes back in time beyond 500 BC (see Fig. 4.6); prior to that date radiocarbon ages are consistently too recent, the underestimate being steady at around 800 years for the three millennia beyond 4000 BC. From 500 BC to AD 1300 there is a tendency for radiocarbon ages to overestimate the calendar age, but not by more than 150 years. It is in the millennia of underestimation that calibration has its archaeological impact and when it became available for application in prehistory there followed a dramatic reappraisal of the relationship of western Europe and the Balkans to the Near East; this was 'the second radiocarbon revolution', the first having been the impact that radiocarbon ages themselves had had already in indicating a greater than expected antiquity for Neolithic developments.[14]

The second aspect is the increased ambiguity in interpretation that usually results from the 'wiggliness' of the calibration curve. As illustrated in Fig. 4.7 the span in calendar date corresponding to the error limit span of the radiocarbon age may be substantially in excess of the latter; in other
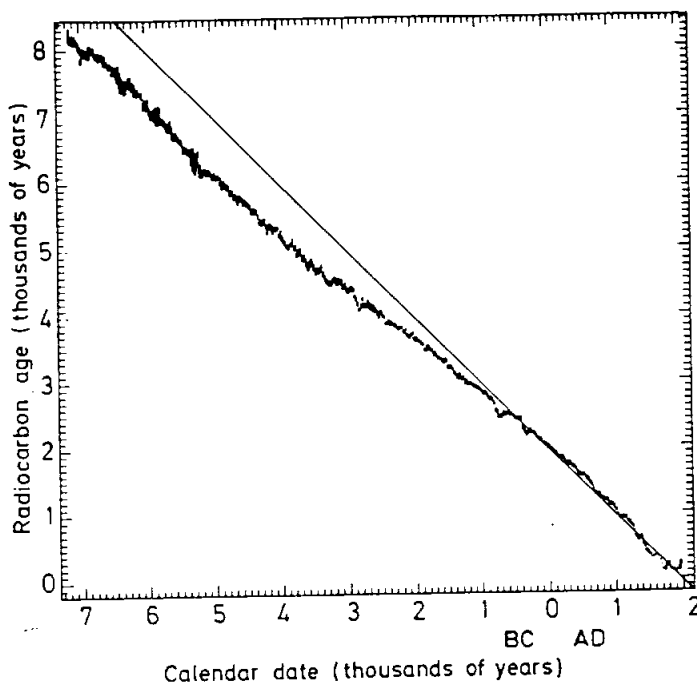
Radiocarbon age (thousands of years)

Fig. 4.6 Relationship between conventional radiocarbon age and calendar date, based on dendrochronologically dated wood samples. The solid line shows the 'ideal' relationship that would exist if the half-life used for calculation of conventional radiocarbon ages was exactly correct. (From Pearson 1987.)

cases there may be several possible calendar date spans corresponding to a single radiocarbon age.

The third aspect concerns the error limit band of the calibration curve itself. Even in a wiggle-free part of the curve this inevitably widens the calendar date span – as illustrated in Fig. 4.8.

Faced with these aspects[15] it is not surprising that some archaeologists throw up their hands in despair. The more effective response is a realistic appraisal of the situation. For despite these complications radiocarbon continues to provide the main chronological framework of prehistoric periods back to 40,000 years ago. It should also be appreciated that the calibration curves have involved many years of dedicated and meticulous effort by the laboratories and dendrochronologists concerned and represent a quite remarkable achievement.

Historical
Until the early 1980s an additional difficulty for archaeologists was that the radiocarbon community could not agree on a common calibration curve. The first one produced was that of Suess (1970) drawn freehand
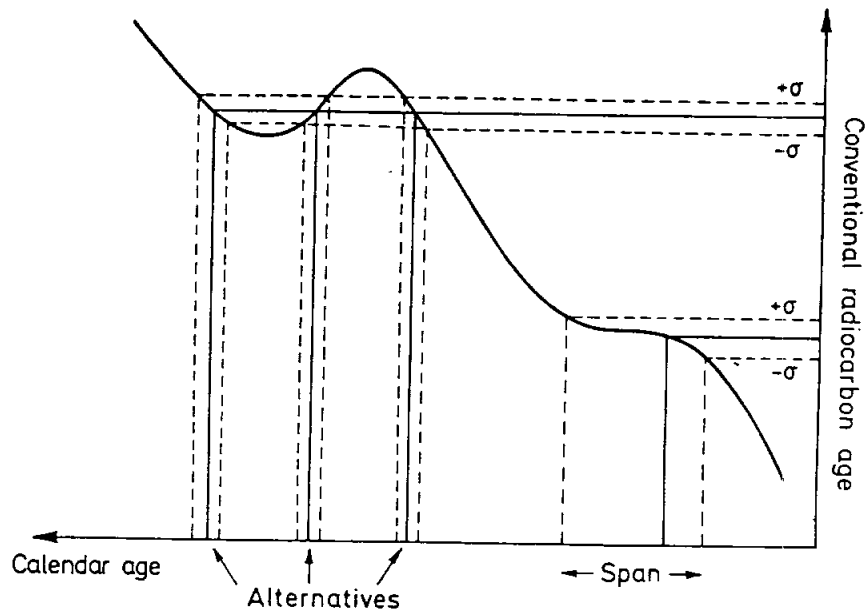
Fig. 4.7 (*Left*) Because of a wiggle in the calibration curve there are three possible calendar ages corresponding to one radiocarbon age. (*Right*) Because of a 'plateau' in the calibration curve the span in calendar age corresponding to the error limits of the radiocarbon age is substantially increased. On the other hand, in the central steep portion the error limits would be reduced (not shown).

by 'cosmic schwung'. At that time the experimental precision attainable for the calibration samples was about ±50 years, substantially worse than the ±20 years now available from high-precision laboratories. Calibration curves were also produced by Ralph *et al.* (1973) and Damon *et al.* (1972), the former being the basis of the much-used MASCA[16] corrections. Another commonly used calibration curve was that of Clark (1975) based on statistical assessment of all the data then available. These various curves, all based on trees from the western USA, showed the same main features, but there were differences in the smoothing procedures employed. Eventually, using mainly the same data, a *consensus calibration* was proposed (Klein *et al.* 1982); this made a careful assessment of the influence of experimental precision and interlaboratory bias (as indicated by measurement of samples of the same date) and a sound statistical basis for conversion was developed. Inevitably, in order to find common ground it was necessary to accept fairly wide error limits for the accuracy of the conversion. Also instead of keeping to the common practice of quoting the span in calendar date that corresponds to ±1 standard error in radiocarbon age (i.e. the 68% level of confidence) the span that corresponds to ±2 standard errors (i.e.
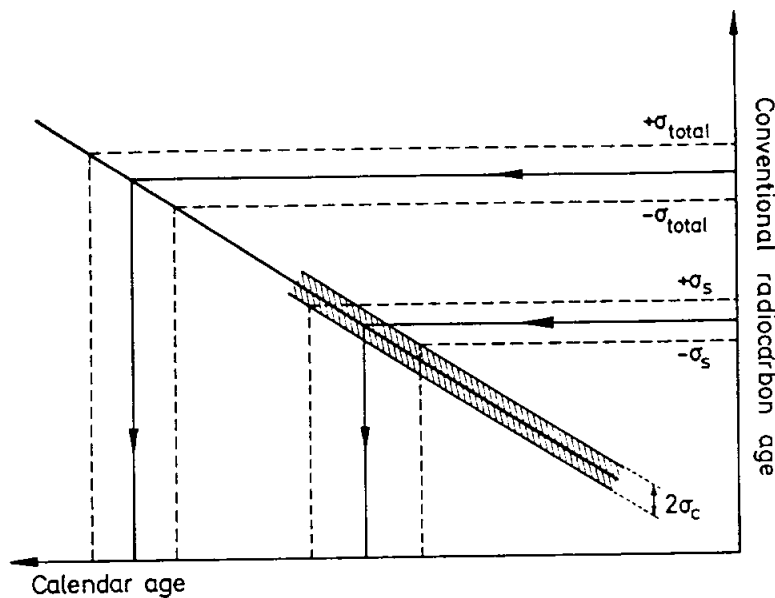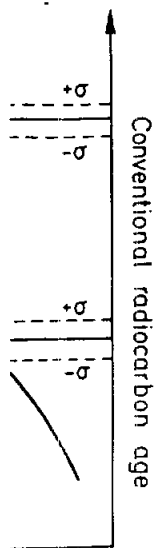
Calendar age

Fig. 4.8 The calibration curve itself has error limits, $\pm\sigma_c$, so that even in the absence of irregularities the calendar age span is wider than the radiocarbon age span to which it corresponds. However, the procedure indicated in the lower part of the figure overestimates the enhancement of the span; the correct procedure (see e.g. Pearson and Stuiver 1986) is to combine the calibration error limits, $\pm\sigma_c$, with those for the sample age, $\pm\sigma_s$ according to $\sigma_{total} = (\sigma_s^2 + \sigma_c^2)^{1/2}$ and use σ_{total} as indicated in top upper part of the figure.

95% level) was used; although the wider spans may be more realistic the different basis for uncertainty assessment does introduce additional confusion. The consensus calibration has now been superseded by the high-precision calibrations which were presented in 1985 at the Twelfth International Radiocarbon Conference at Trondheim, Norway; these opened a new era for archaeologists.

High-precision calibrations
Of particular importance at the conference was the definitive demonstration that there was agreement between calibrations derived from trees growing on the Pacific coast of the USA and trees growing in lowland Europe, derived furthermore in two independent laboratories. These calibrations are the work of the laboratories at Belfast and Seattle and cover the periods 2500–500 BC (Pearson and Stuiver 1986) and 500 BC–AD 1950 (Stuiver and Pearson 1986) with a justified claim to an accuracy of better than ±20 years; because they were replicated in two laboratories they were recognized by the conference as being definitive and were recommended for use by archaeologists. The laboratory at Belfast used the liquid scintillation
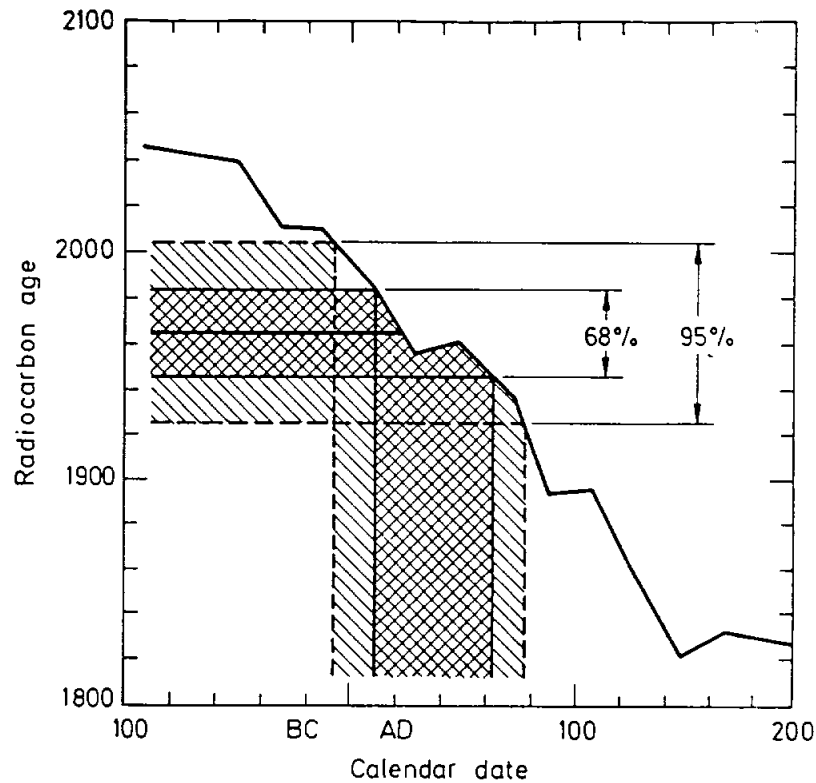

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Fig. 4.9   Calibration of the radiocarbon age of 1964 ± 20 years derived from measurements on a control sample by three AMS laboratories involved in dating the Shroud of Turin (see Damon *et al.*, 1989). For the calibration curve (Stuiver and Pearson 1986) σ_c is only about ± 10 years in this period so that, following the procedure given in the caption to Fig. 4.8, $\sigma_{total} = (20^2 + 12^2)^{1/2} = 22$. The calendar date span corresponding to the 68% level of confidence is AD 10–65, and that corresponding to the 95% level of confidence is 10 BC–AD 80.

technique, with samples spanning 20 years of growth (bidecadal), and at Seattle a gas proportional counter was used, with samples spanning 10 years of growth (decadal); any systematic age difference between the two laboratories was shown to be less than a few years. Whereas the former used mainly Irish oak the latter used Douglas fir and sequoia from the US Pacific coast and oak from south Germany; again there was no significant systematic difference between regions.

Full details of all calibrations presented at the conference, together with precise instructions for utilization, are given in a special issue of *Radiocarbon* (vol. 28–2B). Beyond the two recognized calibrations just mentioned the conference recommended use of the Belfast curve – now extended to 6000 BC (Pearson *et al.* 1989). Further back firmly based

dendrochronological curves extend to 7200 BC and reliable indications, using varve data also, reach 12000 BC. As elsewhere in the present text 'BC' (or 'AD') means calendar date as obtained after calibration; in the terminology recommended by the conference the correct nomenclature would be 'cal BC' (or 'cal AD').

Most of the calibrations reported utilized either 10- or 20-year growth spans. For some, smoothed curves using a 100-year running mean are presented also; these have an uncertainty in radiocarbon age of only a few years.

Probability spectra

Determination of the calendar date span, or spans, that correspond to the 68% error limits in radiocarbon age (or to the 95% limits) is moderately straightforward, examples being given in Figs. 4.9 and 4.10. However, because of the irregular shape of the calibration curve, the distribution of probability within the span(s) is somewhat more complex than the probability curve appropriate to a radiocarbon age (see Fig. 4.1). Increasingly dates are being expressed in terms of probability spectra, such as shown in Figs. 4.11 and 4.12.

These spectra represent the full information that is available from a determination; given the cost and effort involved in measurement it would seem appropriate that space should be found for spectra in publications, inconvenient though this may be. Although it is possible to derive a central date and confidence level spans from the calendar date probability distribution these gloss over the unevenness of the distribution; thus in Fig. 4.11 the probability is rather low in the centre and the 68% confidence level span excludes dates of substantially higher probability. However, there are other statistical approaches (e.g. Leese 1988) which avoid this feature.

Floating tree-ring sequences; 'wiggle-matching'

Samples which have a known spacing in calendar years, such as those formed by the wood of a large timber beam with well-defined annual rings – or an interrelated sequence of such beams, permit more accurate dating than is otherwise possible. Special statistical treatments have been developed (Clark and Renfrew 1972; Clark and Sowray 1973) which are generally applicable, and in cases where the period in question contains irregularities in the calibration curve, 'wiggle-matching' is possible (e.g. Ferguson *et al.* 1966; Suess and Strahm 1970; Pearson 1986). Essentially this latter consists of finding where the wiggle pattern formed by the sequential sample dates best fits the wiggle pattern of the calibration curve. The time span of the wood used for each sample date (which must be of high precision) needs to be either 10 or 20 years, as appropriate to the calibration curve used; hence the sequence needs to extend over at least 50 years. By this

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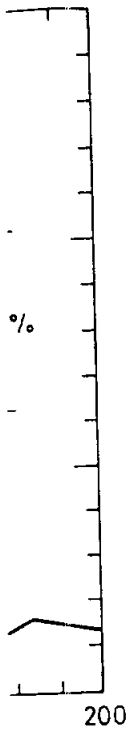
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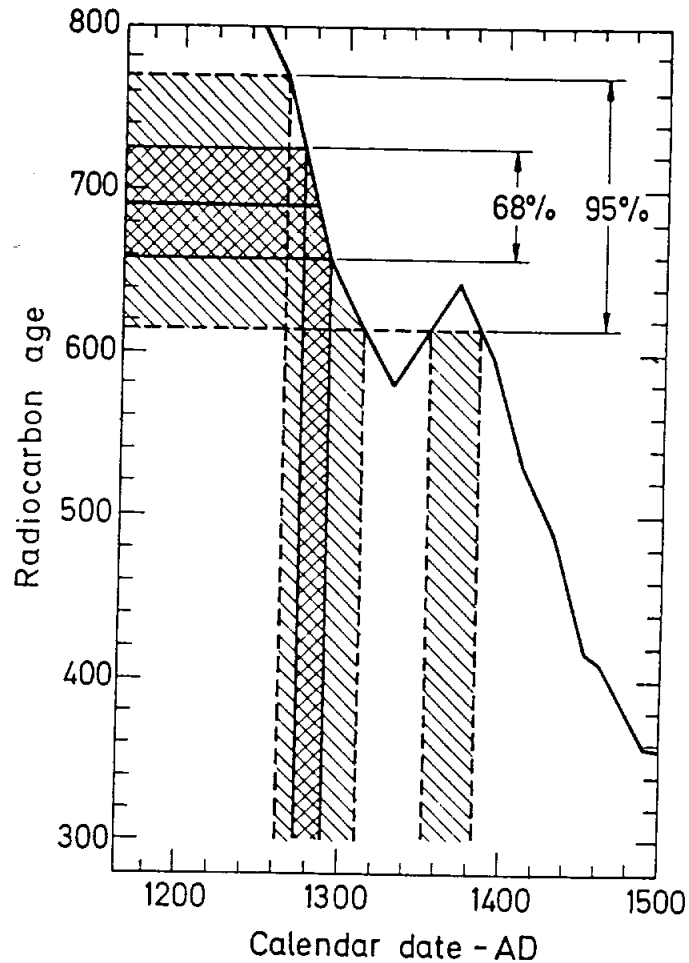ilibrations just
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Fig. 4.10 Calibration of the radiocarbon age of 691 ± 31 years as derived from measurements by three AMS laboratories on linen threads from the Shroud of Turin (see Damon *et al.*, 1989). Following a similar procedure to that for Fig. 4.9 the calendar date span corresponding to the 68% level of confidence is AD 1275–1290; corresponding to the 95% level of confidence there are two possible spans: AD 1260–1310 and AD 1355–1385. Note that because of the steepness of the curve the 68% calendar span is appreciably smaller than the radiocarbon age span to which it corresponds. The calibration curve is that of Stuiver and Pearson (1986).
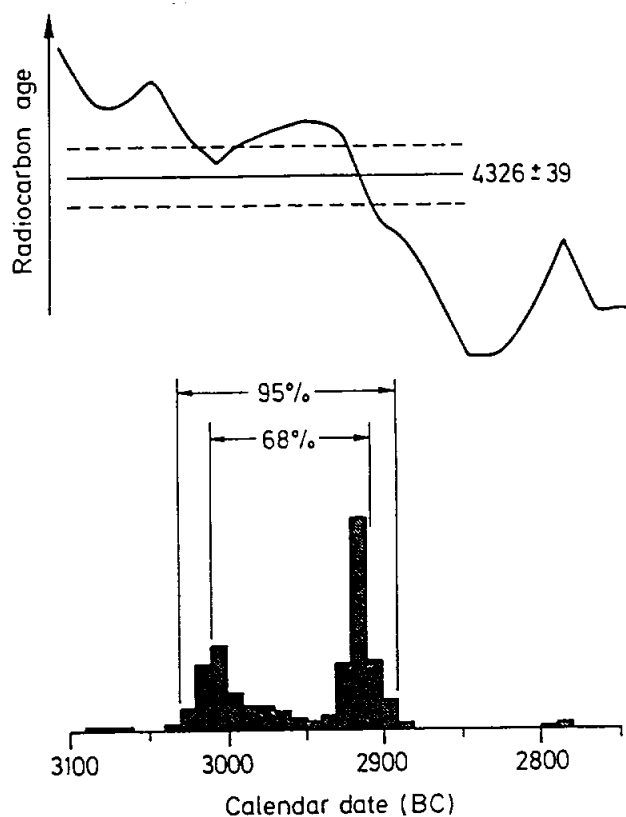
Fig. 4.11 Probability distribution for the calendar age corresponding to a radiocarbon age of 4326 ± 39 years; the upper part shows the calibration curve (Pearson *et al.* 1986) and the histogram below indicates the probability that the calendar date lies in one of the 10 year intervals indicated. The vertical lines indicate the limits of calendar date within which there is a 68% probability of the true date lying; the limits corresponding to 95% probability are also shown. These are not quite the same as the limits of the calendar date span that corresponds to the 68% and 95% levels of confidence limits in the radiocarbon age. The radiocarbon age concerned is the weighted mean for samples from Nubia ('Terminal A-Group') which were contemporaneous with about the beginning of the First Dynasty in Egypt (see Hassan and Robinson 1987, from which this diagram has been obtained[17]).

technique it is possible to obtain quite narrow calendar date spans even in time periods where the calibration curve is flat.

Coherence
Even when the exact separation in calendar years is not known, the coherence of a suite of samples related by stratigraphy, or otherwise, allows better assessment of reliability than can be obtained with unrelated

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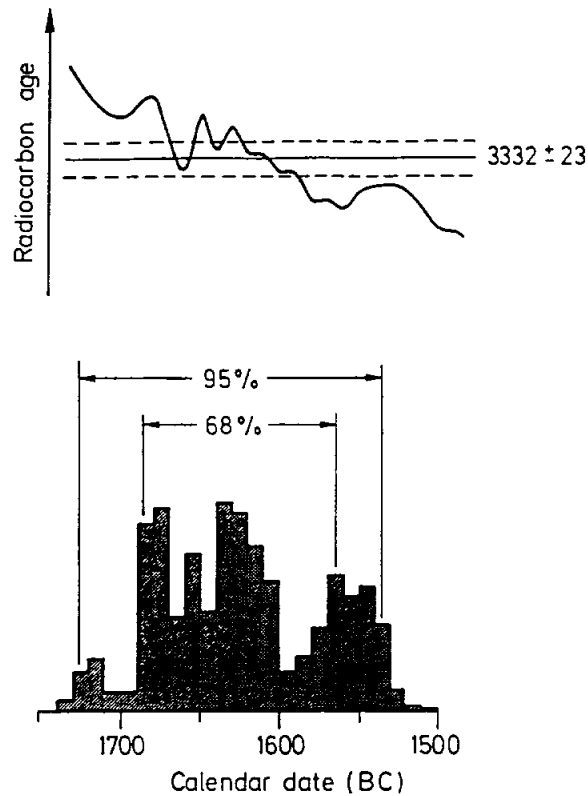
Fig. 4.12 Probability distribution for the calendar date corresponding to a radiocarbon age of 3332 ± 23 years on same basis as for Fig. 4.11 (except that the calibration curve is the decadal one of Stuiver and Becker, 1986). This diagram has been derived by S. W. Robinson (pers. comm.) and the radiocarbon age is based on conventional beta counting determinations made on six fully pre-treated short-lived samples found in a destruction layer associated with the Bronze Age eruption of Thera on the Aegean island of Santorini. Other assessments of the eighteen conventional determinations that are available give lower averages (depending on rejection criteria) but none below 3290 radiocarbon years (see Aitken *et al.*, 1988). Datings of single seeds and grain etc using the AMS technique have now given an average of 3325 ± 30 years (Housley *et al.* 1990) in good agreement with the age illustrated above. The traditional chronology (based on archaeological linkage to the Egyptian calendar) places the eruption *circa* 1500 calendar years BC. As will be seen from the probability spectrum the radiocarbon determinations indicate that an earlier date is much more likely; this is consistent with the revised, 'long', chronology as well as with ice-core and tree-ring evidence – see section 2.3.6. Contrary to the situation in Fig. 4.10 the calibration curve is rather flat here and consequently the 68% range of calendar date probability is substantially wider than the 68% span in radiocarbon age; similarly in respect of 95%.

samples. In most of this chapter we have been concerned with laboratory assessments, but however hard the chef works in his kitchen the ultimate proof of the pudding is in the eating. Figure 4.13 illustrates this.

In judging coherence it is important to pay full regard to the quoted date spans and to remember that at the 68% level of confidence there is a one in three probability that the true date lies outside the quoted span. Thus in checking whether or not two dates are in correct stratigraphic order the spans corresponding to 95% level of confidence should be used; even then there is a one in twenty chance that one of the true dates lies outside the span.

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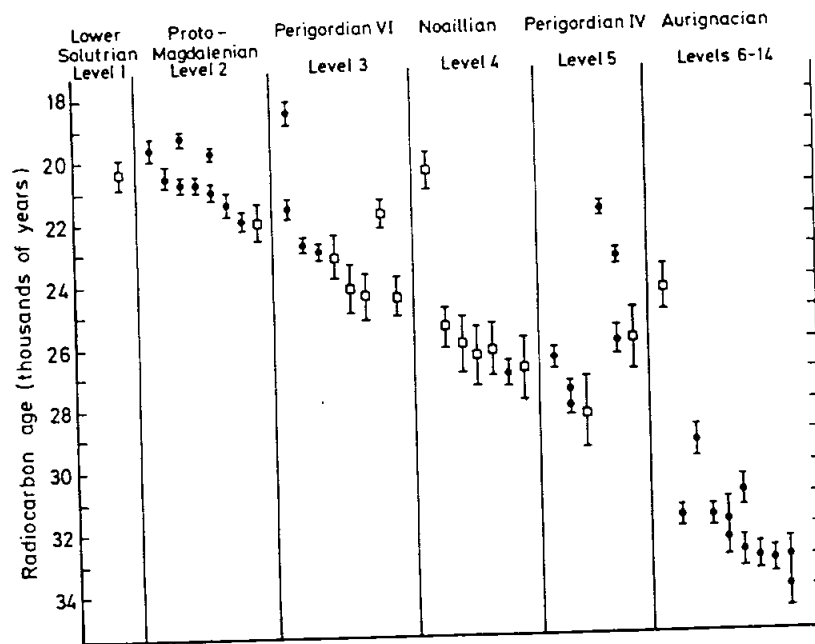
Fig. 4.13 Radiocarbon ages for bone samples, arranged in stratigraphic order, from the Upper Paleolithic site at Abri Pataud, France; closed symbols are for total amino acid extracts dated by AMS (at Oxford); open symbols are for samples dated by beta-decay counting (at Groningen) mostly using collagen. Although the majority are in excellent concordance with stratigraphy there are a few samples for which the date appears to be anomalously too recent; these samples all have a rather small amount of collagen remaining (less than 4% of the original content) suggesting the possibility of contamination by intrusive amino acids from the soil despite precautions taken.
(From Hedges 1987; see also Waterbolk 1971; Mellars and Bricker 1986).

4.5 BEYOND CALIBRATION

Although we may expect gradual extension of the period for which calibration is available through dendrochronology and glacial varve counting, it is unlikely to extend much into the last glaciation. However, other dating techniques are becoming increasingly relevant as far as the long-term trend is concerned. Comparative results using uranium series (Vogel 1987) and thermoluminescence (by H. Valladas, see Aitken 1987) suggest that the period during which radiocarbon gives a substantial underestimate of calender age extends back to at least c. 20,000 years ago. New developments in potassium–argon dating and in uranium-series dating should allow somewhat more precise comparisons to be made, particularly with the latter.

In making such comparisons conventional radiocarbon ages should be multiplied by 1.03 in order to convert to values based on the revised half-life, i.e. 900 years should be added to a radiocarbon age of 30,000 years and 1200 years to one of 40,000.

NOTES

1. As an example consider a proportional counter installation for which the count rate for modern carbon is 16 per minute: for a sample 11,000 years old (two half-lives) the rate will average 4 per minute and so to reach the 10,000 counts necessary for a standard error of ±100 (corresponding to ±1% and hence about ±80 years in age) the counting must be continued for 2500 minutes, i.e. 42 hours. This is one of several factors contributing to the slow and expensive nature of radiocarbon dating.

   The situation worsens for older samples, not only because of the lower count rate but also because the sample count rate becomes comparable with the background count rate observed for a 'dead' sample. Suppose for the same installation the background count rate is 1 per minute and for simplicity assume it to be known precisely and to be constant, which is not necessarily the case. For a sample that is 23,000 years old, i.e. four half-lives, the observed count rate (sample plus background) will average 2 per minute. Hence in the 2 days of counting routinely employed for old samples at many laboratories the total count will be about 6000 with a standard error of ±80. When the background is subtracted the net sample count will be about 3000 but with the same standard error of ±80; the latter corresponds to ±2.7% of the net sample count, i.e. to ±210 years in age.

   The advantage of using a bigger sample may be seen by repeating the above calculation for a scintillation counter for which the modern carbon count rate is 80 per minute and the background 8 per minute.
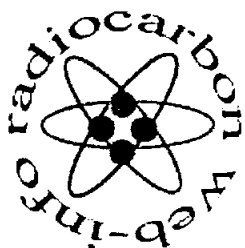
➤ The method	➤ Publication	➤ Bibliography
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➤ Applications	➤ Age calculation	➤ Credits
➤ WWW links	➤ Calibration	➤ What's New
➤ K-12	➤ Pretreatment	➤ Email

BY: THOMAS HIGHAM

"Everything which has come down to us from heathendom is wrapped in a thick fog; it belongs to a space of time we cannot measure. We know that it is older than Christendom, but whether by a couple of years or a couple of centuries, or even by more than a millenium, we can do no more than guess." [Rasmus Nyerup, (Danish antiquarian), 1802 (in Trigger, 1989:71)].

Nyerup's words illustrate poignantly the critical power and importance of dating; to order time. Radiocarbon dating has been one of the most significant discoveries in 20th century science. Renfrew (1973) called it 'the radiocarbon revolution' in describing its impact upon the human sciences. Oakley (1979) suggested its development meant an almost complete re-writing of the evolution and cultural emergence of the human species. Desmond Clark (1979) wrote that were it not for radiocarbon dating, *"we would still be foundering in a sea of imprecisions sometime bred of inspired guesswork but more often of imaginative speculation"* (Clark, 1979:7). Writing of the European Upper Palaeolithic, Movius (1960) concluded that *"time alone is the lens that can throw it into focus"*.

The radiocarbon method was developed by a team of scientists led by the late Professor Willard F. Libby of the University of Chicago in immediate post-WW2 years.
Libby later received the Nobel Prize in Chemistry in 1960:

"for his method to use Carbon-14 for age determinations in archaeology, geology, geophysics, and other branches of science."

According to one of the scientists who nominated Libby as a candidate for this honour;

"Seldom has a single discovery in chemistry had such an impact on the thinking of so many fields of human endeavour. Seldom has a single discovery generated such wide public interest."

(From Taylor, 1987).

Today, there are over 130 radiocarbon dating laboratories around the world producing radiocarbon assays for the scientific community. The C14 technique has been and continues to be applied and used in many, many different fields including hydrology, atmospheric science, oceanography, geology, palaeoclimatology, archaeology and biomedicine.

The 14C Method

There are three principal isotopes of carbon which occur naturally - C12, C13 (both stable) and C14 (unstable or radioactive). These isotopes are present in the following amounts C12 - 98.89%, C13 - 1.11% and C14 - 0.00000000010%. Thus, one carbon 14 atom exists in nature for every 1,000,000,000,000 C12 atoms in living material. The radiocarbon method is based on the rate of decay of the radioactive or unstable carbon isotope 14 (14C), which is formed in the upper atmosphere through the effect of cosmic ray neutrons upon nitrogen 14. The reaction is:

$$14N + n => 14C + p$$
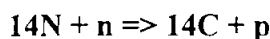
(Where n is a neutron and p is a proton).
The 14C formed is rapidly oxidised to 14CO2 and enters the earth's plant and animal lifeways through photosynthesis and the food chain. The rapidity of the dispersal of C14 into the atmosphere has been demonstrated by measurements of radioactive carbon produced from thermonuclear bomb testing. 14C also enters the Earth's oceans in an atmospheric exchange and as dissolved carbonate (the entire 14C inventory is termed the **carbon exchange reservoir** (Aitken, 1990)). Plants and animals which utilise carbon in biological foodchains take up 14C during their lifetimes. They exist in equilibrium with the C14 concentration of the atmosphere, that is, the numbers of C14 atoms and non-radioactive carbon atoms stays approximately the same over time. As soon as a plant or animal dies, they cease the metabolic function of carbon uptake; there is no replenishment of radioactive carbon, only decay. There is a useful diagrammatic representation of this process given here

Libby, Anderson and Arnold (1949) first discovered that this decay occurs at a constant rate. They found that after 5568 years, half the C14 in the original sample will have decayed and after another 5568 years, half of that remaining material will have decayed, and so on (see figure 1 below). The **half-life** (t 1/2) is the name given to this value which Libby measured at 5568±30 years. This became known as the **Libby half-life**. After 10 half-lives, there is a very small amount of radioactive carbon present in a sample. At about 50 - 60 000 years, then, the limit of the technique is reached (beyond this time, other radiometric techniques must be used for dating). By measuring the C14 concentration or residual radioactivity of a sample whose age is not known, it is possible to obtain the countrate or number of decay events per gram of Carbon. By comparing this with modern levels of activity (1890 wood corrected for decay to 1950 AD) and using the measured half-life it becomes possible to calculate a date for the death of the sample.

As 14C decays it emits a weak beta particle (b), or electron, which possesses an average energy of 160keV. The decay can be shown:

$$14C => 14N + b$$
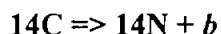
Thus, the 14C decays back to 14N. There is a quantitative relationship between the decay of 14C and the production of a beta particle. The decay is constant but spontaneous. That is, the probability of decay for an atom of 14C in a discrete sample is constant, thereby requiring the application of statistical methods for the analysis of counting data.

It follows from this that any material which is composed of carbon may be dated.Herein lies the true advantage of the radiocarbon method, it is able to be uniformly applied throughout the world. Included below is an impressive list of some of the types of carbonaceous samples that have been commonly radiocarbon dated in the years since the inception of the method:

- Charcoal, wood, twigs and seeds.
- Bone.
- Marine, estuarine and riverine shell.
- Leather.
- Peat

- Coprolites.
- Lake muds (gyttja) and sediments.
- Soil.
- Ice cores.
- Pollen.
- Hair.
- Pottery.
- Metal casting ores.
- Wall paintings and rock art works.
- Iron and meteorites.
- Avian eggshell.
- Corals and foraminifera.
- Speleothems.
- Tufa.
- Blood residues.
- Textiles and fabrics.
- Paper and parchment.
- Fish remains.
- Insect remains.
- Resins and glues.
- Antler and horn.
- Water.

The historical perspective on the development of radiocarbon dating is well outlined in Taylor's (1987) book "Radiocarbon Dating: An archaeological perspective". Libby and his team intially tested the radiocarbon method on samples from prehistoric Egypt. They chose samples whose age could be independently determined. A sample of acacia wood from the tomb of the pharoah Zoser (or Djoser; 3rd Dynasty, ca. 2700-2600 BC) was obtained and dated. Libby reasoned that since the half-life of C14 was 5568 years, they should obtain a C14 concentration of about 50% that which was found in living wood (see Libby, 1949 for further details). The results they obtained indicated this was the case. Other analyses were conducted on samples of known age wood (dendrochronologically aged). Again, the fit was within the value predicted at ±10%. The tests suggested that the half-life they had measured was accurate, and, quite reasonably, suggested further that atmospheric radiocarbon concentration had remained constant throughout the recent past. In 1949, Arnold and Libby (1949) published their paper "Age determinations by radiocarbon content: Checks with samples of known age" in the journal *Science*. In this paper they presented the first results of the C14 method, including the "Curve of Knowns" in which radiocarbon dates were compared with the known age historical dates (see figure 1). All of the points fitted within statistical range. Within a few years, other laboratories had been built. By the early 1950's there were 8, and by the end of the decade there were more than 20.
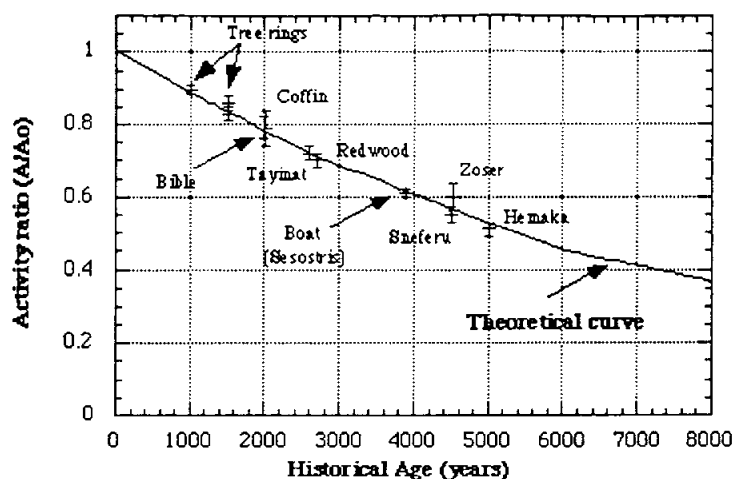
Figure 1: The "Curve of Knowns" after Libby and Arnold (1949). The first acid test of the new method was based upon radiocarbon dating of known age samples primarily from Egypt (the dates are shown in the diagram by the red lines, each with a ±1 standard deviation included). The Egyptian King's name is given next to the date obtained. The theoretical curve was constructed using the half-life of 5568 years. The activity ratio relates to the carbon 14 activity ratio between the ancient samples and the modern activity. Each result was within the statistical range of the true historic date of each sample.

In the 1950s, further measurements on Mediterranean samples, in particular those from Egypt whose age was known through other means, pointed to radiocarbon dates which were younger than expected. The debate regarding this is outlined extensively in Renfrew (1972). Briefly, opinion was divided between those who thought the radiocarbon dates were correct (ie, that radiocarbon years equated more or less to solar or calendar years) and those who felt they were flawed and the historical data was more accurate. In the late 1950's and early 1960's, researchers measuring the radioactivity of known age tree rings found fluctuations in C14 concentration up to a maximum of ±5% over the last 1500 years. In addition to long term fluctuations, smaller 'wiggles' were identified by the Dutch scholar Hessel de Vries (1958). This suggested there were temporal fluctuations in C14 concentration which would neccessitate the calibration of radiocarbon dates to other historically aged material. Radiocarbon dates of sequential dendrochronologically aged trees primarily of US bristlecone pine and German and Irish oak have been measured over the past 10 years to produce a calendrical / radiocarbon calibration curve which now extends back over 10 000 years (more on Calibration). This enables radiocarbon dates to be calibrated to solar or calendar dates.

Later measurements of the Libby half-life indicated the figure was *ca.* 3% too low and a more accurate half-life was 5730±40 years. This is known as the **Cambridge half-life**. (To convert a "Libby" age to an age using the Cambridge half-life, one must multiply by 1.03).

The major developments in the radiocarbon method up to the present day involve improvements in measurement techniques and research into the dating of different materials. Briefly, the initial solid carbon method developed by Libby and his collaborators was replaced with the Gas counting method in the 1950's. Liquid scintillation counting, utilising benzene, acetylene, ethanol, methanol etc, was developed at about the same time. Today the vast majority of radiocarbon laboratories utilise these two methods of radiocarbon dating. Of major recent interest is the development of the Accelerator Mass Spectrometry method of direct C14 isotope counting. In 1977, the first AMS measurements were conducted by teams at Rochester/Toronto and the General Ionex Corporation and soon after at the Universities of Simon Fraser and McMaster (Gove, 1994). The crucial advantage of the AMS method is that milligram sized samples are required for dating. Of great public

interest has been the AMS dating of carbonacous material from prehistoric rock art sites, the Shroud of Turin and the Dead Sea Scrolls in the last few years. The development of high-precision dating (up to ±2.0 per mille or ±16 yr) in a number of gas and liquid scintillation facilities has been of similar importance (laboratories at Belfast (N.Ireland), Seattle (US), Heidelberg (Ger), Pretoria (S.Africa), Groningen (Netherlands), La Jolla (US), Waikato (NZ) and Arizona (US) are generally accepted to have demonstrated radiocarbon measurements at high levels of precision). The calibration research undertaken primarily at the Belfast and Seattle labs required that high levels of precision be obtained which has now resulted in the extensive calibration data now available. The development of small sample capabilities for LSC and Gas labs has likewise been an important development - samples as small as 100 mg are able to be dated to moderate precision on minigas counters (Kromer, 1994) with similar sample sizes needed using minivial technology in Liquid Scintillation Counting. The radiocarbon dating method remains arguably the most dependable and widely applied dating technique for the late Pleistocene and Holocene periods.
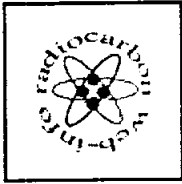
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RLAHA - ORAU


Radiocarbon Dating by AMS
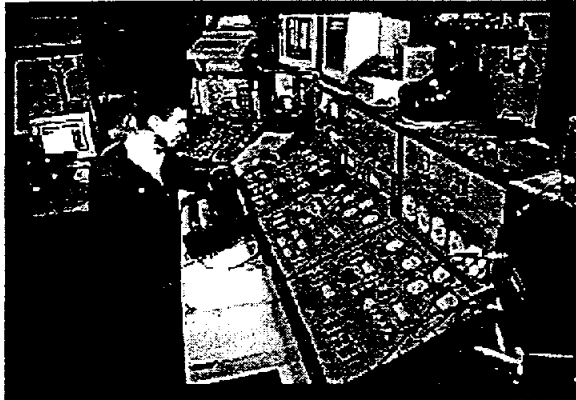
(all photographs are of ORAU (c) James King-Holmes)

In order to measure radiocarbon ages it is necessary to find the amount of radiocarbon in a sample. This can either be achieved by measuring the radioactivity of the sample (the conventional *beta*-counting method) or by directly counting the radiocarbon atoms using a method called Accelerator Mass Spectrometry (AMS).

- How Accelerator Mass Spectrometry works
- Sample preparation for AMS
- Advantages and disadvantages over *beta*- counting
- AMS laboratories

How Accelerator Mass Spectrometry works
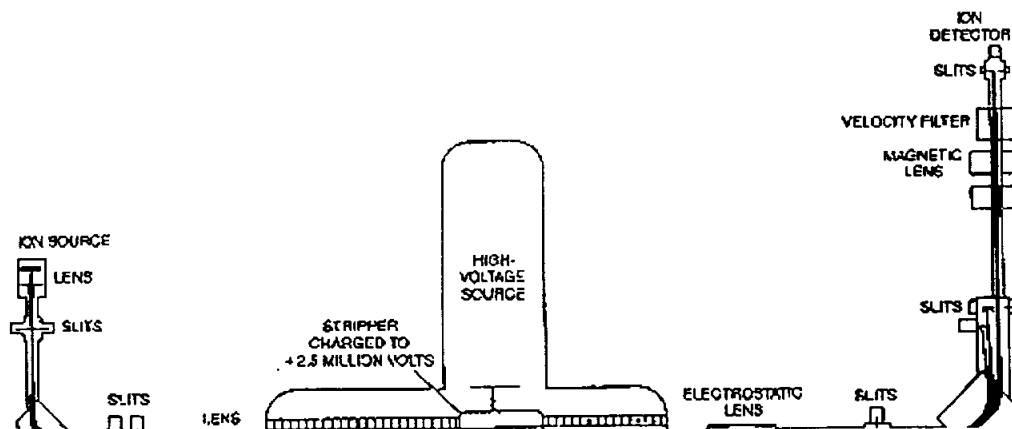
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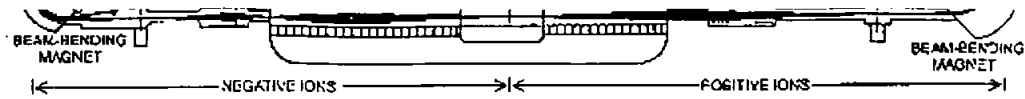
In common with other kinds of mass spectrometry, AMS is performed by converting the atoms in the sample into a beam of fast moving ions (charged atoms). The mass of these ions is then measured by the application of magnetic and electric fields.

The measurement of radiocarbon by mass spectrometry is very difficult because it's concentration is less than one atom in 1,000,000,000,000. The accelerator is used to help remove ions which might be confused with radiocarbon before the final detection.

The sample is put into the ion source either as graphite or as carbon-dioxide. It is ionised by bombarding it with cesium ions and then focused into fast-moving beam (energy typically 25keV). The ions produced are negative which prevents the confusion of 14C with 14N since nitrogen does not form a negative ion. The first magnet is used in the same way as the magnet in an ordinary mass spectrometer to select ions of mass 14 (this will include large number of 12CH2- and 13CH- ions and a very few 14C-ions).
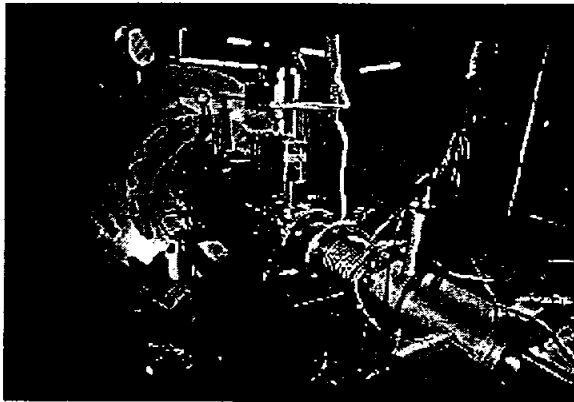
The ions then enter the accelerator. As they travel to the terminal (which is at about 2MV) they are accelerated so much that when they collide with the gas molecules in the central 'stripper canal' all of the molecular ions (such as 12CH2 and 13CH) are broken up and most of the carbon ions have four electrons removed making them into C3+ ions. These are then accelerated down the second half of the tandem accelerator reaching energies of about 8MeV. The second magnet selects ions with the momentum expected of 14C ions and a Wien filter checks that their velocity is also correct.

Finally the filtered 14C ions enter the detector where their velocity and energy are checked so that the number of 14C ions in the sample can be counted.

Not all of the radiocarbon atoms put into the ion source reach the detector and so the stable isotopes, 12C and 13C are measured as well in order to monitor the detection efficiency. For each sample a ratio of 14C/13C is calculated and compared to measurements made on standards with known ratios.

Sample preparation for AMS

Careful sampling and pretreatment are very important stages in the dating process, particularly for archaeological samples where there is frequently contamination from the soil.

Before sampling, the surface layers are usually removed because these are most susceptible to contamination. Only very small quantities are required for the AMS measurement (30ug-3mg of carbon) and so the damage to objects can be minimised.

The chemical pretreatment depends on the type of sample. As an example bones are treated as follows:

- bone powder is produced by drilling the sample
- acid is used to demineralise the bone
- alkali is used to remove humic acids from soil etc.
- the extracted `collagen' is converted to gelatin by heating
- the gelatin is put through an ion exchange column to remove impurities
- the purified sample is freeze dried

Several of these procedures are done in an automated continuous flow system.

After chemical pretreatment the samples are burnt to produce carbon dioxide and nitrogen. A small amount of this gas is bled into a mass spectrometer where the stable isotope ratios of carbon and nitrogen are measured. These ratios provide useful information on the purity of the sample and clues about the diet and climatic conditions of the living organism. The carbon isotope ratio is also used to correct for isotopic fractionation in the radiocarbon measurement.

The carbon dioxide is collected in a glass ampoule or converted to graphite for radiocarbon measurement on the AMS system.

Advantages and disadvantages over *beta-* counting

The main advantages of AMS over the conventional *beta*-counting method is the much greater sensitivity of the measurement. In AMS the radiocarbon atoms are directly detected instead of waiting for them to decay. Sample sizes are thus typically 1000 times smaller allowing a much greater choice of samples and enabling very selective chemical pretreatment. See also specific advantages for Archaeology, Art History, Environmental Science and Biological Tracer Studies

Small sample sizes do have their disadvantages too: greater mobility within deposits and more difficult control of contaminants. The best conventional counters can still achieve higher precision and lower backgrounds than an AMS system assuming a suitably large pure sample can be found. For this reason the calibration curves for radiocarbon have usually been measured using counters.

AMS Laboratories

There are a large number of AMS labs worldwide many of which perform radiocarbon measurements and some of which will also undertake sample pre-treatment. Those currently known to be on the WWW are:

- Australian National University Accelerator Mass Spectrometry
- C14 Labor - Erlangen-Nürnberg
- Center For Accelerator Mass Spectrometry (CAMS) Lawrence Livermore National Laboratory (USA)
- Centre for Isotope Research, Groningen, NL
- NOSAMS, National Ocean Sciences Accelerator Mass Spectrometer Facility at Woods Hole Oceanographic Institution
- NSF - University of Arizona Accelerator Mass Spectrometry Facility
- Oxford University - Radiocarbon Accelerator Unit
- Purdue Rare Isotope Measurement Laboratory (PRIME Lab)
- Rafter Radiocarbon Laboratory (AMS) (New Zealand)
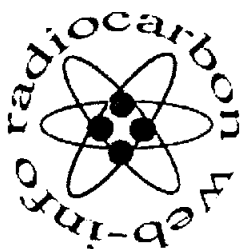
The development of this page will be gradual and contributions are invited. There are many, many interesting applications of radiocarbon dating in a variety of different fields. If you would like to set up information regarding a project in which radiocarbon dating illuminated or solved a problem or in which C14 played a central role, please contact THigham@waikato.ac.nz

ARCHAEOLOGY

- Radiocarbon dating the Dead Sea scrolls Page describing the recent radiocarbon dating of some of the Dead Sea scrolls at the NSF-Arizona AMS facility.
- Dead Sea Scrolls Short press release concerning the recent radiocarbon dating of some of the scrolls.
- Kennewick Man Newspaper reports concerning the 9,200-year-old bones found recently along the banks of the Columbia River in Kennewick, Washington.
- Debert, a palaeoIndian site in Nova Scotia Extensive radiocarbon dating from the Debert site, Nova Scotia indicates occupation between 10 600 and 10700 BP.
- Archaeometry and Stonehenge Presentation of results of excavations and dating of the Stonehenge 20th century excavations project.
- Dating Stonehenge 52 radiocarbon dates have been measured in the reexcavation of parts of this famous archaeological site.
- Datation des peintures de la grotte Chauvet A new radiocarbon series from the recent Ardèche rock art find are the earliest currently known for rock art in the region.
- Recherche en art pariétal préhistorique More research and dates for French rock art sites.
- Archaeological research at Oslonki, Poland The site of Oslonki is dated by 24 radiocarbon dates, which when calibrated to calendar years point to a dating of between 4300 and 4000 B.C.
- Dombate passage tomb, Spain WWW page about the megalithic monument of Dombate (La Corunha, Galicia, NW Spain) with several C14 dates for different moments of the life of the monument (in Spanish).
- The Origins of Angkor Archaeological Project From the University of Otago (New Zealand) and the Fine Arts Department of Thailand, the project is concerned with investigating archaeology of pre-formative Angkorean society of South East Asia. Radiocarbon dating underpins the chronological aspects of the investigation.
- Radiocarbon dating of the Angel site and phase in regional perspective. Sherri Hilgeman and Mark Schurr of the Glenn A. Black Laboratory of Archaeology.
- Radiocarbon chronology from the prehistoric Caborn site, Indiana. by Cheryl Ann Munson (Indiana University) and Marjorie Melvin Jones (University of Southern Indiana).
- Radiocarbon dates from Pinarbasi, near Catal Huyuk, Turkey from the recent excavations of Pinarbasi.
- Northeast PaleoIndian Radiocarbon database.
- Database of radiocarbon dates for British & Irish archaeology Under construction
- Absolute Chronology for Early Civilisations in Austria and Central Europe using 14C Dating with Accelerator Mass Spectrometry

DOI 04452

- Canadian Archaeological Radiocarbon Database.
- Mapping Ancient History A Java based map of Canada, showing the location and spread of dated sites based on the radiocarbon dates held in the Canadian Archaeological Radiocarbon database

OCEANOGRAPHY

- The World Ocean Circulation Experiment (WOCE) The World Ocean Circulation Experiment (WOCE); at the Woods Hole Oceanographic Institution's NOSAMS Facility. Measuring carbon in the Pacific and Indian Ocean to understand better the processes of ocean circulation.
- Ocean sediment C-14 data The Lamont-Doherty Earth Observatory of Columbia University has compiled 974 C-14 dates from 309 ocean sediments cores, covering the period from 40,000 years BP to the present worldwide.

PALAEOENVIRONMENTAL STUDIES

- The America's Project A palaeovegetational reconstruction of the North and South Americam continents using a radiocarbon dated timeframe from 15-9 ky BP.
- Wrangel Island Mammoths Abstract of the *Radiocarbon* article of the fascinating discovery that mamoths were still alive on this subarctic island at 2000 BC.
- TephraBase Radiocarbon Search Search the Tephrabase directory for radiocarbon dated volcanic tephras.
- Dating of the Owens River system, Southern California This lake consisted of a chain of pluvial lakes occupying a succession of closed basins in southeastern California; this site shows details of the radiocarbon dating by AMS of the river system.
- Radiocarbon dating the inundation of the Bering Land Bridge New Evidence on the Timing of Inundation of the Bering Land Bridge, Based on Radiocarbon Ages of Macrofossils.

CALIBRATION AND DENDROCHRONOLOGY

- Laboratory of Tree-Ring Research, University of Arizona.
- Ancient Bristlecone Pine homepage.
- Aegean Dendrochronology Project at Cornell University.
- The International Tree-Ring Data Bank (ITRDB) at the University of Arizona, Tucson
- The Sheffield Dendrochronology Laboratory, Sheffield, England.
- The Dutch Centre for Dendrochronology (RING), Amersfoort, The Netherlands.
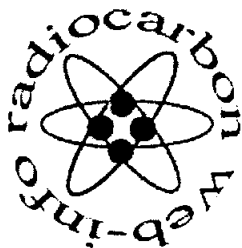- The Climatic Research Unit, University of East Anglia, Norwich, England.

PALAEOCLIMATOLOGY

- Current research in palaeoclimates and solar variation using tree ring dated C14 chronologies at the University of Arizona.
- Palaeoclimates from Arctic Lakes and Estuaries (PALE) Home Page including the PALE Geochronology programme with radiocarbon databases from Iceland, Canada, Europe, Alaska and Russia.
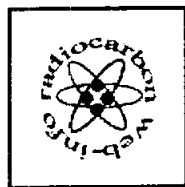
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The method   Publication   Bibliography

Measurement   Corrections   Awards

Applications   Age calculation   Credits

WWW links   Calibration   What's New

K-12   Pretreatment   Email

"Everything which has come down to us from heathendom is wrapped in a thick fog; it belongs to a space of time we cannot measure. We know that it is older than Christendom, but whether by a couple of years or a couple of centuries, or even by more than a millenium, we can do no more than guess. " [Rasmus Nyerup, (Danish antiquarian), 1802 (in Trigger, 1989:71)].

The person who wrote these words lived in the 1800s, many years before archaeologists could accurately date materials from archaeological sites using scientific methods. Rasmus Nyerup's quote reminds us of the tremendous scientific advances which have taken place in the 20th century. In Nyerup's time, archaeologists could date the past only by using recorded histories, which in Europe were based mainly on the Egyptian calendar. They used pottery and other materials in sites to date 'relatively'. They thought that sites which had the same kinds of pots and tools would be the same age. The relative dating method worked very well, but only in sites which were had a connection to the relative scale. Most sites could not be dated. When radiocarbon dating was developed, it revolutionised archaeology, because it enabled them to more confidently date the past, and to build a more accurate picture of the human past. The archaeologist Colin Renfrew (1973) called it the development of this dating method 'the radiocarbon revolution' in describing its great impact upon the human sciences.

How was radiocarbon dating developed?

The radiocarbon method was developed by a team of scientists led by the late Professor Willard F. Libby of the University of Chicago after the end of World War 2.
Libby later received the Nobel Prize in Chemistry in 1960 for the radiocarbon discovery.

Today, there are over 130 radiocarbon dating laboratories around the world producing radiocarbon dates for the scientific community. The C14 method has been and continues to be applied and used in many, many different fields including hydrology, atmospheric science, oceanography, geology, palaeoclimatology, archaeology and biomedicine.

How does radiocarbon dating work?

All plants and animals on Earth are made principally of carbon. During the period of a plant's life, the plant is taking in carbon dioxide through photosynthesis, which is how the plant makes energy and grows. Animals eat plants, and some eat other animals in the food chain. Carbon follows this pathway through the food chain on Earth so that all living things

are using carbon, building their bodies until they die.

A tiny part of the carbon on the Earth is called Carbon-14 (C14), or radiocarbon. It is called 'radio'-carbon, because it is 'radioactive'. This means that its atomic structure is not stable. Radioactive means that the atomic structure of the carbon 14 atom is unstable and there is an uneasy relationship between the particles in the nucleus of the atom itself. Eventually, a particle is emitted from the carbon 14 atom, and carbon 14 disappears. Most of the carbon on Earth exists in a slightly different atomic form, although it is chemically speaking, identical to all carbon.

In the 1940s, scientists succeeded in finding out how long it takes for radiocarbon to disappear, or decay, from a sample of carbon from a dead plant or animal. Willard Libby, the principal scientist, had worked in the team making the nuclear bomb during World War 2, so he was an expert in nuclear and atomic chemistry. After the war he became very interested in peaceful applications of atomic science. He and two students first measured the "half-life" of radiocarbon. The half-life refers to the amount of time it takes for half the radiocarbon in a sample of bone or shell or any carbon sample to disappear. Libby found that it took 5568 years for half the radiocarbon to decay. After twice that time (11000 years), another half of that remaining amount will have disappeared. After another 5568 years, again another half will have disappeared. If you look at the graph below, you will see that after about 50 000 years of time, all the radiocarbon will have gone. Therefore, radiocarbon dating is not able to date anything older than 60 or 70 000 years old. The job of a radiocarbon laboratory is to measure the remaining amounts of radiocarbon in a carbon sample. This is very difficult and requires a lot of careful work to produce reliable dates.

What kind of things can you date using radiocarbon?

Because carbon is very common on Earth, there are alot of different types of material which can be dated by scientists. Below is a list of the different kinds of materials which can be dated:

- Charcoal, wood, twigs and seeds.
- Bone.
- Marine, estuarine and riverine shell.
- Leather.
- Peat
- Coprolites (samples of preserved faeces).
- Lake muds (gyttja) and sediments.
- Soil.
- Ice cores.
- Pollen.
- Hair.
- Pottery.
- Metal casting ores.
- Wall paintings and rock art works.
- Iron and meteorites.
- Bird eggshell.
- Corals and foraminifera.
- Blood residues.
- Textiles and fabrics.
- Paper and parchment.
- Fish remains.
- Insect remains.
- Resins and glues.
- Antler and horn.
- Water.

How did Libby test his method and find out if it worked correctly?

Libby tested the new radiocarbon method on samples from prehistoric Egypt whose age was known. A sample of acacia wood from the tomb of the pharoah Zoser was dated for example. Zoser lived during the 3rd Dynasty in Egypt (2700-2600 BC). Libby figured that since the half-life of C14 was 5568 years, they should obtain a radiocarbon amount of about 50% of that which was found in living wood because Zoser's death was about 5000 years ago. The results they obtained indicated this was the case. Many other radiocarbon dates were conducted on samples of wood of known age. Again, the results were good. In 1949, Libby and his team published their results. By the early 1950s there were 8 new radiocarbon laboratories, and by the end of the decade more than 20.
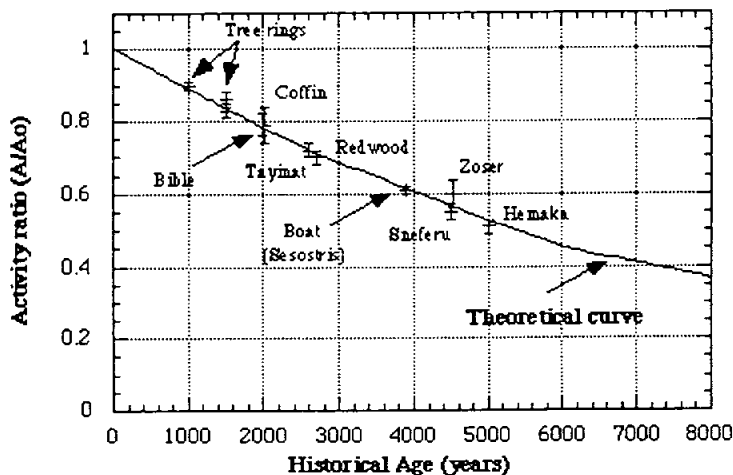
How much material do you need to date using radiocarbon?

A new way of radiocarbon dating was developed in the late 1970s called "AMS Radiocarbon dating". AMS stands for Accelerator Mass Spectrometry. AMS dating is important because using it you can date very small sizes carbon samples. Imagine a grain of rice, this can be dated now with radiocarbon. We can date pollen grains, seeds, tiny pieces of charcoal. What about a hair from someone's head? That too can be dated using AMS! We can now date a variety of very, very small samples, so many more kinds of archaeological and geological samples can be dated than ever before so AMS is a tremendous breakthrough for archaeologists and other researchers.

How much does it cost to date using radiocarbon dating?

The cost varies between different laboratories. On average, a single date will cost about 250 US dollars. The high cost is because it is a big job to date a sample. It takes a long time to change the carbon material into the form it needs to be in to be able to be dated.

What are the oldest things that can be radiocarbon dated?

Anything that is less than about 50 or 60 000 years can be radiocarbon dated. Beyond 60 000 years there is hardly any radiocarbon left in a sample that is original. Often there might be small amounts by this is usually contamination so it gives a date for the material that might be in error. It is very difficult to date material of this age because for a start there is a small amount of c14 in living things, so after a long, long time, there is even less in old material. Often, radiocarbon daters release dates as being 'greater than 50 000 years' or 'greater than 45 000 years' because of the difficulty in reliably giving a date at this age.

What is the youngest thing that can be radiocarbon dated?

This is a difficult one, because we can date pretty much anything from today or in modern times, but getting an actual 'date' is hard. In the 1950s and 60s, people blew up alot of nuclear bombs, and one thing that happened because of this was that alot of radiocarbon was created in the air artificially. Radiocarbon is a side effect of nuclear bombs. In the early 1960s the amount of radiocarbon produced by bombs was bigger than the amount of radiocarbon naturally present! It sounds bad, and nuclear bombs are not pleasant when they are generated, but for science there have been some spinoffs because we have been able to study the movement of this radiocarbon through the environment and learn alot about how radiocarbon is transported naturally. So this has been beneficial. We can also date things that have happened since 1950 rather well because of the sudden jump in radiocarbon on Earth, so that it is possible to figure out within 2-3 years sometimes, the date of a sample.

Generally, we can date things pretty well over the past 1000 years, it becomes difficult from about 1700 AD to 1900 AD because of natural changes in radiocarbon, and since 1950 AD dating is quite possible.

What kinds of famous things have been radiocarbon dated?

There are many examples of famous things being dated. Let's have a look at some examples. The Shroud of Turin is a piece of cloth which was thought to be the burial cloth of Jesus Christ. If this was true, then it should be about 2000 years old. In the 1980s, some tiny pieces of this cloth were sent to 4 AMS Radiocarbon laboratories for radiocarbon testing. The results showed dates of only 650 years ago. The cloth was made in the 1300s, which showed that it was a fake. In the 1300s alot of people made up religious items, pretending they were in fact older than they were, and the Shroud of Turin is one of those.

The Dead Sea Scrolls, are another very famous archaeological discovery which have been dated. They date from the first century BC to the first century AD. They were also dated by AMS a few years ago. There was close agreement between the radiocarbon dates and the dates which had been estimated using the writing styles used on the scrolls, and in some cases the dates recorded on the scrolls themselves.

What about the Iceman? The Iceman is a very famous frozen body found in northern Italy in 1991. Samples of his bones, grass boot, leather and hair were dated, the results showed that he lived almost 5500 years ago (3300-3100 BC), during the age when people first began using copper in Europe. Radiocarbon dating was tremendously important in dating the precise age of the Iceman.

How do you know that radiocarbon really works?

It is possible to test radiocarbon dates in different ways. One way is to date things that you already know the age of. Libby did this when he first developed the method, by dating artefacts of Egyptian sites, which were already dated historically. Another way is to use tree rings. Every year a tree leaves a ring, the rings increase in number over time until a pattern of rings is formed. Sometimes the tree has many hundreds of rings. Scientists can date the age of the tree by counting and measuring the rings. Radiocarbon daters can then date the tree rings and compare the dates with the real age of the tree. This is a very good way of testing radiocarbon, and we now know that there are some differences in radiocarbon dates and real time. Most of the time radiocarbon dating is accurate, but sometimes it is different from the true age by a small amount.

We can also test radiocarbon by comparing the results with the dates produced by other dating methods, and there are many of those. These methods are completely different to radiocarbon dating and use different methods to provide dates. Some of the dating methods

Home   Contents   Subscribers   Authors   Announcements   Info   Search

Radiocarbon-Related Information Sources

Basics · Email List · Product Info · Computer Programs · Databases · Laboratories

Introductions to Radiocarbon Dating

- "Death Starts the Stop-Watch"
  A brief museum-like display, in English and German
- WebInfo - Radiocarbon Dating
  A compendium of online information on the theory and practice of radiocarbon dating, with references to published material.
- See also labs in list followed by the ● info symbol. (Most of the labs also provide detailed technical information about their specific dating techniques.)

Internet Discussion List

- C14-L: Radiocarbon Listserv email list
  (Search the C14-L archives: http://listserv.arizona.edu/lsv/www/c14-l.html)

Product Information

- Packard Instruments: Isotopic analysis products
- Wallac (Finland): Liquid Scintillation Counters

Computer Programs
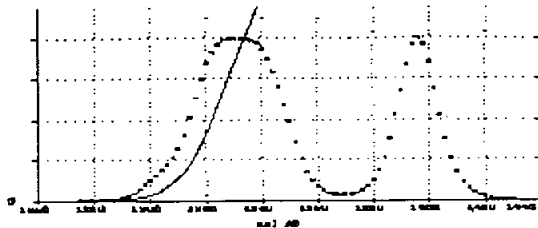
- BCal: Online Bayesian radiocarbon calibration tool. Developed at the School of History and Archaeology, Cardiff University, this allows users to obtain calibrated dates on data sets entered via a Web browser.
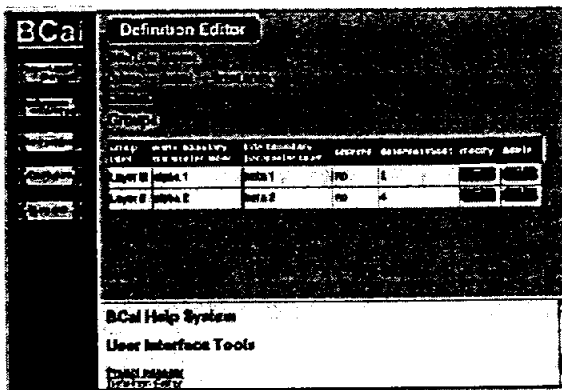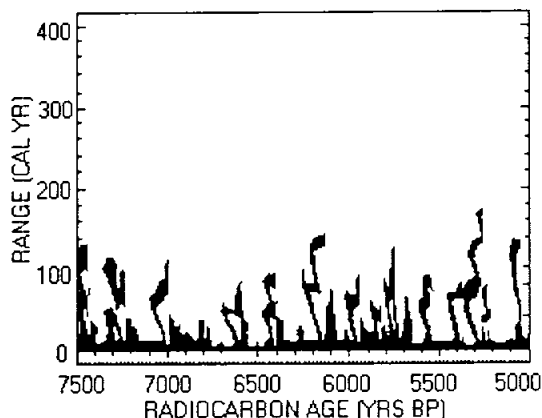
- CAL25: The Groningen Calibration Program: By J. van der Plicht, for DOS, updated with 1998 calibration data set.
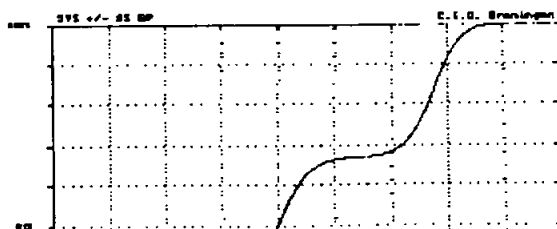
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- CALIB 4: By Stuiver and Reimer, a radiocarbon calibration program for both Macintosh and DOS platforms; French version of the manual available.

- Metabase: laboratory data management software system that can be used by LSC labs
- OxCal by Christopher Bronk Ramsey, a radiocarbon calibration program for Windows which also allows Bayesian analysis of sequences, phases, tree-ring sequences, spans, orders etc.. There is an online manual which is also available as a Windows help file.
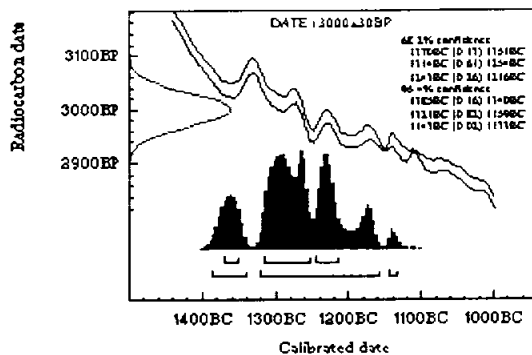
Radiocarbon Databases and Searchable Indexes

- Australia
  - Australian National University Radiocarbon Abstracts. *(NOTE: the database for this set of abstracts of radiocarbon-related publications is about 10 years out of date, but is useful for earlier articles.)*
- Canada
  - Canadian Archaeological Radiocarbon Database
    - Main CARD searchable database of archaeological and vertebrate palaeontological sites in Canada
    - GSC Project: Mapping Ancient History
      Interactive map based on CARD data, illustrating locations of radiocarbon-dated archaeological and palaeobiological sites in Canada for the past 14 millennia
- Italy
  - Searchable database of Mediterranean C-14 Ages and Publications from Dipartimento di Scienze della Terra di Pisa, Italy
- United Kingdom

- United Kingdom
  - o Archaeological Site Index to Radiocarbon Dates from Great Britain and Ireland: database of over 4000 dates from the British Isles
    - Description of the database
    - Search access via the Archaeology Data Service catalogue
  - o Oxford Radicarbon Accelerator Unit datelist index
- United States
  - o National Geophysical Data Center Paleoclimatology Home Page
  - o National Geophysical Data Center Radiocarbon datasets

Radiocarbon Labs

List of Known Active Radiocarbon Labs & Lab Codes

Radiocarbon Labs with WWW Servers

Ⓐ = Lab with AMS (accelerator)   ● = Site has information about ^{14}C method

- Austria
  - o VERA: Vienna Environmental Research Accelerator Ⓐ ●
  - o Absolute Chronology for Early Civilisations in Austria and Central Europe using 14C Dating with AMS (University of Vienna) ●
- Australia
  - o Australian National University - Accelerator Mass Spectrometry Ⓐ
    Explanations and applications lists of several varieties of radiosotope dating.
- Canada
  - o Geological Survey of Canada (GSC) - Radiocarbon Dating
- France
  - o Centre de datation par le RadioCarbone - Université Claude Bernard I, Lyon, France
    Information in French and English: measurement techniques, sample submission forms, etc.
- Germany
  - o Erlangen-Nürnberg University AMS Group; Ⓐ ● same site auf Deutsch ●
  - o Institut für Bodenkunde - Isotopendatierungslabor - University of Hamburg (in German)
  - o University of Heidelberg Institute for Environmental Physics
  - o Leibniz Labor for Radiometric Dating and Isotope Research - Christian Albrechts University, Kiel; Ⓐ same site auf Deutsch
    List of services, pricelists, sample data sheets
- Netherlands
  - o Centre for Isotope Research, Groningen Ⓐ
- New Zealand
  - o Rafter Radiocarbon Laboratory (AMS) Ⓐ
    Price lists for dating, illustrations of pretreatment and measurement equipment.
  - o University of Waikato Radiocarbon Dating Laboratory including:
    - New Zealand Archaeological Date List
    - WebInfo - Radiocarbon Dating ●
- Sweden
  - o University of Lund Department of Quaternary Geology Ⓐ
- Switzerland
  - o University of Zurich Dep't of Geography Radiocarbon Laboratory Ⓐ
    Includes downloadable sample forms   DOI 04460
- United Kingdom
 - o NERC Radiocarbon Laboratory, East Kilbride, Scotland Ⓐ

Information about dating services and grant funding for analysis

- o Oxford University - Research Lab for Archaeology and Radiocarbon Accelerator Unit ⊕
  Information about dating services and OxCal calibration program
- o Queen's University of Belfast - Radiocarbon Laboratory
  Information on dating options, sample size requirements
- o SURRC Radiocarbon Laboratory, Glasgow, Scotland
  Commercial service, quality assurance, submission forms, prices.

- United States

  - o Beta Analytic Radiocarbon Dating--Radiometric, AMS, Stable Isotopes and SEM ⊕
    Beta Analytic is the largest radiocarbon dating facility in the world, currently analyzing 10,000 samples each year for researchers worldwide.
  - o Center for Applied Isotope Studies - University of Georgia
    Radiometric and stable isotope dating and other services
  - o Desert Research Institute Radiocarbon Laboratory - Las Vegas, Nevada
  - o Geochron Laboratories - Cambridge, Massachussets ●
    Isotope analyses for researchers in the fields of geology, economic geology, geochronology, archaeology, anthropology, and hydrology; environmental, metabolic, and food adulteration studies.
  - o Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry (CAMS) ⊕
    Measurements of eight anthropogenic and cosmogenic isotopes.
  - o NOSAMS, National Ocean Sciences Accelerator Mass Spectrometer Facility at Woods Hole Oceanographic Institution ⊕ ●
    Information on AMS dating, World Ocean Circulation Experiment (WOCE)
  - o Purdue Rare Isotope Measurement Laboratory (PRIME Lab) ⊕ ●
    AMS dating of C14 and other radionuclides, chemical sample preparation; newsletter "What's new at PRIME Lab"
  - o T.M.B.Group Inc, Stable Isotope Ratio Laboratory - Miami, Florida
    Stable isotope ratio measurement of $^{13}C/^{12}C$, $^{13}C/^{12}C$, and $^{18}O/^{16}O$
  - o NSF - University of Arizona AMS Facility ⊕
    Information on dating, fees, sample submission form
  - o University of Arizona, Laboratory of Isotope Geochemistry
  - o University of Colorado-INSTAAR Laboratory for AMS Radiocarbon Research ⊕
    Information on services, projects, sample submission.
  - o University of Minnesota, Limnological Research Center
    AMS C-14 Target Preparation Unit, with downloadable sample forms
  - o University of Texas Vertebrate Paleontology & Radiocarbon Laboratory
  - o University of Washington Quaternary Isotope Lab
    Includes download access to CALIB calibration program.

Other Isotope Labs

- Thermal Ionization Mass Spectrometry Page
  A large list of laboratories that perform TIMS on various isotopes

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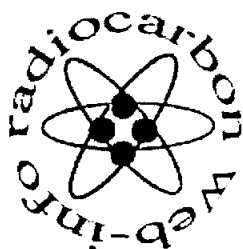
CONTRIBUTED BY: THOMAS HIGHAM

Introduction

The journal *Radiocarbon* was begun in 1958, its main function being the publication of radiocarbon date compilations produced by the world's laboratories. Today, there are many laboratories and few publish comprehensive lists of results, there are far too many dates being calculated for this to be achieved. The publication of radiocarbon dates rests almost totally with the submitter of the material. In many instances, researchers have in recent decades, neglected to publish relevant data describing the sample, laboratory and reference numbers, provenance and reservoir correction details. Such practices seriously undermine the value of radiocarbon dates because they lack a meaningful context. Some of the problems associated with interpreting the corpus of radiocarbon data obtained thus far concern variation in reporting. These may be involved with uncertain reservoir corrections, especially for shell dates, corrections for isotopic fractionation and failure to specify whether the old or new half-life was used.

Publication of dates

There are some crucial pieces of radiocarbon information that ought to be published in papers and media which present radiocarbon dates:

- The individual laboratory code number, which is prefixed to radiocarbon measurements from that particular lab. Thus, ANU-3546 refers to sample 3546 measured at the Radiocarbon Laboratory at the Australian National University, for example. For a list of current radiocarbon laboratories and Lab code numbers, click here.
- The Conventional Radiocarbon Age BP (with its ± error equal to ±one standard deviation).
- The sample isotopic fractionation (deltaC13) value, whether measured or estimated (which should be noted).
- Any estimate of a reservoir correction. Any radiocarbon age which possesses a reservoir correction should be termed a *Reservoir Corrected age* and this age should be given in addition to the Conventional Radiocarbon Age.
- Depending upon the type of publication and the nature of the discipline, D14C should also be published. This is the term which describes the depletion in per mille of C14 (corrected for isotopic fractionation) (More on D14C).

The CRA must always be given in a publication. Unlike calibrated age ranges, CRA's never change (unless laboratories recalculate them).

In terms of calibration, the choice of what to publish is more complicated. Calibrated data changes with successive calibration curves, therefore it is important to inform the reader of the calibration curve which was used, as well as the basic data concerning the conventional radiocarbon age and lab number. In cases where the sample is from the Southern hemisphere it is important to note whether an offset was deducted to account for the difference which exists between the activity of the two hemispheres. In dating shell, note should be made of whether the conventional radiocarbon age was corrected prior to

calibration or whether corrections were made using a local delta-R value. In the calibration pages in this server, information regarding publication of calibrated data is being constructed. Generally, the term "Cal AD" or "Cal BC" is given to describe calibrated age range data. There was a proposal mooted recently in Britain to use the upper and lower cases of "BP" to describe calibrated and conventional dates, bp for instance was to refer to calibrated dates, BP to conventional dates. This was never adopted by the international Radiocarbon community.

International Radiocarbon conferences are held every three years. Here, specialists in the field present papers, new techniques and results for peer perusal, workshops and discussion. In addition, computer databases containing extensive radiocarbon date compilations should become more widely used. An example of such a database can be seen at the University of Waikato Radiocarbon Dating Laboratory where dates measured there for the New Zealand prehistoric sequence have recently been brought online. There are also online radiocarbon databases at the National Geophysical Data Center - Paleoclimatology Home Page and National Geophysical Data Center - Radiocarbon datasets. In addition, there is a searchable database of Italian C-14 Ages and Publications at the Dipartimento di Scienze della Terra di Pisa, Italy. The Palaeoclimates from Arctic Lakes and Estuaries (PALE) Home Page includes the PALE Geochronology programme with radiocarbon databases from Northeastern PalaeoIndian Radiocarbon Database.
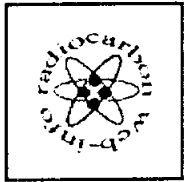
HTML DOCUMENT BY T.HIGHAM.
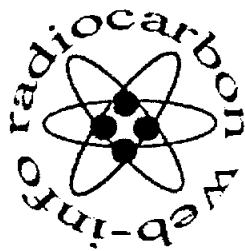
CONTRIBUTED BY: THOMAS HIGHAM

[A **Conventional Radiocarbon Age** or CRA, does not take into account specific differences between the activity of different carbon reservoirs. A CRA is derived using an age calculation based upon the decay corrected activity of the absolute radiocarbon standard (1890 AD wood) which is in equilibrium with atmospheric radiocarbon levels (as mentioned previously, 1890 wood is no longer used as the primary radiocarbon standard, instead Oxalic Acid standards I and II were correlated with the activity of the original standard). In order to ascertain the ages of samples which were formed in equilibrium with different reservoirs to these materials, it is necessary to provide an age correction. Implicit in the Conventional Radiocarbon Age BP is the fact that it is not adjusted for this correction. In this page, we consider natural reservoir variations and variations brought about by human interaction].

Natural Corrections

Reservoir effects

Radiocarbon samples which obtain their carbon from a different source (or reservoir) than atmospheric carbon may yield what is termed **apparent ages**. A shellfish alive today in a lake within a limestone catchment, for instance, will yield a radiocarbon date which is excessively old. The reason for this anomaly is that the limestone, which is weathered and dissolved into bicarbonate, has no radioactive carbon. Thus, it dilutes the activity of the lake meaning that the radioactivity is depleted in comparison to 14C activity elsewhere. The lake, in this case, has a different **radiocarbon reservoir** than that of the majority of the radiocarbon in the biosphere and therefore an accurate radiocarbon age requires that a correction be made to account for it.

One of the most commonly referenced reservoir effects concerns the ocean. The average difference between a radiocarbon date of a terrestrial sample such as a tree, and a shell from the marine environment is about 400 radiocarbon years (see Stuiver and Braziunas, 1993). This apparent age of oceanic water is caused both by the delay in exchange rates between atmospheric CO2 and ocean bicarbonate, and the dilution effect caused by the mixing of surface waters with upwelled deep waters which are very old (Mangerud 1972). A reservoir correction must therefore be made to any conventional shell dates to account for this difference. Human bone may be a problematic medium for dating in some instances due to human consumption of fish, whose C14 label will reflect the ocean reservoir. In such a case, it is very difficult to ascertain the precise reservoir difference and hence apply a correction to the measured radiocarbon age.

Spurious radiocarbon dates caused by volcanic emanations of radiocarbon-depleted CO2 probably also come under the category of reservoir corrections. Plants which grow in the vicinity of active volcanic fumeroles will yield a radiocarbon age which is too old. Bruns (1980) measured the radioactivity of

modern plants growing near hot springs heated by volcanic rocks in western Germany and demonstrated a deficiency in radiocarbon of up to 1500 years. Similarly, this effect has been noted for plants in the bay of Palaea Kameni near the prehistoric site of Akrotiri, which was buried by the eruption of the Thera volcano over 3500 years ago (see Weninger, 1989). The effect has been suggested as providing dates in error for the eruption of Thera which has been linked to the demise of the Minoan civilisation in the Aegean. One plant growing near the emanations had an apparent age of 1390 yr. The volcanic effect has a limited distance. Bruns (1980) found that at 20 m away from the source, plants yielded an age in agreement with that expected. Radiocarbon discrepancies due to volcanic CO_2 emissions are a popular source of ammunition for fundamentalist viewpoints keen to present evidence to show that the radiocarbon method is somehow fundamentally flawed.

Recent Human derived disturbances

Suess or Industrial effect

Since about 1890, the use of industrial and fossil fuels has resulted in large amounts of CO_2 being emitted into the atmosphere. Because the source of the industrial fuels has been predominantly material of infinite geological age (*e.g* coal, petroleum), whose radiocarbon content is nil, the radiocarbon activity of the atmosphere has been lowered in the early part of the 20th century up until the 1950's. The atmospheric radiocarbon signal has, in effect, been diluted by about 2%. Hans Suess (1955) discovered the **industrial effect** (also called after him) in the 1950's. A number of researchers found that the activity they expected from material growing since 1890 AD was lower. The logical conclusion from this was that in order to obtain a modern radiocarbon reference standard, representing the radiocarbon activity of the 'present day', one could not very well use wood which grew in the 1900's since it was affected by this industrial effect. Thus it was that 1890 wood was used as the modern radiocarbon standard, extrapolated for decay to 1950 AD.

Atom bomb effect

Since about 1955, thermonuclear tests have added considerably to the C14 atmospheric reservoir. This C14 is 'artificial' or 'bomb' C14, produced because nuclear bombs produce a huge thermal neutron flux. The effect of this has been to almost double the amount of C14 activity in terrestrial carbon bearing materials (Taylor, 1987).

De Vries (1958) was the first person to identify this 'Atom Bomb' effect. In the northern hemisphere the amount of artificial carbon in the atmosphere reached a peak in 1963 (in the southern hemisphere around 1965) at about 100% above normal levels. Since that time the amount has declined owing to exchange and dispersal of C14 into the Earth's carbon cycle system. The presence of bomb carbon in the earth's biosphere has enabled it to be used as a tracer to investigate the mechanics of carbon mixing and exchange processes. Ellen Druffel has called this the silver lining in thermonuclear bomb testing. The GEOSECS (Geochemical Ocean Section Study) oceanographic programme, for example, involved the collection and measurement of samples of ocean water along a number of Pacific and Atlantic transects to map the presence of bomb carbon and enable modellers to analyse the pathway of radiocarbon and its exchange and residence times. Currently, at the Woods Hole AMS Laboratory, the World Ocean Circulation Experiment (WOCE) is underway, this link shows the transects across the East Pacific ocean where C14 measurements of dissolved inorganic carbon have been obtained. You can see the dispersal

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of bomb carbon into the upper layers of the Pacific. At the National Geophysical data center you can view some measurements of carbon 14 in trees from India showing bomb carbon levels from 1960-1980.

More information here.

More relevant information:

Radiocarbon Calibration

Pretreatment and Contamination

Isotopic fractionation

Summary: The accuracy of radiocarbon dates (modified from Polach, H.A. 1976).

Sources of Error	Effect upon Age Determination	Measures to minimise the error incurred
1. Precision of age determination	Statistical:Typically ±1%Modern or less	Big samples, longer count times, repeat sample assays
2. Inherent a. C14 half-life	Libby half life 3% too low	Multiply CRA's by 1.03 if necessary
b. C13/C12 fractionation	Variable, up to 450 yr for shell.	Stable isotope analyses using Mass Spec.
c. C14 Modern standard	Variable > 80 yr	International crosscheck of secondary standards.
d. Variation in past C14 production rates	0-800 yr, beyond *ca*12 ka not determined	Tree ring calibration; otherwise interpret results in radiometric timescale.
e. Distribution of C14 in nature	Surface ocean latitudinal dependence -400 to -750 yr. Deep ocean -1800 yr.	Interpretation of results.
f. Changes of C14 concentration in the atmosphere.	Industrial effect *ca* -2.5% and atom bomb effect +160% in atmosphere	Interpretation of results
3. Contamination.	Nil to 300 yr up to 15 ka; >20 ka possible beyond 25 ka.	Interpretation of results, analysis and dating of extracted pretreated fractions.
4. Biological age of material	<10 yr to>1000 yr	Identification of species of material in the case of wood and charcoal to short lived samples only.
5. Association of sample and event	Intermediate	Interpretation of results
6. Human	Intermediate	Care in field and laboratory
7. Interpretation of results	Intermediate	Care in interpretation, interdisciplinary approach and collaboration
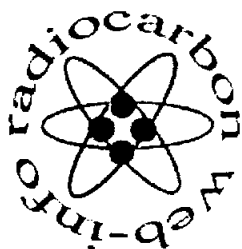
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CONTRIBUTED BY: THOMAS HIGHAM

Much of the information presented in this section is based upon the Stuiver and Polach (1977) paper "Discussion: Reporting of C14 data". A copy of this paper may be found in the *Radiocarbon Home Page*

The radiocarbon age of a sample is obtained by measurement of the residual radioactivity. This is calculated through careful measurement of the residual activity (per gram C) remaining in a sample whose age is **Unknown**, compared with the activity present in **Modern** and **Background** samples. You can get an idea of the relationship between C14 and age at the Carbon Dating calculator page.

Modern standard

The principal modern radiocarbon standard is N.I.S.T (National Institute of Standards and Technology; Gaithersburg, Maryland, USA) **Oxalic Acid I** ($C_2H_2O_4$) . Oxalic acid I is N.I.S.T designation SRM 4990 B and is termed HOx1. This is the International Radiocarbon Dating Standard. Ninety-five percent of the activity of Oxalic Acid from the year 1950 is equal to the measured activity of the **absolute radiocarbon standard** which is 1890 wood. 1890 wood was chosen as the radiocarbon standard because it was growing prior to the fossil fuel effects of the industrial revolution. The activity of 1890 wood is corrected for radioactive decay to 1950. Thus 1950, is year 0 BP by convention in radiocarbon dating and is deemed to be the 'present'. 1950 was chosen for no particular reason other than to honour the publication of the first radiocarbon dates calculated in December 1949 (Taylor, 1987:97).

The Oxalic acid standard was made from a crop of 1955 sugar beet. There were 1000 lbs made. The isotopic ratio of HOx I is -19.3 per mille with respect to (wrt) the PBD standard belemnite (Mann, 1983). The Oxalic acid standard which was developed is no longer commercially available. Another standard, **Oxalic Acid II** was prepared when stocks of HOx 1 began to dwindle. The Oxalic acid II standard (HOx 2; N.I.S.T designation SRM 4990 C) was made from a crop of 1977 French beet molasses. In the early 1980's, a group of 12 laboratories measured the ratios of the two standards. The ratio of the activity of Oxalic acid II to 1 is 1.2933±0.001 (the weighted mean) (Mann, 1983). The isotopic ratio of HOx II is -17.8 per mille. There are other secondary radiocarbon standards, the most common is ANU (Australian National University) sucrose. The ratio of the activity of sucrose with 0.95 Ox was first measured by Polach at 1.5007±0.0052 (Polach, 1976b:122). Later inter-laboratory measurements put the ratio at 1.5081 (Currie and Polach, 1980).

According to Stuiver and Polach (1977), all laboratories should report their results either directly related to NBS Oxalic acid or indirectly using a sub-standard which is related to it.

Background

It is vital for a radiocarbon laboratory to know the contribution to routine sample activity of non-sample radioactivity. Obviously, this activity is additional and must be removed from calculations. In order to make allowances for background counts and to evaluate the limits of detection, materials which radiocarbon specialists can be fairly sure contain no activity are measured under identical counting conditions as normal samples. Background samples usually consist of geological samples of infinite age

such as coal, lignite, limestone, ancient carbonate, athracite, marble or swamp wood. By measuring the activity of a background sample, the normal radioactivity present while a sample of unknown age is being measured can be accounted for and deducted.

In an earlier section we mentioned that the limit of the technique is about 55-60 000 years. Obviously, the limit of the method differs between laboratories dependent upon the extent to which background levels of radioactivity can be reduced. Amongst accelerator laboratories there has been mooted the theoretical possibility of extended range dating to 75 000 yr +, at present this seems difficult to attain because of the problems in accurately differentiating between ions that mimic the mass and charge characteristics of the C14 atom. Beukens (1994) for instance has stated that this means the limit of the range for his Isotrace laboratory is 60 000 yr which is very similar to the conventional range.
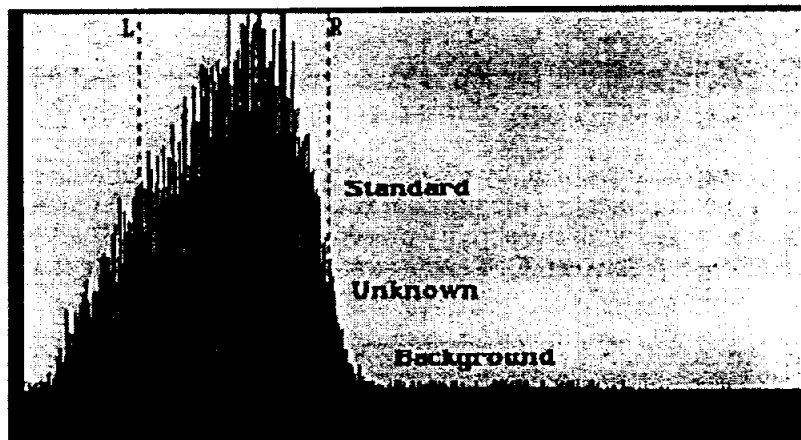
Figure 1: This gif shows the comparison in radioactivity between a sample, or unknown (green area) , a modern standard (dark blue) and a background (small red peaks) derived from beta decay. The scale represents log E (energy).

Conventional radiocarbon ages (BP)

A radiocarbon measurement, termed a **conventional radiocarbon age** (or CRA) is obtained using a set of parameters outlined by Stuiver and Polach (1977), in the journal *Radiocarbon*. A time-independent level of C14 activity for the past is assumed in the measurement of a CRA. The activity of this hypothetical level of C14 activity is equal to the activity of the absolute international radiocarbon standard.

The Conventional Radiocarbon Age BP is calculated using the radiocarbon decay equation:

$$t = -8033 \ln(Asn/Aon)$$

Where -8033 represents the mean lifetime of 14C (Stuiver and Polach, 1977). Aon is the activity in counts per minute of the modern standard, Asn is the equivalent cpm for the sample. 'ln' represents the natural logarithm.

A CRA embraces the following recommended conventions:

- a half-life of 5568 years;
- the use of Oxalic acid I or II, or appropriate secondary radiocarbon standards (*e.g.* ANU sucrose) as the modern radiocarbon standard;
- correction for sample isotopic fractionation (deltaC13) to a normalized or base value of -25.0 per mille relative to the ratio of C12/C13 in the carbonate standard VPDB (more on fractionation and

deltaC13);
- the use of 1950 AD as 0 BP, ie all C14 ages head back in time from 1950;
- the assumption that all C14 reservoirs have remained constant through time.

Three further terms are sometimes given with reported radiocarbon dates. d14C, D14C and deltaC13.

All are expressed in per mille notation rather than per cent notation (%).
d14C represents the per mille depletion in sample carbon 14 prior to isotopic fractionation correction and is measured by:

$$d14C = ((Asn/Aon) - 1)1000 \text{ per mille}$$

D14C represents the 'normalized' value of d14C. 'Normalized' means that the activity is scaled in relation to fractionation of the sample, or its deltaC13 value. All D14C values are normalized to the base value of -25.0 per mille with respect to the standard carbonate (VPDB). D14C is calculated using:

$$D14C = d14C - 2(dC13 + 25)(1 + d14C/1000) \text{ per mille}$$

This value can then be used to calculate the CRA using the equation given above.

$$\text{Radiocarbon age} = -8033 \ln(1 + D14C/1000)$$
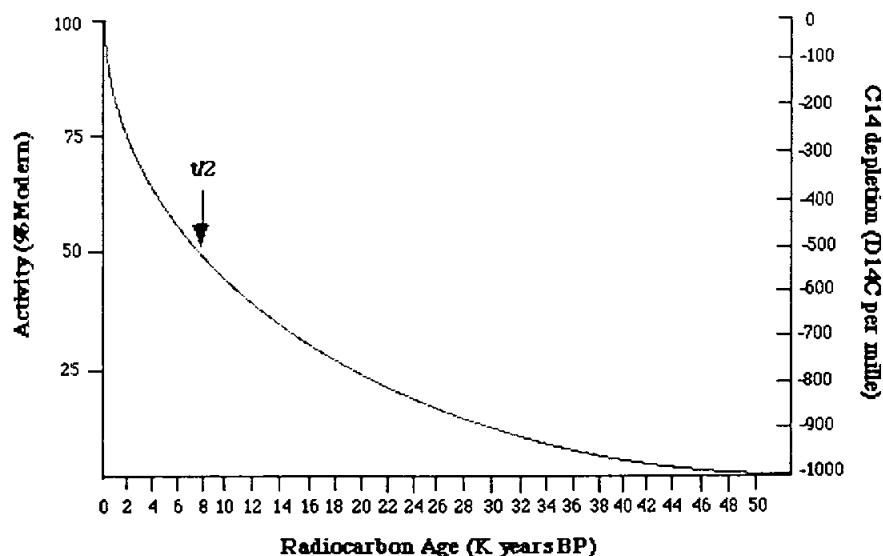
Figure 1: Decay curve for C14 showing the activity at one half-life (t/2). The terms "%Modern", or "pmC" and D14C are shown related in this diagram along with the Radiocarbon age in years BP (Before 1950 AD).

Age reporting

If the reservoir corrected conventional radiocarbon age calculated is within the past 200 years, it should by convention be termed 'Modern' (Stuiver and Polach, 1977:362). If a sample age falls after 1950, it is termed greater than Modern, or >Modern. Absolute percent modern (%M or pMC - 'percent modern carbon') is calculated using:

$$\%M = 100 \times Asn/Aabs$$

or,

Asn/Aon(1/8267(y-1950)) x 100 percent

Where Aabs is the absolute international standard activity, 1/8267 is the lifetime based on the new half life (5730 yr), Y = the year of measurement of the appropriate standard. This is an expression of the ratio of the net modern activity against the residual normalised activity of the sample, expressed as a percentage and it represents the proportion of radiocarbon atoms in the sample compared to that present in the year 1950 AD. Thus, %Modern becomes a useful term in describing radiocarbon measurements for the past 45 years when, due to the influx of artificial radiocarbon into the atmosphere as a result of nuclear bomb testing the 'age' calculation becomes a 'future' calculation.

If the sample approaches D14C = -1000 per mille within 2 standard deviations, it is considered to be indistinguishable from the laboratory background, ie, not able to be separated with confidence from the laboratory countrates which result from a sample which contains no radionuclide. In this instance, a **minimum age** is calculated. An example of a minimum age is >55, 000 yr or >50, 000 yr (Gupta and Polach, 1985).

Should the activity of the sample be indistinguishable from the background activity at 1 standard deviation, it is released as **background.**

Samples whose age falls between modern and background and are given finite ages.Standard errors released with each radiocarbon assay (see below) are usually rounded by convention (Stuiver and Polach, 1977). Again, not all laboratories subscibe to these conventions, some do not round up ages.

Age (yr)	Radiocarbon date rounded to	Error (± value)
0 - 1000	nearest 10	nearest 5 up
1000 - 10000	nearest 10	nearest 10 up
10000 - 25000	nearest 50	nearest 10 up
>25000	nearest 100	nearest 50 up

Standard error

We mentioned previously that statistical analysis is necessary in radiocarbon dating because the decay of C14 although constant, is spontaneous. It is not possible to measure all of the radioactivity in a given sample, hence the need for some kind of statistical analysis of counted data. The distribution of counted C14 decay events will, over time, yield a pattern. The pattern is termed a "normal distribution curve". A normal or "Gaussian" distribution describes the symmetrical bell shaped cluster of events around the average or mean of the data. In a normal distribution, 2 out of 3, or 68% of the values or counts observed will fall within one standard deviation of the average of the data. At two standard deviations, 95% of the observed counts will fall within the range and at three standard deviations, 99% of the counts which comprise the normal distribution will fall within this region. Each radiocarbon date is released as a conventional radiocarbon age with 'standard error'. This is the '±' value and by convention is ± 1 sigma. The standard error is based principally upon counting statistics (but see below).

According to Stuiver and Pearson (1992), the majority of laboratories report the measured counting statistics as a laboratory standard error. This results in considerable under-reporting (Scott, Long and Kra, 1990:253-393; Stuiver and Pearson, 1992:20) because a standard error based upon counting statistics alone does not include additional errors which may be incurred, for example, during sample preparation. Pearson (1979:21) has suggested:

> *"Those involved in radiocarbon dating should be alert to the various possible sources of error and recognize that the precision quoted on a date may be quite unrealistic if the error*

sources have not been investigated in detail".

Gordon Pearson. 1979. "Precise 14C Measurement by LS Counting". *Radiocarbon* 21(1):1-22.

To present a date with a realistic standard error, Pearson (1980; 1983) and Pearson *et al.* (1986:929) have identified the factors which contributed significantly to errors in beta counting using Liquid Scintillation spectrometry. Ostensibly, this research was a precursor to high precision dating of Irish bog oak samples for the calibration of the radiocarbon timescale (Pearson, 1980, 1983; Pearson and Stuiver, 1993). He investigated each principal factor contributing to errors and considered their effect on overall laboratory precision and concluded that a standard error of ±25 radiocarbon years was possible in the Belfast laboratory. Standard errors quoted by the Belfast laboratory, then, are based upon this analysis.

Many laboratories today calculate a **laboratory error multiplier** to account for all errors account for routine variation in reproducibility in radiocarbon dating. Stuiver (Stuiver and Pearson, 1993), for instance, has reported that the standard errors reported in the University of Washington laboratory results are based a lab multiplier. According to Stuiver and Pearson (1993), the error multiplier (or 'K') is a measure of the laboratory reproducibility, incorporating the errors resulting from the preparation of gas, its loading, memory effects and counting statistics. 'K' is defined as the actual standard error divided by the quoted standard error and is usually generated through repeat dating of a standard of known age or consensus age.

In addition, inter-laboratory comparison exercises have been undertaken to evaluate laboratory variation and identify causes for it. We hope to include some information regarding these important programmes run principally by the International Atomic Energy Agency (IAEA) and Glasgow University Department of Statistics.

Accuracy and Precision in Radiocarbon dating

It is important to note the meaning of "accuracy" and "precision" in radiocarbon dating. Accuracy refers to the date being a 'true' estimate of the age of a sample within the range of the statistical limits or ± value of the date. Thus, for the sake of argument, if we were radiocarbon dating a sample of Harold 1's (d. 1066) remains, and obtained a date of 1040±40 AD, we would have dated the event of his death accurately. If however the date were 1000±15 AD, we would be inaccurate. In terms of precision, however, the former is imprecise in comparison to the latter. It can be seen that the date of 1000±15 AD while being highly precise is, in this instance, inaccurate.
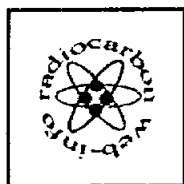
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Radiocarbon Calibration

- Why radiocarbon measurements are not true calendar ages
- How tree rings are used as a radiocarbon record
- How radiocarbon calibration works
- Some conventions
- Calibration programs
- Further reading

Why radiocarbon measurements are not true calendar ages
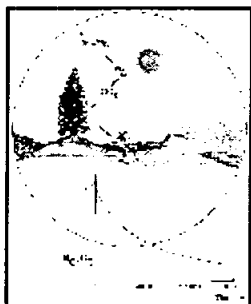
Radiocarbon measurements are always reported in terms of years 'before present' (BP). This figure is directly based on the proportion of radiocarbon found in the sample and is calculated on the assumption that the atmospheric radiocarbon concentration has always been the same as it was in 1950 and that the half life of radiocarbon is 5568 years. For these purposes 'present' refers to 1950 so you do not have to know the year in which the measurement was made.

To give an example if a sample is found to have a radiocarbon concentration exactly half of that for material which was modern in 1950 the radiocarbon measurement would be reported as 5568 BP.

For two important reasons, this does not mean that the sample comes from 3619 BC: firstly the proportion of radiocarbon in the atmosphere has varied by a few percent over time and secondly the true half life of radiocarbon is 5730 years not the original measured value of 5568 years. In order to see what a radiocarbon determination means in terms of a true age we need to know how the atmospheric concentration has changed with time.

How tree rings are used as a radiocarbon record

Many types of tree reliably lay down one tree ring every year. The wood in these rings once laid down remains unchanged during the life of the tree. This is very useful as a record of the radiocarbon concentration in the past. If we have a tree which is 500 years old we can measure the radiocarbon in the

500 rings and see what radiocarbon concentration corresponds to each calendar year.

Using very old trees (such as the Bristlecone Pines in the western U.S.A.) it is possible to make measurements back to a few thousand years ago.
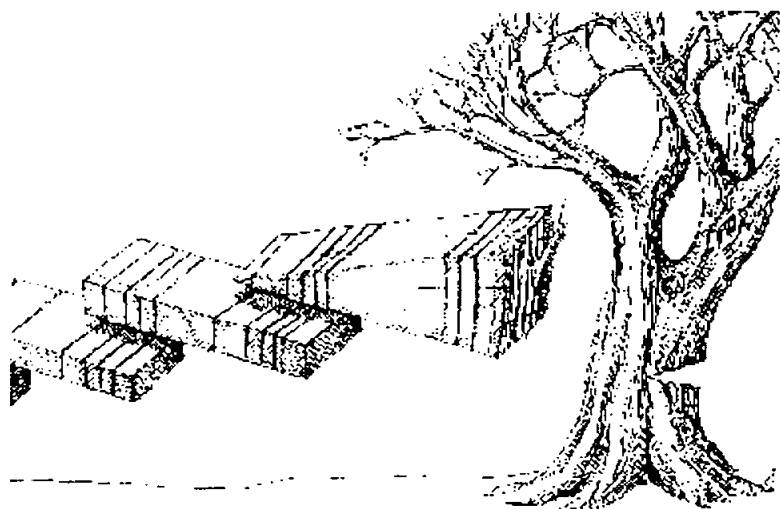
To extend this method further we must use the fact that tree ring widths vary from year to year with changing weather patterns. By using these widths it is possible to compare the tree rings in a dead tree to those in a tree that is still growing in the same region. By using dead trees of different but overlapping ages you can build up a library of tree rings of different calendar ages. This has now been done for Bristlecone Pines in the U.S.A and waterlogged Oaks in Ireland and Germany to provide records extending back over the last 11,000 years.

How radiocarbon calibration works

Calibration of radiocarbon determinations is in principle very simple. If you have a radiocarbon measurement on a sample you can look through the tree ring record for a tree ring with the same proportion of radiocarbon. Since the calendar age of the tree rings is known this then tells you the age of your sample.

In practice this is complicated by two factors: one is that the measurements on both the tree rings and the samples have a limited precision and so there will be a range of possible calendar years; the other is that, given the way the atmospheric radiocarbon concentration has varied, there might be several possible ranges. These effects are most clearly seen by looking at a specific example.

DATE : 3000±30BP
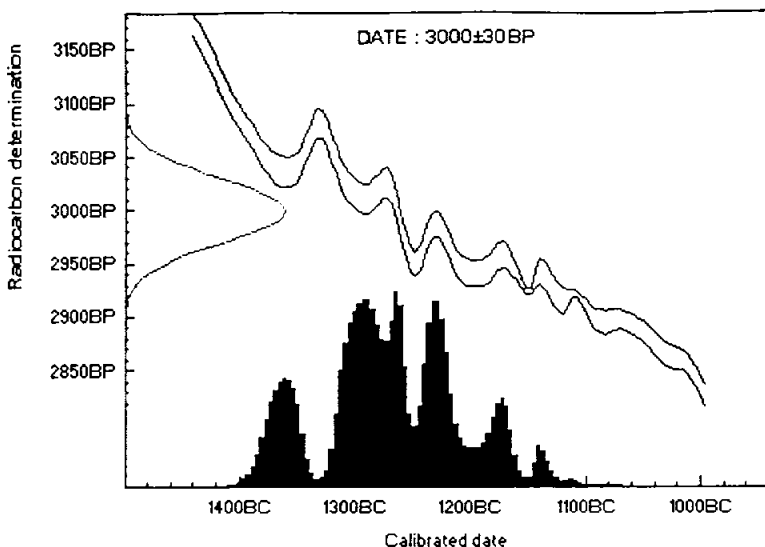
This plot shows how the radiocarbon measurement 3000+-30BP would be calibrated. The left hand axis shows radiocarbon concentration expressed in years 'before present' and the bottom axis shows calendar years (derived from the tree ring data). The pair of blue curves show the radiocarbon measurements on the tree rings (plus and minus one standard deviation) and the red curve on the left indicates the radiocarbon concentration in the sample. The black histogram shows possible ages for the sample (the higher the histogram the more likely that age is).

The results of calibration are often given as an age range. In this case we might say that we can be 95% sure that the sample comes from between 1390CalBC and 1130CalBC.

Some Conventions

This is not intended to be an exhaustive summary of radiocarbon calibration conventions but a brief guide.

- Reporting radiocarbon dates
- The calibrated time scales
- Methods of calculating ranges

Reporting radiocarbon dates

Radiocarbon dates should always be reported either as 'percent modern' or years 'before present' (BP). The first indicates the proportion of radiocarbon atoms in the sample as compared to samples modern in 1950. The second is directly derived from this on the assumption that the half life of radiocarbon is 5568 years and the amount of radiocarbon in the atmosphere has been constant.

The calibrated time scales

Once calibrated a radiocarbon date should be expressed in terms of CalBC, CalAD or CalBP. The Cal prefix indicates that the dates are the result of radiocarbon calibration using tree ring data. These values should correspond exactly to normal historical years BC and AD. The term CalBP means the number of years before 1950 and can be directly compared to calendar years.

Methods of calculating ranges

There are two main methods used for calculating age ranges from the calibration curve:

The first method to be employed was called the `intercept method' because it can be done by drawing intercepts on a graph. This method will tell you the years in which the radiocarbon concentration of tree rings is within two standard deviations of your measurement (eg between 2940BP and 3060BP for the measurement 3000+-30BP).

A slightly different method is now more often used which is called the `probability method'. This requires a computer since the calculations are more complicated. It gives the time range from which you can be 95% sure the sample came.

Calibration programs

There are a number of calibration programs available including the original DOS program CALIB and the Windows program OxCal.

Further reading

- Aitken M.J. 1990 *Science-based dating in archaeology* London, Longman
- Stuiver M. and R.S. Kra eds. 1986 Calibration issue, Proceedings of the 12th International 14C conference *Radiocarbon* **28**(2B) 805-1030
- Stuiver M., A. Long A., and R.S. Kra eds. 1993 Calibration issue *Radiocarbon* **35**(1)
- The online manual for OxCal

See also the OxCal reference list.

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Email: orau@rlaha.ox.ac.uk
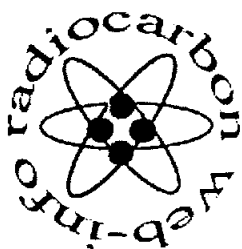
➤ The method	➤ Publication	➤ Bibliography
➤ Measurement	➤ Corrections	➤ Awards
➤ Applications	➤ Age calculation	➤ Credits
➤ WWW links	➤ Calibration	➤ What's New
➤ K-12	➤ Pretreatment	➤ Email

CONTRIBUTED BY: THOMAS HIGHAM

When the C14 method was originally developed, Libby and his research team had to assume that the ratios of the carbon isotopes they were measuring had been altered only by 14C decay (Taylor, 1987:3) and that the sample material accurately represented the event to be dated. Sample materials deposited in archaeological or geological contexts seldom remain in pristine condition, of course, they are often degraded and altered chemically. Libby realized that the residual carbon 14 of some samples would be thus affected and suggested that some materials would be more accurate for dating than others. He predicted that charcoal would be the most effective, shell, the least.
The following types of sample have been commonly radiocarbon dated:

- Charcoal, wood, twigs and seeds.
- Bone.
- Marine, estuarine and riverine shell.
- Leather.
- Peat
- Coprolites.
- Lake muds (gyttja) and sediments.
- Soil.
- Ice cores.
- Pollen.
- Hair.
- Pottery.
- Metal casting ores.
- Wall paintings and rock art works.
- Iron and meteorites.
- Avian eggshell.
- Corals and foraminifera.
- Speleothems.
- Tufa.
- Blood residues.
- Textiles and fabrics.
- Paper and parchment.
- Fish remains.
- Insect remains.
- Resins and glues.
- Antler and horn.

Since the 1950's, a number of researchers have concentrated on investigating and reducing the effects of this post-depositional contamination. This field of inquiry is known as **sample pretreatment** and it is concerned with removing post-depositional contaminants by isolating sample fractions containing carbon which is autochthonous and therefore accurately dates the event in question.

This section is divided into a number of areas: DOI 04476

This section is divided into a number of areas:

- Submission of samples for dating
- Contamination
- Assessing the effects of pretreatment
- Physical pretreatment methods
- Chemical pretreatment methods
- Summary of pretreatments by material

Introduction

Submission of samples:

The key issue in sample pretreatment is that there is no method, or methods, that can be universally applied to all types of material from archaeological or geological contexts. Pretreatments are designed to remove the contaminating substances that have affected the sample during its post-depositional history. If pretreatments were able to be uniformly implemented, there would have to be a uniform and predictable array of post-depositional characteristics between all samples. Clearly, this is not the case. Each sample submitted for dating has its own specific depositional history. The variety in environment and post-depositional features is reflected in the variety and complexity of pretreatment procedures and the variety of different types of dateable material (see above). Nevertheless, there are certain laboratory procedures which are associated with specific sample types and environments, and a number of accepted and often repeated pretreatment methods. These are described in detail below.

The laboratory decides on the most effective pretreatment procedure through a careful examination of each submitted sample. A number of variables feature in this consideration, one of the most important concerns the environment within which the sample was deposited. The lab must consider the possibility of contamination in each sample it dates and depends upon information supplied by the submitter and collector of the material for its assessment. The submitter should supply information detailing the type of environment from which the sample was obtained and commenting on the presence of rootlet intrusion and contaminants.

There is more information about AMS Sample Preparation and pretreatment at the Oxford AMS lab, the Rafter Radiocarbon Lab and the PRIME AMS lab.

The Radiocarbon Laboratory at the University of Texas at Austin, a conventional laboratory, also has information about pretreatments and the routine methods used in their laboratory.

The submitter should also describe the relationship between the material and the geological, or archaeological context to be dated. A stratigraphical diagram should be drawn to enable the dater to understand completely the site and origin of the material, and to consider the ability of the lab to adequately date the sample in question. The submitter should also indicate the degree of accuracy and precision required. Sometimes, a precise date is not needed and pretreatment methods designed to reduce errors will not be necessary. Many commercial laboratories have different charges for dating depending on the precision (and speed) that is required. A high-precision date may involve the lab in more intensive pretreatment and labour and consequently costs are higher.

Submitters should send as much sample as possible because of the destructive nature of certain pretreatment techniques. This is particularly relevant for laboratories which use conventional methods of dating. Bone dating, for example, requires large amounts of sample because the fractions which are usually extracted comprise a small percentage of the total material and the target fractions decompose rapidly. Often, submitted samples are divided and one portion retained as a reference in case the original sample is lost, or a further date required.

Sometimes, submitters perform basic pretreatments, usually involving a wash in distilled water and the removal of root material. This should be reported in the submission forms accompanying samples sent to the laboratory.

Contamination

Contamination may be artificially or naturally caused. Artificial contamination may be blamed on human negligence during the collection and processing of samples. Contaminants often include ash from tobacco, hair and fibres, paper from packing material and oil or grease (Hogg, 1982:21). Natural contamination occurs in the post-depositional environment. Samples may be contaminated by material which make any radiocarbon result either too old or too young. The most common source of contamination by modern carbon is caused by rootlet intrusion. Organic samples such as wood, charcoal, soil and bone are especially prone to this and should be examined closely before, and after collection, for evidence of root penetration (Hogg, 1982:18). Contamination may also be caused by humic acids circulating throughout the soil. Humics are the decayed remnants of dead plants. They may exchange carbon or adhere to samples that have large surface areas and make any radiocarbon results too young. This surface exchange is termed 'adsorption' and is especially common in samples such as peats, charcoals and muds.

Certain samples, especially shell, may show evidence of isotopic exchange or recrystallisation. Isotopic exchange occurs when shells exchange carbon with percolating ground acids. This alters their isotopic ratios and affects their 'true' age. The exchange usually occurs on the exterior shell surfaces in terrestrial environments and is common in samples found below the water table (Hogg, 1982:18). An analysis of the carbon isotope ratios using a mass spectrometer will reveal the extent of any exchange. A correction factor may be applied or the sample rejected on this basis. Recrystallisation refers to the modification of shell aragonite to calcite, often involving an exchange with modern calcite and a subsequent altering of isotopic ratios.

In investigating the extent and effect of these types of sample contamination, the radiocarbon laboratory is faced with two major problems. First, it has to identify precisely the nature and size of contamination. Second, it needs to assess its magnitude and direction of change (Gupta and Polach, 1985:129).

Olsson (1974), and Gupta and Polach (1985:129-134) have considered the nature of this relationship between sample, contaminant and magnitude of error. They suggested that by "guesstimating" the age difference between the 'true' sample age and that of the contaminant, and calculating the relative size of the contaminant in the sample, it was possible to determine the extent of the error caused by the contaminant and apply a correction. A set of graphs were shown by the authors' to show the range of errors associated with samples contaminated by older and younger carbon. In general, the older the sample, the greater became the effect of contamination, even if the percentage of contaminant to sample was small (see Table 1). This consideration is based on the assumption that any contamination was instantaneous (Gupta and Polach, 1985:130). More complex problems arise when the contaminating fraction changes temporally in size.

	% Contamination by modern carbon					
	0%	1%	5%	10%	25%	50%
At 900 BP	900 (0)	890 (1)	850 (5)	810 (11)	670 (26)	440 (51)
	% Contamination by old carbon					
At 900 BP	0%	1%	5%	10%	25%	50%
	900 (0)	980 (9)	1320 (47)	1770 (97)	3280 (264)	6630 (637)

Table 1: The effect of contamination by old and modern carbon upon a sample with a 'true age' of 900 BP. Figures in brackets give the % error introduced by the contaminant (table from Caughley, 1988).

The other major issue in sample contamination concerns samples which contain small errors. Dates which are clearly too old or young are easily recognised and investigated, those that contain less significant errors are more difficult to identify. According to Olsson (1979), the danger is that these dates will often be considered to be reliable when they are not because they fall close to the expected age.

## Assessing the effect of treatment

There are a number of ways to guage the effects of pretreatment upon samples. The most common is to analyse and date the different fractions that have been removed. This will reveal the magnitude of error. If the dates from sample and contaminant are close, the associated error will be insignificant, however, if there is a major difference, the errors will rise. If different fractions give statistically identical results then it is concluded that no significant contamination has occurred. Another more complex method, concerns the analysis of the chemical properties of successively removed fractions. This enables the investigator to identify the types of contaminants present and their concentration, and determine the success of pretreatments. This quantitative method targets specific contaminants and measures them as a percentage of the total sample. It is a costly measure and is usually confined only to research programmes or to very important samples. A third method is cross-checking. The original date is 'checked' by dating other contemporaneous materials. Similarly, the date may be assessed using reliable cultural and stratigraphic markers as chronological reference points. For example, in Mycenean, Minoan and Cycladic archaeology, reliable chronological markers exist in the form of pottery, which varies both stylistically and temporally through the bronze age, providing a useful reference. A final, though less reliable method, is the analysis of the amount of carbon dioxide produced in combustion or hydrolysis, in proportion to the size of the sample. The rationale here is that successful pretreatments should maximise the amounts of pure carbon dioxide produced, proportional to sample size. The assumption is that the CO_2 produced is not contaminated.

By dating the fractions removed, then, it may be possible to consider whether pretreatments have revealed a 'truer' age. An example of such a study may be seen in the recent work of Head *et al.* (1989), who implemented a geochronological research programme in loess deposits in China, near Xian. Humic contamination was expected because of the discovery of rootlet intrusion and the muddy and wet texture of the deposit. Humic acids are mobile, decay products from recently dead plants which leach down through site profiles, being adsorbed by certain receptive substances and affecting 'true' dates. The usual method for removing humic acids is through treatment with base solutions, most commonly, sodium hyroxide (NaOH). Often, by increasing the polarity of these washes, more effective removal of humics is possible. Each wash results in a base soluble fraction and a base insoluble fraction. Both can be analysed for contaminants, or dated. If dates from the two fractions vary significantly then it may be assumed that some degree of contamination has occurred. Sometimes the base insoluble fraction will be deemed the most reliable fraction, because the base pretreatments will have extracted the humic acid contamination. Conversely, the base soluble fraction may be considered more reliable, because the humic component will be a terrestrial humic acid, that is, a contemporaneous fraction of the peat. Deciding which sample fraction was reliable in Xian was made by analysing a number of complex variables, for example; the elemental atomic ratios for the fractions, which indicate the types of humic substances in the stratum; optical density measurements, which reveal approximately the time a humic substance has been present in the sample; solvent extraction analysis, which may show the type of contaminant residue; and 14C determinations, which enable comparison of the dates from the two fractions. Through these analyses it was possible for Head et al to guage the effect and origin of contamination and estimate the success of the pretreatment. They found in this case, that the base soluble fraction was the most reliable for dating. The insoluble fraction revealed ages that were considered too young. The clay component which formed the basis of the insoluble fraction was providing a matrix suitable for adsorption of contaminants and attracting young humic substances (Head et al, 1989; 685-689).

There are two major types of pretreatment applicable to carbonaceous samples:

- Physical pretreatment

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- Chemical pretreatment
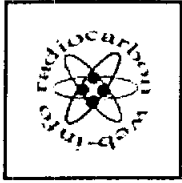
HTML DOCUMENT BY T.HIGHAM.
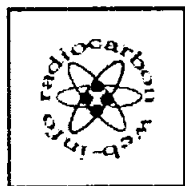
Physical Pretreatment Methods.

Physical pretreatment refers to any pretreatment not involving chemicals. Gupta and Polach (1985) divide this into two parts; the removal of obvious contamination; and the reduction in size of the sample (Gupta and Polach, 1985;13-16). The most common methods of removal include separation of sample and rootlets using tweezers and magnification, and the scraping of the contaminated exterior layer using a surgical scalpel, dental drill and carborundum paper. The rationale behind this is that the exterior surfaces will show the effects of contamination, or isotopic exchange, first. Fragments of charcoal are scraped clean with a scalpel, larger bones have the outer layer excised with a drill and shells have the 'chalky' exterior removed with dental equipment. Physical pretreatment can be preferable to using chemicals because it enables the radiocarbon specialist to be selective in which parts of the sample are removed. The use of chemicals often results in the destruction of pure sample material.

The pretreatment of shell is a good example. The outer layers of shell may be removed using drills and carborundum paper, beneath a fume hood, designed to remove the dust from the laboratory environment. The aim of drilling being to isolate one fraction of the shell material. The section considered to be most reliable for dating is aragonite, the less stable crystal form of the two shell carbonates (the other being calcite). Aragonite is selected because it will show the effects of recrystallisation first. Recrystallisation describes an isotopic exchange. In the post-depositional environment, certain shells incorporate new calcite from other sources of carbonate. This shell may be of a different age and isotopic ratio and will affect radiocarbon determinations. This process is termed recrystallisation. It is difficult to test for recrystallisation on shell calcite, because it is hard to differentiate between sample and contaminant, but it is easily apparent on aragonite. A test for calcite peaks in the aragonite samples of shell by X-ray diffraction places limits on the probability that recrystallisation has occurred.

Usually, calcite that has recrystallised becomes chalky and white and this is the fraction targetted for removal by drilling. The other method commonly employed in shell pretreatment is 'acid-washing'. The acid most often used is hydrochloric acid (HCl). A dilute HCl solution (usually 5-10% conc.) is added to the shells, which are shaken for approximately ninety seconds while the acid dissolves a portion of the shell exterior.

After initial pretreatment, the samples are usually crushed and reduced in size to increase the surface area prior to further pretreatment, acid evolution or combustion. Shell, rock and bone samples are often crushed in a mortar and pestle. Wood is either splintered using a hammer and chisel, or ground into sawdust in a mill. Charcoal is usually ground in a petrie dish or mortar and pestle. Soil samples are slurried and wet seived prior to acid pretreatment. Distilled water and seives are used to separate soil, mud and peat samples into 'fine' and 'coarse' fractions. The coarse fraction is submitted to the archives as a reference sample, while the fine fraction is acid washed and eventually dated.

On to the Chemical Pretreatment pages...

HTML DOCUMENT BY T.HIGHAM.

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Chemical Pretreatment Methods

DISCLAIMER: The pretreatments described below are not universally applied in all radiocarbon laboratories, there may be slight variations in some of the procedures between different laboratories and radiocarbon specialists. For detailed information regarding the pretreatment procedures employed by a specific laboratory it is necessary to contact the laboratory in question. Data given below is merely intended as a guide only.

- Pretreatment of organic matter; charcoal, peat etc.
- Pretreatment of Bone
- Analytical chemistry of Bone
- Wood pretreatment
- Shell pretreatment
- Summary of pretreatments by material

Pretreatment of organic matter: Charcoal, peat, lake muds.

Many samples from terrestrial environments, such as wood, charcoal and peat, will often contain small amounts of absorbed carbonates from percolating groundwater. This material is non-contemporaneous and must be removed. Usually, dilute HCl (10% conc.) is used in this treatment. It is added to the sample in a beaker which is placed on a hot plate and heated until slowly boiling. After approximately one hour it is removed and placed into a buchner funnel. The buchner apparatus uses the pressure of flowing water to create a vacuum. By increasing the rate of flow, one can increase the effect of the vacuum. A glass filter is placed at the bottom of the funnel and dampened with distilled water (dist. H_2O). Afterwards, the sample is placed on top of the filter paper and a number of litres of distilled water poured in and drawn through the sample by the vacuum effect. The aim is to reduce the pH levels of the sample to a neutral level by continual rinsing. During this treatment, regular litmus readings are taken to determine the extent of the acidity remaining. Once the pH level is reduced, two sample fractions are left; an acid insoluble fraction and an acid soluble fraction. The soluble fraction should contain the carbonate contaminants and as such is seldom used for dating purposes, except when there is a need to know the age and nature of the contamination. The acid insoluble fraction should contain the original, pristine sample, minus the carbonate contaminants, if the acid wash has had its desired effect. It is placed in a petrie dish or beaker and dried in an oven prior to combustion or further pretreatment.

HCl acid washing is usually applied to samples destined for combustion. Because HCl reacts with carbonate to produce CO_2, its use in pretreatment work is restricted to non-carbonate samples.

Sodium hydroxide (NaOH) treatment is usually associated with the removal of humic acid contamination from soils, wood, charcoal and peat samples. Humic acids are the mobile decay products of biological materials deposited in the vicinity of the sample matrix. They are easily incorporated by sample materials, affecting the ages of each. There are two major decay contaminants; humic acids and fulvic acids. The humic fraction is acid insoluble and is removed using a base extraction method. The fulvic fraction however, is soluble in acid and may be removed using an HCl wash.

The most common method of treating samples thought to be contaminated with these substances is the acid-base-acid method (ABA), sometimes called the acid-alkali-acid (AAA) method. After being physically pretreated and reduced in size, the sample is washed in hot diluted (10%) HCl in a beaker for approximately one hour, or until the reaction appears to have ceased. It is then rinsed in a buchner funnel with distilled water to reduce the pH levels towards neutral. Following this, the sample is immersed in a 5% diluted, boiling NaOH solution for approximately one hour, after which it is rinsed or centrifuged

again. The NaOH treatment produces two fractions, base soluble and insoluble. The former may be kept for dating purposes by being acidified, rinsed and dried in an oven. The latter too, must be acidified because the NaOH pretreatment sometimes involves an exchange between the NaOH and atmospheric CO_2. The NaOH absorbs CO_2 from the surrounding air. The final acid wash ensures that any such contamination is removed. The insoluble fraction usually contains the sample minus the contaminant and is the dateable component.

Sometimes, samples undergo a solvent extraction prior to ABA pretreatment to remove contaminants such as resins and waxes. A soxhlet extractor is the most common apparatus used in the extraction method. This apparatus continually recycles the solvents being used so that they do not have to be replaced. Solvents are heated in a round-bottomed flask and evaporate up through a siphon into a condenser. Upon condensing they drip down through the pyrex wool covering the sample and then through the sample itself, leaching the contaminants through the profile and dissolving them. As the pressure increases in the sample tube, the solvents are gradually deposited back into the original flask, whereupon the process is repeated. The contaminants are collected in the flask and either dated, stored for analysis, or discarded. The samples most often given solvent pretreatments such as this are wood, soil organics, peat and charcoal, from specific environments.

A variety of solvents may be used in the extraction process, depending on the type of material and the contaminants present. The most common involves using three solvents, beginning with a chloroform/ethanol mixture ($CHCl_3$ and ETOH) at a ratio of 2:1. This is run through the sample until the solvents appear muddy and dirty. The solvent soluble materials are removed and dried in an oven. A second extraction is carried out using alcohol (C_2H_5OH) which continues until the siphon is clear. The procedure is repeated with water and the sample is removed and dried in an oven before further pretreatment or combustion. Other solvent extractions using ethyl acetate, acetone and benzene/ethanol will be dicussed later.

Bone

CONTRIBUTED BY: FIONA PETCHEY

(For more detail see Taylor 1982, 1992; Stafford et al 1987:25; 1988:2257; Brown et al. 1988:171; Gurfinkel 1987:46; van Klinken and Mook 1990:155).

The first radiocarbon measurements on bone were on naturally burned bone (Arnold and Libby 1951; De Vries and Barendesen 1954). Soon after Libby (1952:44) stressed concern over the low organic carbon content, porous structure and possible effects of putrefaction and chemical alteration on the bone. Only two samples of whole bone had been measured at this time, and both gave young dates. More recently the context of one of the samples (C-558 initially thought to be from a Folsom level at Lubbock Lake, Texas) has been placed in doubt (Taylor 1992:376). Consequently, while there had been little work in this area , bone did not appear in Libby's 1952 listing of suitable sample materials, though burned bone was ranked alongside charcoal at the top.

However, the obvious importance of bone to the chronology of many sites saw a continued interest in bone as a dating medium. The major problem was traced to the use of whole bone to generate CO_2 for 14C measurements, whereby contamination from both carbonates and organics could enter the date. Initial efforts to remove the indigenous organics from the bone included techniques such as the artificial pyrolysis of bone by May (1955) whose process was designed to minimise loss of residual organics, acid digestion and dialysis (Munnich 1957), and the gelatinization of "collagen" (Sinex and Faris 1959). Despite these attempts problematic dates still persisted. In a review of the literature up to 1960, Olson (1963:61-65, in Taylor 1992:377) noted that bone dates were most often rejected. Proof that humates were the predominant contaminant in decalcified bone was finally given by De Vries (in Vogel and Waterbolk 1963). A variety of techniques were developed to remove this matter: Initially the pretreatment procedure used on charcoal was adopted whereby decalcified bone is extracted with 0.1 to 0.5 M NaOH (Berger and Libby 1966; Haynes 1967); conversion of the sample to gelatin by Longin

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(1971); and later Protsch (1975) combined the HCl, NaOH and gelatinization steps. This is the general "collagen" extraction procedure used today in carbon dating and dietary analysis (i.e. DeNiro and Epstein 1981).

By the mid-70's a number of reviews and evaluations of bone dating were being undertaken (e.g. Olsson et al. 1974; El-Daoushy et al. 1978). One group at the Uppsala laboratory proposed the use of different fractions (acid soluble and acid insoluble) for the majority of bones on the basis that it would be improbable for contaminants to cause the same error in different fractions. Unfortunately the yields from the different fractions were often insufficient for conventional dating techniques (Taylor 1992:381-3).

Initial descriptions of experiments demonstrating the feasibility of accelerator or cyclotron-radiocarbon-based isotopic measurements appeared in 1977 (Muller 1977). The advent of AMS enabled dating of small amounts of material, of material with very low organic carbon content, and multiple 14C determinations of different organic fractions (Taylor 1982:46, 1992:37; Gillespie et al. 1984:165). While this was a clear advantage in the dating of bone, the use of smaller samples required a clearer separation of the organic and inorganic portions. Therefore, more emphasis had to be placed on the purity of the sample (Protsch 1991:284).

Cation exchange chromatography had initially been introduced for the dating of problem samples (Ho *et al.* 1969). The large sample sizes and excellent preservation of collagen in the bones at the La Brea tar pits, California, made these C14 measurements possible, but proved to be too expensive and impractical for the large samples required with conventional dating methods. The advent of AMS changed this. Initial chromatographic techniques involved the hydrolysis of the extracted "collagen", but the incomplete removal of humic acids by gelatinization, alkali and acid treatments often resulted in cross linkages with residual impurities when hydrolysed. Attempts to remove humates prior to hydrolysis using XAD resins (Stafford et al. 1988; Law and Hedges 1989; Law et al. 1991) and decolourising charcoal (Gillespie et al. 1984) still failed to remove exogenous amino acids associated with soil contaminants (Hassan and Hare 1978). More recently to aid in the understanding of the series of reactions that can take place during diagenesis and pretreatment, van Klinken (1994) has used sample yields during enzymatic cleavage to screen the degree of cross linking.

To counteract possible contamination products, techniques based on the molecular weight and size of the collagen molecule have been used. Brown, Nelson, Vogel and Southon (1988) modified the Longin method of "collagen" extraction by adding an ultrafiltration step (gel electrophoresis) designed to exclude low molecular weight species (see also Gillespie 1989). Another approach developed to purify collagen for stable isotope analysis involves the use of collagenase, which preferentially isolates tripeptides of known length from the surviving collagen fragments (DeNiro and Weiner 1988a, b; van Klinken and Hedges 1992; van Klinken 1994).

Other attempts have concentrated on identifying relatively uncontaminated parts of bone. The isolation of "aggregates" which were identified as having potentially a better protected environment for collagen survival was undertaken by DeNiro and Weiner (1988b), but do not give reliable results from bone with a low collagen content (Hedges and van Klinken 1992:285-6). Recently several researchers have noted the use of non-collagenous components for dating seriously degraded bone. Long, Wilson, Ernst, Gore and Hare (1989:238) have suggested that phosphoproteins may be protected from degradation as they bond to the apatite structure. Gillespie (1989:240) noted the existence of osteocalcin, osteonectin and other phosphoproteins, proteoglycans, and glycoproteins as well as blood proteins, which may display differential survival characteristics to collagen.

The first suite of 14C measurements of a non-collagenous protein were undertaken on osteocalcin by Ajie, Kaplan, Slota and Taylor (1990). Osteocalcin makes up 1% of total bone protein and appears to bind tightly to hydroxyapatite, suggesting a good possibility of being protected from contamination. Further, it has not been detected in many species of bacteria, plants or invertebrates (Hauschka 1980 in Taylor 1992:389). However, osteocalcin values on two skeletons from the Haverty site (Los Angeles) gave disproportionably old values, which if correct would signify the oldest human remains in the western hemisphere (Taylor 1992:396). It may be that for osteocalcin to be a suitable medium, isolation of essential amino acids may need to be performed (Sobel and Berger 1994).

Apatite Fraction.

Early C14 studies using the inorganic or carbonate fraction of bone were in most cases clearly false, usually too young (Berger et al. 1964; Tamers and Pearson 1965). Haynes investigated the reliability of using the bone apatite fraction and concluded that erroneous apatite dates can result from carbon exchange in the apatite structure during recrystallization, and/or surface exchange reactions (Haynes 1968:688). Studies into separation of the in situ primary apatite fraction from diagenetic carbonates were initiated in the 1960's and 1970's (e.g. Haynes 1968; Hassan 1976; Hassan et al. 1977). Hass and Banewics (1980) reported more encouraging results, and the demonstration that careful etching with acetic acid can enable the residual carbonate to maintain a biogenetic d13C signal (Lee-Thorp et al. 1989) suggests possibilities. But no-one has so far demonstrated that the indigenous carbonate can be extracted reliably and separated from diagenetic carbonate (see Stafford et al. 1991; Hedges and van Klinken 1992:285; Taylor 1982:458; Gillespie et al. 1984:165).

Teeth

Good results have generally been obtained from teeth (e.g. van Klinken and Mook 1990:158), though CO2 exchange with the atmosphere may be more efficient in teeth than initially thought (John Head pers. comms. 27/6/95). Recent studies on CO2 from teeth do, however, indicate that secondary carbonates may be identified from stable isotope values, suggesting that reliable 14C determinations may possibly be obtained on tooth enamel (Hedges et al. 1994).

Analytical chemistry of Bone

As it became obvious that the state of preservation of collagen is vital for 14C accuracy, researchers began to examine biochemical indices that might be useful in characterising collagen (Taylor 1992:380). Those "finger-prints" which have been adopted to assess the degradation of bones include measurement of the nitrogen content of bone, stable carbon and nitrogen isotopes and the nitrogen/carbon ratio, a collagen like amino acid pattern, the presence and relative concentration of hydroxyproline, infra red spectra and tests for metal ions derived from humic contaminants.

Total collagen content

"Collagen" can be estimated by percentage nitrogen in the whole sample, or by measuring the nitrogen content in the decalcified extract. Fresh, dry, defatted, compact bone from large mammals contains on average between 4 and 5% organic nitrogen by weight, though variations do occur depending on maturity and size of mammal (Garlick 1969:503, 509). However, such measurements do not indicate if the nitrogen is wholly present as collagen, nor the extent of non-nitrogenous organic material (Hedges and van Klinken 1992:282).

Stable C and N isotopes

A basic assumption in the stable or radiometric isotope analysis of bone is that collagen is thought to retain 13C/12C and 15N/14N values postmortem even though collagen is known to degrade with time after death. However, as each amino acid has a unique isotopic value, diagenesis of collagen will theoretically alter the isotope value of the resulting organic fraction (Hare and Estep 1983; Tuross et al. 1988), while humates also have an effect on the isotopic composition of bone depending upon their concentration, 13C , 14C and 15N compositions (Stafford et al. 1988:2257). In some cases, the traditional pretreatments (i.e. HCl, EDTA, NaOH and gelatinization) may further change the observed isotopic values (Tuross et al. 1988:929, 934), though ion exchange chromatography does not seem to cause any major variations (Stafford et al. 1988).

C/N ratio

Carbon/nitrogen values can be taken either on the whole bone or extract of. Carbon/nitrogen values of 2.9-3.6 from gelatinous extracts of bone are though to be indicative of collagen with diagenetically

unaltered carbon and nitrogen values, while high values (ie >>4) indicate extensive diagenesis, or a high proportion of exogenous carbon possibly from sample preparation, non-collagenous proteins or contaminants (Stafford et al. 1988:2266; Tuross et al. 1988:931; Hedges and van Klinken 1992:282-3).

Amino acids

Several studies have investigated the possibility of using amino acid composition and/or racemisation values as a means of characterising indigenous organics in bone samples (Hassan and Hare 1978:115-116). Some workers suggest that the absence of the collagen amino acid signature indicates the presence of contamination (Wyckoff 1972). Others (e.g. Hare 1980) have suggested that in some cases where the organic content is extremely low (below 0.4 to 0.1% N), the amino acid pattern may reflect the indigenous non-collagenous protein residue rather than contamination. A number of factors may also alter the collagenous amino acid "finger-print": The different pretreatments effect the total amino-acid composition of the bone, while differential loss of amino acids and peptides may occur during diagenesis due to differences in solubility, effect of temperature and susceptibility to oxidation or deamination, to name a few (Hedges and van Klinken 1992:283, 285). Attempts to identify a non-collagenous composition has seen the use of the Gly/Asp ratio (DeNiro and Weiner 1988a; Long et al. 1989; Law and Hedges 1989; Weiner and Bar-Yosef 1990; Hedges and van Klinken 1992:282-3). Glycine is abundant in collagen, whereas aspartate is abundant both in bone non-collagenous proteins and in most (including bacterial) protein, and therefore discrepancies in the relative amounts of each are a sensitive test for contaminants.

Infra red spectroscopy

Qualitative IR spectroscopy has been used to estimate the purity of the protein under analysis (DeNiro and Weiner 1988a, b; Law et al. 1991), as well as to assess the degree of recrystallization of hydroxyapatite (Weiner and Bar-Yosef 1990). However, with archaeological materials complex spectra may be obtained due to diagenesis and contamination (Law et al. 1991:308, 311), so at present this technique cannot identify impurities less than the >5-10% level (Hedges and van Klinken 1992:283).

Ion beam analysis

Analysis of light elements (F, N, P and Na) and trace metals using X-ray specta has been done by Redvers-Newton and Coote (1994) in order to identify the presence of metal complexes which form in the presence of humic materials. Again the complex spectra may be obtained and due to diagenesis and exogenous organic matter.

All these analytical techniques for collagen assessment have met with only limited success, depending on the preservation state of the bone itself. In an attempt to achieve a better chemical characterisation of the fraction selected for dating Stafford, Brendel and Duhamel (1988) used a number of these criteria to classify bone preservation (see Table 1). Unfortunately, there is currently no consensus as to biogeochemical methods which can be routinely used in bones exhibiting very low or trace amounts of collagen (i.e. lost >95% of their protein)(Taylor 1992:386-7). As a consequence Hedges and van Klinken (1992:282) suggest an age limit of 18ka as older dates are more sensitive to modern contamination.

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	Class I: [Modern]	Class II: [very well to well preserved]	Class III: [Moderately well preserved]	Class IV: [Poorly preserved]	Class V: [Extremely poorly preserved]
Whole bone % Nitrogen	4.5-3.5	3.5-0.6	0.9-0.4	0.5-0.1	0.1-<0.01
Characteristic amino acids: Residues per 1000 nominal values	Hydroxyproline 90 Aspartic acid 50 Glutamic acid 70 Proline 120 Glycine 330 Alanine 105-110 Arginine 55	90 50 70 120 330 120 45	90 50 70 120 330 120 45	90 50 70 120 300-330 120 45	30-80 50-100 70-130 100-180 260-300 100-120 40-45
Physical characteristics of whole bone	High compressive and tensile strength; spiral and conchoidal fracturing; dense mineral matrix.	Bone becomes white and chalky w. loss of concoidal fracturing: exteria hard and waxy. Less N than fracturing becomes uneven, perpendicular to the bone axis. >80wt% of protein.	Interior and exteria chalky, surface hardness decreases and porosity increases with decreasing %N. Uneven hackly fractures.	Continued decrease in hardness and increase in porosity.	Soft. Hard if inorganic replacement has occurred.
Gelatin	>or=90wt% of collagen	>80wt%of protein	>50wt% protein	2-50wt% protein	<10-20% of protein

(After Stafford et al. 1988:2258).

Wood

In instances where there is contamination by secondary carbonate deposition or humic acids the pretreatments described above for charcoal are applied as equally to wood. Water is used to collect the remains of starch from wood and bone samples. Starch consists of two fractions, μ-amylose and amylopectin, the former is soluble in water, the latter not. When aqueous, the μ-amylose forms a precipitate and changes into the insoluble form which sits in a layer above the water solution where it is collected for dating. The process usually begins with the ground or milled sample being placed in a beaker of distilled water and either left standing for 3-5 days or slowly boiled for several hours and left overnight. The sample and water are then filtered into a buchner flask and the process repeated; fresh water is added and the solution heated and left to stand. A test for starch presence is conducted using iodine and 10% potassium iodine solution. The solution will turn blue if starch is present.

Holocellulose

The holocellulose fraction is targetted for dating when the laboratory requires the autochthonous sample carbon or in cases where the wood for dating is old or severely contaminated. It is the carbohydrate fraction, the structural element of the wood and is considered most reliable for dating. The use of cellulose is widely used in dendrochronological studies (Taylor, 1988:47). Pearson (1983), for example, used a holocellulose pretreatment in his important work on the Irish bog oak chronology where it was crucial that all contaminants were removed and only pristine sample dated (Pearson, 1983:21). There is a variety of different methods for cellulose extraction beginning with the removal of resins and waxes. The key apparatus in these techniques is again the soxhlet extractor.

Wood sample is usually chopped and milled prior to pretreatment. Organic solvents are used initially to remove resins and waxes from the wood. As mentioned above, ethanol, ethyl acetate, benzene and acetone may be used in the solvent extractions. The samples should also be thoroughly washed in water

to remove any carbon absorbed from the solvents used.

After the waxes and resins have been removed by solvent extraction, the milled wood is placed into a buchner flask containing 800 mls of distilled water and 3 mls of concentrated HCl (or 30 mls 10% conc.). Into this is added an amount of NaClO2 (sodium chlorite). The actual amount varies with the size and density of the sample in question. About 7.5 grams of sodium chlorite is used for every 25 grams of sample but this varies between labs. The sample, distilled water, HCl and NaClO2 are placed on an 70-80° C heat source (warming flask), with a cover glass for approximately four hours. The sample is then rinsed in a buchner flask using distilled water. White cellulose should remain. This is placed in a beaker to which is added 5%w/v concentrated NaOH. This is heated. The base treatment will remove any further contaminants from the wood, but also absorbs atmospheric carbon, therefore an acid wash using 10% HCl is always implemented afterwards. Often, the laboratory will wash in the base in a Nitrogen (N2) environment thus minimising atmospheric exchange. Finally, the sample is rinsed with distilled water until the pH level is neutral (pH=7). The sample cellulose is then removed, placed in a petrie dish and stored in an oven to dry before combustion and dating.

Lignin is a wood substance that makes up 25-35% of softwood species and 17-25% of hardwood species. According to Head (1982:221), lignin is made up of polymer chains formed into a 3-dimensional network. It is resistant to certain of the chemical reactions causing degradation in wood samples in the natural environment. It is not hydrolysed by acids, for example, whereas cellulose is. Many lignin substances are soluble in alkalis, however, they absorb metal ions in solution and may be vulnerable to degredation from bacterial action. Head (1982) has shown that the extent and characteristics of degradation can be analysed using x-ray diffraction, to examine the pattern and structure of wood, although these techniques require some refinement before they become generally used. These analyses have shown that it is possible to reconstruct the post-depositional environment of certain wood fractions and be able to recommend applicable pretreatments, once that information is known.

Lignin can be extracted from wood cellulose using a strong acid such as sulphuric acid.

Shell

The most common fraction of shellfish remains which have been dated is the inorganic calcium carbonate. Certain samples may show evidence of isotopic exchange, or recrystallisation. Recrystallisation involves the dissolution of primary aragonite, which forms the major crystalline carbonate fraction in most shells, and the subsequent reprecipitation or recrystallisation of the carbonate in a calcite structure. Often this process will alter the isotopic ratio of the carbonate and affect the 'true' age because bicarbonates of different age may be present in the post-depositional matrix. The exchange usually occurs on the exterior shell surfaces in terrestrial environments and is common in samples found below the water table. Recrystallised shells may often show a 'chalky' or powdery exterior (Taylor, 1987; Aitken, 1990). In cases where the suspected recrystallised shell is an aragonitic secreter, x-ray diffraction analysis will reveal the presence or extent of calcite and the sample may rejected or accepted in the light of the result. Where the shell is composed mineralogically of calcite, visual observation is the only method for considering recrystallisation. Submitters should collect hard, non-porous, thick shells with fresh surfaces and preserved textures to minimise the possiblity of post-depositional isotopic exchange. Also, it is a good idea to obtain aragonitic secreting species which inhabit the intertidal zones or a few metres below that, so the age obtained from the shellfish can be reliably compared with the marine shell reservoir corrections commonly available around the world (see Stuiver and Braziunas, 1993).

Shells are pretreated chemically using an acid wash procedure which removes the exterior shell where contamination through isotopic exchange is most likely to have occurred post-depositionally. In some laboratories, the exterior surfaces are ground using drills to remove the outer layer and obtain the fresh fraction for dating.
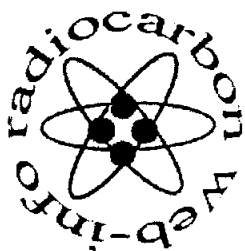
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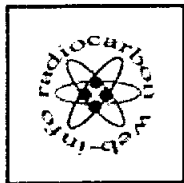
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