

## Radiocarbon dating in archaeology: methods and applications

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We discuss the physical principles of radiocarbon dating and its use in archaeometry. A detailed outline of error assessment and quality assurance is given. Correct sample selection, sample provenance, and contamination evaluation procedures are discussed. We give examples of  $C^{14}$  dating in the context of Australian and New Zealand archaeology.

### 1. INTRODUCTION

*“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 millennium, we can do no more than guess.”*

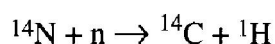
Rasmus Nyerup, 1802[1].

Nyerup's words illustrate poignantly the critical power and importance of dating in archaeology; to provide an independent means of measuring the age of past events. Radiocarbon dating is one of the most significant discoveries in archaeological research. Oakley[2] suggested its development meant an almost complete re-writing of the evolution and cultural emergence of the human species. Clark[3] wrote that were it not for radiocarbon dating, “we would still be foundering in a sea of imprecision's sometime bred of inspired guesswork but more often of imaginative speculation”. Writing of the European Upper Palaeolithic, Movius[4] concluded that “time alone is the lens that can throw it into focus”.

It is now fifty years since Willard Libby and his co-workers developed the radiocarbon dating technique. In the intervening years it has become established as the premier method for dating prehistory in the Holocene and Late Pleistocene periods. In addition, there have been significant advances in routine analysis, methodology and instrumentation, while our understanding of the sources of error in archaeological dating has increased. In this chapter, we outline the basis of the method and tackle some of the significant developments. We then consider the basis for archaeological radiocarbon dating and illustrate its use with some archaeological case studies.

## 2. The method

The underlying principles of radiocarbon dating are well known. Carbon is essential for life on Earth, it is the building block of plants and animals. There are three principal isotopes of carbon on Earth;  $^{12}\text{C}$  (98.89% of the global carbon budget),  $^{13}\text{C}$  (1.11%) and  $^{14}\text{C}$  (0.00000000010%). Each are identical chemically, but  $^{14}\text{C}$  is unstable, or radioactive, because it contains extra neutrons in its nucleus.  $^{14}\text{C}$  is created in the upper atmosphere through the action of cosmic rays, which impact the Earth, forming thermal neutrons. A secondary effect of this production is an impact upon the isotope  $^{14}\text{N}$  that results in the emission of a proton and a particle of  $^{14}\text{C}$ :



Very soon after production,  $^{14}\text{C}$  is oxidised and becomes  $^{14}\text{C}$ -labelled  $\text{CO}_2$  (i.e.  $^{14}\text{CO}_2$ ). This  $^{14}\text{CO}_2$  enters plant and animal lifeways via photosynthesis and exchange with Surface Ocean water.  $^{14}\text{C}$  is eventually incorporated within all living organisms throughout the biosphere (Figure 1).

The  $^{14}\text{C}$  concentration of a plant or animal is maintained in equilibrium during its lifetime with the level of atmospheric  $^{14}\text{C}$ . As soon as the organism dies, decaying  $^{14}\text{C}$  is no longer replaced and a state of increasing disequilibrium begins. As  $^{14}\text{C}$  decays it emits a weak beta particle, or electron ( $\beta^-$ ):



Libby and his collaborators measured the half-life, or period when half the  $^{14}\text{C}$  in a given body of carbon could be expected to decay, at  $5568 \pm 30$  years. Libby used this half-life to calculate an exponential decay curve showing predicted  $^{14}\text{C}$  levels back through time. The method was tested by dating samples of known-age Egyptian material and dendrochronologically-dated wood, the results of which were within the statistical limits of the curve[5] (Figure 2). It is now known that the so-called "Libby half-life" underestimates the true half-life by ~3%. A more accurate value was later calculated to be  $5730 \pm 40$  years (the so-called Cambridge half-life). Nevertheless, by convention, the Libby half-life is used when computing radiocarbon determinations for the sake of historical continuity. The resulting error is essentially corrected for by the conversion of radiocarbon determinations to calendar years through the application of a calibration curve measured using the same half-life.

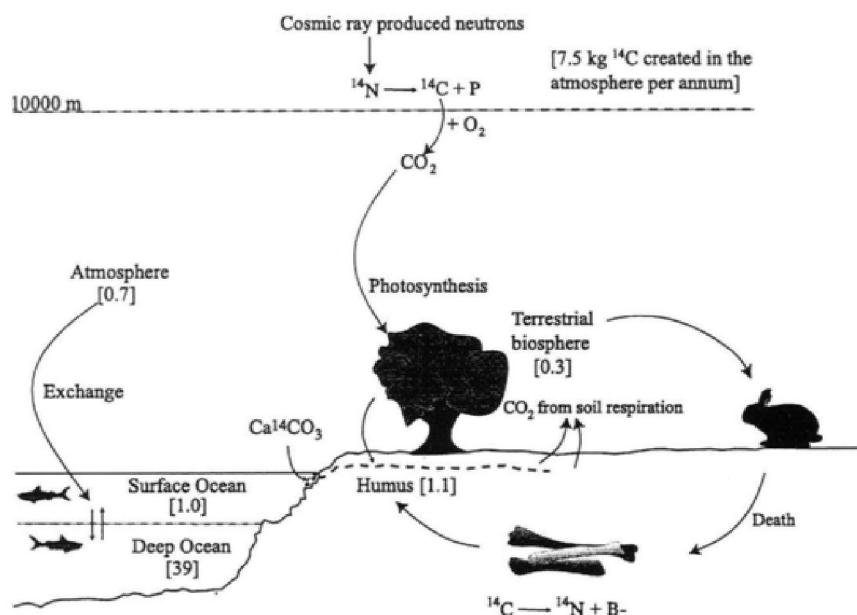


Figure 1. Pathways of  $^{14}\text{C}$  in nature. Figures in brackets represent  $^{14}\text{C}$  contents in million million tonnes within each of the selected reservoirs[6].

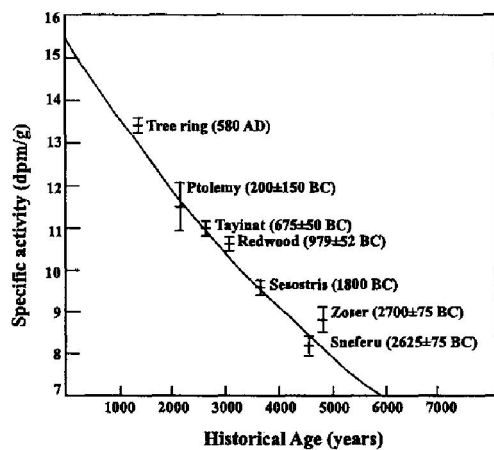


Figure 2. The first check of known-age samples with radiocarbon content, originally published by Arnold and Libby [7]. This is based on Libby[8]. The theoretical curve was calculated using the half-life of 5568 years. The activity is represented in disintegrations per minute per gram carbon (dpm/g).

### 3. Age calculation

The carbon in the Earth's biosphere forms compounds with many different elements. This means that there is a tremendous range of materials that may conceivably be dated (Table 1). Herein lies one of the principal advantages of the method for dating in archaeology. The task of a radiocarbon laboratory is to determine the  $^{14}\text{C}$  concentration of carbonaceous samples of unknown age. This is understandably complex because  $^{14}\text{C}$  is a low-level isotope, present at a ratio of 1.5 atoms of  $^{14}\text{C}$  for every 1 000 000 000  $^{12}\text{C}$  atoms in modern material. The measurement of radiocarbon activity is achieved to routine levels of *ca.* 1.0—0.3% (see below) either radiometrically, by measuring beta decay events (represented by counts per minute per gram of carbon—cpm/g/C) or, using direct ion detection accelerator mass spectrometers (AMS), by measuring  $^{14}\text{C}$  concentration ratios.

Table 1

Carbon materials that are commonly radiocarbon dated in archaeology (denoted by \*), and some of those which have been dated experimentally. Some samples are only able to be dated using AMS radiocarbon techniques because they are commonly small in size (these are denoted by +) (see below).

Charcoal, wood, twigs and seeds*	Wall paintings and rock art works+
Bone*	Iron
Marine, estuarine and riverine shell*	Avian eggshell
Leather*	Corals *
Peat*	Blood residues+
Coprolites	Textiles and fabrics*
Lake muds and sediments*	Paper and parchment*
Soil*	Fish remains
Pollen+	Insect remains+
Hair+	Resins and glues
Pottery	Antler and horn*
Metal casting ores	

Stuiver and Polach[9] have defined the conventions for the reporting of conventional radiocarbon ages, which are now widely adopted:

1. calculation using the Libby half-life of  $5568 \pm 30$  yr;
2. ages calculated with respect to a modern reference standard whose activity is correlated to wood grown in 1890 AD and normalised for decay to 1950 AD;
3. ages released in years BP ('Before Present'), with 'present' being 1950 AD (the year of the publication of the first radiocarbon determinations by Libby, Anderson and Arnold [10]);
4. a correction for sample isotopic fractionation, with  $\delta^{13}\text{C}$  normalisation to  $-25.0\text{‰}$  with respect to (wrt) the VPDB standard carbonate (Vienna PeeDee Belemnite)[11];
5. assumption that there is constancy in radiocarbon levels during the past.

Laboratories report ages with reference to accepted standards. The *absolute international standard activity* is defined as 95% of the activity of the U.S National Institute of Standards and Technology (NIST) Oxalic Acid 1 (termed HOX 1), in 1950 AD, which is normalised for isotopic fractionation to a  $\delta^{13}\text{C}$  of -19.0‰ (see below). Declining amounts of Oxalic Acid 1 resulted in the introduction of a new standard, Oxalic Acid II (HOXII)[12].

Absolute measurements are difficult to achieve due to measurement efficiency parameters. Instead, a ratio of the activity of the unknown sample and standard is determined under identical experimental conditions. The measurement is not therefore absolute, but relative. Stuiver and Polach[13] defined the activity ratio as  $A_{\text{SN}}/A_{\text{ON}}$ , where  $A_{\text{ON}}$  is the modern standard activity measured in the laboratory and normalised for isotopic fractionation, and  $A_{\text{SN}}$  is the normalised activity of the sample whose age is unknown. The conventional radiocarbon age may then be calculated with reference to the average lifetime of  $^{14}\text{C}$  (the average lifetime of  $^{14}\text{C}$  is -8033 yr, so 1% of the  $^{14}\text{C}$  in a sample of carbon will decay every 80 years), using the radiocarbon decay equation:

$$-8033 \ln\left(\frac{A_{\text{SN}}}{A_{\text{ON}}}\right)$$

'ln' is the natural logarithm. Since both  $A_{\text{SN}}$  and  $A_{\text{ON}}$  are defined with respect to 1950 AD, this measured ratio, and the radiocarbon age from which it is derived, does not change, irrespective of the year of measurement.

The background limit for the  $^{14}\text{C}$  method is reached by about ten half-lives (approximately 55 000 years). This limit varies under different laboratory and experimental conditions. Significant reductions to the background limit can be achieved by shielding the measurement system from cosmic radiation. It has been suggested that AMS systems might one day have the potential to extend beyond the effective limit because of enhanced detection efficiencies, but this has yet to eventuate. In practice, a range of post-depositional contamination and system errors effectively limit the potential for dating very old archaeological samples.

Although the decay of  $^{14}\text{C}$  is constant, it is also random, which means that repeat measurements of sample activity should cluster around the "true" age of the sample, producing a Gaussian or normal distribution. Radiocarbon ages are therefore expressed with a one standard deviation '±' value, so they comprise an age ( $y$ ), and a standard error ( $\sigma$ ). Consider a radiocarbon age of  $2500 \pm 200$  BP, for instance. This means that the "true" age has a 68% ( $1 \sigma$ ) chance of falling between 2300 and 2700 BP. Some archaeologists opt for a more conservative two standard deviation value, which means that the "true" age has a 95% ( $2 \sigma$ ) chance of falling between the range (i.e.,  $y + 2 \sigma$ ,  $y - 2 \sigma$ , or 2100—2900 BP).

Standard errors are based principally on measurement statistics. In radiometric counting systems, the principal influence on the standard deviation is the length of the measurement time and the number of recorded decay events during that time. Larger fractions of the same carbon sample will produce more counts. High Precision (HP)  $^{14}\text{C}$  laboratories therefore utilise longer counting times as well as increased sample sizes[14](Figure 3). Consider a sample which has an activity of 7 cpm/g/C. This sample will produce 10000 counts in 24 hours, and yield a standard deviation of  $\pm 100$  yr (where  $s.d = \sqrt{\text{total counts}}$ ). The standard error quoted with a radiocarbon determination will therefore be

1%, or  $\pm 80$  years. Doubling the sample size will yield twice the counts in the equivalent counting time, so 20000 counts will be obtained, with an equivalent reduction in standard error to 0.7%, or  $\pm 60$  years.

In natural biochemical processes, such as photosynthesis, plants preferentially take up  $^{12}\text{C}$  over  $^{14}\text{C}$ . This 'fractionation' can result in an error of *ca.* 0—400 years in an uncorrected radiocarbon age. Because the depletion in  $^{14}\text{C}$  is twice that of  $^{13}\text{C}$ , one means to correct for fractionation is to measure the ratio of  $^{13}\text{C}/^{12}\text{C}$  and then correct the measured activity of  $^{14}\text{C}$ . The depletion in  $^{13}\text{C}$  from the international standard carbonate (VPDB) is termed  $\delta^{13}\text{C}$  and is expressed in parts per thousand ( $\text{‰}$ , per mille).

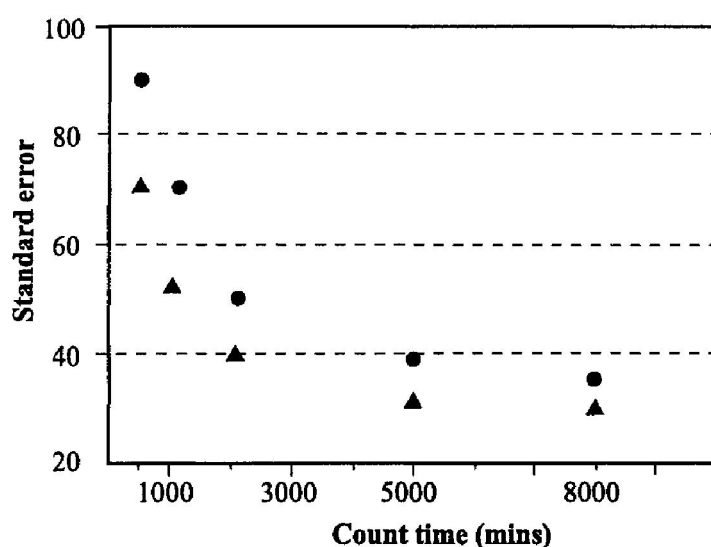


Figure 3. Relationship between measurement time and standard error in 3 (●) and 5 mL (▲) samples of benzene ( $\text{C}_6\text{H}_6$ ). Data from the Waikato Radiocarbon Laboratory<sup>[15]</sup>.

In Table 2, the  $\delta^{13}\text{C}$  values for commonly dated samples are listed. Without correction, there is an age change in an uncorrected radiocarbon age of 16 years, with every 1 $\text{‰}$  change in  $\delta^{13}\text{C}$ . The correction is made by using the  $\delta^{13}\text{C}$  to normalise the sample activity to an agreed base of  $-25 \text{‰}$  wrt VPDB. Problems have arisen for archaeologists where it is unclear whether laboratories have or have not corrected for isotopic fractionation. The  $\delta^{13}\text{C}$  value for marine shell (*ca.* 0  $\text{‰}$ ), for example, is equivalent to *ca.* -400 years, coincidentally the same as the average oceanic reservoir correction *ca.* +400 years, so in the past many laboratories applied no  $\delta^{13}\text{C}$  or reservoir correction to shell, because they were approximately equal to one another. The majority of laboratories now provide routine  $\delta^{13}\text{C}$  corrections, or estimate the  $\delta^{13}\text{C}$  value for the particular sample type and correct on that basis.

Not all radiocarbon samples come from an environment, or reservoir, which is in equilibrium with atmospheric  $^{14}\text{C}$ . If they are not they may produce "apparent ages". As described above, marine organisms living in equilibrium with the ocean surface layer, for

example, will yield radiocarbon ages *ca.* 400 years older than contemporary terrestrial organisms[16]. This is known as the 'marine reservoir effect'. Oceanic ages may be corrected once the extent or size of the reservoir effect is known. Other apparent ages are produced from samples of plants growing near volcanic fumaroles<sup>[17]</sup>, lacustrine environments, or gastropods living on limestone deposits[18].

In the modern era, two types of human activities have modified atmospheric <sup>14</sup>C concentration. The first is the industrial (or Suess effect)[19] effect which refers to the emission of CO<sub>2</sub> from fossil sources which contain no <sup>14</sup>C due to their extreme age. The effect has been to dilute the <sup>14</sup>C in the post-1880 AD atmosphere by *ca.* 2%. The second is the nuclear effect. Beginning the mid-1950s<sup>[20]</sup>, there was an increase in <sup>14</sup>C in the atmosphere from nuclear testing, peaking in 1963-5 *ca.* 100% above normal levels. Since then, the level of atmospheric <sup>14</sup>C has been declining as the 'bomb' carbon enters the biosphere (Figure 4).

Table 2  
Variations in  $\delta^{13}\text{C}$  in nature[21].

Material	$\delta^{13}\text{C}$ ‰ (per mille)
Marine HCO <sub>3</sub>	-1 ± 2
Marine CO <sub>3</sub>	0 ± 2
VPDB $\delta^{13}\text{C}$ standard	0
Soil CO <sub>2</sub>	-5 ± 3
Speleothems	-9 ± 3
Atmospheric CO <sub>2</sub>	-9 ± 2
Bone apatite and original carbonate	-12 ± 3
Grains, seeds, maize, millet (C4 plants)	-10 ± 2
Freshwater plants (submerged)	-16 ± 4
Grasses arid zone, sedges	-13 ± 3
Straw, flax	-14 ± 3
Marine organisms (organic)	-15 ± 3
Succulents (cactus, pineapple etc)	-17 ± 2
NIST Oxalic acid 1 standard (HOXI)	-19 ± 1
NIST Oxalic acid 2 standard (HOXII)	-17.6 ± 1
Bone collagen (C3 diet), wood cellulose	-20 ± 2
C3 plants, grains (wheat, etc). Graphite, coal	-23 ± 3
Wood, charcoal (C3 plants)	-24 ± 3
Recent wood	-25 ± 3
Tree leaves, wheat, straw etc	-27 ± 2
Peat, humus	-27 ± 3

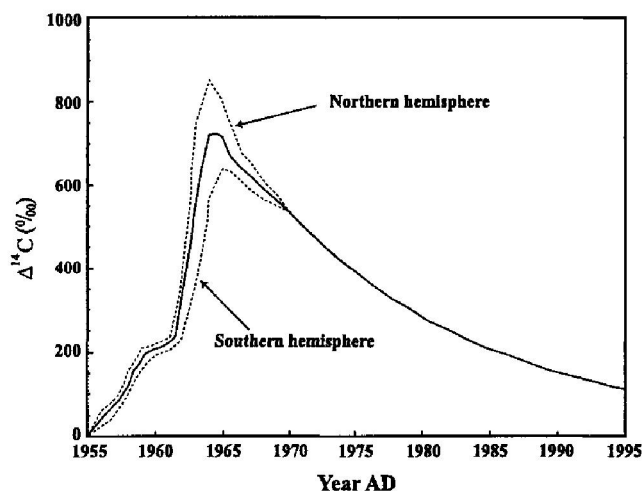


Figure 4: Influence of ‘bomb’ carbon in the Earth’s atmosphere since 1955 AD. Midline represents average mean atmosphere. Note the lag in the uptake of bomb carbon in the Southern Hemisphere and the steady decline in  $^{14}\text{C}$  through the last three decades. Based on Peng, Key and Östlund[22].  $\Delta^{14}\text{C}$  represents the per mille (‰ parts per thousand) depletion in  $^{14}\text{C}$ .

#### 4. MEASUREMENT METHODS

Three methods of measuring residual  $^{14}\text{C}$  activity are used today in radiocarbon dating; Liquid Scintillation Spectrometry (LSC), Gas Proportional Counting (GPC) and Accelerator Mass Spectrometry (AMS). LSC and GPC are both conventional, or radiometric techniques which rely on the measurement of  $^{14}\text{C}$  decay events. AMS is a direct ion counting technique.

The LSC method involves the conversion of sample carbon to a suitable counting solvent, usually benzene ( $\text{C}_6\text{H}_6$ ). Benzene is targeted because it has a high proportion of carbon atoms and excellent light transmission qualities. The measurement of the beta activity ( $\beta^-$ ) within the sample benzene is made by addition of an organic compound called a scintillator which, in the presence of ionising radiation, traps emitted beta particles within the benzene and then emits a photon in response. There is a quantitative relationship between the process of beta decay and photon emission. Commercially available LS spectrometers employ photomultiplier tubes which register an electronic pulse proportional to the energy of the beta particle when a photon is detected[23].

GPC was the successor to the modified “solid-carbon” geiger technique, with which Libby had made the first  $^{14}\text{C}$  measurements. GPC detects ionising radiation within a gas sample, using electrodes located in a shielded counter. The majority of laboratories utilise  $\text{CO}_2$  or acetylene[24], the purity of which is critical. An advantage of GPC systems is their flexibility in terms of gas sizes, from 10 mL to 7.5 L[25]. Mini-counters developed during the



1980s have resulted in the reduction in required sample size to <1 g C, but long count times are required for reasonable precision.

Until recently, archaeologists required samples comprising 2–4 g C for each radiometric measurement, but since the 1970s, AMS has enabled milligram-sized samples to be dated (Table 3) and, therefore, expanded the range of possible radiocarbon sample types. Accelerators operate on the principle that when a stream of atomic particles is deflected from a straight trajectory, those of lower mass will be deflected from their path to a larger extent than those which have higher mass. AMS involves an ion accelerator and powerful magnets, which effectively select and then separate  $^{14}\text{C}$  and  $^{12}\text{C}$  (or  $^{13}\text{C}$ ) according to their atomic mass, and measures their ratio. AMS extends the sensitivity of regular mass spectrometers which operate at a typical  $^{14}\text{C}$  abundance sensitivity of  $10^{-6}$ – $10^{-10}$ , to  $\sim 10^{-15}$ [26]. This increase is critical when it is remembered that  $^{14}\text{C}$  is present in modern atmospheric  $\text{CO}_2$  at  $10^{-12}$ .

Table 3

Sample size requirements for typical radiometric and AMS systems. Weights are a guide only, requirements may vary between different laboratories.

Material	Dry weight		
	Radiometric dating (ideal weight)	Radiometric dating (minimum weight)	AMS dating
Wood and charcoal	8–12 g	1 g	5–10 mg
Carbonates	35 g	5 g	15 mg
Peat~	5–10 g	1 g	0.1–1 g
Bone~	100–200 g	20–80 g	1 g
Lake sediment~	30–100 g	10–20 g	1 g

NB: ~ranges reflect varying carbon content (weights approximate).

There are a number of advantages to dating by AMS. Measurement times are significantly shorter (*ca.* 1 hour per sample) because the technique involves direct ion counting (equivalent radiometric measurement times range from about 30–50 hours per sample). AMS also enables poorly preserved or contaminated samples to be more rigorously pretreated and still yield a sufficient sample size, while different fractions of the same sample may be dated to determine the extent of contamination. On the other hand, small samples suitable for AMS dating are sometimes more mobile in archaeological contexts. In addition, radiometric samples are more likely to yield an ‘average’ age in samples that are contaminated, because exogenous carbon will often be proportionally less concentrated and more homogenised than in a comparable small sample. Milligram-sized AMS samples are also more prone to laboratory-induced contamination during pretreatment and processing due to their small size[27]. Finally, radiometric systems in general continue to produce higher levels of measurement precision, although the lower sample size constraints of AMS systems allow multiple  $^{14}\text{C}$  measurements.

Suggestions of a complete dominance of radiocarbon laboratories by AMS systems[28], [29], are yet to come to fruition. The majority of  $^{14}\text{C}$  facilities are radiometric, which are much cheaper to construct and maintain. Nevertheless, it is widely recognised that AMS has ushered in another revolution in archaeological dating applications.

## 5. QUALITY ASSURANCE

One question, which arises in radiocarbon analysis, concerns the reliability and reproducibility of results from different laboratories. The majority of the world's laboratories adhere to generally agreed protocols to ensure Quality Assurance (QA). This involves intercomparison exercises, regular measurement of radiocarbon standards, determination of reproducibility based on replication of QA samples, and set written and database protocols.

A series of international intercomparison exercises amongst the radiocarbon community has been undertaken to enable laboratories to analyse standard samples of varying age[30][31], as well as maintaining in-house programmes of Quality Assurance. The IAEA[32][33] and TIRI[34][35][36] intercomparisons provided a bank of reference samples which were sent to participating laboratories for radiocarbon analysis. The TIRI samples, for instance, included barley (modern), Belfast pine (4500 BP), IAEA cellulose (modern), peat (3800 BP), whale bone (12700 BP) and calcite (background), amongst others. The results are compiled, anomalous determinations are set aside and consensus values determined by the coordinators. These values are then used to determine bias and offsets amongst laboratory results.

These exercises demonstrated that a significant degree of variation was present. In particular, radiocarbon laboratories have tended to underestimate standard errors. This has led to the adoption of a 'laboratory error multiplier' by many laboratories. This value is generated by repeat measurements of standards and used to increase routine standard errors to take into account variations in reproducibility.

## 6. Archaeological dating

### 6.1 Sample selection and provenance

Accurate radiocarbon dating depends crucially upon the care and attention attached to both the analytical chemistry performed on carbonaceous samples and the measurement of residual  $^{14}\text{C}$  in the laboratory, as well as the rigour of the archaeological investigation (see Table 7 for summary). Precise archaeological dating begins with the careful mapping of the stratigraphic location of the cultural remains, the documentation of the contextual association between material selected for dating, and the inferred cultural activity or archaeological event which is to be dated. In reality, this can be exceedingly complex because of the difficulties often encountered in establishing precisely what is being dated, and how the material relates to that perceived *event*. The misassociation of sample and event is almost certainly the principal source for error in dating archaeological sites which are less than 2-4 half-lives old.

We refer to the event to be dated as the *target event*. This might be, for example, the deposition of a shell midden, the construction of a house, or the manufacture of a spear. A radiocarbon determination may incorporate error because the dated event spans a significant period of time and result in a *pre-event age*. The construction of a large ceremonial structure, for example, might conceivably involve many phases of construction over many years. If the archaeologist is unsure of the sequence of construction and if a single phase is dated with a single radiocarbon determination, there is a strong possibility that the structure may contain a degree of pre-event age. It is the task of the archaeologist to infer the length of time and contextualise the level of offset between archaeological event and scientific date. Similarly,

accurate dating can be affected by *post-event age*, which results in ages that are too young. One example is the reuse of material in archaeological sites[37], or the retouching of rock art.

Table 4

Inferred dating strength in archaeology. Based on Mook and Waterbolk[38].

Strength	Description
1	<i>Robust determination.</i> The target event and determined age have no offset or bias because the material <i>is</i> that event. These samples comprise “single entities” [39], rather than combined, homogenised samples of possible varying age. Examples: bone with butchery marks in which the date of butchery is sought, rice dated in pottery temper where the date of manufacture of the pot is sought.
2	<i>Very strong determination.</i> There is a strong probability that the material dated and the event share the same true age. The relationship is implied strongly by functionality and context. Example: preserved wood within a grave context, charcoal from a hearth.
3	<i>Strong determination.</i> While there is no absolute direct relationship between the event and the material to be dated, there is a realistic expectation that they are contemporaneous. Examples: shells from a concentrated feature within an occupation layer of a site, charcoal from a lens within an occupation layer.
4	<i>Tentative determination:</i> The material dated is only related to the event on the basis of an interpretation, which may or may not be robust. The radiocarbon determination may be interpreted after the event as reliable or unreliable based upon additional chronological information. Examples: grave fill charcoal which may or may not have been taken in prehistory from pre-event layers, midden shell which has been recently redeposited, disseminated charcoal from agricultural soils which may originate from old pre-existing trees.

Another potential problem is caused by sample constituent errors, including *inbuilt age* [40]. Inbuilt age is defined as the difference in age between the death of the sample and the archaeological event which is to be dated. In the case of wood, it is the combination of *growth age* (the age of old wood in a tree) and *storage age* (the time the tree was lying around before it was used)[41]. Inbuilt age produces non-systematic offsets causing the radiocarbon determination to be too old.

The relative ‘strength’ of any particular sample to be dated may be ranked (Table 4), so that the greatest confidence is placed on samples such as bone associated with butchery or burial, where the material belongs to an identified archaeological event. The advantages of ranking radiocarbon determinations have been demonstrated by the work of Kuzmin and Tankersley[42] who applied rankings to their analysis of the  $^{14}\text{C}$  corpus from Eastern Siberian Palaeolithic sites, which resulted in a clearer understanding of the chronology in question.

## 6.2 CONTAMINATION

One advantage of dating using  $^{14}\text{C}$  is the wide range of available carbonaceous materials. This inherent advantage is compromised to an extent because over time it becomes increasingly unlikely that original carbon will resist contamination by foreign, or exogenous carbon. Contamination results in age shifts from the 'true age' by an amount influenced both by the percentage of the contaminant within the sample and by the age of the contaminant (Table 5). For example, contamination from sources which contain no radioactive carbon (i.e. background) introduce a larger proportional shift in error in young samples, whereas old samples are more significantly affected by young contaminants.

Table 5

The influence of contamination upon a sample of carbonaceous material 900 BP in age.

Sample 'true age'	Age of contaminant	% of sample composed of contaminant					
		0%	1%	5%	10%	25%	50%
900 BP	Modern <sup>†</sup>	900 (0)	890 (1)	850 (5)	810 (11)	670 (26)	440 (51)
900 BP	Background <sup>^</sup>	900 (0)	980 (9)	1320 (47)	1770 (97)	3280 (264)	6630 (637)

<sup>^</sup>: contamination with sample which contains no  $^{14}\text{C}$ . <sup>†</sup>: contamination with carbon equivalent to the radiocarbon activity of  $^{14}\text{C}$  from 1950 AD. Figures in brackets represent the percentage shift in age from 'true age'. Table adapted from Caughley[43].

A range of routine pretreatment chemistries has been applied to isolate original carbon in dateable materials and remove a majority of non-sample contaminants (Table 6).

Table 6

Routinely applied pretreatments on regularly dated materials.

Sample	Pretreatment
Bone	Exterior surfaces removed with a drill and the sample is crushed. Bone collagen (protein) is isolated after heating with weak acid. A NaOH wash may also be used to remove humic contaminations. Greater purification is achieved by extracting bone gelatin from the collagen.
Charcoal/ wood	Fragments are selected and any adhering surface contamination removed. The sample is crushed and acid washed to remove non-sample carbonates. An alkali treatment is used with samples suspected of soil humic contamination, followed by an acid wash to remove precipitated atmospheric $\text{CO}_2$ .
Lake muds/ soil/ peat	Similar pretreatments to charcoal and wood. The isolation of plant macrofossils, fine and coarse fractions may be employed to determine a more reliable age.
Shell/ coral	Exterior surfaces are cleaned. A dilute HCl acid wash may be used to remove areas of further contamination.

Sometimes, more rigorous pretreatments must be applied to samples which originate from problematic environments. In the case of old wood, for instance, resins, lignins and waxes can be removed to isolate cellulose, the carbohydrate fraction of the wood[44]. Bone which is at risk of contamination or degradation may be pretreated to fractions which are specific only to bone, including individual or total amino acids[45].

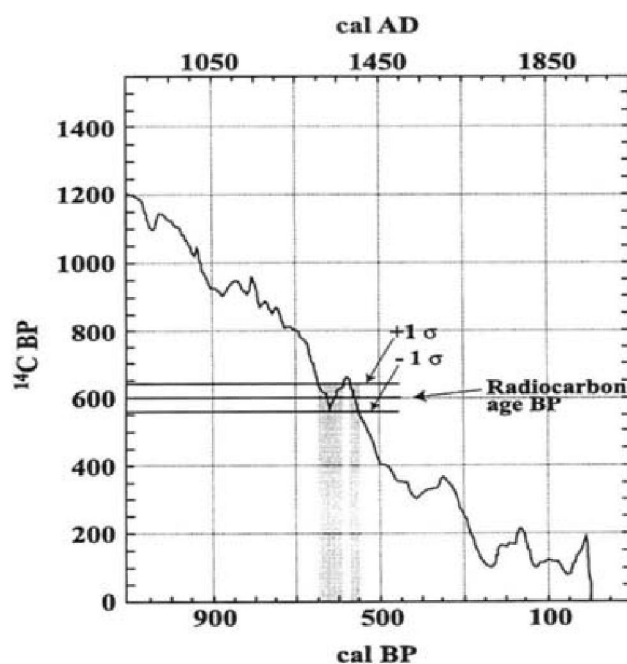


Figure 5. Calibration of a radiocarbon determination of  $600 \pm 40$  BP using the 1998 INTCAL calibration dataset[46]. “Wiggles” in the calibration curve mean that there is a bimodal calendar age range for this radiocarbon determination. The shaded area shows the calendar age ranges which can be read off the x-axis. The CALIB computer programme shows that the calendar age at  $1 \sigma$  is 1300-1370 cal AD (650-580 cal BP) and 1380-1405 cal AD (570-565 cal BP).

## 7. Calibration

The assumption that the concentration of  $^{14}\text{C}$  in each radiocarbon reservoir has remained constant was addressed early in the history of the method and found to be unsustainable[47]. Archaeological sites in Europe and the Mediterranean which had been dated by comparative methods, played a central role in first determining that the relationship between secular time and radiocarbon years was not linear[48]. It is now known that the  $^{14}\text{C}$  production rate is influenced by short term variations in the bombardment of the upper atmosphere by cosmic rays[49], a slow long-term increase in the intensity of the geomagnetic dipole over the last 30 000 years, and changes in ocean ventilation patterns during the last deglaciation. This results

in fluctuations or “wiggles” in the concentration of radiocarbon in the biosphere over time (see Figure 5).

Past atmospheric variation in  $^{14}\text{C}/^{12}\text{C}$  production has been reconstructed for the Holocene period using dendrochronologically-dated oak and pine from Europe and North America[50][51]. This has enabled the calibration of radiocarbon determinations to calendar time back to 11 850 cal BP[52]. Beyond this date there is a paucity of suitable wood for extending the calibration curves, so a range of other proxies have been utilised, including corals dated by  $^{230}\text{Th}/^{234}\text{U}$  [53][54] which span the period 11 850—24 000 cal BP[55], and laminated sediments[56]. The 1998 INTCAL dataset integrates these various proxies and covers the period 0—24 000 BP<sup>[57]</sup>. INTCAL 98 enables the calibration of surface ocean samples using a marine curve, which models the movement of radiocarbon within and into the ocean[58][59].

While the calibration of radiocarbon determinations appears to be a simple process, it is hampered by two factors. The first is that radiocarbon standard errors can make it difficult to distinguish absolutely the corresponding calendar date for a radiocarbon measurement. The second is caused by the “wiggles” in the calibration curve which mean that the calibration of single radiocarbon determinations can result in multiple intercepts along the curve and more than one possible age range. Understandably, this can provide serious interpretive problems for archaeologists. Using a section of the 1998 INTCAL curve a radiocarbon age of  $600 \pm 40$  BP is calibrated by running a horizontal line from 600 BP, to the points which intersect the calibration curve (Figure 5). In this example there are four intercepts. From the intercepts, vertical lines are drawn to the point where they bisect the  $x$ -axis and the same is done at  $1 \sigma$  either side of the  $^{14}\text{C}$  age to give the corresponding calendar age range. In this example, the “wobble” in the calibration curve results in bimodal age ranges, either of which could theoretically contain the “true” age. A calibrated radiocarbon age is referred to in “cal AD/BC” or in “cal BP”.

A recent approach has been to calibrate radiocarbon data in combination with archaeological evidence. Archaeological information in the form of relative stratification (phases, sequences), historic evidence (coins, written texts), information derived from the boundaries of the event (*termini post* and *ante quem*) and artefactual evidence[60][61] assume importance in the dating of an archaeological site. Bayesian statisticians have incorporated this *a priori* (prior) information along with radiocarbon data to determine calendrical age for archaeological contexts. Computer software programmes, such as OxCal[62] and Date Lab[63], and the Internet-based BCal[64] have made this Bayesian approach to calibration much more accessible to archaeological users.

## 8.0 CASE STUDIES

To the archaeologist falls the task of interpreting the results generated by the radiocarbon laboratory. Ideally, the task of dating ought to be a collaborative process between laboratory and field archaeologist, with samples chosen on the basis of both archaeological and dating suitability. In this section, we focus upon actual dating problems which impact critically upon archaeological interpretations.

Table 7

Influences on the reliability of archaeological radiocarbon determinations. After Polach[65].

Error source	Direction, size of error	Means to reduce error
<b>Archaeological variables</b>		
Misassociation, <i>pre-</i> and <i>post-</i> event age	Old or young	Rigorous attention to stratigraphy and geomorphology
Human contamination (hair, petrol, oil, waxes, paper etc)	Old or young	Care during excavation, rigour attached to sample collection and storage
Inbuilt age of wood (growth age)(see text)	Older (non-systematic)	Screening of samples and selection of short-lived twigs/seeds
Inbuilt age of wood (storage age)	Older	Selection of charcoal from species which are not durable
<b>Radiocarbon variables</b>		
Half-life of radiocarbon	Libby half-life is 3% too low	Calibrate results, or multiply Libby age by 1.03
Sample isotopic fractionation	0-450 years (if $\delta^{13}\text{C}$ estimated)	Measurement of $\delta^{13}\text{C}$
Laboratory induced fractionation	Young or old	Check $\delta^{13}\text{C}$ values, rerun if in doubt. Rigorous lab chemistry
Measurement precision	Increases statistical uncertainty	For radiometric samples: increase counting times and sample sizes. In AMS dating: multiple measurement
Distribution of $^{14}\text{C}$ in nature	Surface ocean 300—700 years: too old. deep ocean 1400--1800 years too old	Determine reservoir effect (or $\Delta R$ offset) using samples of known age, or marine shell-terrestrial pairs.
Variation in past $^{14}\text{C}$ production rates	$\pm 5\%$ <: beyond the limit of calibration curve: error difficult to quantify	Calibration of archaeological samples using established calibration curves
<b>Environmental variables</b>		
Post-depositional contamination	Old or young depending on source	Physical and chemical pretreatment. Experimentation to determine the most reliable fractions
Recrystallisation of $\text{CO}_3$	In closed system — none; in open system — older or younger	X-ray diffractometry of carbonate to check for recrystallisation of calcite
Bioturbation, geoturbation	Old or young	Rigorous attention to stratigraphy and geomorphology.
Hard water effect (marine/lacustrine)	Old	Comparison with paired terrestrial samples
Upwelling effect (marine samples only)	Old	Avoid marine samples, date terrestrial samples only

### 8.1 Single radiocarbon determination from New Zealand

In the first case study, we shall consider a simple example of a radiocarbon dating exercise, by following the process of dating a single sample from the site, to the laboratory.

At Kawatea, Little Okains Bay, New Zealand, scattered artefacts including a prehistoric fishhook, human hair and trade knives were collected from the surface of a cave in the 1890s. In the 1960s, the cave was excavated. From the cave floor, the stratigraphy comprised 15 cm of cave roof dust, 60 cm of midden remains belonging to the so-called Classic Maori culture (*ca.* 1500—1769 AD), and 13 cm of Archaic phase midden (*ca.* 1250-1500 AD). Moa bone, mussel shells and fire stone chips were excavated from this lower context.

No samples were submitted for radiocarbon analysis after the excavation, but some of the material was stored in the Okains Bay Museum, where many local Maori and European artefacts are held. Museum staff decided to submit a sample of moa bone to date other artefacts found at Okains Bay and to aid the writing of a local history of the area.

A moa leg bone, weighing 127 grams, was brush cleaned at the Museum, and then packed in double polythene bags, which were carefully labelled. The packaged samples were sent to the Waikato Radiocarbon Dating, in New Zealand, along with a completed sample submission form containing information on the sample material, its location, an estimated age, and other relevant data. Upon arrival at the laboratory, the sample was given an accession number, and the submitter was notified that it had arrived safely.

The bone was physically pretreated in the laboratory, by cleaning with a scalpel and dental probe and then washing in an ultrasonic bath. The bone was then crushed to a fine powder and chemically pretreated to isolate a fraction of the original protein. The bone powder was reacted with 2% concentrated HCl, rinsed and dried. This yields acid insoluble “collagen”. The sample was then gelatinised, by heating in weakly acidic (pH=3) water at 90° C for 4 hours, rinsed and dried. Finally, the bone gelatin was freeze-dried, weighed and queued in the laboratory for benzene synthesis.

The gelatin was converted from its carbonaceous form, into benzene, a process that takes three days. First it was combusted to produce carbon dioxide. The measured gas was then reacted with molten lithium at 800°C to produce lithium carbide ( $\text{Li}_2\text{C}_2$ ). Afterwards, distilled water was added to the  $\text{Li}_2\text{C}_2$  to produce acetylene ( $\text{C}_2\text{H}_2$ ) which was then allowed to sublime onto a vanadium catalyst that converts three acetylene molecules into one molecule of benzene by a process called catalytic trimerisation. The weight of benzene produced was 2.98 grams.

The radiocarbon activity of the benzene was determined using one of the laboratory's LS spectrometers. The sample was counted for 2500 minutes, and produced a total of 66360 counts during that time ( $26.371 \pm 0.1$  cpm). This data was compared with a laboratory standard of ANU sucrose measured previously in the same spectrometer in the same glass vial, which recorded an activity of 28.404 cpm. The radiocarbon age was calculated using the radiocarbon decay equation on one of the laboratory computers.



$$\begin{aligned}
& -8033 \ln\left(\frac{A_{SN}}{A_{ON}}\right) \\
& = -8033 \ln\left(\frac{26.371}{28.404}\right) \\
& = -8033 \ln(0.92842557) \\
& = -8033(-0.074265058) \\
& = 596 \text{ years BP}
\end{aligned}$$

The calculated age was rounded up to 600 years BP. The standard error was calculated at  $\pm 35$  years (a measurement precision of 0.43%), so the conventional radiocarbon age for the moa bone sample from Okains Bay, was  $600 \pm 35$  BP. This radiocarbon age was calibrated using the 1998 INTCAL calibration curves and yielded a bimodal calibrated age range (1285—1305 and 1365—1385 AD at  $1 \sigma$ ). This calendar age was slightly earlier than the estimated age of 1400—1500 AD, which the archaeologist involved in the project, provided, but very similar to the earliest phase of moa hunting identified in the South Island of New Zealand.

## 8.2 DATING AT THE LIMITS OF THE RADIOCARBON METHOD: AUSTRALIA

The expansion of humans into the “new lands” of the Americas, Australia and the Pacific has been linked to the extinction of a range Pleistocene animals and environmental changes associated with anthropogenic influences[66]. In these regions, dating by  $^{14}\text{C}$  assumes central importance to the identification of the earliest cultural evidence and the decipherment of human impacts. In Australia, dating the first humans extends the radiocarbon method to its limits.

One of the problems with archaeological dating in Australia is the lack of unambiguous stylistic and artefactual markers through time, as well as a paucity of clear faunal changes to provide independent chronometers of site age[67]. Developments in dating techniques over the past 40 years have extended the antiquity of humans in Australia from 9000 BP in the 1960s[68]<sup>1</sup>, to 32000 BP in the early 1970s<sup>[69]</sup> to *ca.* 40 000 BP since that time<sup>[70]</sup>. The accuracy of the *ca.* 40 000 BP date is the subject of considerable debate. Jones, Roberts and others<sup>[71][72]</sup> have argued that these results represent an ‘event horizon’[73] caused by the influence of small amounts of contaminants in old samples, rather than being representative of the earliest human presence in Australia as Allen and others have argued[74]. In the early 1990s, the application of TL (Thermoluminescence) and OSL (Optically Stimulated Luminescence) techniques resulted in ages of 50—60 000 years at two sites in northern Australia[75][76] which lent support to a prehistoric chronology which exceeds 40 000 years.

Allen and Holdaway[77] compared the distribution of geological and archaeological determinations from published and unpublished works to determine the robustness of this supposed radiocarbon event horizon (Figure 6). They argued that if the barrier at 40 000 BP were a real phenomenon, then  $^{14}\text{C}$  determinations would be affected by it whether they were from archaeological or natural, non-cultural sites. The archaeological data did not challenge the threshold, but the geological data yielded ages which exceeded it. Allen and Holdaway[78] concluded therefore that the radiocarbon barrier had not influenced the

distribution of the radiocarbon results at *ca.* 40-50 000 years BP because if it had, geological determinations would have been similarly affected.

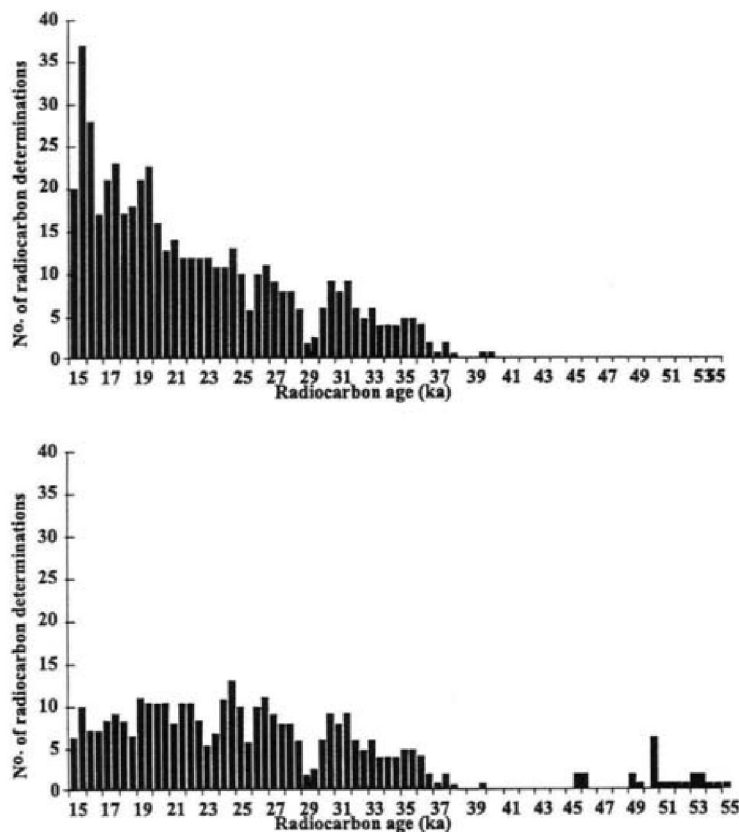


Figure 6. Radiocarbon determinations from Australian archaeological (above) and geological (below) sites which predate 14999BP (from Allen and Holloway [82]).

A number of scholars have criticised this approach. Webb[79], for instance, has shown that some of the series of pre-40 000 BP determinations in the geological distribution were dated in the Groningen laboratory where the samples were assayed using a technique called isotopic enrichment of  $^{14}\text{C}$ [80] designed to extend the range of dating using radiocarbon. Once these determinations are removed, the disparity between the two datasets is reduced considerably.

Chappell *et al.* [81] have shown that materials which are close to, or beyond, the radiocarbon limit tend to cleave asymptotically to a date of *ca.* 40-50 000 BP, due principally to unremoved contamination. They suggest that the oldest dated determinations from archaeological sites in Australia are probably affected by this asymptotic trend. One example of this trend is illustrated in the dating of kauri (*Agathis australis*) tree logs from coastal sand

barriers in northern New South Wales. The sand barriers within which the logs were collected were estimated on geomorphological grounds and  $^{230}\text{Th}/^{234}\text{U}$  dating of corals, to be between 120 and 130,000 years old. Sixteen radiocarbon ages on wood fractions, including resins, humates, humic acids and cellulose ranged from *ca.* 11000 BP to 43000 BP, with only two registering results determined to be beyond background and two yielding minimum or 'greater than' ages (Figure 7). There are lessons from this not just for Australian archaeological radiocarbon dating, but also for dating in other late Quaternary contexts, where the age of archaeological sites approaches the potential limit of the  $^{14}\text{C}$  technique.

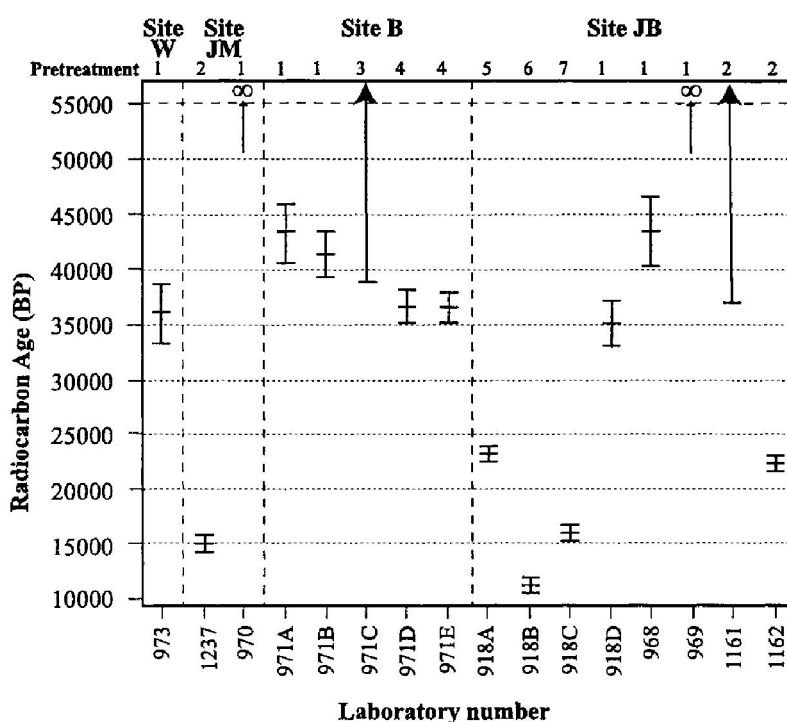


Figure 7: Radiocarbon determinations of kauri (*Agathis australis*) from four sites on coastal dunes in NSW, Australia, whose age is greater than 60 000 years. Ages are given with  $\pm 1 \sigma$  error bars. Numbers refer to dated fractions of the wood. 1: cellulose (these ought to be most reliable); 2: humate; 3: humic; 4: wood residue; 5: 'as is' wood (i.e. untreated); 6: resin; 7: humic and fulvic acid. All determinations from the Australian National University Radiocarbon Laboratory, Canberra. Only two determinations are background (denoted  $\infty$ ) age. Two others yielded 'greater than...' ages (ANU-1161 & 971C- denoted  $\rightarrow$ ). Data reproduced from Chappell *et al.* [82].

### 8.3 Testing the reliability of novel sample types

Whilst the ubiquity of carbon in the biosphere ensures a range of possible dating materials, it is necessary to ensure that novel materials are reliable prior to routine  $^{14}\text{C}$  determinations being assayed. First, it is important to consider whether the organism

originates from a reservoir which is in equilibrium with atmospheric  $^{14}\text{C}$ , or not, and to ascertain whether it is susceptible to post-depositional contamination. This can be achieved by comparison with reliable sample types from identical stratigraphic contexts or by some other independent means of dating[83]. In addition, a potential radiocarbon material must be shown to give reproducible radiocarbon results. Reproducibility is demonstrated when multiple  $^{14}\text{C}$  assays of a novel type, as a group, produce results which are statistically indistinguishable.

An investigation into the reliability of dating snapper fish bone (*Pagrus auratus*) from New Zealand archaeological sites demonstrates this need for careful evaluation of novel sample types. In New Zealand, the earliest archaeological sites date from the mid-13<sup>th</sup> century AD. Many of these Archaic phase sites were, however, dated in the late 50s and early 60s. Since then, advances in the dating of routine sample materials have led to the re-evaluation of many determinations. At sites such as Shag River Mouth[84] and Wairau Bar[85] in the South Island, for instance, re-dating has suggested that both were brief prehistoric occupations (< 50 yr) rather than extensive occupations covering centuries. Unfortunately, many of these key sites cannot be reexcavated and any attempt at re-dating relies heavily on archived material and therefore a limited choice of sample type. For three of these early sites; Houhora[86] and Twilight Beach (northern North Island), and Rotokura (northern South Island)[87], large amounts of snapper bone, which had been initially collected for faunal analysis, was available for dating.

The ability to date fishbone is beneficial for archaeologists because it is common in many archaeological coastal midden sites and it is directly correlated with an identifiable archaeological event, in this instance fishing. The reliability of this sample type for radiocarbon dating had been questioned, however, because of earlier erroneous fishbone determinations and the possibility that some species incorporate carbon from the deep ocean [88]. Snapper do not, however, extend significantly into  $^{14}\text{C}$  depleted waters which exist below 200m[89][90] and none of the archaeological snapper populations were located in areas where old  $^{14}\text{C}$ -depleted water upwells[91]. Moreover, radiocarbon results of otoliths from modern and historic snapper collected on the eastern North Island coast compare favourably to radiocarbon determinations of surface water, modern shellfish and historic shell[92].

Enough well-preserved snapper bone was isolated from each of the sites to produce three to four radiocarbon determinations. The  $^{14}\text{C}$  results of the bone gelatin were compared to assess reproducibility, and the calibrated results compared to radiocarbon determinations on identified charcoal and shell from the same contexts.

Radiocarbon determinations of snapper from all three sites were indistinguishable from one another, supporting the requirement of reproducibility of determinations from this novel sample type (Figure 8). At Houhora and Twilight Beach, the reservoir-corrected snapper gelatin pooled results overlapped with pooled charcoal and shell determinations and yielded acceptable 14<sup>th</sup> and late 14<sup>th</sup> to early 15<sup>th</sup> century dates respectively. The single shell determination for Rotokura (1300—1340 Cal AD at 1  $\sigma$ ), however, was statistically different to the pooled charcoal and shell results for the site. It is thought likely that the shell sample was from a sub-fossil source. The late 14<sup>th</sup> to early 15<sup>th</sup> century result for charcoal and fish bone gelatin is an acceptable estimated time for the deposition of Layer 4 at Rotokura on the basis of artefactual and economic evidence[93]. Overall, the preliminary results suggest that snapper bone gelatin is a reliable radiocarbon sample type, while the radiocarbon

determinations for all three sites support the developing scenario of a rapid phase of early exploration and colonisation in New Zealand[94].

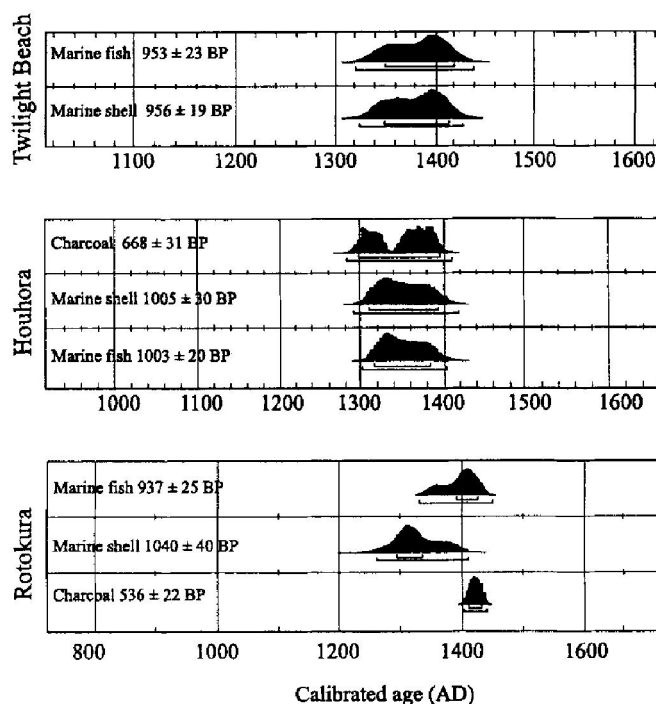


Figure 8: Calibrated radiocarbon determinations of snapper bone gelatin from three archaeological sites in New Zealand. The radiocarbon determinations were calibrated using OxCal, with the INTCAL 98 calibration curves.

#### 8.4 Determining the presence of contamination : The Cuello case.

Bone collagen is subject to alteration following the death of the animal via a combination of chemical, physical and biological processes. The decay process involves the breakdown of soft tissue, which is manifested as a loss of collagen and a corresponding increase in susceptibility to humic and non-humic contaminants. Many of these contaminants do not interact chemically with the sample and can be removed physically or chemically. Unfortunately, some do react with the fraction to be dated and may affect the radiocarbon age.

The general problem of radiocarbon dating bone, particularly in more extreme circumstances (i.e. both reduced collagen content and contaminated bone) is the subject of much active research[95][96]. One avenue involves monitoring the effect of sample pretreatment combined with careful analytical assessment of the bone prior to dating. This relies on the assumption that contamination can be detected and if necessary, the sample rejected. Law *et al.*[97], for example, attempted to obtain a reliable radiocarbon chronology from the Mayan site of Cuello, in Belize by using infra-red spectroscopy combined with a

selective pretreatment regime to isolate a representative protein/peptide fraction from highly degraded, contaminated bone.

A number of charcoal  $^{14}\text{C}$  dates from Preclassic contexts at Cuello had supported a "long" chronology, with the Preclassic spanning *ca.* 2500 BC—AD 250. This contradicted the conventional ceramic chronology which, on stylistic grounds, suggested a Middle Preclassic (*ca.* 300 BC—600 BC) date for the ceramics from the earliest deposits. A subsequent set of charcoal determinations produced a short chronology spanning 750 BC—AD 250. No satisfactory explanation could be given as to why radiocarbon determinations from adjoining excavations with visibly contiguous stratigraphy should yield such contrasting results[98].

A fresh approach was to date carefully selected short-lived material from the relevant layers where the contemporaneity of the samples with the archaeological context was assured. Initial attempts to date bone were unsuccessful[99]. A number of reasons were suggested for these initial bone dates being in error, including:

- low collagenous protein remaining;
- high bone degradation and/or environmental contamination resulting from deposition in a tropical environment;
- possible contamination by PVA/PV-OH, used to consolidate fragile bone after excavation.

Four additional human bone samples were therefore selected for dating. To monitor the effectiveness of different pretreatments on such contaminated bone, four fractions were isolated from each; total acid-insoluble, NaOH leached fraction ("crude collagen"); crude gelatin; ion exchange purified gelatin ("ion-exchanged gelatin"); and amino acids from hydrolyzed ion-exchanged gelatin[100]. The progressive cleanup of the sample was monitored by comparison of infra-red spectrographs of control samples ("finger print" spectra of PVA/PV-OH (Figure 9 B1) and modern hydrolysed collagen (Figure 9 B2)) with archaeological human bone samples. Amino acids were also isolated from unconsolidated animal bone to test whether this pretreatment method could provide satisfactory radiocarbon determinations for unconserved samples from this site.

The infra-red analysis confirmed that the crude collagen fraction retained considerable proportions of contaminants. The pretreatment method used on the original bone determinations from Cuello (ion-exchange purification of a collagen hydrolysate) would therefore have left soil-derived amino acid contaminants. Gelatinisation before ion-exchange removed more of these contaminants. Gelatinisation of the protein fraction also resulted in the removal of infra-red peaks associated with the consolidant from most of the samples except the heavily contaminated Burial 62. The spectrum of the gelatinisation residue from Burial 62 (Figure 9 A2) was similar to that for PV-OH (Figure 9 B1), though the lack of definition indicated that additional environmental contaminants were also present. Generally, the similarity of most archaeological spectra from the site (for example Figure 9 A3) to that of partially hydrolysed modern collagen (Figure 9 B2), suggested that there had been breakdown of the archaeological proteins, possibly caused by diagenesis, or as a result of the gelatinisation procedure. An absence of contamination could not be guaranteed, however.

It was hypothesized that ion exchange purification of the gelatin, prior to subsequent hydrolysis and separation of total amino acids, would remove an even greater proportion of

soil contaminants and improve the reliability of radiocarbon determinations. Confirmation that the cleanup of these samples had been successful was demonstrated when the  $1725\text{cm}^{-1}$  and  $1220\text{cm}^{-1}$  absorption peaks associated with carboxylic acid ( $-\text{COOH}$ ) disappeared and the  $-\text{COO}^-$  peak at *ca.*  $1400\text{cm}^{-1}$  appeared following the ion-exchange procedure (Figure 9 A1). This occurs when ammonium salts ( $-\text{COONH}_4^+$ ) are formed, a reaction that would have exposed any masked contamination peaks.

Acceptable  $^{14}\text{C}$  determinations were obtained from the unconsolidated control samples and the purified amino-acid fractions isolated from the consolidated samples. Radiocarbon results of the intermediate fractions (crude gelatin, and crude collagen) improved as the degree of purification increased. For the better preserved samples the  $^{14}\text{C}$  determinations were fairly uniform throughout the pretreatment process. The largest discrepancy in the determinations was yielded from the gelatinisation residue from Burial 62, demonstrating the effect of contamination by the consolidant and possibly also from humic materials.

Overall, the amino acid radiocarbon determinations of the human burial remains from Cuello supported an occupation beginning in the late second millennium BC. This is over one millennium shorter than the radiocarbon chronology initially determined for the site, but several centuries older than that indicated by the "short" chronology[101]. Recent re-evaluations of the ceramic chronology advanced by Andrews and Hammond[102] have lent support to these conclusions.

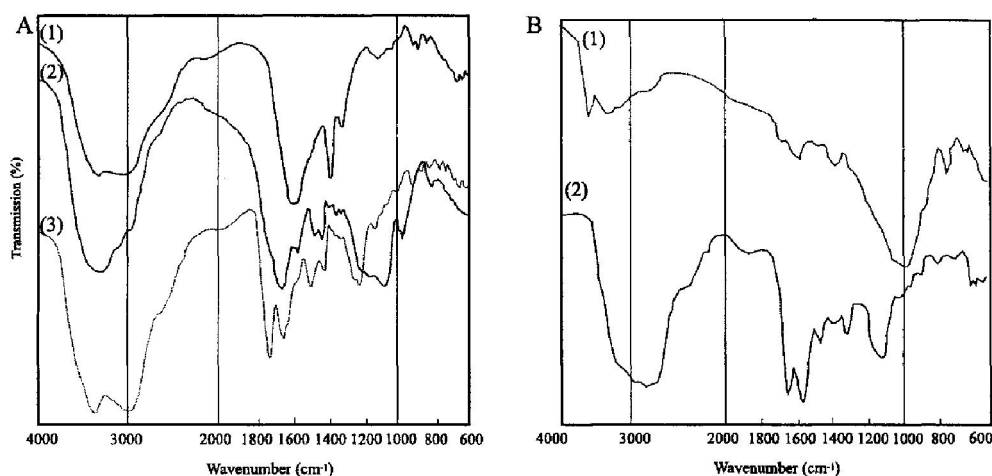


Figure 9: Infra-red spectra from the site of Cuello, Belize. A: prehistoric human bone (1):  $\text{NH}_4^+$  form from Burial 7, after ion exchange (2): crude gelatin from Burial 62. (3) peptized gelatin extracts from Burial 7. B: standards; (1): PV-OH. (2): Modern bovine collagen after partial hydrolysis.

## 9. CONCLUSIONS

The chronological range of  $^{14}\text{C}$  covers a span of time covering about 60 000 years. During this time, modern humans expanded throughout the Old and New Worlds, and

agriculture and more complex forms of social organisation become discernible in the archaeological record. Although it began as a method devised by physicists and chemists, the successful application of radiocarbon dating in archaeology depends upon rigorous attention to sample provenance and stratigraphy in order to determine the age of dated events, coupled with an ongoing liaison with the radiocarbon laboratory to produce results which are both accurate and precise.

Avenues of further research which will continue to enhance the application of the radiocarbon method include the development of more optimized measurement methods, such as GC-AMS<sup>103</sup>], the development of a new generation of smaller sized AMS facilities[104], as well as improved sample pretreatment methods[105] and the extension of the calibration curve beyond 24 ka. Novel sample types also continue to be introduced for more routine dating applications due principally to the enhanced sensitivities of AMS systems (e.g. pollen and carbon from rock art sites[106]). The second fifty years of radiocarbon dating promises to be as exciting and stimulating as the first.

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