Introduction to Radiocarbon Determination by the Accelerator Mass Spectrometry Method

AMS Counting

There are three principal isotopes of carbon which occur naturally - ^{12}C, ^{13}C (both stable) and ^{14}C (unstable or radioactive). These isotopes are present in the following amounts ^{12}C - 98.89%, ^{13}C - 1.11%, and ^{14}C - 0.00000000010%. Thus, one carbon-14 atom exists in nature for every 1,000,000,000,000 or (1 in a trillion) carbon-12 atoms in living material. The radiocarbon method is based on the rate of decay of the radioactive or unstable carbon isotope 14 (^{14}C), which is formed in the upper atmosphere through the effect of cosmic ray neutrons upon nitrogen-14.

The reaction is:

$$^{14}N + n => {}^{14}C + p$$

(Where n is a neutron and p is a proton)

The ^{14}C formed is rapidly oxidized to $^{14}CO2$ and enters the earth's plant and animal life ways through photosynthesis and the food chain. The rapidity of the dispersal of ^{14}C into the atmosphere has been demonstrated by measurements of radioactive carbon produced from thermonuclear bomb testing. ^{14}C also enters the earth's oceans in an atmospheric exchange and as dissolved carbonate [the entire ^{14}C inventory is termed the carbon exchange reservoir (Aitken, 1990)]. Plants and animals which utilize carbon in biological food chains take up ^{14}C during their lifetimes. They exist in equilibrium with the ^{14}C concentration of the atmosphere; that is, the number of ^{14}C atoms and non-radioactive carbon atoms stays approximately the same over time. As soon as a plant or animal dies, they cease the metabolic function of carbon uptake; there is no replenishment of radioactive carbon, only decay.

Libby, Anderson and Arnold (1949) were the first to measure the rate of this decay. They found that after 5568 years, half the ^{14}C in the original sample will have decayed and after another 5568 years, half of that remaining material will have decayed, and so on (see figure 1 below). The half-life (*t* 1/2) is the name given to this value which Libby measured at 5568±30 years. This became known as the Libby half-life. After 10 half-lives, there is a very small amount of

radioactive carbon present in a sample. At about 50,000-60 000 years, then, the limit of the technique is reached (beyond this time, other radiometric techniques must be used for dating). By measuring the ^{14}C concentration or residual radioactivity of a sample whose age is not known, it is possible to obtain the count rate or number of decay events per gram of Carbon. By comparing this with modern levels of activity (1890 wood corrected for decay to 1950 AD) and using the measured half-life, it becomes possible to calculate a date for the death of the sample.

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

$$^{14}C => {}^{14}N + b$$

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

It follows from this that any material which is composed of carbon may be dated. Herein lies the true advantage of the radiocarbon method – it is able to be uniformly applied throughout the world on any material that contains residual carbon.

Because of this, laboratories from around the world are producing radiocarbon assays for the scientific community. The ^{14}C technique has been and continues to be applied and used in many different fields including hydrology, atmospheric science, oceanography, geology, palaeoclimatology, archaeology, biomedicine and materials science.

The Accelerator Mass Spectrometry method of direct ^{14}C isotope counting was first performed in 1977 by scientific research teams at Rochester and Toronto, the General Ionex Corporation, and soon after additional measurements were carried out at Simon Fraser and McMaster Universities (Gove, 1994).

Radiocarbon dating using Accelerator Mass Spectrometry (AMS) differs from the decay counting methods in that the amount of ^{14}C in the sample is measured directly, rather than by waiting for the individual radioactive decay events to occur. This makes the technique 1,000 to 10,000 times more sensitive than decay counting. The enhanced sensitivity is achieved by accelerating sample atoms as ions to high energies using a particle accelerator and using nuclear particle detection techniques. Additionally because of the increased sensitivity, counting times are greatly reduced (minutes to hours, instead of days) and sub-milligram sample sizes can be routinely measured. Because of this, a greatly

increased range of sample types and sizes can now be measured that previously gas-proportional or LSC counting techniques could not.

In the ^{14}C AMS technique, the element of interest (sample carbon) is chemically separated from the original sample, converted to graphite, pressed into a cathode (sample target holder) where it forms a solid graphite plug or layer, and is then placed into a sputter ion source of an accelerator.

This methodology outlines the general graphite sample preparation (chemistry) and AMS counting procedures at Beta Analytic Inc. for organic and carbonate samples. Through this process, the CO2 produced from carbonaceous raw materials is cryogenically purified (separated from non-combustible gases) and reduced to solid graphite for measurement in an AMS.

Conversion of Sample Carbon to Graphite

Sample Pretreatment

Each sample must first be pretreated or the material of interest isolated to ensure that only the primary carbon of interest will be analyzed. As many different types of carbon-containing compounds are present, different pretreatment regimes have been developed to concentrate and isolate the particular carbon fraction of interest prior to dating _(See Pretreatment Glossary – Standard Pretreatment Protocols at Beta Analytic)_.

_CO_2 Generation_

The pretreated sample carbon is first oxidized to CO_2 either by combustion in an Oxygen stream or through direct reaction with reduced Cupric Oxide (metal wire / powder) for organics or through acid hydrolysis for carbonates.

Combustion OR Acid Hydrolysis

Organic + O2 + ΔH => CO2   Carbonate + H3PO4 => CO2

(Sample) (900°C) (Sample)
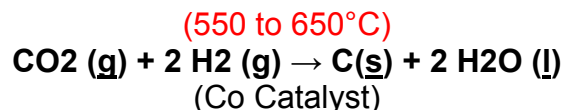
Organic + CuO + ΔH => CO2

(Sample) (900°C)

The CO_2 generated is then cryogenically purified by removing water vapor and any non-combustible/condensable gases by passing through a series of dry-ice / Methanol water traps (~ -78°C) and depending on the sample type a series of liquid Nitrogen / Pentane slush traps (~ -129°C).

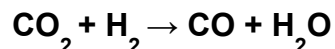## Conversion of CO_2 to Graphite (Graphitization reaction)

To produce the small amounts of elemental carbon from CO_2 for measurement in an AMS, we use the Bosch reaction (Manning and Reid, 1977) that is a chemical reaction between carbon dioxide and hydrogen that produces elemental carbon (graphite), water and heat.

The reaction takes place as two successive reductions; first to carbon monoxide and then to carbon, which permeates and adheres to the surface of the Cobalt powder (catalyst). More details on graphitization techniques and catalysts can be found in Vogel et al, 1984.
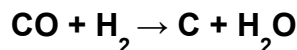
The overall reaction is as follows:

<p style="text-align:center">(550 to 650°C)</p>

$$CO2\ (\underline{g}) + 2\ H2\ (\underline{g}) \rightarrow C(\underline{s}) + 2\ H2O\ (\underline{l})$$

<p style="text-align:center">(Co Catalyst)</p>

However, the above reaction is actually the result of two separate reactions. The first reaction - the water-gas shift reaction is a fast one:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

The second reaction controls the overall reaction rate:

$$CO + H_2 \rightarrow C + H_2O$$

During the graphitization procedure, cryogenically cleaned, dry CO_2 produced from the combustion or acid hydrolysis is transferred cryogenically (with Liquid Nitrogen @ -196°C)* to a specially designed graphitization cell under vacuum that is composed of Vycor glass, Pyrex glass and Stainless Steel (modified design after Lloyd et al, 1991).

NOTE: Prior to the introduction of the CO_2 over the cobalt catalyst in the graphitization cell, the cobalt is pre-conditioned to remove any carbon contaminants by being evacuated then purged with Hydrogen multiple times and finally reduced over ¾ atmosphere of hydrogen for 1-2 hours at 550°C to 650°C.

The pre-conditioned graphitization cell contains either a 4.5 mg or 3.5 mg aliquot of Cobalt metal powder (a mixture of 85% Alfa Aesar -400 mesh, and 15% Alfa Aesar Puratronic -22 mesh) that is specific to the size of the sample being graphitized.

Based on the amount of CO_2 generated during the combustion, the CO_2 is cryogenically transferred to a graphitization cell containing and amount of Cobalt

that is 3x greater in weight than the amount of carbon (3:1 ratio), then an aliquot of Ultra-Pure Research Grade Hydrogen is added such that the amount of Hydrogen is 3x greater in volume as the sample CO_2 (3:1 ratio). The graphitization cell is then placed into a 550°C to 650°C oven for a period of 10-12 hours while the water produced during the graphitization is continuously removed, via a cold finger that is part of the graphitization cell, by a dry-ice Methanol slush (-78°C).

After 10-12 hours have passed, the pressure in the graphitization cell is inspected to ensure that the reaction has gone to completion (that the CO_2 has been converted to graphite with a minimum yield falling in the range of 80-100%). If the reaction has not reached completion, the graphitization cell is returned to the oven, and reacted again for a period of 4-10 hrs. If the reaction does not reach an 80-100% completion following the second graphitization attempt, the sample is analyzed again starting from combustion.

If the graphitization has gone to completion, the graphitization cell is placed under a vacuum and allowed to warm to room temperature causing all water vapor formed during the graphitization reaction to be pumped away, leaving the graphite dry. The graphite is then purged 1x with ultra-pure (99.999) Argon which has passed through an ascarite molecular sieve to remove any CO2 and a silicone drying agent to remove any water vapor. This is then followed by pumping to a vacuum and then purged again with ultra-pure (99.999) Argon to equalize with atmospheric pressure. The graphitization tube is then removed from the graphitization cell and capped with an Al-foil cover and placed in a test tube rack ready to be loaded into a cathode for AMS counting.

AMS Cathode (Target) Loading

The prepared graphite sample is placed into an AMS cathode (target) by pouring the graphite directly from the graphitization tube into the cathode. The graphite powder is then compressed to a minimum of 150 psi (gauge reading) in an Arbor press or by hammering with a press-pin.

The surface of the graphite (target face) is optically inspected to ensure that the graphite appears to be smooth and homogenous (i.e. the graphite does not appear uneven or mottled in coloration). The cathode (target) is then placed into a cathode wheel and placed into the AMS along with the necessary Modern Standards (OXI and/or OXII, organic and carbonate blanks, TIRI known age standards (organic and or carbonate) and sufficient blind QA samples (samples previously measured by LSC and/or AMS) for C14/13 and C14/12 detection.

AMS Counting

As is common with other kinds of mass spectrometry, AMS counting is performed by converting the atoms in the sample (graphite) into a beam of fast moving ions

(charged atoms). The mass of these ions is then separated by the application of magnetic and electric fields and measured by nuclear particle detection techniques. The measurement of radiocarbon by mass spectrometry is very difficult because its concentration is less than one atom in 1,000,000,000,000 (one-trillion) atoms. Thus the accelerator is used to help remove ions that might be confused with radiocarbon before the final detection.

The sample is put into the ion source (as graphite) and is ionized by bombarding it with Cesium ions and then focused into a fast-moving beam. The ions produced are negative which prevents the confusion of ^{14}C with ^{14}N since nitrogen does not form a negative ion. The first bending magnet is used in the same way as the magnet in an ordinary mass spectrometer to select ions of mass 14 (this will include large number of $^{12}CH^{2-}$ and $^{13}CH^{-}$ ions and a very few $^{14}C^{-}$ ions). The ions then enter the accelerator. As they travel to the terminal detector they are accelerated sufficiently such that when they collide with the gas molecules in the stripper, all of the molecular ions (such as $^{12}CH_2$ and ^{13}CH) are broken up allowing most of the Carbon ions to pass through to a second bending magnet which further separates the ions with the mass and momentum expected of ^{14}C, ^{13}C, and ^{12}C.

Finally the filtered ^{14}C ions enter the detector where their velocity and energy are checked so that the number of ^{14}C ions in the sample can be counted. Not all of the radiocarbon atoms put into the ion source end up reaching the detector and so the stable isotopes, ^{12}C and ^{13}C are measured as well in order to monitor the detection efficiency. For each sample, a ratio of $^{14}C/^{13}C$ is calculated and compared to measurements made on standards with known ratios.

Uncertainties in AMS

Soon after the first AMS spectrometers were developed, the quality of AMS measurements was demonstrated through comparisons of the error in the mean of a series of n AMS measurements for a sample (external error) to the counting statistics of the measured total counts, N, in that series of measurements (internal error). If µ is the mean of a group of individual measurements, each with variance σ2 (here assumed equivalent for all measurements), the fractional precisions were shown to be equivalent:

$$\sigma^2_{ext} = \sigma^2 / n \, (n-1)\mu^2 = \sigma^2 \, int = 1/ N_{total}$$

Indeed, equivalence of the standard error in the mean of AMS measurements to the precision expected from counting statistics demonstrated the degree to which

the spectrometer and its operation are free of systematic error. (Wölfli, et al., 1983; Donahue, Jull, & Zabel, 1984; Farwell, et al., 1984; Suter, et al., 1984).

The development of a uniform sample material for ^{14}C AMS, filamentous or fullerene graphite (Vogel et al, 1984), provided intense ion beams for all samples and standards, bringing the internal and external uncertainties into routine equivalence for precise (σ ≤1%) AMS quantification. (Bonani, et al., 1987; Vogel, at al., 1987).

Sample Isotopic Fractionation (Stable Isotope Ratios 13/12C)

In order to provide radiocarbon determinations that are both accurate and precise, it is necessary to measure the stable isotopes of ^{13}C and ^{12}C and their ratio. This is performed by extracting a small amount of the CO_2 generated during the combustion or acid hydrolysis and measuring the 13/12C ratio relative to the PDB mass-spectrometry standard. This ratio is later used in the calculation of the radiocarbon age and error to correct for isotopic fractionation in nature.

Fractionation during the geochemical transfer of carbon in nature produces variation in the equilibrium distribution of the isotopes of carbon (^{12}C, ^{13}C and ^{14}C). Craig (1953) first identified that certain biochemical processes alter the equilibrium between the carbon isotopes. Some processes, such as photosynthesis for instance, favors one isotope over another, so after photosynthesis, the isotope ^{13}C is depleted by 1.8% in comparison to its natural ratios in the atmosphere (Harkness, 1979). Conversely the inorganic carbon dissolved in the oceans is generally 0.7% enriched in ^{13}C relative to atmospheric carbon dioxide.

The extent of isotopic fractionation on the ^{14}C/^{12}C ratio, which must be measured accurately, is approximately double that for the measured ^{13}C/^{12}C ratio. If isotopic fractionation occurs in natural processes, a correction can be made by measuring the ratio of the isotope ^{13}C to the isotope ^{12}C in the sample being dated. The ratio is measured using an ordinary mass spectrometer. The isotopic composition of the sample being measured is expressed as delta13C which represents the parts per thousand difference (per mille) between the sample carbon-13 content and the content of the international PDB standard carbonate (Keith et al., 1964; Aitken, 1990). A d13C value, then, represents the per mille (part per thousand) deviation from the PDB standard. PDB refers to the Cretaceous belemnite formation at Peedee in South Carolina, USA. This nomenclature has recently been changed to VPDB (Coplen, 1994).

In summary, isotopic fractionation refers to the fluctuation in the carbon isotope ratios as a result of natural biochemical processes as a function of their atomic mass (Taylor, 1987). Variations as such are unrelated to time and natural radioactive decay. It is common practice in radiocarbon laboratories to correct radiocarbon activities for sample fractionation. The resultant ages are termed

"normalized", meaning the measured activity is modified with respect to -25 per mille wrt VPBD. The correction factor must be added or subtracted from the conventional radiocarbon age.

The deltaC13 value for a sample can yield important information regarding the environment from which the sample comes or the mixtures of materials used to produce it because the isotope value of the sample reflects the isotopic composition of the immediate environment. In the case of shellfish, for example, marine shells typically possess a dC13 value of between -1 and +4 per mille, whereas river shells possess a value of between -8 and -12 per mille. Therefore, in a case where the precise environment of the shell is not known, it is possible to determine the most likely by analysis of the dC13 result.

Fractionation also describes variations in the isotopic ratios of carbon brought about by non-natural causes. For example, samples may be fractionated in the laboratory through a variety of means. Usually, this is due to lack of attention to detail and incomplete conversion of the sample from one stage to another or from one part of the laboratory to another. In Liquid Scintillation Counting, for example, incomplete synthesis of acetylene during lithium carbide preparation may result in a low yield and concurrent fractionation. Similarly, the transfer of gases in a vacuum system may involve fractionation error if the sample gas is not allowed to equilibrate throughout the total volume. Atoms of larger or smaller mass may be favored in such a situation. If, however, the entire sample is converted completely from one form to another (e.g. solid to gas, acetylene to benzene) then no fractionation will occur.

Radiocarbon Age and Error Calculation

Much of the information presented in this section is based upon the paper Stuiver, M. and Polach, H.A. 1977. Discussion: Reporting of ^{14}C data. *Radiocarbon* 19; 355-63.

The radiocarbon age of a sample is obtained by measurement of the residual radioactivity. This is calculated through careful measurement of the residual activity (per gram C) remaining in a sample whose age is unknown, compared with the activity present in Modern and Background samples.

Modern Standard

The principal modern radiocarbon standard is N.I.S.T (National Institute of Standards and Technology; Gaithersburg, Maryland, USA) Oxalic Acid I (C2H2O4). *Oxalic acid I* is N.I.S.T designation SRM 4990 B and is termed HOx1. This is the International Radiocarbon Dating Standard. Ninety-five percent of the activity of Oxalic Acid from the year 1950 is equal to the measured activity of the *absolute radiocarbon standard* which is 1890 wood. The 1890 wood was chosen

as the radiocarbon standard because it was growing prior to the fossil fuel effects of the industrial revolution.

The activity of 1890 wood is corrected for radioactive decay to 1950. Thus 1950, is year 0 BP by convention in radiocarbon dating and is deemed to be the 'present'. The year 1950 was chosen for no particular reason other than to honor the publication of the first radiocarbon dates calculated in December 1949 (Taylor, 1987;97).

The Oxalic acid standard was made from a crop of 1955 sugar beet. There were 1000 lbs made. The isotopic ratio of HOx I is -19.3 per mille with respect to (wrt) the PBD standard belemnite (Mann, 1983). The Oxalic acid standard which was developed is no longer commercially available. Another standard, *Oxalic Acid II* was prepared when stocks of HOx 1 began to dwindle. The Oxalic acid II standard (HOx 2; N.I.S.T designation SRM 4990 C) was made from a crop of 1977 French beet molasses. In the early 1980s, a group of 12 laboratories measured the ratios of the two standards. The ratio of the activity of Oxalic acid II to 1 is 1.2933±0.001 (the weighted mean) (Mann, 1983). The isotopic ratio of HOx II is -17.8 per mille.

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

Background Detection

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

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

Conventional radiocarbon ages (BP)

A radiocarbon measurement termed a conventional radiocarbon age (or CRA) is obtained using a set of parameters outlined by Stuiver and Polach (1977), in the journal *Radiocarbon*. A time-independent level of ^{14}C activity for the past is assumed in the measurement of a CRA. The activity of this hypothetical level of ^{14}C activity is equal to the activity of the absolute international radiocarbon

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

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

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

A CRA embraces the following recommended conventions:

• a half-life of 5568 years;
• the use of Oxalic acid I or II as the modern radiocarbon standard;
• correction for sample isotopic fractionation (deltaC13) to a normalized or base value of -25.0 per mille relative to the ratio of ^{12}C/^{13}C in the carbonate standard VPDB (more on fractionation and deltaC13);
• the use of 1950 AD as 0 BP, ie all ^{14}C ages head back in time from 1950;
• the assumption that all ^{14}C reservoirs have remained constant through time.

Additional terms are sometimes requested to be or reported with, or in lieu of the standard Conventional Radiocarbon Age BP result from which all others are mathematically derived. These are the "Measured Radiocarbon Age BP", Percent Modern Carbon (pMC), Mean Biobased Result (expressed in %), Percent Mean Biogenic Carbon Content, Percent Biomass CO2, Fraction Modern Carbon (fmdn or fMC) as well as d14C, D14C, delta 14C, Δ14C and delta 13/12C (all of which are expressed in per mille notation (%) rather than per cent notation.)

d14C represents the per mille depletion in sample carbon 14 prior to isotopic fractionation correction and is measured by;

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

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

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

This value can then be used to calculate the CRA using the equation given above.
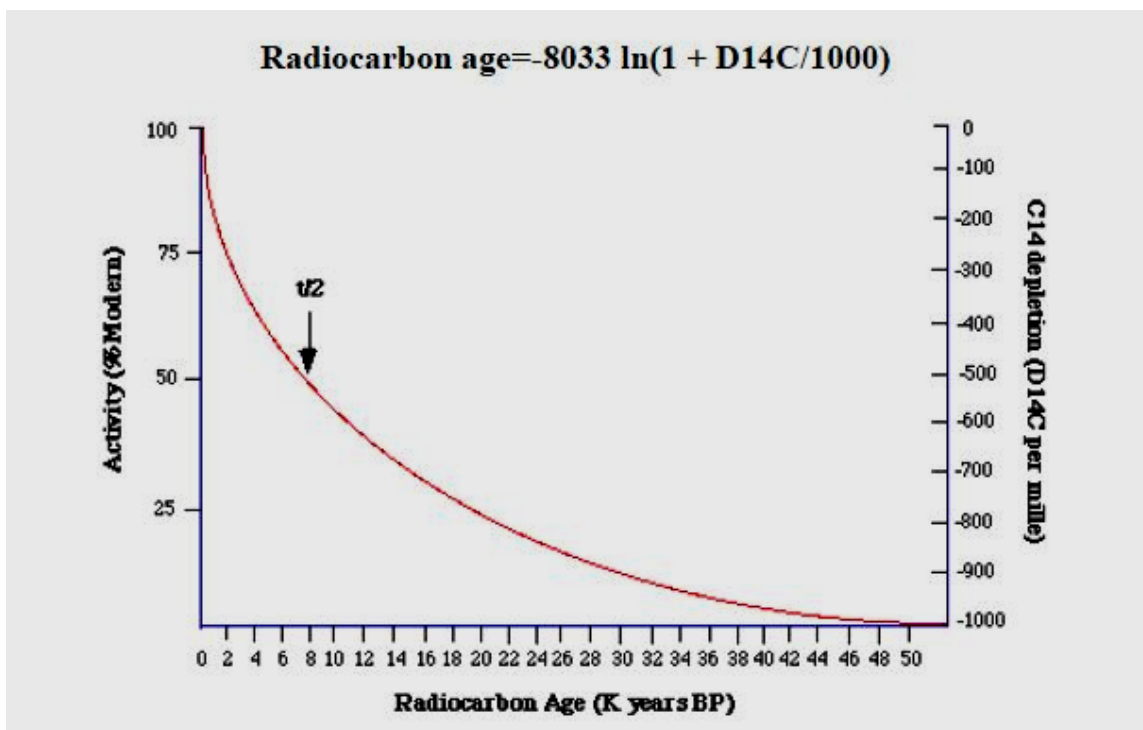
Radiocarbon age=-8033 ln(1 + D14C/1000)

Figure 1 - Decay curve for ^{12}C showing the activity at one half-life (t/2). The terms "%Modern" or "pMC" and D14C are shown related in this diagram along with the Radiocarbon age in years BP (Before 1950 AD).

Age reporting

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

%M=100 x Asn/Aabs

or

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

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

the influx of artificial radiocarbon into the atmosphere as a result of nuclear bomb testing, the 'age' calculation becomes a 'future' calculation.

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

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

Standard Error and Sources of Error

Statistical analysis is necessary in radiocarbon dating because the decay of ^{14}C although constant, is spontaneous. It is not possible to measure the entire radioactivity in a given sample, hence the need for some kind of statistical analysis of counted data. The distribution of counted ^{14}C decay events will, over time, yield a pattern. The pattern is termed a "normal distribution curve".

A normal or "Gaussian" distribution describes the symmetrical bell shaped cluster of events around the average or mean of the data. In a normal distribution, 2 out of 3, or 68% of the values or counts observed will fall within one standard deviation of the average of the data. At two standard deviations, 95% of the observed counts will fall within the range and at three standard deviations, 99% of the counts which comprise the normal distribution will fall within this region.

Each radiocarbon date is released as a conventional radiocarbon age with 'standard error'. This is the '±' value and by convention is ± 1 sigma. The standard error is based principally upon counting statistics, however other sources of error are possible and their effects are listed below:

Summary; The accuracy of radiocarbon dates (modified from Polach, H.A. 1976). Sources of Error	Effect upon Age Determination	Measures to minimize the error incurred
1. Precision of age determination	Statistical; Typically ±1%Modern or less	Big samples, longer count times, repeat sample assays
2. Inherent a. ^{14}C half-life	Libby half life 3% too low	Multiply CRA's by 1.03 if necessary
b. ^{12}C/^{13}C fractionation	Variable, up to	Stable isotope analyses

	450 yr for shell.	using Mass Spec.
c. ^{14}C Modern standard	Variable > 80 yr	International crosscheck of secondary standards.
d. Variation in past ^{14}C production rates	0-800 yr, beyond *ca*12 ka not determined	Tree ring calibration; otherwise interpret results in radiometric timescale.
e. Distribution of ^{14}C in nature	Surface ocean latitudinal dependence -400 to -750 yr. Deep ocean -1800 yr.	Interpretation of results.
f. Changes of ^{14}C concentration in the atmosphere.	Industrial effect *ca* -2.5% and atom bomb effect +160% in atmosphere	Interpretation of results
3. Contamination	Nil to 300 yr up to 15 ka; >20 ka possible beyond 25 ka.	Interpretation of results, analysis and dating of extracted pretreated fractions.
4. Biological age of material	<10 yr to>1000 yr	Identification of species of material in the case of wood and charcoal to short lived samples only.
5. Association of sample and event	Intermediate	Interpretation of results
6. Human	Intermediate	Care in field and laboratory
7. Interpretation of results	Intermediate	Care in interpretation, interdisciplinary approach and collaboration

Accuracy and Precision in Radiocarbon Dating

It is important to note the meaning of "accuracy" and "precision" in radiocarbon dating. Accuracy refers to the date being a 'true' estimate of the age of a sample within the range of the statistical limits or ± value of the date. Thus, for the sake of argument, if we were radiocarbon dating a sample of human bones from an individual who we knew died in 1066 AD and obtained a date of 1040±40 AD, we would have dated the event of his death accurately. If however the date obtained were 1000±15 AD, we would be inaccurate.

In terms of precision, however, the former is imprecise in comparison to the latter because of the larger stated error value. As such it can be seen that the date of 1000±15 AD while being highly precise is, in this instance, inaccurate.

Reservoir Effects

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

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

One of the most commonly referenced reservoir effects concerns the ocean. The average difference between a radiocarbon date of a terrestrial sample such as a tree, and a shell from the marine environment is about 400 radiocarbon years (see Stuiver and Braziunas, 1993). This apparent age of oceanic water is caused both by the delay in exchange rates between atmospheric CO_2 and ocean bicarbonate, and the dilution effect caused by the mixing of surface waters with upwelled deep waters which are very old (Mangerud 1972). A reservoir correction must therefore be made to any conventional shell dates to account for this difference. Human bone may be a problematic medium for dating in some instances due to human consumption of fish, whose ^{14}C label will reflect the ocean reservoir. In such a case, it is very difficult to ascertain the precise reservoir difference and hence apply a correction to the measured radiocarbon age.

Spurious radiocarbon dates caused by volcanic emanations of radiocarbon-depleted CO_2 probably also come under the category of reservoir corrections. Plants which grow in the vicinity of active volcanic fumaroles will yield a

radiocarbon age which is too old. Bruns *et al.* (1980) measured the radioactivity of modern plants growing near hot springs heated by volcanic rocks in western Germany and demonstrated a deficiency in radiocarbon of up to 1500 years through comparison with modern atmospheric radiocarbon levels. Similarly, this effect has been noted for plants in the bay of Palaea Kameni near the prehistoric site of Akrotiri, which was buried by the eruption of the Thera volcano over 3500 years ago (see Weninger, 1989). The effect has been suggested as providing dates in error for the eruption of Thera which has been linked to the demise of the Minoan civilization in the Aegean. One modern plant growing near the emanations had an apparent age of 1390 yr. The volcanic effect has a limited distance however. Bruns *et al.* (1980) found that at 200 m away from the source, plants yielded an age in agreement with that expected. They suggested that the influence of depleted CO_2 declined rapidly with increasing distance from the source. Radiocarbon discrepancies due to volcanic CO_2 emissions are a popular source of ammunition for fundamentalist viewpoints keen to present evidence to show that the radiocarbon method is somehow fundamentally flawed.

Suess or Industrial Effect

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

Atom Bomb Effect

Since about 1955, thermonuclear tests have added considerably to the ^{14}C atmospheric reservoir. This ^{14}C is 'artificial' or 'bomb' ^{14}C, produced because nuclear bombs produce a huge thermal neutron flux. The effect of this has been to almost double the amount of ^{14}C activity in terrestrial carbon bearing materials (Taylor, 1987).

De Vries (1958) was the first person to identify this 'Atom Bomb' effect. In the northern hemisphere the amount of artificial carbon in the atmosphere reached a peak in 1963 (in the southern hemisphere around 1965) at about 100% above normal levels. Since that time the amount has declined owing to exchange and

dispersal of ^{14}C into the earth's carbon cycle system. The presence of bomb carbon in the earth's biosphere has enabled it to be used as a tracer to investigate the mechanics of carbon mixing and exchange processes.