

Radiocarbon

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DISCUSSION

REPORTING OF ^{14}C DATA

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INTRODUCTION

Count rates, representing the rate of ^{14}C decay, are the basic data obtained in a ^{14}C laboratory. The conversion of this information into an age or geochemical parameters appears a simple matter at first. However, the path between counting and suitable ^{14}C data reporting (table 1) causes headaches to many. Minor deflections in pathway, depending on personal interpretations, are possible and give end results that are not always useful for inter-laboratory comparisons. This discussion is an attempt to identify some of these problems and to recommend certain procedures by which reporting ambiguities can be avoided.

I. RADIOCARBON DATING STANDARD

It is widely recognized that all laboratories should report their results either directly related to NBS oxalic acid or indirectly by using a sub-standard which is directly related to the NBS oxalic acid (Olsson, 1970). The internationally accepted radiocarbon dating reference value is 95 percent of the activity, *in AD 1950*, of the NBS oxalic acid normalized to $\delta^{13}\text{C} = -19$ per mil with respect to (wrt) PDB (Olsson, 1970; R, 1961, v 3). Although the ^{14}C activity of oxalic acid is changing with time, the activity of the international standard defined above does not change. It will be named the *absolute international standard activity* (AISA) in further discussion.

Most laboratories, in their calculations, use an activity value A_{ON} that is 95 percent of the measured net oxalic acid activity (count rate) A_{Ox} today, normalized for ^{13}C fractionation according to

$$A_{\text{ON}} = 0.95A_{\text{Ox}} \left(1 - \frac{2(19 + \delta^{13}\text{C})}{1000} \right).$$

Measurements of $\delta^{13}\text{C}$ are relative to the PDB standard. The activity A_{ON} depends on the year of measurement (y) and has to be corrected for decay between 1950 and year (y) of actual counting date. The *absolute international standard activity* is given by

$$A_{\text{abs}} = A_{\text{ON}} e^{\lambda(y-1950)} \quad \text{where } \lambda = \frac{1}{8267} \text{ yr}^{-1},$$

eg, the measured A_{ON} is today about 0.3 percent lower than A_{abs} .

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2. ISOTOPIC FRACTIONATION CORRECTION

It is strongly desirable that all workers report $\delta^{13}\text{C}$ values, either measured or estimated relative to PDB. By convention, the ^{13}C isotopic fractionation in all samples, irrespective of environment, is taken into account by normalizing to -25 per mil wrt PDB, the postulated mean value of terrestrial wood. The normalized sample activity A_{SN} relates to the measured sample activity A_{S} as follows:

$$A_{\text{SN}} = A_{\text{S}} \left(1 - \frac{2(25 + \delta^{13}\text{C})}{1000} \right),$$

where $\delta^{13}\text{C}$ is measured or estimated in per mil wrt PDB. This equation is a generally used approximation of the more precise $A_{\text{SN}} = A_{\text{S}} 0.975^2 / (1 + \delta^{13}\text{C}/1000)^2$ (Stuiver and Robinson, 1974).

3. RADIOCARBON AGE CALCULATION

The radiometric age of a sample is calculated by assuming a time-independent atmospheric ^{14}C level in all past times. The specific activity (activity per gram C) of this hypothetical atmospheric carbon level, after normalizing to -25 per mil for ^{13}C , is by definition equal to the specific activity of the absolute international standard A_{abs} . For a Libby half-life of 5568 yrs, and when measured in 1950, the age (t) of a sample before 1950 AD is therefore given by

$$t = -8033 \ln \frac{A_{\text{SN}} (\text{in } 1950)}{A_{\text{ON}} (\text{in } 1950)}$$

The actual measurements of sample and oxalic acid activities were, of course, not made in 1950. The measured ratio $A_{\text{SN}}/A_{\text{ON}}$, however, does not change with time. It stays equal to the 1950 ratio because both sample and oxalic acid lose their ^{14}C at the same rate. Thus the calculated age (t), given by $t = -8033 \ln A_{\text{SN}}/A_{\text{ON}}$, is a fixed number independent of the year of measurement. It always implies an age prior to AD 1950 (ie, AD 1950 equals 0 yrs BP).

Ages (yrs) calculated in the above manner ($t = -8033 \ln A_{\text{SN}}/A_{\text{ON}}$) are called *conventional radiocarbon ages* (years BP). This term implies:

- A. the use of the 5568 yr half-life (mean life 8033 y),
- B. the assumption of constancy of ^{14}C atmospheric level during the past,
- C. the use of oxalic acid (direct or indirect) as a standard,
- D. isotopic fractionation normalization of all sample activities to the base of $\delta^{13}\text{C} = -25$ per mil (relative to the $^{13}\text{C}/^{12}\text{C}$ ratio of PDB),
- E. the year 1950 is automatically the base year, with ages given in years BP (ie, present is AD 1950).

4. RESERVOIR EFFECT

The calibration of the oxalic acid standard (in 1958) was based on the age corrected ^{14}C activity of AD 1890 tree-rings in equilibrium with 1890 atmospheric CO_2 . When reservoirs differ in specific ^{14}C content

from the atmosphere, an age adjustment is needed. A *conventional radiocarbon age*, as defined in section 3, does take into account ^{13}C fractionation but not differences in ^{14}C specific activity of reservoirs which arise from effects other than isotopic fractionation. It is recommended that a *conventional radiocarbon age* is always reported without adjustment; a *reservoir corrected age BP* should be given separately. The adopted reservoir corrections should be given (and referenced) with the sample description.

The above procedure necessitates a reservoir correction, for example, for marine shell ages because the *conventional radiocarbon age* takes only ^{13}C fractionation into account. The corrections for ^{13}C fractionation and reservoir ^{14}C deficiency cancel each other more or less for shells from non-polar regions and many laboratories have adopted the convenient practice of forgetting — and not mentioning — the two corrections. The recommended procedure should eliminate possible ambiguity: all *conventional radiocarbon ages* are to be ^{13}C corrected, and estimates of reservoir corrections, when needed, are to be given separately.

5. STATISTICAL UNCERTAINTY OF AGE DETERMINATION

The *conventional ^{14}C age* is accompanied by a standard error, based on the number of accumulated counts of the sample, oxalic acid, and background, plus additional errors caused by inaccuracies in voltage, pressure, temperature, dilution, et cetera. The standard error should include the error in ^{13}C ratios. For measured $^{13}\text{C}/^{12}\text{C}$ ratios the contribution to the standard error is small, but it may be significant for estimated isotope ratios. The spread in isotope ratios, and the influence on standard errors when $\delta^{13}\text{C}$ ratios are estimated, are given in figure 1 (reproduced by permission from Polach, 1976). The error in the conventional ^{14}C half-life should NOT be included in the standard error. The statistical uncertainty of the age determination, the standard error of the *conventional ^{14}C age*, is given as \pm one *standard deviation*.

6. DEPLETION OR ENRICHMENT WRT STANDARD

To give the relative differences between either uncorrected or ^{13}C corrected sample activity (count rate) and measured oxalic acid activity, one can define

$$d^{14}\text{C} = \left(\frac{A_S - A_{ON}}{A_{ON}} \right) 1000 \text{ per mil} = \left(\frac{A_S}{A_{ON}} - 1 \right) 1000 \text{ per mil}$$

and

$$D^{14}\text{C} = \left(\frac{A_{SN} - A_{ON}}{A_{ON}} \right) 1000 \text{ per mil} = \left(\frac{A_{SN}}{A_{ON}} - 1 \right) 1000 \text{ per mil}.$$

Thus the *conventional radiocarbon age*, as defined in section 3, is given by

$$t = -8033 \ln \left(1 + \frac{D^{14}\text{C}}{1000} \right).$$

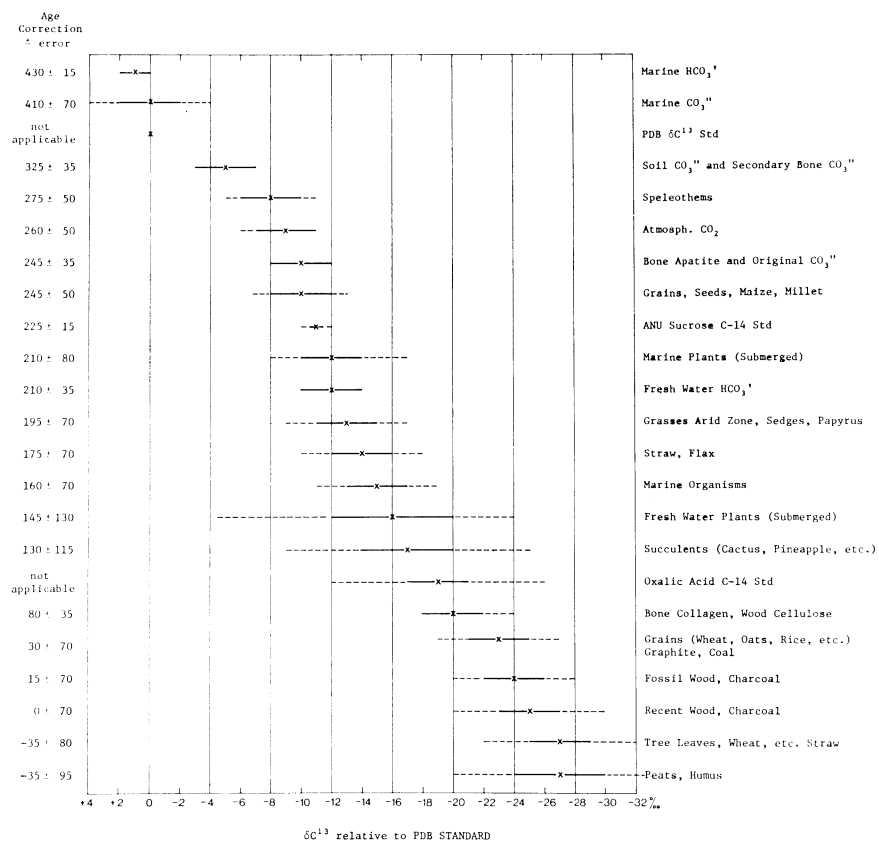


Fig. 1. C variation in nature. The suggested mean values, to be used when estimating $\delta^{13}\text{C}$ of samples are given as (x) and the suggested appropriate error of estimation (never less than $\pm 2\%$) is given by solid lines. The variations in ^{14}C standard are due to laboratory fractionation only. The large range in $\delta^{13}\text{C}$ of some datable materials does not always allow to apply effectively a correction based on an estimate of the mean value. Note that the \pm error of the age correction due to spread of $\delta^{13}\text{C}$ values is often of the same order of magnitude or larger than the common statistical uncertainty (\pm error) of the age determination. When a measured $\delta^{13}\text{C}$ correction is not applied, the AGE CORRECTION is to be added (arithmetically) to the isotopic fractionation uncorrected radiocarbon age determination and the error of estimation of mean $\delta^{13}\text{C}$ value (due to their spread in nature) must be correctly combined with the statistical uncertainty of the age determination. The isotopic fractionation corrected age is therefore the sum of the radiocarbon age and its error ($A \pm a$) and the isotopic fraction age correction and its error ($B \pm b$). The corrected age ($A \pm a$) + ($B \pm b$) equals $(A + B) \pm (a^2 + b^2)^{1/2}$. This correction, within limits given by solid lines, is necessary when valid comparison of reported ages of a variety of organic materials is sought. (After Polach, 1976, reproduced by permission of the editor).

As discussed, the measured activity ratios A_S/A_{ON} and A_{SN}/A_{ON} do not change with time because both sample and oxalic acid lose ^{14}C at the same rate. As a result $d^{14}\text{C}$ and $D^{14}\text{C}$ values are independent of the year of measurement.

7. PERCENT MODERN

Percent Modern is seldom used in chronological studies, and it is now recommended that in such studies only the $\delta^{13}\text{C}$ ratio and the *conventional ^{14}C age BP* be given. The 8th International Conference on Radiocarbon Dating (Proceedings, 1972) accepted the replacement of $D^{14}\text{C}$ per mil by *percent Modern*, equated to the activity ratio $A_{SN}/A_{ON} \times 100$ percent. We consider this term superfluous. However, for geochemical and ^{14}C equilibria (distribution of ^{14}C in nature) studies, the new term "absolute" *percent Modern* (pM) is desirable. It is defined as follows

$$\text{pM} = \frac{A_{SN}}{A_{\text{abs}}} \times 100 \text{ percent} = \frac{A_{SN}}{A_{ON}e^{\lambda(y-1950)}} \times 100 \text{ percent},$$

where (y) is the year of Oxalic measurement, and $\lambda = 1/8267 \text{ yr}^{-1}$ is based on the 5730 yr half-life. When the years of collection and measurement are not identical, A_{SN} has to be corrected for the decay that took place between year of collection and measurement (table I).

The measured and $\delta^{13}\text{C}$ -normalized oxalic acid activity A_{ON} declines with age, and if the reservoir activity has remained constant, then the measured activity ratio A_{SN}/A_{ON} is dependent upon the year of measurement of Oxalic acid. The "absolute" *percent Modern* makes this ratio constant and meaningful for many specialized studies.

When relating a *conventional radiocarbon age* to "absolute" *percent Modern* (pM) as defined above, the year of measurement (y) becomes important. Thus,

$$t + \frac{y - 1950}{1.03} = -8033 \ln \frac{\text{pM}}{100} .$$

8. AGE CORRECTION, $\delta^{14}\text{C}$, Δ , AND $\Delta^{14}\text{C}$

When comparing sample ^{14}C activities with oxalic acid activity, an age correction may be needed. For instance, for a tree-ring grown in year (x) and measured during year (y), the age corrected activity is $A_{\text{ge}}e^{\lambda(y-x)}$. The age correction is based on the 5730 yr half-life ($\lambda = 1/8267 \text{ yr}^{-1}$). In the first proposed use of $\delta^{14}\text{C}$ and its associated $\Delta^{14}\text{C}$ (Broecker and Olson, 1959), it was also clearly stated that the comparison of sample activity should be with the activity of an age corrected international standard. As the actual intercalibration measurements of wood/oxalic were made in 1958, it was in the first instance suggested by Broecker and Olson (1959) that the oxalic activity should be corrected back to AD 1958. Since then it has become the custom to use the year 1950 as the base year for all radiocarbon measurements (Godwin, 1962). The age correction of oxalic acid standard has been made to the base year of 1950 for the calculation of the activity of the *absolute international standard* (Olsson, 1970), referred to in section 1.

TABLE 1
Calculation procedure for ^{14}C ages and geochemical parameters

	SAMPLE	OXALIC ACID
NET ACTIVITY; NORMALIZED FOR COUNTING VOLUME, MASS CHANGE, DILUTION, IMPURETIES, ETC. ACTIVITY IN COUNTS PER MINUTE	A_S	A_{OX}
NORMALIZATION FOR ISOTOPE FRACTIONATION. ALL $\delta^{13}\text{C}$ VALUES WITH REGARD TO PDB	$A_{SN} = A_S \left[1 - \frac{2(\delta^{13}\text{C}_S + \delta^{13}\text{C}_O)}{1000} \right]$	$A_{ON} = .95A_{OX} \left[1 - \frac{2(\delta^{13}\text{C}_O + \delta^{13}\text{C}_O)}{1000} \right]$
ABSOLUTE INTERNATIONAL STANDARD ACTIVITY (CORRECTED FOR DECAY SINCE 1950)		$A_{ABS} = A_{ON} e^{\lambda(y-1950)}$
x = YEAR OF GROWTH y = YEAR OF MEASUREMENT	λ in Table always $\frac{1}{8267} \text{yr}^{-1}$	
	GEOCHRONOLOGICAL SAMPLES	GEOCHEMICAL SAMPLES WITHOUT AGE CORRECTION
PER MIL DEPLETION OR ENRICHMENT WITH REGARD TO STANDARD	$d^{14}\text{C} = \left[\frac{A_S}{A_{ON}} - 1 \right] 1000 \text{ ‰}$	$\delta^{14}\text{C} = \left[\frac{A_S}{A_{ABS}} - 1 \right] 1000 \text{ ‰}$ *
Equivalent equation		$\delta^{14}\text{C} = \left[\frac{A_S e^{\lambda(y-x)}}{A_{ABS}} - 1 \right] 1000 \text{ ‰}$
PER MIL DEPLETION OR ENRICHMENT RELATIVE TO STANDARD NORMALIZED FOR ISOTOPE FRACTIONATION	$D^{14}\text{C} = \left[\frac{A_{SN}}{A_{ON}} - 1 \right] 1000 \text{ ‰}$	$\Delta = \left[\frac{A_{SN}}{A_{ABS}} - 1 \right] 1000 \text{ ‰}$ *
Equivalent equation		$\Delta = \left[\frac{A_{SN} e^{\lambda(1950-x)}}{A_{ABS}} - 1 \right] 1000 \text{ ‰}$
APPROXIMATE RELATIONSHIP	$D^{14}\text{C} = d^{14}\text{C} - 2(\delta^{13}\text{C}_S + 25) \left(1 + \frac{\delta^{14}\text{C}}{1000} \right)$	$\Delta^{14}\text{C} = \delta^{14}\text{C} - 2(\delta^{13}\text{C}_O + 25) \left(1 + \frac{\delta^{14}\text{C}}{1000} \right)$
Conventional radiocarbon age BP, based on 5568 yr. half life $\lambda = 8033 \text{ yr}^{-1}$	$t = -8033 \ln \frac{A_{SN}}{A_{ON}}$	
ALWAYS REPORT	$\delta^{13}\text{C}$ and conventional radiocarbon age	$\Delta^{14}\text{C}$, $\delta^{14}\text{C}$ and $\delta^{13}\text{C}$
OPTIONAL	$d^{14}\text{C}$ and $D^{14}\text{C}$	$P = \frac{A_{SN}}{A_{ABS}} 100 \text{ ‰}$ *

When year of collection z differs from year of measurement y , either A_S or A_{SN} should be replaced by respectively $A_S e^{\lambda(y-z)}$, $A_{SN} e^{\lambda(y-z)}$, or A_S and A_{SN} kept unchanged but oxalic acid corrected for decay between year of collection and 1950 only. This procedure is applicable only when marked in the table by an asterisk.

Thus $\delta^{14}\text{C}$ is here defined as the relative difference between the *absolute international standard* and sample activity corrected for age, but not for $\delta^{13}\text{C}$.

$$\delta^{14}\text{C} = \left(\frac{A_s e^{\lambda(y-x)}}{A_{\text{abs}}} - 1 \right) 1000 \text{ per mil},$$

where (y) is the year of measurement and (x) the year of growth.

The $\delta^{14}\text{C}$ term has also often been used in instances where sample age correction is not possible. According to the 8th International Radiocarbon Conference in Wellington, New Zealand, the $\delta^{14}\text{C}$ (and its associated Δ term) should be used only when samples have been age corrected (Proc., 1972). When age correction is impossible, one can use $d^{14}\text{C}$ and $D^{14}\text{C}$, as defined in the previous section. However, $\delta^{14}\text{C}$, Δ , and $\Delta^{14}\text{C}$ values have been and are used extensively in oceanography where age corrections are not possible. Both age-corrected and non-age corrected $\delta^{14}\text{C}$, Δ , and $\Delta^{14}\text{C}$ values seem to be with us for an indefinite period, and therefore the radiocarbon dater must clearly define their meaning each time he uses these terms. Age corrected oxalic acid activity (the *absolute international standard activity* A_{abs}) should always be used when calculating the $\delta^{14}\text{C}$, $\Delta^{14}\text{C}$ values. For oceanographic samples

$$\delta^{14}\text{C} = \left(\frac{A_s}{A_{\text{abs}}} - 1 \right) 1000.$$

When the years of collection and measurement are not identical, A_s has to be corrected for the decay that took place between year of collection and measurement (table I).

After normalization for $\delta^{13}\text{C}$, the relative difference between age corrected sample activity $A_{\text{SN}} e^{\lambda(y-x)}$ and the absolute standard is

$$\begin{aligned} \Delta &= \left(\frac{A_{\text{SN}} e^{\lambda(y-x)}}{A_{\text{abs}}} - 1 \right) 1000 \text{ per mil} \\ &= \left(\frac{A_{\text{SN}} e^{\lambda(1950-x)}}{A_{\text{ON}}} - 1 \right) 1000 \text{ per mil}. \end{aligned}$$

For oceanographic samples,

$$\Delta^{14}\text{C} = \left(\frac{A_{\text{SN}}}{A_{\text{abs}}} - 1 \right) 1000 \text{ per mil}.$$

$D^{14}\text{C}$ and $d^{14}\text{C}$, as well as $\Delta^{14}\text{C}$ and $\delta^{14}\text{C}$, can be tied to each other through the following expressions:

$$D^{14}\text{C} = d^{14}\text{C} - 2(\delta^{13}\text{C} + 25) \left(1 + \frac{d^{14}\text{C}}{1000} \right) \quad (1)$$

and

$$\Delta^{14}\text{C} = \delta^{14}\text{C} - 2(\delta^{13}\text{C} + 25) \left(1 + \frac{\delta^{14}\text{C}}{1000} \right). \quad (2)$$

These are the expressions commonly used for the calculation of $D^{14}C$ and $\Delta^{14}C$ values. They are, however, only approximations derived from a combination of the equations in sections 6 and 8. The precise relationship

$$\Delta^{14}C = 1000 \left(\left(1 + \frac{\delta^{14}C}{1000} \right) \frac{0.975^2}{\left(1 + \frac{\delta^{13}C}{1000} \right)^2} - 1 \right)$$

is given in Stuiver and Robinson (1974). As it has been customary so far to use relationships (1) and (2) in making corrections for isotopic fractionation, their continued use is recommended.

9. REPORTING OF AGES CLOSE TO MODERN

Chronological samples can be reported as *MODERN* when the reservoir-corrected, *conventional radiocarbon* age is less than 200 yrs; *> MODERN* when A_{SN} is greater than A_{ON} . However, in these instances, $D^{14}C$ must also be reported in addition to the required $\delta^{13}C$ value.

10. REPORTING OF AGES CLOSE TO BACKGROUND

In order to retain maximum possible information when reporting ages close to *background*, the following procedures are recommended:

When sample activity A_{SN} is less than twice the standard deviation σ of A_{SN} the resulting age should be reported as " $>x$," where the minimum age x is the conventional ^{14}C age calculated for an $A_{SN} + 2\sigma$ sample activity. $A_{SN} = 0$ has to be substituted for negative A_{SN} values. When the sample activity differs less than one σ from the background, the statement, "Sample activity not distinguishable from background," should be given. When measured sample activity is between 1 and 2σ , an "apparent" age can be added.

$D^{14}C$ values should also be reported in all the above cases because their error ($\pm sD^{14}C$) is normally distributed round the value of $D^{14}C$, whilst the \pm error of the *AGE* is log-normally distributed round the age BP , making it inappropriate for error weighted (pooled mean) calculations (Polach, 1969).

11. ROUNDING OFF

The magnitude of the standard error determines the rounding off of a conventional ^{14}C age. It is standard practice in the physical sciences to give one more digit than can be accurately accounted for. In reporting the standard error, the first two digits should be retained. For instance, 8234 ± 256 and $42,786 \pm 2322$ are rounded, respectively, to 8230 ± 260 and $42,800 \pm 2300$. When the standard error is less than 100 yrs, rounding off to the nearest multiple of ten is recommended between 50 and 100 yrs, and rounding off to the nearest multiple of five below 50 yrs.

RECOMMENDATIONS

For chronological studies, *ie*, geological, archaeological, et cetera samples, where the measurement of age is the most important aspect, the following quantities based on the 5568 yr half-life ($\lambda = 1/8033 \text{ yr}^{-1}$) are critical and should be reported:

- A. $\delta^{13}\text{C}$ ratio — actual measured or estimated value wrt PDB.
- B. The *conventional radiocarbon age* BP , as defined in section 3, with its \pm *error* expressed as \pm one standard deviation.
- C. The estimate of “reservoir” correction (sec. 4) when a *reservoir corrected age* is given in addition to the *conventional radiocarbon age*.
- D. An optional parameter for reporting is D^{14}C : The per mil *depletion* or *enrichment* wrt 0.95 Oxalic, (normalized for isotopic fractionation of both Oxalic and sample).

For geochemical samples, dendrochronological samples, reservoir equilibria, and diffusion models, the following quantities, with age corrections based on 5730 yr half-life ($\lambda = 1/8267 \text{ yr}^{-1}$) are critical and should be reported:

- A. $\delta^{13}\text{C}$ ratio — actual measured or estimated value wrt PDB,
- B. *Percent modern*, as defined in section 7, (if applicable) or
- C. $\delta^{14}\text{C}$ and $\Delta^{14}\text{C}$ or Δ (depending on the user's past preferences), as given in sections 8 and 9, with clear indication if an age correction has been applied to any of these terms.

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