Quantum-mechanical equilibrium isotopic fractionation correction to radiocarbon dating: a theory study

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Abstract This paper relates the quantum–mechanical equilibrium isotopic fractionation correction to the radiocarbon dating method by Eq. 9, and also shows the significant influence of temperature on the method. It is suggested that the correction is a function of the frequencies and temperature of a specific sample and these two variables can be evaluated theoretically by the ab initio quantum calculations and experimentally by analyzing the clumped-isotope ratios in it, respectively. This paper also suggests that the $^{14}C/^{12}C$ ratio in the atmosphere in geological time can be calculated by Eq. 10.

Keywords Quantum mechanics · Isotopic fractionation correction · Radiocarbon dating

Introduction

Radiocarbon dating is a chronological method which uses radioisotope carbon-14 (^{14}C) to investigate the ages of carbonaceous samples [1, 2]. ^{14}C atom forms in the nuclear reaction:

$$n + {}^{14}_{7}N^{1+} \rightarrow {}^{14}_{6}C + p$$
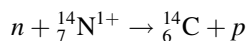
where p is the proton, N is the atom of nitrogen, n is the neutron resulting from the cosmic ray. Then ^{14}C spreads

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throughout the atmosphere and forms carbon dioxide ($^{14}CO_2$) when it reacts with oxygen. Finally $^{14}CO_2$ permeates the carbon cycling resulting in preserving ^{14}C in carbonaceous matters. When sampled, the carbonaceous materials become clocks due to the decaying ^{14}C in them.

Since the half-life of ^{14}C is moderate, i.e. 5568 ± 30 [1] or 5730 ± 40 years [3], Grosse and Libby [4] at the University of Chicago developed the radiocarbon dating method. To achieve high accuracy calendar dates by this method, scientists had advanced several calibration methods, including tree rings [5], annually laminated sediments [6], corals [7, 8], INTCAL98 [5], INTCAL04 [9], and INTCAL09 [10]. The calculations of such calibrations are based on the conventional formula, which was given by Stuiver and Polach in 1977 [2]. In this formula, the correction of the isotopic fractionation plays a significant role. The correction is that the difference in $\delta^{13}C$, normalized to 'the postulated mean value, i.e. −25 per mil with respect to PDB, of terrestrial wood', simply indicates a double change of that in $\delta^{14}C$ within the carbonaceous matters. However, neither might this quantitative relation always be true for specific processes such as chemical processes in which the factor is 1.9 [11, 12], nor does the conventional formula itself include the effect of temperature, at which the sample formed, on the fractionation correction. The following section tries to relate the equilibrium isotopic fractionation correction, depending on the temperature, to the radiocarbon dating method. And the conclusions are listed in the final section.

Assumptions and derivations

The derivations in present paper are based on the postulate: samples are well preserved without chemical exchange

after they formed. This is the second assumption of Libby's [1]. Here does not use Libby's first assumption because published works shows the variability of ^{14}C in the atmosphere [11–17]. This variability is due to the varying intensities of cosmic radiation with time [18], and the release of ^{12}C and ^{14}C into the atmosphere by, for example, burning of fossil (known as Suess effect [19–21]) and explosion of nuclear bombs [22], respectively.

As mentioned above, $^{14}CO_2$ in the atmosphere is the significant medium to preserve ^{14}C into the carbonaceous matter, XC_n, where X stands for the stoichiometry of all atoms except carbon (C) in the sample, and n for the number of C in it. This process involves an isotope reaction [23, 24]:

$$^{14}CO_2 + \frac{1}{n}X^{12}C_n \overset{K}{\rightleftharpoons} {}^{12}CO_2 + \frac{1}{n}X^{14}C_n \tag{1}$$
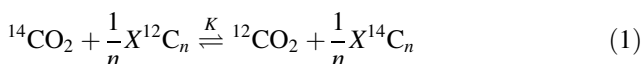
where K is the equilibrium constant, depending at most on the temperature T [25].

Incorporation of ^{14}C into the carbonaceous matter XC_n, assuming no further exchange, starts the radiocarbon clock. The number of ^{14}C in XC_n at $t = 0$, $N^{14C}_{XC_n,0}$, and that at present $t = t$, $N^{14C}_{XC_n,t}$, follow an exponential decay:

$$N^{14C}_{XC_n,t} = N^{14C}_{XC_n,0}\,e^{-\lambda t} \tag{2}$$

where $1/\lambda = 8033$ year (Libby value) is the mean life of ^{14}C.

Now let $N^{12C}_{XC_n}$ denote the number of ^{12}C in XC_n. Division of Eq. 2 by $N^{12C}_{XC_n}$ gives

$$\frac{N^{14C}_{XC_n,t}}{N^{12C}_{XC_n}} = \frac{N^{14C}_{XC_n,0}}{N^{12C}_{XC_n}}\,e^{-\lambda t} \tag{3}$$

since $N^{12C}_{XC_n}$ was not altered after the sample formed. In this equation, the left side and the first term of the right side represent the ratio of $^{14}C/^{12}C$ in the sample at $t = t$ and $t = 0$, respectively.

The $N^{14C}_{XC_n,0}\big/N^{12C}_{XC_n}$ ratio in Eq. 3 can be evaluated by studying the equilibrium constant K of reaction 1 at $t = 0$. For reaction 1, the molality-scale equilibrium constant is [25]

$$K = \frac{[X^{14}C_n]^{\frac{1}{n}}[^{12}CO_2]}{[X^{12}C_n]^{\frac{1}{n}}[^{14}CO_2]} = \frac{\left(\frac{[X^{14}C_n]}{[X^{12}C_n]}\right)^{\frac{1}{n}}}{\frac{[^{14}CO_2]}{[^{12}CO_2]}} = \frac{\frac{N^{14C}_{XC_n,0}}{N^{12C}_{XC_n}}}{\frac{N^{14C}_{CO_2,0}}{N^{12C}_{CO_2}}} \tag{4}$$

with the last term expressing the concentration by the number of ^{14}C and ^{12}C in those two chemicals: $N^{14C}_{CO_2,0}$ and $N^{12C}_{CO_2}$ are the numbers of ^{14}C and ^{12}C in CO_2 in the atmosphere at $t = 0$, respectively. This term is the $^{14}C/^{12}C$ ratio in XC_n divided by that in CO_2, and it is just the

expression of the fractionation factor, α, defined by experimental chemists, giving $K = \alpha$. For theoretical chemists, α is the ratio of reduced partition function ratios (RPFRs) between those two substances [23, 24]. Since the factor α is unique for a specific process, we have

$$\frac{\frac{N^{14C}_{XC_n,0}}{N^{12C}_{XC_n}}}{\frac{N^{14C}_{CO_2,0}}{N^{12C}_{CO_2}}} = \alpha = \frac{RPFR_{X^{14/12}C_n}}{RPFR_{^{14/12}CO_2}} \tag{5}$$

or

$$\frac{N^{14C}_{XC_n,0}}{N^{12C}_{XC_n}} = \frac{RPFR_{X^{14/12}C_n}}{RPFR_{^{14/12}CO_2}}\frac{N^{14C}_{CO_2,0}}{N^{12C}_{CO_2}} \tag{6}$$

where

$$RPFR =$$

$$\left(\frac{\sigma^{12C}}{\sigma^{14C}}\prod_k^{3N-6(5)}\frac{u^{14C}_k}{u^{12C}_k}\frac{\exp\left(-u^{14C}_k/2\right)}{\exp\left(-u^{12C}_k/2\right)}\frac{1-\exp\left(-u^{12C}_k\right)}{1-\exp\left(-u^{14C}_k\right)}\right)^{1/n} \tag{7}$$

in which σ is the symmetry number, $u = hc\omega/k_BT$, h is the Planck's constant, c is the speed of light, ω is the frequency in cm^{-1}, k_B is the Boltzmann constant, T is the temperature.

Substitution of Eq. 6 into Eq. 3 gives

$$\frac{N^{14C}_{XC_n,t}}{N^{12C}_{XC_n}}e^{\lambda t} = \frac{RPFR_{X^{14/12}C_n}}{RPFR_{^{14/12}CO_2}}\frac{N^{14C}_{CO_2,0}}{N^{12C}_{CO_2}} \tag{8}$$

Use of the natural logarithm to Eq. 8 leads to

$$t = \frac{1}{\lambda}\left(\ln\left(RPFR_{X^{14/12}C_n}\right) - \ln\left(RPFR_{^{14/12}CO_2}\right)\right.$$
$$\left. - \ln\left(\frac{N^{14C}_{XC_n,t}}{N^{12C}_{XC_n}}\right) + \ln\left(\frac{N^{14C}_{CO_2,0}}{N^{12C}_{CO_2}}\right)\right) \tag{9}$$

This equation shows that the time t the clock recorded is a function of ω, T, $N^{14C}_{XC_n,t}\big/N^{12C}_{XC_n}$, $N^{14C}_{CO_2,0}\big/N^{12C}_{CO_2}$ and other physical constants. The first two terms in the right side of above equation is called the isotopic fractionation correction to the radiocarbon dating method.

For a specific sample, the accurate value of ω and $N^{14C}_{XC_n,t}\big/N^{12C}_{XC_n}$ in Eq. 9 can be directly evaluated by ab initio quantum calculations [23, 24, 26–31] and accelerator mass spectrometry (AMS) technique [32–42], respectively. The methods to evaluate T and $N^{14C}_{CO_2,0}\big/N^{12C}_{CO_2}$ are illustrated below.

T in Eq. 9 is the unique temperature at which the sample formed and recorded. According to Eq. 5, α is a function of temperature, and this allow us to find the inverse function of α to evaluate T: that is, if $\alpha = f(T)$, then we have $T = f^{-1}(\alpha)$

which gives T if α is known. If α is, however, given by the theoretical calculations, T locates in an interval of temperatures at which XC_n can form [26–29] rather than at a unique temperature the specific sample formed. So we have to experimentally measure the isotope ratios kept in the sample, and then get the unique α and, therefore, the unique T.

A good example of such case is to determine T by studying the clumped-isotopes in calcite [43, 44]. The equilibrium constant $K3866$ (or Δ_{47}, See definitions and details of experiments in Refs. [43, 44]) of clumped-isotopes in calcite can be given as a function of T from 273.15 to 1273.15 K by theoretical predictions [44], while a specific sample such as Calcite HA4 in Ref. [43] only formed at $323.15 \pm 2(1\sigma)$ K with $K3866 = 1.00053 \pm 0.011(1\sigma)$. Therefore, as Ref. [43] did, one might use the experimental results of clumped-isotope ratios in the calcite rings of the stalagmite to determine $K3866$, and then compare this value to the experimental fitted polynomial, $T = f^{-1}(K3866)$, to get T [43]. Since samples (formed in reaction 1) such as stalagmites and trees are in a single phase, Ts recorded by them are suggested to be experimentally given by studying the clumped-isotopes [45–50] kept in them.

$N_{CO_2,0}^{14C} / N_{CO_2}^{12C}$ in Eq. 9 is unknown now, but the method to evaluate it can be given. Rewriting Eq. 8, we have

$$\frac{N_{CO_2,0}^{14C}}{N_{CO_2}^{12C}} = \frac{\text{RPFR}_{14/12\,CO_2}}{\text{RPFR}_{X^{14/12}C_n}} \frac{N_{XC_n,t}^{14C}}{N_{XC_n}^{12C}} e^{\lambda t} \tag{10}$$

In this equation, the left side is the $^{14}C/^{12}C$ ratio in the atmosphere and the right side shows information from a sample: the isotope fractionation factor α of $^{14/12}C$ between CO_2 and the sample, the AMS results of $^{14}C/^{12}C$ ratio in it, and the time t which can be directly given by examining the number of the growth rings of, for example, a tree. With such information on the samples, Eq. 10 gives the ratio of $^{14}C/^{12}C$ in the atmosphere where the sample formed in the geological time.

If the $^{14}C/^{12}C$ ratio in the past atmosphere were generated in future literature, we shall obtain a new relationship between this $^{14}C/^{12}C$ ratio and t. Then we expect a reasonable reference value (which plays the role as absolute international standard activity A_{abs} does in the conventional formula [2]) of $\left(N_{CO_2,0}^{14C} / N_{CO_2}^{12C}\right)_{\text{ref}}$ that makes Eq. 9 to work. This is beyond the ability, and thus a limitation, of this theoretical paper: we cannot set the last term in Eq. 9 down now.

Conclusions

From the above derivations, the conclusions can be drawn as follows:

(1) This work introduces us a new dimension, the temperature T, to study radiocarbon dating.

(2) The mechanism of isotopic fractionation correction to radiocarbon dating method is clear. This correction, shown in Eq. 9, is a function of ω and T resulting from studying the equilibrium isotopic reaction 1. Since the fractionation caused by reaction 1 cannot happen in the classical mechanism and it can be derived only from quantum mechanism [23, 24], the correction is a quantum-mechanical equilibrium isotopic fractionation correction to radiocarbon dating.

(3) One application of this work, as Eq. 9 shows, is to explain why so many calibrations, shown in the introduction, are needed for radiocarbon dating. The reasons for the need are:

(a) The first comes from the difference of carbonaceous matters. This is shown by 'XC_n' in the first term of Eq. 9 when we suppose a constant T and a fixed $^{14}C/^{12}C$ ratio in the last term. For example, carbonaceous matters XC_n are fiber and calcite in tree rings and corals [5, 51], respectively. These chemicals have different vibrations ω and therefore different RPFRs at the same T;

(b) The second is from the temperature. Since α between, for example, calcite and carbon dioxide in Eq. 9 is generally not a linear function of T [26–28], T affects t in a non-linear way if the last two terms in Eq. 9 are constants. For example, as shown in Ref. [43], the temperature of one ring of calcite differs from that of another;

(c) The third is due to the variation of $^{14}C/^{12}C$ ratio in the atmosphere. If the first three terms in Eq. 9 are fixed, then t is a function of the variation of $^{14}C/^{12}C$ ratio. As published works showed [11–14], there is no linear function to describe this ratio as a function of t: this ratio affects t in some non-linear way. Briefly, these three parameters separately have a non-linear relationship with t.

In the nature, the relationship between t and the three parameters is more complex. When reaction 1 happened, these three influence factors might change together with the latitude and the altitude or the depth and in seasonable scale or even hundred-year scale [11–14, 52–54]. Consequently, the years given by conventional formula deviate from a straight or linear line and need to be calibrated when high accuracies are required. It is apparent that Eq. 9 itself contains more information than the conventional

one [2] and, if Eq. 9 were used to determine the years of samples, the deviation would be significant small.

(4) Another application of present work, as Eq. 10 shows, is to generate the $^{14}C/^{12}C$ ratio in the atmosphere in the geological history by studying the examples of which the 'growth years' can be directly examined.

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