

RADIOCARBON DATING: REVOLUTIONS IN UNDERSTANDING*

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Radiocarbon dating has undergone a number of ‘revolutions’ in the past 50 years. This is in part because it is a field in continuous development, but perhaps more because of its profound impact on archaeology and the nature of interdisciplinary research. In order to understand the use of radiocarbon as a dating tool, it is necessary to understand the life cycle of radiocarbon, from its production in the upper atmosphere, through its sequestration in reservoirs and samples and its final decay. Different elements in this life cycle lead to complications, or subtleties that need to be understood if we wish to develop high-resolution chronologies. Most of the changes that have influenced radiocarbon dating are revolutions in understanding of the natural world in disparate academic disciplines. More than ever, it is necessary for users of radiocarbon to understand and engage with the science that underlies the method.

KEYWORDS: AMS, CALIBRATION, CHRONOLOGY, PRE-TREATMENT, RADIOCARBON

INTRODUCTION

It is no coincidence that the journal *Archaeometry* was founded within a decade of the discovery of radiocarbon dating by Libby (Libby *et al.* 1949): the idea of creating a Research Laboratory for Archaeology from which the journal grew was first mooted by Lord Cherwell in February 1950, in the hope that radiocarbon would only be the first of many scientific methods that could revolutionize archaeology. Radiocarbon dating is still perhaps the single scientific method that has had the most profound influence on the study of archaeology and it is therefore interesting to look at the interplay between the scientific method and its application to archaeology, a subject that itself has changed almost beyond recognition in the past 50 years.

This paper is not intended to be a history of the development of radiocarbon, but an inevitably individual perspective of the method as it is today. However, in looking at the way the method works, it is worth looking at why it has been so influential and also why there have been so many radiocarbon ‘revolutions’ (Renfrew 1973; Atkinson 1975; Linick *et al.* 1989; Taylor 1996; Mellars 2006). For a method or approach to be able to revolutionize a subject is normally considered a good thing, but radiocarbon seems to have managed rather too many revolutions for the good of either archaeology or the application of science to the arts.

THE RADIOCARBON LIFE CYCLE

In order to understand properly the radiocarbon dating method, and its development, it is necessary to have a basic understanding of how radiocarbon is produced and how it gets into the different parts of the environment.

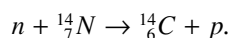
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Because radiocarbon has a relatively short half-life (usually given as 5730 a, but see the section on radioactive decay below), there is essentially no primordial radiocarbon and so it is present in different quantities in different reservoirs due to a dynamic equilibrium between its production (largely in the upper atmosphere) and its loss through radioactive decay. The reason that the method works at all is that both the production and the processes of dispersion through the environment do not change too much over time. However, whereas with dating methods such as uranium series or argon/argon dating we usually have techniques for determining the initial concentration of the parent isotopes in the sample, with radiocarbon we can only estimate this from our knowledge of the past environment. The methods for measuring radiocarbon have changed a great deal in the past few decades. However, the principal reason why our interpretation of older radiocarbon dates has changed so radically is that our understanding of the past environment, and in particular the radiocarbon life cycle, has changed so much.

Production

Radiocarbon can be produced through a number of nuclear reactions; however, the most important one for radiocarbon dating is the reaction



This reaction takes place largely in the upper atmosphere, where thermal neutrons, resulting from a cascade of reactions from cosmic rays, react with the nitrogen atoms in air. Some production is also possible even at ground level, but the rates are some two orders of magnitude lower (Mak *et al.* 1999), at about 1×10^{-4} atoms $\text{g}^{-1} \text{s}^{-1}$. In principle, this might result in radiocarbon being formed *in situ* at ground level. The processes involved are very complex because of moderation of neutrons and attenuation of cosmic rays, and the fact that other production reactions involving oxygen are also possible. However, as an order of magnitude estimate let us consider a protein with a CN atomic ratio of 3.2. The number of stable carbon atoms present in such a protein per gram of nitrogen is $3.2N_A/14 = 1.37 \times 10^{23}$ atoms g^{-1} and the number present from steady state *in situ* production would be 2.5×10^7 atoms g^{-1} or a ${}^{14}\text{C}/{}^{12}\text{C}$ ratio of about 1.8×10^{-16} , corresponding to a radiocarbon age of some 70 ka. Most samples dated do not contain as much nitrogen as this and are also usually buried sufficiently below the surface to reduce any such effects further. For these reasons, *in situ* production is not normally considered to be a significant issue in dating unless there is exposure to high neutron doses from other sources.

The global production rate of radiocarbon in the atmosphere is surprisingly poorly known. The production rate can be estimated by modelling the reaction (O'Brien 1979; Masarik and Reedy 1995) or calculating from the current concentrations and the global carbon budget (Suess 1965; Damon *et al.* 1978) and these all lead us to think that the global production rate is in the range $2\text{--}3$ ${}^{14}\text{C}$ atoms $\text{cm}^{-2} \text{s}^{-1}$. However, attempts to directly measure the production rate either at ground level (Mak *et al.* 1999) or at altitude (Bronk Ramsey *et al.* 2007) do not agree well with these estimates. Fortunately, from a dating point of view the actual production rate is not required; all we need to know is the concentration in the atmosphere.

Variations in production rate occur due to changes in the cosmic ray flux incident on the solar system, and due to variations in the Earth's magnetic field that shields the Earth from the charged particles. On the timescales we are considering in radiocarbon dating, we would expect the overall cosmic ray flux to the solar system to remain fairly constant, although there

may be individual events such as supernovae that do occasionally contribute significantly (Damon *et al.* 1995). The screening ability of the Earth's magnetic field is, however, affected by solar activity and by the primary strength and direction of the magnetic field itself, and these can lead to very significant variations in radiocarbon production rate. Because of the complications of the carbon cycle, these effects can be difficult to unravel. Measurements on the isotope ^{10}Be , which is formed in a similar way but which precipitates out much faster, gives a much more direct measure of production rate (see, e.g., Muscheler *et al.* 2004).

Ultimately, the most important conclusion to draw from the production process itself, from the point of view of radiocarbon dating, is that it is expected to fluctuate on a whole range of timescales. This is something that has been recognized and assessed from the very earliest days of the method (Anderson and Libby 1951). The short-term fluctuations are highly damped by the large reservoir of carbon in the active carbon cycle, but are sufficient to generate short-term wiggles in the radiocarbon calibration curve, which effectively limits the precision of radiocarbon calibration of single samples to at best a century or so (95.4% confidence) or in many cases much worse, quite regardless of the measurement precision.

One final radiocarbon production mechanism is important in dating. This is the anthropogenic production of radiocarbon during atmospheric nuclear bomb tests, and particularly those of the 1960s. These gave rise to a massive influx of radiocarbon, almost doubling the concentration in the atmosphere in the mid-1960s. The concentration is still falling and will in a few years (probably within the next decade) fall to the pre-bomb values.

Dispersal in the environment

Once radiocarbon has been produced in the upper atmosphere, it is thought to rapidly form ^{14}CO (93%) (Pandow *et al.* 1960), which is then slowly oxidized to $^{14}\text{CO}_2$ in a reaction involving the OH free radical (Lelieveld *et al.* 2006), or directly forms $^{14}\text{CO}_2$ (7%), although some recent experiments suggest that more may form $^{14}\text{CO}_2$ directly (Ramsey *et al.* 2007). The $^{14}\text{CO}_2$ then is mixed through the tropopause into the troposphere. The radiocarbon from nuclear weapons testing in the 1960s, although masking the natural production of radiocarbon in this period, has been studied in detail (Hua and Barbetti 2004), and shows the very rapid mixing of radiocarbon within each hemisphere and the slower mixing between hemispheres. Measurements of radiocarbon are almost always relative to the concentration of the stable isotopes. This means that even if the radiocarbon production remains constant, rising CO_2 concentrations, such as those seen since the Industrial Revolution, will result in a lowering of the $^{14}\text{C}/^{12}\text{C}$ ratio (Tans *et al.* 1979).

For the period prior to direct atmospheric measurements, carbon incorporated into tree rings provides a continuous record of the atmospheric concentration of radiocarbon in the atmosphere both for the Northern Hemisphere (Reimer *et al.* 2004b) and the Southern Hemisphere (McCormac *et al.* 2004). These tree-ring records extend back to the start of the Holocene and into the Late Glacial. In principle, they provide a growing-season average of the atmospheric concentration for each year, although in practice the measurements are mostly made at a decadal resolution (averaging across the decade). Further back than this, varved lakes have the possibility of giving similar information (Kitagawa and van der Plicht 2000), but at present the varve counting is too uncertain to give us a reliable long-term timescale. The post-bomb atmospheric data and the tree-ring data suggest that within a hemisphere there is unlikely to be significant regional variation on a large scale, and although small effects have been seen (Kromer *et al.* 2001) these seem most likely to be the result of different growing seasons in different regions.

However, most measurements made are from northern Europe and North America, and there are indications that there may be small but significant offsets in Japan (Nakamura *et al.* 2007), where there may be a significant effect from ocean upwelling. It is also documented that there can be local variation close to volcanic vents (Pasquier-Cardin *et al.* 1999), but such effects seem to be very localized. Industrial-scale release of fossil fuel derived CO₂ can have a large local effect, with a 4.4% reduction in the proportion of radiocarbon reported in Poland at the height of their use of coal as a fuel (Kuc and Zimnoch 1998), and this could be relevant in the use of radiocarbon for forensic dating.

The radiocarbon in the atmosphere is in dynamic equilibrium with that in the surface oceans due to exchange through the water surface. However, whereas the atmosphere has a mixing time of the order of weeks, the much larger carbon reservoir provided by the surface oceans is much slower to mix and is itself in exchange with the deep ocean (a larger reservoir still). The net effect of this is that the ocean surface is on average depleted by about 5% (corresponding to about 400 ¹⁴C years). A simple box model can be used to estimate this effect and direct measurements made in different regions (Hughen *et al.* 2004b). Inevitably, the exchange of carbon with the atmosphere and mixing of deep ocean waters with those of the surface has a great deal of geographical variation. Considerable effort has gone into trying to estimate the local variation in oceanic radiocarbon concentration, and these data are summarized in the CHRONO Marine Reservoir Database (<http://calib.qub.ac.uk/marine/>), which allows for correction of this effect (Stuiver *et al.* 1998). However, even this does not really deal with the issue completely, since most of the measurements made in this sort of study look at the concentrations in the oceans in recent centuries (though prior to nuclear weapons testing). Ocean circulation and climate are obviously not in a steady state and so the reservoir offsets seen today will not be the same as those prevailing in the past (see, e.g., Ascough *et al.* 2007). So even the surface oceans are an inhomogeneous reservoir whose relationship with the atmosphere varies spatially and temporally. Measurements of radiocarbon concentration are, in themselves, a valuable tool in understanding the details of oceanic circulation (Key *et al.* 2002). Unfortunately for dating applications, the oceanic circulation is an unwanted complication and it is usually only possible to make allowance for the spatial component of the variability.

For the periods for which we do not have any tree-ring data, the marine environment provides key records of past radiocarbon concentration, both from corals, which can be uranium-series dated (Bard *et al.* 1998; Cutler *et al.* 2004; Fairbanks *et al.* 2005; Chiu *et al.* 2007), and foraminifera deposited in sediments, whose timescale can be linked to other chronologies (Bard *et al.* 2004; Hughen *et al.* 2004b, 2006). These records are used both to estimate the global average surface ocean radiocarbon concentration (Hughen *et al.* 2004a) and to infer the value for the atmosphere (Reimer *et al.* 2004b). In doing this, we have to make assumptions about the relationship between these reservoirs. In practice, the radiocarbon in any one region of the ocean will vary relative to the surface oceanic average. This variability, first seen in places where there is significant ocean upwelling (Monges Soares 1993), is much more likely to be the rule than the exception. All of these records are of great intrinsic interest as, quite apart from their ability to provide information for dating, they also give information on past changes in the global carbon cycle (Hughen *et al.* 2004a). However, with the exception of tree rings, all of the records have potential problems that need to be understood (Bronk Ramsey *et al.* 2006).

The other main types of reservoir relevant to radiocarbon dating are lakes and rivers. Here, we know even less than we do about the oceans. Such freshwater systems not only act as reservoirs in their own right and exchange CO₂ with the atmosphere, but also incorporate carbon

from carbonates of geological origin. This, in principle, means that the radiocarbon concentration can lie anywhere between the levels in the atmosphere and those of the bedrock (effectively zero). In fluvial systems, the actual radiocarbon concentrations will vary seasonally and will depend on details of the recent weather conditions. In larger lakes, the variation will generally be slower and reflect longer-term climate trends. Indeed, measurements of this kind can be very useful in determining past environmental conditions (Stein *et al.* 2004). In some instances, the carbon in these reservoirs can become locked into speleothems or tufas, which, if they can be dated by other means (e.g., uranium-series methods), can be used to infer the past concentrations of the isotope (Beck *et al.* 2001).

Incorporation into organisms

Were radiocarbon only present in the main carbon reservoirs, it would only be useful in the study of their mechanisms. The isotope is useful for the dating of organic material only because it becomes fixed into organisms during their life.

The main way in which carbon enters the biosphere from the main atmospheric and aquatic carbon reservoirs is through the process of photosynthesis in green plants, including algae. It is ultimately this photosynthesis reaction that is the dated event associated with the radiocarbon dating method. At this stage, carbon dioxide, with its ambient proportion of radiocarbon, is incorporated into the plant. The uptake process does involve some fractionation or preferential take-up of the lighter isotopes, particularly in the C3 form of photosynthesis, but this can be accounted for by measurements of the stable isotopes ^{12}C and ^{13}C .

In the case of simple plants, the proportion of radiocarbon provides a snapshot of the reservoir in which the organism lived. Many such organisms, however, will be at the bottom of the food chain and will pass on this signature to other higher organisms. On the other hand, longer-lived plants lay down cellulose in cells, which subsequently die and cease to exchange carbon with the living part of the plant. This is most obvious in trees from temperate climates where there are annual tree rings, but all woody plants do this and, in such cases, the plant retains a record of the ambient radiocarbon isotope ratio over a more prolonged period.

Although most plants take their carbon as CO_2 directly from the air, or from the water in the case of aquatic plants, there are some more complicated environments, most notably peat, where the sources of carbon are more complex (Christen *et al.* 1995; Pancost *et al.* 2000; Blaauw *et al.* 2004).

In the case of animals, their carbon comes from plant material either directly (in the case of herbivores) or by a more circuitous route through the food chain (in the case of carnivores and omnivores). Fortunately, most plant-eating animals feed on this year's growth of plants, as they are unable to digest woody material. Terrestrial food chains are also sufficiently short that in most instances the carbon in any animal's diet will have been fixed from the atmosphere within the past few years. It should be remembered, however, that some animals, such as detritus-feeding beetles, will be ingesting carbon that might have been photosynthesized some years before. Perhaps the most extreme effect of this sort is seen in land snails, which are able to incorporate carbonate from geological age limestone into their shells (Goodfriend and Stipp 1983).

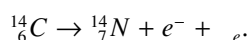
Just as plants lay down carbon in large molecules of the polymer cellulose, animals also lay down carbon in polymers during their lifetime. Some of these, such as keratin (horn, nails, feather and hair) cease to exchange carbon with the rest of the organism as soon as they have been formed and therefore retain a detailed temporal isotopic record. Other proteins, on the

other hand, are continuously turned over. In some structures where there are also carbon-containing mineral components (such as bone) the turnover rate is low and in a few instances (e.g., shell and tooth enamel) there is effectively no turnover (Spalding *et al.* 2005). When dating long-lived animals, all of these considerations can be important (Shin *et al.* 2004).

Most animals live in one environment and also draw their food from it. However, some animals spend time in different parts of the biosphere (e.g., amphibians, some fish etc.) and others, most notably humans, get their food from a whole variety of sources. This means that the carbon they incorporate will ultimately come from different primary reservoirs (Lanting and van der Plicht 1998; Cook *et al.* 2001, 2002).

Radioactive decay

The decay of radiocarbon takes place through beta decay:



Like all radioactive decay, this is a random process, which can take place at any time from the formation of the radiocarbon. The rate of decay is determined by the half-life, for which two values are often quoted. The first of these is the Libby half-life 5568 ± 30 a (Anderson and Libby 1951), which is used in the calculation of radiocarbon ‘dates’, and the second is the so-called Cambridge half-life of 5730 ± 40 a (Godwin 1962), which is thought to be a more accurate reflection of the true decay rate. However, the half-life is really not that well known and some scholars think that it may be substantially longer, perhaps as much as 6000 a (Chiu *et al.* 2007), since this might make better sense of some of the long-term records. This is an important issue when using radiocarbon to study the changes in the global carbon circulation in the past 50 ka. As with the overall radiocarbon production rate, this is an area where further fundamental research is certainly needed.

From the point of view of dating, the key thing about the radioactive decay is that once photosynthesis has locked carbon from the environment into the organism, the proportion of radiocarbon will then fall off exponentially at a rate that is quite independent of any chemical or physical conditions (such as temperature, pH, atomic bindings etc.).

Sample survival

Even during the life of an organism, its constituent parts are constantly being broken down and reformed. Once an organism dies, many of these processes take place rapidly and usually little remains after a few years. However, in some conditions, most notably waterlogged deposits and very dry conditions, there is better preservation. It is always important to remember that such survival is exceptional and therefore will not be representative of the original assemblage of organisms present.

Exactly what survives in the ground and how, is a complex topic: in some conditions, such as acidic peat accumulations, there may be virtually no mineral components remaining but organic preservation may be very good, as in the case of bog bodies. In hot dry conditions the reverse is likely to be true, with very good mineral preservation and poor preservation of proteins (Hedges and van Klinken 1992). Ultimately, remains of this sort become fossilized, with full replacement of the original material by minerals from the surrounding matrix. Even before this happens, the mineral components of bone and shell often exchange carbon with dissolved carbonate and so do not retain the original radiocarbon ratio signal.

Table 1 *Main stable molecular forms of carbon used in ^{14}C dating*

<i>Molecular form</i>	<i>Material</i>
Cellulose (polysaccharide)	Wood and plant remains
Chitin (polysaccharide)	Arthropod exoskeletons
Collagen (protein)	Bone and teeth
Keratin (protein)	Hair, horn, nails, claws and beaks
Lipids (glycerides)	Animal fats and vegetable oils
Aragonite (calcium carbonate)	Mollusc shells, corals and speleothems
Calcite (calcium carbonate)	Speleothems and cremated bone
Amorphous carbon (elemental carbon)	Charcoal or charred plant remains

The organic materials that survive intact for longest, with their original complement of carbon atoms, are normally the polymers or larger crystals as shown in Table 1. Of course, the carbon from organisms that degrade is not lost, but is often present in the form of small mobile molecules such as humic acids. Such components cannot, however, be related back to a single organism or to a well-defined photosynthesis event.

Even when carbon does remain in some stable form, there will usually be many other more mobile carbon-containing compounds and other contaminants that become incorporated into the material remains of an organism. These contaminants will have different origins and so will not share the same isotopic signal.

THE DATING METHOD

Extracting original material

The first stage in the dating method is usually to take a sample that relates to a single organism. The aim of the method is to determine the time at which the carbon in that organism was isolated from the atmosphere or the aquatic environment. This type of dating is sometimes referred to as ‘single-entity’ dating (Ashmore 1999). In other cases, it might be appropriate to date a mixture of entities—as in the case of bulk peat or coral, where a whole community of organisms is sampled together; the assumption in such cases is that the community all lived and died at the same time. In still further cases, we take samples of inorganic material such as speleothems, which have directly assimilated carbon from the environment at their time of formation.

The selection of samples from an archaeological context requires considerable archaeological expertise, principally because it is important that the sample taken relates directly to some event or process of archaeological interest. Conceptually, the process of archaeological excavation consists of the recovery of material and contextual information that can be related back to the original human activity and environmental conditions. The first stages of the radiocarbon dating methodology are essentially an extension, on a finer scale, of this same process: the radiocarbon scientist must essentially ‘excavate’ the sample to recover original carbon-containing components that can be related back to the original organism(s) and, in doing so, must try to gather as much information as possible about the sample, which might be useful in interpreting any radiocarbon measurements made. Just as every site is different, so every radiocarbon sample is different in terms of the degree of preservation and the range of contaminants present. For

Table 2 *The effect of contamination: the rough effect on the radiocarbon age of contaminants of different ages in comparison to a typical age uncertainty quoted*

	¹⁴ C age (a)				
	0	5 000	10 000	20 000	40 000
Typical uncertainty	30	40	60	130	700
1% modern	0	-70	-200	-840	-7 180
1% geological	80	80	80	80	80
1% 1000 a younger	n.a.	-11	-11	-11	-11
1% half age	0	-30	-70	-200	-840

this reason, although standardized methods can be applied, this does not mean that all samples will behave in the same way.

The first stage of sample pre-treatment is normally physical cleaning and inspection. It is important, for example, that root penetration is recognized and dealt with at this stage, before the chemical processes that follow. At this stage there are also sometimes visible signs of other contamination, such as the use of glues or preservatives. This stage of the pre-treatment is a simple extension of what has started in the field, the aim being to separate the sample from its surrounding matrix.

The next stage is the purification of the original components of the samples. This is normally performed by chemical pre-treatment of some sort, the aim of which is to reduce the contaminants present in the sample from the environment and to minimize the addition of further contaminants. Most, though not all, environmental contaminants are comparable in age to the samples or younger: such contamination is generally more important in old samples. Laboratory contaminants are usually either free from radiocarbon (of geological origin) or modern—either can be critically important, as can be seen in Table 2.

For high-precision dating, where effects of the order of 10 years are important for recent samples, it is evident from Table 2 that modern and geological age contaminants need to be kept below about 0.1%, or about 10 µg C, in a typical accelerator mass spectrometry (AMS) sample (Bronk Ramsey *et al.* 2004a). We are less sensitive to contaminants that are roughly the same age as the sample, where levels of contamination up to 1% are acceptable. The same goes for the dating of very old material: we need to ensure that modern contamination remains below 0.1%, and that contaminants that are roughly half the age of the sample will not become too important until they get above about 1%—in such cases, contaminants that are similar in age or much older are not an issue.

For many sample types, fairly simple pre-treatment methods are sufficient for recovering original material from samples. For organic samples, these methods are usually variants of the acid–base–acid (ABA) methods in which an initial acid treatment removes carbonate precipitated on to the samples from groundwater, the base (or alkali) stage removes humic acid contaminants from the sediment and a final acid stage removes any carbonate dissolved from the air during the pre-treatment. For inorganic samples, acid is often used on its own, after an initial etch, to extract CO₂ from the aragonite or calcite that forms the sample. The reason why these methods often work well is that the samples retain original material in large molecules (cellulose, allotropes of carbon or calcite/aragonite crystals) in reasonably high purity, with contaminants that are only loosely bound or are sufficiently close in age not to compromise the dating accuracy.

Much development work has gone into finding ways to better purify and characterize the main components used for dating. Two good examples are charcoal and bone. In the case of charcoal, further chemical oxidation stages are found to be good at removing trace contaminants, which are significant in the dating of very old poorly preserved charcoal in the 'acid–base–oxidation' (ABOX) methods (Bird *et al.* 1999, 2002, 2003) and careful characterization of charcoal by Raman spectroscopy can also be used to screen samples that may contain contamination after less rigorous methods have been applied (Alon *et al.* 2002; Cohen-Ofri *et al.* 2006). With bone, there have been several attempts to improve on the most widely used simple protein extraction (Longin 1971). These include further molecular size selection using ultra-filtration (Brown *et al.* 1988), the use of ninhydrin to specifically extract the carboxylic carbon from the bone collagen (Nelson 1991) and the selection of particular peptides, which are unlikely to be present in contaminant protein fragments (Hedges and van Klinken 1992; van Klinken *et al.* 1994). As with the ABOX methods, the main impact of these newer methods has been on the dating of older samples (Higham *et al.* 2006a,b; Jacobi *et al.* 2006; Mellars 2006). However, as with all more complex methods, there are potential drawbacks because of the balance to be struck between removal of contaminants and addition of laboratory contaminants during the extra stages. In the case of ultra-filtration of bone, the method, as it was originally applied, was markedly less accurate for recent bones (Bronk Ramsey *et al.* 2004b).

The term 'compound-specific' dating is sometimes applied to some of the more elaborate pre-treatment methods, but it is questionable whether this is a meaningful qualitative distinction. Some of the main molecular species (calcium carbonate, chitin and cellulose) used in dating are compounds anyway in that they are mixtures of elements in a fixed ratio. The allotropes of carbon are not compounds in that they only contain one element, but are nonetheless often of one origin and can be effectively purified. Likewise, some of the proteins dated (collagen and keratin) are not strictly compounds, since the exact arrangement of amino acids varies. However, these large-chain polymers are still much more likely to be original to a specific organism than some individually selected specific amino acids, which might also occur in smaller protein fragments introduced into a sample during degradation.

In terms of normal dating applications, it is important to retain as much of the original material as possible. This is partly because contaminants introduced during the dating process need to be kept below 0.1% and this is easier the larger the sample is; indeed, very large samples (of the order of grams of carbon) are ideal for very high precision work such as the measurements of tree rings for radiocarbon calibration (Reimer *et al.* 2004b). It is also because the precision of the measurement fundamentally depends on the number of ^{14}C atoms present. For this reason, it is most unlikely to be possible to carry out high-precision measurements of samples with only the order of micrograms of carbon or less. These sample size considerations mean that measurements on specific compounds that are only present in low abundance will not replace measurements on the main components of the sample.

Dating of specific trace compounds is certainly useful in some circumstances. These circumstances can be divided into three main categories:

- Samples that otherwise contain no carbon suitable for dating—such as the specific lipids present in pottery, which are most likely to come from food (Stott *et al.* 2001, 2003).
- Samples where the different compounds might have different radiocarbon ratios—such as the individual amino acids in humans consuming both marine and terrestrial food, where stable isotope and ^{14}C measurements on these amino acids is likely to be very effective at unravelling the mixture of carbon from different reservoirs (McCullagh *et al.* 2005, 2006).

- Compounds present in sediments, which are of interest in their own right, such as biomarkers and other organic species (Eglinton *et al.* 1996, 1997). The aim in such applications is usually to understand the processes that take place during and after sedimentation. In principle, where such compounds are of primary interest, such measurements might give date information but, of course, there is no direct linkage to a specific organism and so the precise meaning of the date is unclear.

In general, the aim of pre-treatment methods for the dating of samples (as opposed to components of sediments that derive from multiple organisms) is to extract carbon that was present in the original organism. Almost all of the most successful methods for accurate and precise dating work on the large and stable molecular forms of carbon that survive comparatively well and are present in sufficient abundance to allow precise measurement.

Measuring isotopic ratios

The measurement of radiocarbon is difficult, because it is present in such low abundance, with the $^{14}\text{C}/^{12}\text{C}$ ratio being in the range 10^{-12} – 10^{-15} . This low abundance puts a fundamental statistical limit on the precision of a radiocarbon date: if there are only n radiocarbon atoms present, then the relative precision of any isotope ratio measurement is limited to $1/\sqrt{n}$, even assuming 100% detection efficiency. That means that for a measurement with a precision of 25 years (0.3%), you need to have at least 10^5 atoms present, which implies 2 μg C for a modern sample, or about 10 μg C for a sample that is 12 ka old. No technical development can overcome this fundamental limitation.

The aim of the measurement stage in the technique is to measure the isotope ratio accurately at as high a precision as possible. The two main methods employed are decay counting methods (using liquid scintillation and gas proportional counters) and accelerator mass spectrometry (AMS), where the radiocarbon atoms are directly detected. Ultimately, there are three related considerations here: detection efficiency, instrument precision and sample purity.

Detection efficiency is paramount in determining the precision from counting statistics. AMS methods that count the atoms directly are much more efficient than counting methods that only count those atoms that decay. Typical total AMS detection efficiencies are about 1%, and at best about 5% (with ion source efficiencies of 10% and stripper efficiencies of 50%), which means that the actual carbon sample size theoretically needed is between five and 10 times the fundamental limit for any given precision (i.e., 40–200 μg C for a modern sample and 200–1000 μg C for a 12 ka sample with a precision of 25 years), with typical sample sizes of the order of a milligram of carbon. For a counter counting for a whole month, the best possible detection efficiency (with all decays detected) is about 0.001% and so the required sample sizes are about a thousand times higher than for AMS, and of the order of a gram of carbon.

Instrument stability is a very different issue from detection efficiency and here, at least until recently, the complexity of AMS instruments meant that the instrument itself put significant limits on the precision of the measurements. With the instruments introduced in the past decade or so, AMS measurements are more often limited by counting statistics or uncertainties in sample purity (Steier and Rom 2000; Bronk Ramsey *et al.* 2004a). Instrument stability is, however, still an issue in that there is usually a limit to how long a single target can be measured with high stability, and this means that very high precision measurements are usually achieved by the measurement of multiple targets. Counting instruments, which are intrinsically simpler, can still achieve better overall precision where there is sufficient sample and sufficient counting time (Stuiver *et al.* 1998; Hogg *et al.* 2002).

Sample purity is another area where AMS is not necessarily better than the older counting methods. The advantage of AMS is that a smaller sample size is needed and so in some instances it may be possible to use a pre-treatment method (such as ABOX for charcoal, or ultra-filtration for bone) that cannot be applied while retaining a large sample size. However, in many cases, if the sample is large enough for conventional measurement, there is a suitable method for thorough pre-treatment (e.g., for well-preserved wood or calcite) and the larger sample size makes it much easier to keep any laboratory-derived contaminants well below the level at which they would be significant. With AMS, even after the purification of the sample, it is necessary to combust the sample to CO₂ and then, usually, to reduce it to graphite; these two stages inevitably introduce some carbon (typically about 1 µg C) and uncertainties in this value, and the composition of this carbon limits the precision of the measurement for very small samples. This is one reason why in practice > 100 µg C is often needed for good precision. This is an area where considerable progress is being—and has been—made, which will help in the measurement of small samples (Hua *et al.* 2004; Santos *et al.* 2007). Another approach is to bypass the production of gas and use the CO₂ directly in the ion source (Bronk Ramsey and Hedges 1997). This method is good for small samples, although the overall efficiencies quoted are similar to those for graphite. Because the operation of such sources is more complex than that of graphite sources and the measurement times are generally longer, the principal advantage may be for samples < 50 µg C, where online combustion can be used. Online GC and HPLC applications are also possible with such sources, with much lower combustion backgrounds (Bronk Ramsey *et al.* 2004a), but as the quantities of carbon in each peak are typically of the order of 1 µg C or less, such methods cannot yield precision suitable for dating, and are unlikely ever to do so unless many repeat analyses are made.

Over the past 50 years there has been a steady improvement in measurement methods, with improvements in precision and efficiency. The most significant development is undoubtedly the introduction of accelerators for the direct detection of radiocarbon, allowing a whole range of smaller samples to be measured. New smaller accelerators (Suter *et al.* 2000) reduce the capital cost of setting up such facilities, but in themselves do not yet offer any improvement in measurement precision. The measurement stage of the process is no longer the most critical element in determining precision and accuracy, except for the very smallest samples. We can also say that, with few exceptions, the measurements made decades ago are still valid within their quoted error limits. The problems in radiocarbon dating most often arise either in the pre-treatment stage of the process or in the interpretation of the radiocarbon measurement.

The radiocarbon age

A radiocarbon measurement is just a measurement of the isotope ratios ¹⁴C/¹²C and ¹³C/¹²C, the latter usually being expressed in terms of δ¹³C. The reason for measuring both stable isotopes is that we can then correct for any mass-dependent fractionation that has taken place in any of the processes described above, from the fixing of the carbon from the atmosphere right down to the measurement process itself. Having corrected for this fractionation, we compare the ratio to that measured on standards whose radiocarbon atoms are also decaying. This relative ratio *f* is best expressed as F14C, the fraction of the value expected for material from 1950 (Reimer *et al.* 2004a). The term ‘%modern’ and a range of other variants are also often used, although this term is ambiguous, as it is sometimes corrected for fractionation and sometimes not.

There is an argument for saying that once we have radiocarbon calibration data extending over the whole time range of the method, we should simply leave the measurement in the form

F14C, as we do for material from after 1950. However, before that is the case, users of the method like to have some idea of the age that is implied by the measurement, and so the measurement is usually converted to a radiocarbon 'date' y on the assumption of constant radiocarbon concentration equal to that of the atmosphere in 1950 and a decay of the radiocarbon on the Libby half-life of 5568 a. The relationship is given by the following set of equations:

$$\begin{aligned}y &= -8033 \ln(f), \\|dy| &= 8033|df/f|, \\ \sigma_y &= 8033 \sigma_f/f.\end{aligned}$$

Sometimes, for very old dates, the uncertainty is given in an asymmetric form. However, in some ways this is misleading, since this probability distribution in radiocarbon years is non-Gaussian. It can be argued that it is better to use the differential form given above, which can easily be directly related back to $f \pm df$, which is the primary form of the measurement (and for which the errors are more closely Gaussian) or, indeed, simply to quote such old ages as F14C values.

As the radiocarbon date is essentially a first rough guess at the age based on Libby's state of knowledge back in the 1950s, it should come as no surprise to us now that it is often very different from the true age.

INTERPRETATION OF DATES

Since a radiocarbon measurement is essentially only an isotope ratio measurement, to use it for chronological purposes it needs to be interpreted in the light of our knowledge of the past environment. The first two stages of this are to work out which reservoir(s) provided the carbon present in the sample and then to compare our measurement to those on samples of known age from the relevant environment—the process usually referred to as 'calibration'. We then need to use our knowledge of the organism itself to assess the significance of this calibrated date in terms of the archaeological questions that we are addressing. In short, we need to unravel the details of the radiocarbon life cycle outlined above.

Assessing the organism's place in the environment

At this stage, we need to use our knowledge of how organisms incorporate carbon into their fabric, as discussed above. In many instances it is obvious where an organism derives its carbon: green plants from the atmosphere and herbivores indirectly the same, green aquatic plants from dissolved CO₂ in water, and so on. However, in other instances organisms derive carbon from more than one source and so it would be useful to be able to estimate the proportions.

In archaeology, it is clearly most important to be able to do this for humans, who have a notably variable and mixed diet. To some extent, this can be achieved by the measurement of stable isotope ratios in dietary studies. However, given that the radiocarbon ratios in different reservoirs differ from those of the atmosphere by about 5% in the case of the ocean, and often more in the case of hard water rivers, any uncertainty in our knowledge of the contribution of non-terrestrial food sources compromises our ability to get good chronological resolution. Because of the natural variability in stable isotopes *within* any one environment, we can rarely apportion proportions with a precision of better than 10%, effectively adding an uncertainty of greater than 40 years to our deduced calendar ages. There may be cases where we can be sure that humans were not using non-terrestrial resources, but these must be rare—and if we simply

have no evidence of their use, this does not mean that we can rule it out at a low level. This is an important issue for large, high-resolution dating studies focusing on human bone, as deduced ages might be systematically older by a few decades.

In addressing these issues, one method that may provide better resolution than simple bulk stable isotope assays is the use of stable isotope measurements on specific amino acids, since different amino acids are usually drawn from different sources of the diet (McCullagh *et al.* 2006).

Comparing with records of past radiocarbon concentration

Assuming that we can establish with some certainty the pool from which the carbon in a sample was drawn, our radiocarbon measurement can be assessed in the light of our knowledge of the past environment and the decay rate of radiocarbon. If we do not have any reliable information on this, we can make plausible assumptions (e.g., that the past radiocarbon ratio was as it was in 1950) and use our estimates of the half-life of radiocarbon to estimate the age of the sample. With such an estimate, or guess, it is very difficult to give quantitative uncertainties—or if we do, they will certainly be very large.

Ideally, we have material of known age whose carbon is drawn from the same pool as our sample. This is true for the atmosphere in the period where we have dendrochronologically dated wood (Reimer *et al.* 2004b). It is also true for the period since 1950, when we have direct atmospheric measurements (Hua and Barbetti 2004). In these cases, all we need to do is to compare the radiocarbon measurement for our sample with the reference measurements. In practice, rather than comparing directly to the individual measurements, we put together a radiocarbon calibration curve that gives our best estimate (with quantified uncertainties) for the measurement that we would get for a sample of any age within the range of the data (Buck and Blackwell 2004). Such curves are typically expressed in terms of radiocarbon years except for the period after 1950, but it is better both conceptually and mathematically to consider them as a fractionation corrected isotope ratio in F14C. In terms of the algorithms of calibration, this makes almost no difference until the measurements approach background: here, the measurement uncertainty in F14C is more closely Gaussian. There are essentially two methods of calibration in use. The first is the intercept method, in which one visually examines the overlap, at one or two standard deviations between the measurement made and the reference curve (Stuiver and Reimer 1986). The other method calculates a probability density function for the age of the sample and is implemented in most calibration programs (Stuiver and Reimer 1993; van der Plicht 1993; Bronk Ramsey 2001). If the radiocarbon measurement is expressed as $f_m \pm \sigma_{f_m}$ and the reference curve is given as $f(t) \pm \sigma_f(t)$, we deduce that

$$P(t) \propto \frac{\exp\left[-\frac{(f_m - f(t))^2}{2(\sigma_{f_m}^2 + \sigma_f^2(t))}\right]}{\sqrt{\sigma_{f_m}^2 + \sigma_f^2(t)}}$$

In OxCal4, the comparison is made in F14C as expressed here. In older versions of OxCal, and in other programs, the comparison was made in radiocarbon ages. This will only make a significant difference as calibration becomes possible towards the limit of the technique. Once we have a probability distribution like this, the range of probable values can be calculated using the highest probability density (HPD) range, typically at the 95.4% level.

The calibration process is often thought of as adding a lot of uncertainty to the age. Of course, the reality is that the radiocarbon 'age' is simply a first guess without properly quantified

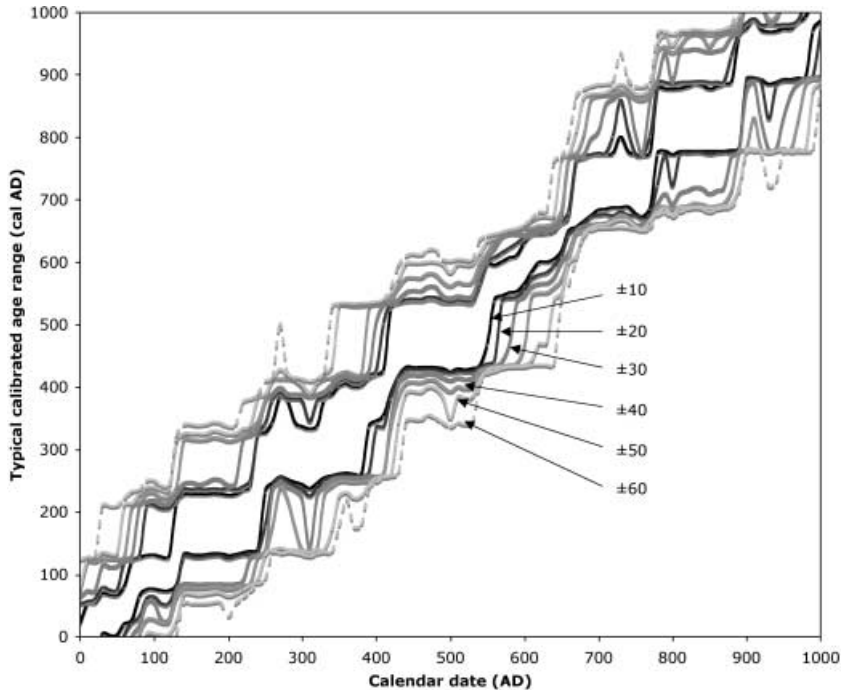


Figure 1 The typical calibrated age range (95.4%) plotted against the calendar date of the sample for the first millennium AD for precision of measurements ranging from ± 10 to ± 60 , using IntCal04. Although moving from a precision of ± 60 to ± 30 does make a significant difference, further improvements in precision only give a marginal improvement in calendar resolution for most true ages.

uncertainties, and it is only after calibration that we can assess the age in absolute terms. However, what is certainly the case is that regardless of the measurement precision, because of the need for calibration it is not possible to get very high calendrical precision for most of the radiocarbon timescale, partly because of the state of our knowledge, but more fundamentally because of the sort of variability in radiocarbon concentrations over time. In practice, this means that for single samples, increasing measurement precision to much less than 0.3%, or 30 ^{14}C years, does not result in appreciably better precision in establishing age (see Fig. 1).

Our knowledge of the radiocarbon concentration in the atmosphere after 1950 is such that, for short-lived material, radiocarbon measurements can be used for dating purposes with calendrical precisions of only a few years (Reimer *et al.* 2004a).

As explained above, our knowledge of other reservoirs is much less secure. With the oceans, we have some good longer-term records that extend well into the last glacial period, but relating these to the global ocean average, local coastal waters or—even more so—the atmosphere is difficult to do precisely, because of the variability in the Earth's climate. However, where these records are dependable, calibration curves may be produced, which are our best estimates of these values, and the same method as for calibrating our radiocarbon measurements can be used. Where we only have one record of radiocarbon, or several records that do not agree well, it seems better not to term them *calibration* curves, whilst recognizing that it can still be

useful to *compare* these records to measurements on samples of unknown age (van der Plicht *et al.* 2004; Bronk Ramsey *et al.* 2006; Mellars 2006; Tzedakis *et al.* 2007). What we need to remember in these cases is that all our conclusions are based ultimately on one interpretation of one record—while unconfirmed, any such conclusions should really be classed as a first (well-informed) guess that might later be proved wrong.

The significance of the age of a sample

Once we have found the possible range of dates for a sample, we need to consider the significance of the age. The dated event is the isolation of carbon from some large reservoir. As discussed above, we need to use our knowledge of how carbon becomes fixed into an organism or other structure, making a distinction between events (such as the fixing of carbon in a tree ring or the growth of hair and wool in animals) and longer-term processes that may extend over several years (such as the growth and remodelling of bone).

Relating the date of the organism to the archaeological context is another matter of considerable importance. This is essentially a matter of archaeological interpretation, but we can draw out some general principles, which were set out as long ago as 1971 (Waterbolk 1971). For each sample, it is important to consider the age at time of deposition and the certainty of association with the date of archaeological interest. There is, in short, no substitute for thinking carefully about how the radiocarbon-dated events relate to the archaeological processes. Some types of sample, such as scatters of charcoal, are hard to interpret; others, such as articulated bone of short-lived herbivores, are in general much more useful. In other instances, the context of the sample need not be critically important if there is a direct relationship between the sample and the human activity. This is true in the case of human-modified bone in looking for the presence of early humans, or domesticated cereal grains when dating early agriculture.

The issues at stake here have been well understood for decades; however, there are many instances in which they are ignored. In some ways, the much easier access to radiocarbon dates now can tempt people not to think in detail about each date and simply treat large numbers of dates as data to be summarized. In some cases this may be fine, but there are some dangers of systematic biases creeping in if, for example, a large number of samples are residual or old in their context—or if a spread in dates is assumed to relate to a long period of activity, whereas it is really due to intrusive and residual material within a context.

When radiocarbon date outliers (i.e., dates that do not make sense archaeologically) are encountered, these are sometimes due to some measurement problem, but much more often they are due to misinterpretation of the sample context.

Synthesis of chronological information

Because of calibration, any single radiocarbon measurement will inevitably have limited precision on the calendar scale, and so in many cases it is imperative that we use series of radiocarbon dates to address archaeological issues at the required resolution. In doing so, it is inevitable that we have to use information other than that measured on the sample in the laboratory. The synthesis of chronological information of all kinds is something that has developed considerably over the past 50 years.

The most common situation encountered in dating is where we have several radiocarbon measurements, all of which relate in some way to the same event. If, as is usually the case, all of the samples draw their carbon from the same reservoir (e.g., the atmosphere), then our

different radiocarbon dates are all independent assessments of the radiocarbon concentration of that reservoir at a particular time (after radioactive decay)—in other words, all of the samples should have the same underlying F14C value. In such instances, all of the radiocarbon measurements should be combined, before calibration. Since the measurements have Gaussian uncertainty distributions, it is possible to take the error-weighted mean and sample variance. In making such a combination, however, it is important to test the assumption that all the ratios are the same. The most widely used method uses a form of χ^2 test (Ward and Wilson 1978); essentially what this does is to see if there is compelling evidence (95% confidence) that the dates do *not* all relate to the same event.

If we are dealing with more complicated situations in which we wish to analyse groups of dates (rather than groups of radiocarbon measurements), we need ways of dealing with the probability density functions that come from the calibration. Since these distributions are not Gaussian, many of the simple methods from classical statistics that might be applied are not applicable. For this reason, Bayesian statistics have become very important in this type of analysis.

The simplest, and yet the most powerful, form of analysis of this kind is applied in situations in which we have material with known age increments. In most cases this is wood with annual tree rings, although in principle it can apply in other situations—such as varved lakes, where the number of years that separate the growth of the material being dated is known. In all such cases, a set of radiocarbon measurements can be obtained that should reflect the changes in the reservoir radiocarbon concentration over that period. The changes seen may be matched to those in the calibration curve, and indeed this type of dating is often referred to now as ‘wigggle-match dating’ (Christen and Litton 1995; Bronk Ramsey *et al.* 2001; Galimberti *et al.* 2004). The matching process can either be carried out by a simple least squares fit (which only gives the most likely fit for the data) or by a Bayesian analysis, which gives a range of possible fits, with probabilities. It turns out that this approach to dating can give very precise results: fewer than 10 measurements, spaced at decadal intervals, can give 95% probability ranges of only a few decades. The precision is actually often better than could be obtained if the calibration curve were a simple straight line, because well-characterized and rapid changes in the radiocarbon in the atmosphere can be identified. There are, however, some limits to this method, which need to be borne in mind. First, the calibration data itself is mostly only measured at decadal intervals, and so no further information will be gained by measuring at a resolution of less than this—and, indeed, the mathematical methods employed for this type of analysis actually assume that, at the resolution of the measurements, the adjacent points on the calibration curve are independently measured. Second, it is important to address the possibility of systematic offsets in the measurements and the calibration curve, either through measurement bias or local variation (e.g., in growth season). The latter problem can be dealt with by applying a systematic ΔR offset uncertainty of the order of a decade.

At many archaeological sites, of course, long-lived wood is not preserved and, even when it is, it often cannot be directly related to the archaeological events of interest. For this reason, a wide range of techniques have been developed to enable us to deal with situations where we have less prescriptive information. In almost all cases, there is some additional information available—we might, for example, know that all of the samples relate to a single phase of activity at a site. In other cases we might know that there are several phases of activity, one after another—or, indeed, a series of samples whose dates must lie in a particular order. It became apparent over a decade ago that Bayesian statistics, and Markov chain Monte Carlo (MCMC) methods, could be used to put this type of information together with the radiocarbon

determinations themselves to provide an integrated interpretation of the chronology of a site or region (Buck *et al.* 1991, 1992; Buck and Millard 2004). These methods have been incorporated into statistical packages such as OxCal, BCal and DateLab (Bronk Ramsey 1994, 1995, 1998, 2001; Buck *et al.* 1999; Jones and Nicholls 2002) and further developed to include deposition models and other kinds of constraints (Blaauw *et al.* 2003; Christen 2003; Blaauw and Christen 2005; Blockley *et al.* 2007; Bronk Ramsey 2008).

It is important to understand the relationship between calibrated radiocarbon dates and statistical integration of these measurements using other archaeological information from a site or culture under study. Many contrast the two as relating the scientific measurement and the archaeological interpretation (the latter, by implication, being less precise). In reality, the situation is not this black and white. The radiocarbon measurement itself is, it is true, a purely scientific matter—although, despite that, not without its problems, because of the nature of the material. Radiocarbon calibration can be seen as an interpretation of the measurement within the large-scale (in some cases, global) environment, and any further statistical integration with archaeological or more local environmental information only extends this process. In some instances, the local information is actually better understood than the global environmental information on which calibration rests.

Bayesian analysis has proved to be very useful in archaeological research (Bayliss and Ramsey 2004). It is applied in two different classes of study. The first is of single sites, where stratigraphic information is used to constrain samples relative to one another and in groups (Cleal *et al.* 1995; Bruins *et al.* 2005; Bayliss *et al.* 2007a; Meadows *et al.* 2007). From such studies, it is now possible to tackle archaeological issues almost on the scale of single generations, rather than the several centuries possible with single radiocarbon dates (Bayliss *et al.* 2007b). Of course, such studies place reliance on the integrity of the archaeological information included in the analyses. However, equally importantly, and perhaps less obviously, they also demand much more in terms of the reliability of the radiocarbon measurements, the calibration data sets and the interpretation of the radiocarbon data in the environmental context.

The other class of radiocarbon study in which Bayesian methods have found their place is those studies in which radiocarbon dates from archaeological phases are analysed together in order to better understand the chronology of regions or cultures (Needham *et al.* 1998; Manning *et al.* 2006; Sharon *et al.* 2007). These studies are, in a sense, rather different in nature—the groupings on which they are based are not from actual stratigraphic information from a specific site; they are based on an interpretation, or a range of possible interpretations, of the regional chronology, and frequently make assumptions about synchronous changes that take place across a region. It is frequently assumed, for example, that particular types of ceramic or bronze artefact come into use and go out of use at particular times. Such changes are, of course, not really events but gradual processes. If the changes take place within a few years, this may not matter, within the resolution of the chronology, but if they take a generation or so, this may be significant. These assumptions are usually, and certainly should be, made explicit in the analysis, and consequently the results of the analysis are contingent on these interpretations being correct. Others might interpret the same information in significantly different ways.

The problems of variable radiocarbon content in the atmosphere distort and defocus our view of the passage of time. The statistical methods now available to deal with calibrated dates act like a corrective lens to overcome these problems. However, with this clearer image other problems are also thrown into sharper focus: the statistical methods do not overcome any methodological shortcomings in the radiocarbon method itself.

CHRONOLOGY

Expectations

To those who do not study it in detail, science is often viewed with a mixture of awe and mistrust. Because of its technical complexity, it is assumed that the answers arising from it will be exact and unequivocal. Fortunately, the study of archaeology has become much more scientific over the past 50 years and, as a result, archaeologists have often engaged closely with the scientific disciplines that are needed for their research. This has been essential in developing the techniques and in ensuring that they are properly applied.

To some extent, the pressures of both commercial archaeology and academic research are undermining the holistic view of scientific evidence. There is a tendency to wish to hive off aspects of the work into stand-alone 'modules' or 'packages' that can deliver a 'specification'. There is a temptation to assume that the chronological work package will provide 'dates' and the interpretative package will interpret the results. This makes sense from a business point of view, because interaction between groups of people is expensive, and it is usually best to assume that the output from one package can be used without too much thought as the input to another, since thought is something that is hard to specify, and is usually the first thing to be jettisoned when we are under pressure.

In some ways, radiocarbon should be able to work in this way. The actual measurement of the radiocarbon isotope ratio is a scientific measurement, like any other, and considerable effort has been put into inter-laboratory inter-comparisons (Boaretto *et al.* 2002; Scott 2003; Scott *et al.* 2005) to ensure that results are repeatable and reliable. However, most of this effort has been expended on well-characterized material. If we are to interpret radiocarbon measurements on samples in terms of chronology, there is much more that needs to be considered and thought about. There is an expectation that as the method has developed and become more precise, all of this has become routine and no longer needs to be considered. This is far from the truth. Although the measurements themselves have become markedly more precise (and hopefully not less accurate), this means that we need to be even more careful now about the chain of reasoning that allows us to go from a radiocarbon measurement to an understanding of chronology. A more powerful telescope needs more careful handling, and is no easier to use than a pair of binoculars. The same is true for a dating method that now, together with the statistical methods used, allows us to look at a temporal resolution an order of magnitude finer than was possible just a couple of decades ago.

The application of radiocarbon dating for high-resolution chronology is not something that can be undertaken without a commitment to serious thought about exactly what the radiocarbon dates mean, an understanding that involves a mixture of different sciences and archaeological interpretation.

The chain of reasoning

The key elements in the chain of reasoning needed in radiocarbon-based chronology are shown in Figure 2. Essentially, these trace back the passage of carbon from the original environment to the sample as measured in the laboratory.

The dating process starts well before the measurement takes place. Samples are recovered from archaeological sites, and their contexts evaluated. They may then be stored, and in some instances conserved and curated in museums. Only after this are samples selected for dating on the basis of a dating strategy. There are many choices made at this stage, which are critical to the



Figure 2 The major elements of radiocarbon dating. The 'History' of the sample includes everything relating to the sample prior to 'Investigation'. The latter incorporates all of the physical actions carried out on the sample. The final stage of the dating process is 'Interpretation', which aims to uncover the main elements of the sample 'History'.

understanding of the radiocarbon date in chronological terms. Once in the laboratory, the samples are pre-treated, in order to try to extract original material in a purified form (see the discussion above). This stage is intended to remove contaminant carbon that has entered the sample during diagenesis, but will also, at some level, add carbon itself.

The measurement itself should be relatively straightforward. By the use of standards, backgrounds and secondary standards, it is possible to ensure that measurements are repeatable and their uncertainties well characterized. It is after this stage that the chain of interpretative reasoning begins, and where most of the potential problems arise.

The radiocarbon ratio measured in the laboratory must be related back to that of the original organism. In doing this, the effectiveness of the pre-treatment methods must be assessed in the light of the changes to the sample that have taken place in the environment and in any subsequent storage. This is not straightforward. Standard materials used for validating dating methods are inevitably different from the real samples from a particular site. In some cases it is possible to use background material (beyond the range of radiocarbon) from the same sequence (Nadeau *et al.* 2001); however, in many archaeological contexts this is not possible. Many of the problems with dating very old material by radiocarbon have arisen because of the difficulties at this stage of the chain of reasoning (Bird *et al.* 1999, 2002, 2003; Higham *et al.* 2006a,b; Jacobi *et al.* 2006; Mellars 2006).

Given a radiocarbon ratio for the original material, the next stage is calibration and this brings in information of two main types.

Logically first is information on the organism itself: we need to assess from which reservoirs the organism will draw its carbon, and in what proportions. As discussed above, this is simple in some cases but difficult in others. In practice, these problems can often be overcome by selection of the most suitable samples and, in general, problems with this stage of the process usually result in inconsistent results that require explanation (Lanting and van der Plicht 1998; Cook *et al.* 2001, 2002). It is possible to see the potential here, though, for systematic chronological bias if, for example, the dating relies solely on human bone.

Having identified the reservoir(s) from which the carbon originates, we must then make use of the record of past radiocarbon concentration embodied in the calibration curve. This is undoubtedly where the greatest shifts in understanding have taken place over the past five decades, and these revolutions in understanding have led to the greatest upheavals in archaeological chronology. The reason for this is clear, since this is a bottleneck in the chain of reasoning. The interpretation of all radiocarbon dates is mediated by the calibration curve and so uncertainties here carry through to everything deduced from the dating method. Other potential problems in radiocarbon dating (choice of samples, pre-treatment methods, reservoir effects) are almost all problems that are mitigated by the use of different sample types, multiple measurements and other forms of replication.

Finally, we come to the analysis of multiple radiocarbon dates in their archaeological or environmental context. This stage is clearly dependent on the other information that is incorporated into the analysis. Such information is very different from site to site, and from case to case. For this reason, it is unlikely that this stage will lead to major misinterpretation of chronology. The main risks come in the higher precision that is obtainable, which makes the earlier stages in the chain of reasoning more critical (Bayliss *et al.* 2007b).

Instability and revolution

Looking back at the development of radiocarbon, it is interesting to reflect on some of the major changes. Apart from the initial discovery of the method and the development of AMS, which were clearly revolutionary in the best sense, most of the other developments and changes have been more incremental. Three main strands have been dominant:

- The study of past radiocarbon levels through tree rings, marine sediments and corals and the development of calibration curves has put at our disposal a huge amount of information not available at the inception of the method. The improvement in our understanding of the past environment has led to the most significant changes in the interpretation of radiocarbon measurements, inevitably overturning the earliest guesses of what they might mean.
- Improved pre-treatment methodologies and better quantification of the uncertainties due to pre-treatment have improved the accuracy of the method and, perhaps most significantly, addressed the problem of radiocarbon dates near the limit of the technique being systematically too young.
- A much better understanding of the diversity of diet, particularly of humans, has led to a realization that multiple reservoirs of carbon need to be considered in the calibration of human bone dates. This has led to some reassessment of particular sites, but has not led to major chronological shifts.

The radiocarbon revolutions that we have seen are essentially revolutions in our understanding of the environment, of the biology of organisms and the chemistry of sample degradation. These essentially reflect the general intellectual developments in a broad range of subjects over the latter half of the 20th century.

The only area where radiocarbon is perhaps different from other scientific methods is the great reliance on the primary calibration records, through which everything is interpreted. The necessity for these records for the effective use of radiocarbon dating makes everyone eager for new data that will extend reliable calibration. This means that there is a great temptation to use single records for this purpose before they are properly replicated. This has led to the potential for the chronology of most of the Upper Palaeolithic and late Middle Palaeolithic to be interpreted on the basis of a single data set. This is clearly a recipe for instability, and it is the reason why the radiocarbon community repeatedly warns of the dangers of such an approach (van der Plicht *et al.* 2004; Bronk Ramsey *et al.* 2006).

FUTURE PROSPECTS

Our understanding of the past environment

The next few years are very likely to see the development of comprehensive radiocarbon calibration records, extending over the whole range of the method. This will have a very significant impact on our ability to use radiocarbon as an absolute dating technique, comparable with other methods, in the period before 26 000 cal BP. We are also rapidly gaining a better understanding of the time dependency of marine reservoir effects, which are unlikely to provide comprehensive local records, but at least should serve to better quantify the uncertainty in reservoir effects over time. Of course, as with previous improvements in understanding, this will not necessarily make things simpler. It is likely, for example, that there will be some significant reversals in the radiocarbon calibration curve. For this reason, the order and spacing of radiocarbon dates will not necessarily correspond with those of the underlying events on a calendar scale. The changes in gradient affect our understanding of rates of change in significant ways (Mellars 2006).

Measurement methodology

Measurement methodology is likely to continue to improve, both in terms of pre-treatment, providing better accuracy, and measurement techniques (principally AMS), providing better

precision. As discussed above, improved precision for single samples is not necessarily that useful on its own, but with statistical methods for synthesis of information, it can provide substantially improved chronological resolution. AMS instruments are also likely to become smaller and easier to operate, allowing larger numbers of actual radiocarbon measurements to be made. Most of the work involved in radiocarbon dating is already in the pre-treatment stages, which, if anything, are becoming more elaborate. For this reason, the most important impact of the greater availability of AMS instruments might be better precision and use of greater numbers of replicate measurements on samples and standards, and the routine measurement of different chemical fractions.

Compound-specific dating is likely to find more applications in areas where there are no other methods for obtaining a reliable date. However, for reasons of sample size, it is not likely that these methods will replace those on more abundant carbon-containing molecules for routine dating.

Finally, when considering measurement, we should remember that counters and AMS are not the only methods of directly detecting radiocarbon, and it could be that other methods might ultimately provide better sensitivity, especially for small samples. One such method is laser-assisted isotope ratio analysis (LARA), which at least has the potential to measure radiocarbon at natural abundance (Murnick *et al.* 2007). In principle, since the sample is not used during the measurement, such methods allow for repeated measurement and therefore might be able to approach 100% detection efficiency. At present, the sensitivity of such systems is too low by several orders of magnitude, and they are currently being developed for biomedical applications where higher radiocarbon concentrations are encountered. In this area, they might prove more effective than gas ion sources and AMS for compound-specific tracer work.

Methods of interpretation

Undoubtedly, the most cost-effective way to improve dating resolution is to use the statistical methods now available for synthesizing a range of chronological information. This is an area where there is likely to be considerable development, not just in terms of the statistical methods themselves, but also in better and wider application of the methods that are already available.

The areas where there are likely to be the greatest improvements are in specific models applicable to particular depositional processes, and in the handling of the really large data sets that are now being built up in some areas of archaeology.

Ensuring stability

It is to be hoped that the next few years will see developments in radiocarbon dating that build on what we already have, but do not result in the disruption and instability of the dependent disciplines, which has sometimes been seen in the past. What is certain is that, with the changes taking place, the application of radiocarbon dating, and the interpretation of radiocarbon dates, will not become simpler. If we are all to benefit from the developments described above, it is important that both laboratories and users of radiocarbon continue to engage in a dialogue over the underlying issues. Radiocarbon dating should not be viewed as a black box, which occasionally has to be shaken because it does not give the right answer.

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