4.7. Carbon Contamination and Fractionation
Carbon Contamination

Because the ratio $^{14}\text{C}/^{12}\text{C}$ in a sample decreases with increasing age - due to the continuous decay of $^{14}\text{C}$ - a small added impurity of modern natural carbon causes a disproportionately large shift in age.

$$\frac{^{14}\text{C}}{^{12}\text{C}}(t) = \frac{^{14}\text{C}}{^{12}\text{C}}(t_0) \cdot e^{-\lambda (t-t_0)}$$

E.g. a 50,000 year old sample will appear as only ~35,000 year old! It should have shown $^{14}\text{C}/^{12}\text{C}$ ratio of $3 \cdot 10^{-15}$ but 1% modern impurity increases it to $1.2 \cdot 10^{-14}$. This corresponds to the younger age.
Mathematical Exercise

A fraction $x$ of $^{14}$C contamination, that occurred at time $t_{\text{cont}}$, changes the real age $t_{\text{real}}$ to an apparent observed age $t_{\text{obs}}$.

\[
\frac{N(t_{\text{obs}})}{N_0} = (1-x) \cdot \frac{N(t_{\text{real}})}{N_0} + x \cdot \frac{N(t_{\text{cont}})}{N_0}
\]

\[
e^{-\lambda \cdot t_{\text{obs}}} = \left(e^{-\lambda \cdot t_{\text{real}}} + x \cdot e^{-\lambda \cdot t_{\text{cont}}} - x \cdot e^{-\lambda \cdot t_{\text{real}}} \right)
\]

\[
x = \frac{e^{-\lambda \cdot t_{\text{obs}}} - e^{-\lambda \cdot t_{\text{real}}}}{e^{-\lambda \cdot t_{\text{cont}}} - e^{-\lambda \cdot t_{\text{real}}}}
\]

For modern contamination $t_{\text{cont}} = 0$

\[
x = \frac{e^{-\lambda \cdot t_{\text{obs}}} - e^{-\lambda \cdot t_{\text{real}}}}{1 - e^{-\lambda \cdot t_{\text{real}}}}
\]
Contamination in the Shroud

Crucifixion 36 AD ⇒ $t_{\text{real}} = 1952$ y;
Measured age: $t_{\text{obs}} = 690$ y

$T_{1/2} = 5730$ y; $\lambda = 1.21 \cdot 10^{-4}$

$$x = \frac{e^{-\lambda t_{\text{obs}}} - e^{-\lambda t_{\text{real}}}}{e^{-\lambda t_{\text{cont}}} - e^{-\lambda t_{\text{real}}}}$$

For contamination in fire at 1532 AD ⇒ $t_{\text{cont}} = 456$ y
$x = 0.83$

For modern day contamination ⇒ $t_{\text{cont}} = 0$
$x = 0.62$

Amount of modern carbon must be nearly doubled!
Deviation in Age Determination

Determine the deviation in time $\Delta t$, if at time $t_{cont}$ a fraction $x$ contamination of $^{14}$C occurred!

\[ e^{-\lambda \cdot t_{obs}} = x \cdot e^{-\lambda \cdot t_{cont}} + (1-x) \cdot e^{-\lambda \cdot t_{real}} \]

\[ \frac{e^{-\lambda \cdot t_{obs}}}{e^{-\lambda \cdot t_{real}}} = e^{-\lambda \cdot (t_{obs} - t_{real})} = x \cdot \frac{e^{-\lambda \cdot t_{cont}}}{e^{-\lambda \cdot t_{real}}} + 1 - x = x \cdot e^{-\lambda \cdot (t_{cont} - t_{real})} + 1 - x \]

\[ \Delta t = t_{real} - t_{obs} = \frac{1}{\lambda} \cdot \ln \left( x \cdot \frac{e^{-\lambda \cdot t_{cont}}}{e^{-\lambda \cdot t_{real}}} + 1 - x \right) \]

For modern contamination $t_{cont}=0$

\[ \Delta t = t_{real} - t_{obs} = \frac{1}{\lambda} \cdot \ln \left( x \cdot e^{\lambda \cdot t_{real}} + 1 - x \right) \]
Deviation from real Age by Contamination

\[ t_{\text{real}} = \Delta t + t_{\text{obs}} = \frac{1}{\lambda} \ln(x \cdot e^{\lambda \cdot t_{\text{real}}} + 1 - x) + t_{\text{obs}} \]

Observed age 690 years

Recent contamination
Turin fire contamination

Considerable contamination necessary to reach “desired” age
long term deviation from real age

\[ \Delta t = t_{\text{real}} - t_{\text{obs}} = \frac{1}{\lambda} \ln \left( x \cdot e^{\lambda t_{\text{real}}} + 1 - x \right) \]

with 1% contamination
real age: 7000 y
deviation: ~100 y
apparent age: 6900 y

real age: 34000 y
deviation: ~4000 y
apparent age: 30000 y

real age: 50000 y
deviation: ~15000 y
apparent age: 35000 y
a 16000 y old sample contaminated with 3% of modern material will appear ~1400 y too young.
To be original, the shroud needs a >50% contamination with modern material.
Contamination with old Material

The deviation between real age and observed age $\Delta t$ can be calculated in terms of time difference between the age of the sample $t_{real}$ and the age $t_{cont}$ of the contaminant $^{14}$C, $t_{real} - t_{cont}$.

\[
e^{-\lambda t_{obs}} = x \cdot e^{-\lambda t_{cont}} + (1 - x) \cdot e^{-\lambda t_{real}}
\]

\[
e^{-\lambda (t_{obs} - t_{real})} = x \cdot e^{-\lambda (t_{cont} - t_{real})} + 1 - x
\]

\[
\Delta t = t_{real} - t_{obs} = \frac{1}{\lambda} \cdot \ln \left( x \cdot e^{\lambda (t_{real} - t_{cont})} + 1 - x \right)
\]
contamination of sample with "dead carbon" (fossil fuel etc) will cause an increase in the apparent age of sample material (see dead rabbit example) because the sample shows less $^{14}\text{C}/^{12}\text{C}$ as it should, simulating an older age for the sample.

e.g. 5000 y old sample contaminated with 20% of 16000 y old material will yield a date which is $\sim$1300 y too old.
Fractionation

Natural chemical or physical processes can fractionate the carbon isotopes during the up-take and alter the $^{13}\text{C}/^{12}\text{C}$ and also the $^{14}\text{C}/^{12}\text{C}$ isotopic ratio. This requires some correction.

e.g. photosynthesis enriches lighter isotopes → the carbon in a plant has a relatively higher $^{12}\text{C}/^{14}\text{C}$ ratio than the atmosphere.

Fractionation is expressed in terms of $\delta^{13}\text{C}$ that is a measure of the deviation of the isotopic ratio $^{13}\text{C}/^{12}\text{C}$ from a standard material (e.g. PDB belemnitella americana or wood).

The typical $\delta^{13}\text{C}$ varies between +2‰ to -27‰ and needs to be determined for the material to be dated. Additional fractionation may occur during the chemical preparation of the sample.
Fractionation effects

The fractionation $\delta^{13}C$ is defined from $^{13}C/^{12}C$ isotopic ratios for the sample (sm) and the standard (st) as:

$$
\delta^{13}C \equiv 1000 \cdot \left[ \frac{\left( \frac{^{13}C}{^{12}C} \right)_{sm}}{\left( \frac{^{13}C}{^{12}C} \right)_{st}} - 1 \right]
$$

A negative value $\delta^{13}C$ means that the sample is isotopically lighter than the standard probe. This fractionation effect also influences $^{14}C$ and makes sample appear older. A less negative value $\delta^{13}C$ means that the sample is also enriched in $^{14}C$. This makes sample appear younger.

For these corrections is assumed that the $^{14}C/^{13}C$ ratio scales with the $^{13}C/^{12}C$ ratio!
Fractionation standard

Fractionation of $^{14}\text{C}$ is defined in terms of the one for $^{13}\text{C}$:

$$\delta^{13}\text{C} \equiv 1000 \cdot \left[ \frac{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{sm}} - \frac{^{13}\text{C}}{^{12}\text{C}}_{\text{st}}}{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{st}}} \right]$$

$$\delta^{14}\text{C} = 2 \cdot \delta^{13}\text{C}$$

often calculated relative to a standard value $\delta^{13}\text{C}_{\text{wood}} = -25\%$
Fractionation corrections

Corrections can be made for fractionation effects by first assessing the specific $^{13}\text{C}$ content of the sample because the $^{14}\text{C}$ fractionation is known to be twice that of $^{13}\text{C}$. This yields correction formula:

$$\frac{^{14}\text{C}}{^{12}\text{C}}|_{\text{corr}} = \frac{^{14}\text{C}}{^{12}\text{C}}|_{\text{uncorr}} \cdot \left(1 - \frac{2 \cdot (25 + \delta^{13}\text{C})}{1000}\right)$$

Example: the material has $\delta^{13}\text{C} = -12 \%$
(since isotopically heavier than wood standard $\delta^{13}\text{C}_{\text{wood}} = -25 \%$, it will appear younger than it is.)

$^{14}\text{C}/^{12}\text{C}|_{\text{uncorr}} = 5.00 \cdot 10^{-13}$
this gives:

$^{14}\text{C}/^{12}\text{C}|_{\text{corr}} = 4.87 \cdot 10^{-13}$
Age correction

sample has δ^{13}C = -12 ‰ and appears younger:

\[ t_{uncorr} = \frac{1}{\lambda} \cdot \ln \left( \frac{(^{14}C/^{12}C)_{org}}{(^{14}C/^{12}C)_{uncorr}} \right) = 8266.64 \cdot \ln \left( \frac{1.3 \cdot 10^{-12}}{5.0 \cdot 10^{-13}} \right) = 7898.86 \text{ y} \]

\[ t_{corr} = \frac{1}{\lambda} \cdot \ln \left( \frac{(^{14}C/^{12}C)_{org}}{(^{14}C/^{12}C)_{corr}} \right) = 8266.64 \cdot \ln \left( \frac{1.3 \cdot 10^{-12}}{4.87 \cdot 10^{-13}} \right) = 8116.64 \text{ y} \]

\[ t_{corr} - t_{uncorr} = 218 \text{ y} \]
Approximate formula

The age correction can be approximated by a simple empirically derived formula for material with a certain fractionation of $\delta^{13}C$ in units $‰$.

$$t_{corr} - t_{uncorr} \approx 16 \cdot (\delta^{13}C + 25) \text{ [y]}$$

Previous example $\delta^{13}C = -12 \text{ }‰$

$$t_{corr} - t_{uncorr} \approx 16(-12 + 25) = 208 \text{ y}$$

agreement within statistical uncertainties!
Fractionation in the Shroud

\[ \frac{^{14}C}{^{12}C}_{\text{corr}} = \frac{^{14}C}{^{12}C}_{\text{uncorr}} \cdot \left(1 - \frac{2 \cdot (25 + \delta^{13}C)}{1000}\right) \]

The observed \(^{14}C/^{12}C\) ratio corresponds to an age of 690 years. Believing the shroud originated in 36 AD forces to expect a “real” \(^{14}C/^{12}C\) ratio of \(1.021 \cdot 10^{-12}\), because much more should have decayed. Enrichment in heavy isotopes \((^{13}C, ^{14}C)\) by fractionation would make the shroud apparently younger. What would be the fractionation \(\delta^{13}C\) and the corresponding enrichment in \(^{13}C\)?

\[ \frac{^{14}C}{^{12}C}_{\text{obs}} \equiv 1.194 \cdot 10^{-12}; \quad \frac{^{14}C}{^{12}C}_{\text{real}} \equiv 1.021 \cdot 10^{-12}; \]
Required Change in $^{13}$C Abundance

\[
\delta^{13}C = 500 \cdot \left(1 - \frac{^{14}C}{^{12}C}_{\text{corr}}\right) - 25 = 500 \cdot \left(1 - \frac{^{14}C}{^{12}C}_{\text{real}}\right) - 25 = 47.4
\]

Far higher than observed in natural material (typically +2 to -27)

Possible enrichment at combustion conditions is still under debate!
Summary

Carbon Contamination and Fractionation are natural processes which have to be taken into account in the final analysis of the data. They can cause significant systematic errors if not considered properly. In fact these systematic errors resemble the main source of uncertainty in all radioactive dating results and are typically much larger than the standard statistical uncertainties which are determined by experimental parameters e.g. sample size or counting conditions.