ARE THE FRACTIONATION CORRECTIONS CORRECT: ARE THE ISOTOPIC SHIFTS FOR $^{14}C/^{12}C$ RATIOS IN PHYSICAL PROCESSES AND CHEMICAL REACTIONS REALLY TWICE THOSE FOR $^{13}C/^{12}C$?

John Southon

Keck Carbon Cycle AMS laboratory, Earth System Science Department, University of California, Irvine, California 92697-3100, USA. Email: jsouthon@uci.edu.

ABSTRACT. Conventional radiocarbon calculations correct for isotopic fractionation using an assumed value of 2.0 for the fractionation of ^{14}C relative to ^{13}C. In other words, isotopic discrimination in physical and chemical processes is assumed to cause relative shifts in $^{14}C/^{12}C$ ratios that are exactly double those of $^{13}C/^{12}C$. This paper analyzes a 1984 experiment that produced a value for the fractionation ratio in photosynthesis of 2.3, which is used to this day by some researchers in the fields of hydrology and speleothem geochemistry. While the value of 2.3 is almost certainly incorrect, theoretical work suggests that the true value may indeed deviate from 2.0, which would have significant implications for ^{14}C calculations.

INTRODUCTION

As is well known, radiocarbon measurements must be corrected for isotopic fractionation in order to place ^{14}C dates on different materials on a common timescale. In conventional ^{14}C calculations (Stuiver and Polach 1977), these corrections are based on $^{13}C/^{12}C$ ratios ($\delta^{13}C$ values) with an assumed value of 2.0 for the fractionation for ^{14}C relative to ^{13}C (Craig 1954). In other words, isotopic discrimination in physical and chemical processes is assumed to cause relative shifts in the $^{14}C/^{12}C$ ratio that are exactly double those of $^{13}C/^{12}C$. In a more general treatment (Craig 1954; Wigley and Muller 1981), it is assumed that for some fractionating process $A \rightarrow B$, the fractionation factor α for $^{14}C/^{12}C$ ratios varies as the equivalent factor for $^{13}C/^{12}C$ ratios raised to some power b:

$$\alpha_{14} = \alpha_{13}{}^b \text{ or } b = \ln\alpha_{14}/\ln\alpha_{13} \tag{1}$$

where R is a $^{14}C/^{12}C$ or $^{13}C/^{12}C$ isotope ratio and $\alpha = R_A/R_B$ is the ratio of isotope ratios for the initial and final constituents. But since $\ln(1+x) \approx x$ for $x \ll 1$:

$$b = \ln(1+\varepsilon_{14})/\ln(1+\varepsilon_{13}) \approx \varepsilon_{14}/\varepsilon_{13} \tag{2}$$

where $\varepsilon = R_A/R_B - 1$ is the fractionation for the process $A \rightarrow B$. Hence, b is simply the ratio of the relative shifts $\Delta R/R$ for $^{14}C/^{12}C$ and $^{13}C/^{12}C$.

A $^{14}C/C$ ratio or ^{14}C-specific activity A_S is related to the $^{14}C/^{12}C$ ratio by

$$A_S = {}^{14}C/C = {}^{14}C/({}^{12}C + {}^{13}C)$$

$$= ({}^{14}C/{}^{12}C)/[1 + {}^{13}C/{}^{12}C_{PDB}(1+\delta^{13}C/1000)]$$

$$\approx ({}^{14}C/{}^{12}C)/(1 + {}^{13}C/{}^{12}C_{PDB}) \text{ to parts in } 10^4$$

where $^{13}C/^{12}C_{PDB}$ is the $^{13}C/^{12}C$ ratio for the PDB standard (=0.01124). Therefore, A_S closely approximates a $^{14}C/^{12}C$ ratio scaled by a constant factor, and the same fractionation corrections apply. Since measured A_S values are corrected to $\delta^{13}C = -25‰$, the fractionation-corrected specific activity A_{SN} normalized to the modern ^{14}C standard A_{ON} is

$$A_{SN}/A_{ON} = A_S/A_{ON}[(1-25/1000)/(1+\delta^{13}C/1000)]^b \tag{3}$$

Using $(1+x)^b \approx 1 + bx$ for $x \ll 1$,

$$A_{SN}/A_{ON} \approx A_S/A_{ON}/[1 - b(\delta^{13}C + 25)/1000] \tag{4}$$

and for $b = 2$ this gives the familiar formula (Stuiver and Polach 1977),

$$A_{SN}/A_{ON} \approx A_S/A_{ON}/[1-2(\delta^{13}C+25)/1000]$$

The ^{14}C age is then given by

$$\text{Age} = -8033\ln(A_{SN}/A_{ON}) \tag{5}$$

where 8033 yr is the mean ^{14}C lifetime based on the Libby half-life. The measured specific activity of the OX1 standard must also be fractionation-corrected, to a δ^{13}C of -19‰:

$$A_{ON} = 0.95A_{OX1}[(1-19/1000)/(1+\delta^{13}C_{OX1}/1000)]^b$$

but this effect is small, since measured δ^{13}C values for OX1 are typically very close to the nominal -19‰.

In an early paper on high-precision GEOSECS ^{14}C results, Stuiver and Robinson (1974) noted that theoretical studies of chemical reactions suggest that the true value of b is ~1.9, rather than 2.0 as originally proposed by Craig (1954). Since this result has important implications for ^{14}C calculations, a derivation based on work by Bigeleisen and Mayer (1947) is included here in Appendix A. Detailed reaction calculations for a variety of chemical equilibria have typically produced values for b in the range of 1.85–1.9 (Stern and Vogel 1971; Hartshorn and Shiner 1972), though calculations by Saliege and Fontes (1984) suggest b ~2.05 for reactions involving CO_2.

The consequences for ^{14}C calculations of possible variations from $b = 2.0$ were explored in detail by Wigley and Muller (1981), who concluded that the effects were typically insignificant. However, this is no longer necessarily true. For example, suppose $b = 2.3$ (the reason for this choice is explained in the "Results and Corrections" section below), and consider how this would affect ^{14}C dates on marine carbonate ($\delta^{13}C = 0$‰) or C_4 plant material ($\delta^{13}C = -13$‰). Based on Equations 3 and 4,

$$(A_{SN}/A_{ON})_b = (A_{SN}/A_{ON})_{2.0} [(1-25/1000)/(1+\delta^{13}C/1000)]^{b-2.0}$$

$$\approx (A_{SN}/A_{ON})_{2.0} [1-(b-2)(\delta^{13}C+25)/1000]$$

Therefore, $$\Delta(A_{SN}/A_{ON})/(A_{SN}/A_{ON}) = -(b-2)(\delta^{13}C+25)/1000 \tag{6}$$

where Δ is a small change. Differentiating Equation 5 and substituting from Equation 6 yields,

$$\Delta(\text{age}) = 8033(b-2)(\delta^{13}C+25)/1000$$

Therefore, correcting A_{SN}/A_{ON} using $b = 2.0$ instead of 2.3 would introduce shifts in the fractionation-corrected ratios A_{SN}/A_{ON} of 7.5‰ and 4‰ for marine carbonate and C_4 plant material, respectively, equivalent to ^{14}C age shifts of 60 and 30 yr. Since ^{14}C measurement precisions as low as ±20 yr are now relatively common, these shifts represent serious errors. The effects of some of these offsets would effectively be hidden; for example, biases in marine carbonate and speleothem ages relative to those of terrestrial plants would appear as shifts in marine reservoir ages and dead-carbon corrections, respectively. However, others—notably in comparisons of ages of C_3 and C_4 plants or of activities of biological materials vs. air samples—would not.

A few studies have produced experimental evidence for fractionation ratios greater than 2.0 for carbon isotopes that, if confirmed, would have serious consequences for ^{14}C determinations. Craig (1954) summarized early work, and references to later experiments are found in Saliege and Fontes

(1984), hereinafter SF84. In general, these experiments have received little attention, but one result—from SF84—is used by some researchers in modeling studies of groundwater hydrology and speleothem geochemistry and is the subject of this paper.

THE SF84 EXPERIMENTS

Methods

In 1975 and again in 1977, SF84 measured the ^{14}C-^{13}C fractionation ratio for photosynthesis directly, by growing plants under well-monitored conditions and determining the isotopic composition of the ambient CO_2 and the fixed biomass. The site chosen was 10 km west of the town of Chartres, 80 km southwest of Paris and ~15 km northwest of the nearest major highway (Autoroute 11 from Paris to Le Mans). Experiments were carried out using both C_3 and C_4 plants: *Heliotropium europaeum* (European heliotrope, C_3); *Phaseolus vulgaris* (common bean, C_3); *Zea mays* (maize, C_4), grown from seed outdoors in a rural setting. Plants were grown in pots filled with vermiculite or carbonate-free soil, elevated 2 m above ground in an open field to minimize localized effects from respired CO_2 from nearby vegetation. CO_2 was collected throughout the growth period by pumping ambient air through a saturated barium hydroxide solution, in a chamber that was well baffled to ensure 100% collection efficiency and thus avoid fractionation between atmospheric CO_2 and the precipitated barium carbonate. A photoelectric cell was used to turn the pumping system on and off to ensure that CO_2 was collected only when the plants were photosynthesizing at levels above the compensation point, i.e. where photosynthesis exceeded respiration and there was a net gain of biomass.

At the end of the 1-month growth period, the total biomass was harvested and the precipitated barium carbonate was recovered. Samples were processed to CO_2 and synthesized to benzene using standard techniques, and ^{14}C was measured by liquid scintillation counting (LSC). Large quantities of benzene (~8.5 g for the 1977 samples) were synthesized to produce high LSC count rates, in order to reduce ^{14}C measurement uncertainties to ~0.15% at 1 σ. $δ^{13}$C values for ambient CO_2 and for plant material were measured on CO_2 aliquots from acidified carbonate, and from directly combusted dried biomass as well as combusted benzene, using a double-collector isotope ratio mass spectrometer (VG602D).

Results and Corrections

The SF84 experimental data and the calculations leading to the fractionation ratio results appear in their Tables 4–6 and are summarized here as Table 1. Recall that the fractionation ratio *b* is given by $b = ε_{14}/ε_{13}$, where *R* is an isotope ratio and $ε = R_A/R_B–1$ is the fractionation for the process $A → B$. Therefore, in Tables 1 and 2:

$$b = (A_{air}/A_{plant}–1)/[(1+δ^{13}C_{air}/1000)/(1+δ^{13}C_{plant}/1000)–1]$$

where *A* are measured ^{14}C-specific activities and $δ^{13}$C has the usual meaning.

Although these experiments appear to have been well planned and carried out, the initial results shown in Table 1 were highly surprising and difficult to explain. Not only was the fractionation ratio of 2.6 for CO_2 to C_3 plant tissue well above the expected value of ~2.0, but the results for the C_4 maize clustered tightly around a remarkable value of 3.9. That is, the fractional differences between the ^{14}C/^{12}C ratios for ambient CO_2 and C_4 plant material were almost *4 times* the equivalent shifts in the ^{13}C/^{12}C ratios for the same samples. Note that the fractionation ratios for CO_2 to C_3 and to C_4 plants have been cited as 2.6 and 2.3, respectively (e.g. Wigley and Muller 1981:184), but either the C_4 value refers to a corrected value (see below) or it was misquoted.

Table 1 Isotopic data from the Saliege and Fontes (1984) experiments.

Collection/ growth period	$\delta^{13}C$ (‰)	±	^{14}C activity (cpm/g)	±	^{13}C fractionation[a] ε_{13}	$\pm^d$	^{14}C fractionation[b] ε_{14}	$\pm^d$	Ratio $\varepsilon_{14}/\varepsilon_{13}$	Error[c,d] ±	Error[c,e] ±
1975 (6/14 – 7/14)											
Air	−8.08	0.07[f]	10.210	0.014[f]							
Maize	−12.05	0.1	10.060	0.020	0.00405	0.00014	0.01491	0.00246	3.71	0.62	0.90
Heliotrope	−26.78	0.07[f]	9.725	0.025[f]	0.01925	0.00012	0.04987	0.00307	2.60	0.16	0.22
1977 (6/21 – 7/21)											
Air	−7.80	0.1	9.982	0.020							
Maize 1	−12.50	0.07[f]	9.795	0.020	0.00476	0.00012	0.01909	0.00251	4.01	0.53	0.88
Maize 2	−12.28	0.07[f]	9.805	0.020	0.00453	0.00012	0.01805	0.00251	3.98	0.56	0.92
Bean	−25.88	0.07[f]	9.500	0.020	0.01856	0.00012	0.05074	0.00265	2.73	0.14	0.22

[a]ε_{13} = fractional change in $^{13}C/^{12}C$ ratio = $(1+\delta^{13}C_{air}/1000)/(1+\delta^{13}C_{plant}/1000)-1$.
[b]ε_{14} = fractional change in $^{14}C/^{12}C$ ratio = $A_{air}/A_{plant} - 1$ where A are counted ^{14}C-specific activities.
[c]Errors are dominated by radiocarbon uncertainties and the resulting uncertainty in ε_{14}.
[d]Error propagated from $\delta^{13}C$ and ^{14}C-specific activity uncertainties shown (data from SF84 Tables 4 and 5).
[e]Error from final uncertainties in SF84 Table 6 (see text).
[f]Mean of 2 determinations.

It was clear to SF84 that these unexpected results required explanation, and they considered several alternatives:

i) Because air was sampled uniformly through the daylight hours while photosynthesis varied according to light levels, the pumped air was subject to isotopic variations that may not have been recorded in the fixed biomass carbon;

ii) Stomatal conductance of CO_2 into plant foliage is not a simple diffusion process and, therefore, the theoretical basis for the expected 2.0 ratio for photosynthesis does not hold;

iii) The plant tissue incorporated small amounts of ^{14}C-dead carbon, which they hypothesized was delivered to their growth pots via meteoric input (i.e. rainwater) and subsequently taken up by root absorption.

The third alternative is attractive because it explains why the initial results from C_4 plants were so extreme: the shifts in ^{14}C activity for the C_4 plants relative to atmospheric CO_2 are far smaller than for C_3 (Table 1), so the same dilution effect by dead carbon has a much greater effect on the CO_2-C_4 differences. This was the explanation adopted by SF84. By correcting the ^{14}C results for the dead-carbon contribution (with $\delta^{13}C$ assumed to be unaffected) using slightly different assumed values for the contamination in the 2 experiments (0.6% in 1975 and 0.8% in 1977), they found that all of the experimentally determined values could be brought into close agreement, with a mean value of the ^{14}C-^{13}C fractionation ratio of 2.3. This value was subsequently adopted in influential modeling papers on the geochemistry and dating of groundwater and speleothems (Fontes 1992; Genty and Massault 1999) and still appears in some publications by researchers attempting to model speleothem ^{14}C (Fohlmeister et al. 2011; Hodge et al. 2011; Rudzka et al. 2011).

If this result is valid, i.e. if the $^{14}C/^{12}C$ versus $^{13}C/^{12}C$ fractionation ratio for photosynthesis (and potentially for other processes) is significantly different from 2.0, all corrections for isotopic fractionation according to Stuiver and Polach (1977) are suspect, and significant errors have been introduced into all ^{14}C age calculations involving large fractionation corrections—an unknown but probably non-negligible percentage of all of the ^{14}C dates that have ever been produced. The purpose of this paper is to examine the experimental results that produced the initial elevated SF84 results and the corrections applied to those data; and to investigate whether the reported results do in fact support the existence of fractionation ratios significantly different from 2.0.

THE DEAD-CARBON HYPOTHESIS

Root Uptake of ^{14}C-Depleted DIC

The proposed explanation for the initial SF84 results relies on meteoric input of dead carbon to the growth pots, presumably originating from carbonate dust scavenged by the rainfall. (In fact, direct input of dust from local agricultural activity and its subsequent dissolution may be more likely.) Uptake by the plants of dissolved inorganic carbon (DIC) via root absorption and its subsequent fixation in the plant tissues then diluted the ^{14}C content of the biomass sufficiently to mimic very large discriminations against ^{14}C, while leaving the ambient air measurements unaffected.

This process may indeed take place, albeit at very low levels. Chartres lies in a region of the Paris basin where sedimentary carbonate bedrock is common, so the presence of old carbonate in dust from soil tillage, etc., is plausible. SF84 cite experiments by Olsson et al. (1972) who found anomalous ^{14}C depletions in biomass from tomato plants grown in media containing "old" and "dead" carbonate. Additionally, ^{13}C and ^{14}C tracer experiments (Amiro and Ewing 1992; Ford et al. 2007 and references therein) have confirmed that DIC uptake does occur in some plants, including *Phaseolus vulgaris*. However, as summarized by Enoch and Olesen (1993) and Ford et al. (2007), different experiments have produced sharply different estimates of the extent to which the process occurs, including cases where the effect is so small as to be unmeasurable. The only common ground in the literature seems to be a widespread agreement that the carbon contribution to fixed biomass from root uptake is at most a few percent of the input from photosynthesis, and probably much less.

A difficulty with this explanation is that it requires very large inputs of dead carbon. ^{14}C levels in the atmosphere and plant material in these experiments, expressed as fraction modern (F^{14}C, Reimer et al. 2004) were ~1.30–1.35 (SF84 Table 4), and the dead-carbon input was presumed to have lowered the ^{14}C content of the biomass by about 0.7%, say from F^{14}C = 1.33 to F^{14}C = 1.32. By mass balance, where x is the ^{14}C content of the soil DIC and assuming 3% of the total biomass is derived from root uptake,

$$0.03(x) + 0.97(1.33) = 1.32, \text{ or } x = 1.00$$

Thus, for root input to provide the necessary depletion, the ^{14}C content of the DIC in the growth pots must be reduced to F^{14}C = 1.00, or 75% that of the ambient CO_2. This requires a sustained input of dead carbon to the pots equal to one-third of the contemporary carbon respired by the plant roots themselves. Data from maize field studies (Amos et al. 2005) show soil fluxes during the growing season of 50–150 kg C/ha-d for densities of ~10^5 plants/ha. Taking the median flux value and assuming that 50% of this is from root respiration (Bond-Lamberty et al. 2004), the minimum dead-carbon input required is $(1/3)(0.5)(10^5 \text{ g/ha-d})/(10^5 \text{ plants/ha})$, or about 0.17 g C per plant per day. The total required for 4 plants per pot (two are shown in the pot cross-section in SF84 Figure 1) over a 30-day experiment would be 20 g C, or 170 g of $CaCO_3$ as dust or DIC. In a pot with ~1 m^2 surface area, this is equivalent to ~1.7 T/ha. Since pH control in acid agricultural soils involves deliberate limestone applications of ~2.5 to 25 T of $CaCO_3$/ha (Power and Prasad 1997), an incidental input of 1.7 T/ha seems very high. Furthermore, this calculation assumes a high value for the root uptake contribution to biomass and ignores any near-ambient contribution to soil respiration from the decay of fast-turnover soil organic matter. Less conservative assumptions would increase the required input of dead carbon several-fold.

A more fundamental problem is that the SF84 corrections assumed that the fraction of biomass attributable to root uptake and fixation of DIC was the same for C_3 and C_4 plants, and between different C_3 species, but no supporting evidence was presented. Since plant water uptake and transpiration and photosynthetic efficiency are all highly variable between plant species and photosynthetic pathways
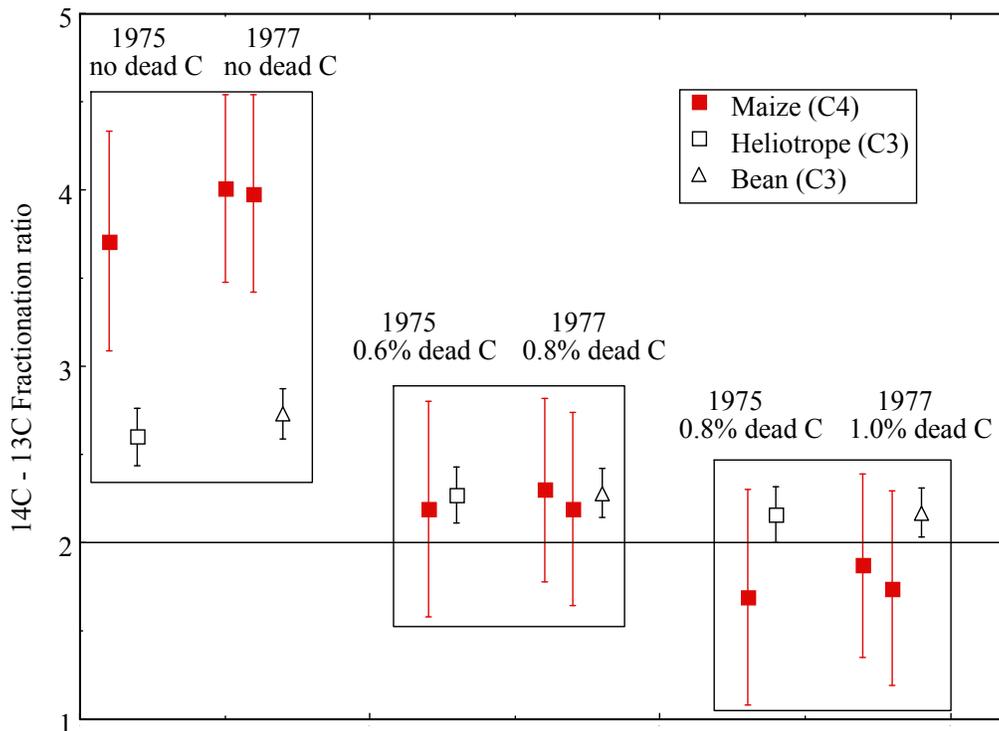
Figure 1 Ratios of the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ fractionations between atmospheric CO_2 and plant tissue, from SF84. The 3 boxes show: i) uncorrected data from the original experiments; ii) data corrected for dead-carbon inputs as per SF84; iii) data corrected for slightly larger dead-carbon inputs as discussed in the text. Note that the uncertainties shown are the smaller of 2 sets derived from the original data (see text) and are ~30% smaller than the final errors quoted in SF84 Table 5.

as well as in response to environmental conditions, such uniformity seems unlikely. This is true even if DIC uptake is simply a passive byproduct of water use, but there is evidence that DIC is actively taken up in some circumstances (Amiro and Ewing 1992; Ford et al. 2007), which suggests scope for even more variability. Of course, this uncertainty over how much DIC is incorporated into plant biomass does not necessarily invalidate the SF84 hypothesis for the dead-carbon source. However, unless the dead-carbon fixation is precisely determined as a fraction of the net photosynthetic uptake for all of the plant species in the SF84 studies, the initial results cannot be corrected in any meaningful way and fractionation ratios for ^{14}C and ^{13}C cannot be derived from those data.

Diurnal Variations of Fossil Fuel CO_2

A possible alternative explanation for the ^{14}C depletions contains elements of SF84's proposed mechanism i) and iii): a time-varying fossil fuel (i.e. dead carbon) component of the ambient CO_2 was sampled unequally by the biomass and the continuously pumped air. In some plants, including at least some maize varieties (Kalt-Torres et al. 1987; Ding et al. 2006), photosynthesis rates drop in the early afternoon. Contributing causes include decreased stomatal conductance to reduce transpiration under progressive drying through the day, and feedbacks to limit photooxidative damage to the photosynthetic apparatus (Long et al. 1994; Kang et al. 2000). Stratification in the atmospheric boundary layer over land is greatest at night and decreases through the day until mid-afternoon, as unequal warming of the surface promotes atmospheric instability and increased mixing with the free troposphere (Liu and Liang 2009). Consequently, CO_2 concentrations from surface sources, includ-

ing fossil fuel pollution, may be at their highest under morning conditions despite increased emissions during the day. If variations in photosynthetic activity translated into a morning bias for the carbon that was ultimately fixed as structural biomass in the SF84 experiments, the plant material may have been depleted in ^{14}C relative to air that was sampled uniformly through the daylight hours. Note that equivalent interactions between long-term (~weeks) shifts in fossil fuel pollution and variations in photosynthesis rates can be ruled out, because consecutive 2-week air samples from 1975 returned identical ^{14}C results.

This explanation requires the presence of large time-varying concentrations of fossil fuel CO_2 at the experimental site, which would be surprising for a rural setting. However, SF84 Table 4 shows "$\delta^{14}C_{mod}$" values for ambient CO_2 based on the 1975 and 1977 month-long air monitoring at the site. Recall that $\delta^{14}C$ is the fractional offset of a sample activity from the absolute ^{14}C standard with no correction for isotopic fractionation (Stuiver and Polach 1977):

$$\delta^{14}C = A_S/A_{abs} - 1$$

This notation is rarely used, but it is logical in a paper questioning the validity of the normal fractionation corrections, and it seems clear that $\delta^{14}C_{mod}$ in SF84 and Stuiver and Polach's $\delta^{14}C$ are identical. (Note that because the experiments were conducted in 1975 and 1977 and the samples must have been measured before 1984, any decay corrections are negligible, regardless of whether or not they are included in $\delta^{14}C_{mod}$.) Application of the usual fractionation corrections to the $\delta^{14}C_{mod}$ data yields $F^{14}C$ values for the pumped air of 1.306 and 1.279 for 1975 and 1977, respectively. These are substantially lower than mid-1975 and mid-1977 results of $F^{14}C = 1.373$ and 1.340 for CO_2 in clean air from the high-altitude Jungfraujoch station (Levin et al. 1985). The ^{14}C depletions of ~0.067/ 1.37 and 0.061/1.34, or 4.5 to 5% of the clean air value, are far greater than those observed in the northern Netherlands (Van der Laan et al. 2010) and in Heidelberg, Germany (Levin et al. 2008), and are comparable with the largest offsets found by Riley et al. (2008) between urban areas of the Los Angeles basin and remote regions of northern California. They confirm that substantial fossil fuel CO_2 was indeed present at the SF84 site, perhaps from very local sources that were unrecognized and/or fortuitously were not operating when the researchers were present.

Evidence for changing isotopic composition of the ambient CO_2 at the SF84 site comes from $\delta^{13}C$ measurements on CO_2 from flask samples collected at 20:00 hr on several days in June and July of 1977. $\delta^{13}C$ varied over a large range, between –7.7 and –9.2‰ (SF84 Table 4). The latter value is significantly depleted relative to measured the monthly mean of about –8‰, indicating that a large input from a very depleted source was present on at least some occasions. However, this does not prove that variable levels of pollution were present, because biomass respiration and fossil fuel CO_2 have similarly light $\delta^{13}C$, and it does not address the timing of any variations in $^{14}CO_2$ at the site. Therefore, while the SF84 data do provide some support for a fossil fuel source, the origin of the dead carbon in the plant tissues remains an open question.

Importantly, the fossil fuel explanation shares another major drawback of the original SF84 hypothesis: there is no basis for assuming that the fossil fuel carbon fraction in the biomass of the various species in the SF84 experiments is the same. Indeed, given the varying diurnal cycles of photosynthetic activity documented in the literature and the disparate explanations proposed for the behavior of different species under different conditions, this seems *a priori* unlikely. Hence, once again there is no reasonable way to correct the SF84 data to compensate for the dead-carbon contamination, and therefore the results cannot be used to determine fractionation ratios for ^{14}C and ^{13}C.

ARE THE CORRECTED SF84 FRACTIONATION RATIOS DIFFERENT FROM 2.0?

As discussed above, attempts to correct the initial SF84 results require major assumptions about the constancy of dead-carbon input for different plant species that cannot be justified. Nevertheless, it is instructive to ignore this fundamental problem and to recreate the calculations from the original paper. Table 2 reproduces the corrections for dead-carbon input from SF84 Table 7, and it also includes propagated errors for the corrected fractionation ratios, which are important for determining whether the corrected ratios are significantly different from 2.0. These errors are dominated by the ^{14}C measurement uncertainties and the resulting uncertainty in the $^{14}C_{air}/^{14}C_{plant}$ ratios, and were determined in 2 ways. First, the errors shown in SF84 Table 6 for the uncorrected fractionation ratios were back-propagated to determine the equivalent errors in the $^{14}C_{air}/^{14}C_{plant}$ ratios, then the dead-carbon corrections were applied to those ratios and final errors were recalculated. Second, the uncertainties quoted in SF84 Table 4 and 5 for the original ^{14}C and ^{13}C data were forward-propagated in the usual way. For the latter case, errors for mean values were derived from the scatter of individual results and also from the propagated 1σ uncertainties, and the larger of the two was used. Note that in both cases, the final uncertainties are almost unchanged when dead-carbon corrections are applied because the $^{14}C_{air}/^{14}C_{plant}$ ratios change by less than 1%.

Table 2 Corrections to Saliege and Fontes (1984) fractionation ratios for dead-carbon input.

	^{14}C fract.[a]		Ratio	^{14}C fract.[a]		Ratio	^{14}C fract.[a]		Ratio	Error[b,c]	Error[c,d]
	ε_{14}	$\pm$[b]	$\varepsilon_{14}/\varepsilon_{13}$	ε_{14}	$\pm$[b,c]	$\varepsilon_{14}/\varepsilon_{13}$	ε_{14}	$\pm$[b,c]	$\varepsilon_{14}/\varepsilon_{13}$	$\pm$	$\pm$
1975	No corr. for dead C			Corr. for dead-C input of 0.6%[e]			Corr. for dead-C input of 0.8%[e]				
Maize	0.01491	0.00246	3.71	0.00882	0.00244	2.19	0.00679	0.00243	1.69	0.61	0.89
Heliotrope	0.04987	0.00307	2.60	0.04357	0.00303	2.27	0.04147	0.00302	2.16	0.16	0.22
1977	No corr. for dead C			Corr. for dead-C input of 0.8%[e]			Corr. for dead-C input of 1.0%[e]				
Maize 1	0.01909	0.00251	4.01	0.01094	0.00248	2.30	0.00890	0.00247	1.87	0.52	0.87
Maize 2	0.01805	0.00251	3.98	0.00991	0.00248	2.19	0.00787	0.00247	1.74	0.55	0.91
Bean	0.05074	0.00265	2.73	0.04233	0.00261	2.28	0.04023	0.00261	2.17	0.14	0.22

[a]ε_{14} = fractional change in $^{14}C/^{12}C$ ratio = $A_{air}/A_{plant}-1$ where A are counted ^{14}C-specific activities.
[b]Error propagated from $\delta^{13}C$ and ^{14}C-specific activity uncertainties from SF84 Tables 4 and 5.
[c]A_{air}/A_{plant} changes by <1% when dead-carbon corrections are applied, so the absolute errors in ε_{14} and in $\varepsilon_{14}/\varepsilon_{13}$ are almost unchanged from Table 1.
[d]Error propagated from final uncertainties in SF84 Table 6 (see text).
[e]$A_{plant}(corr) = A_{plant}/(1-D)$ where D is the dead-carbon input.

This exercise revealed a surprising inconsistency: the propagated measurement errors produce final uncertainties that are ~30% smaller than those shown in the last column of SF84 Table 6. The source of this discrepancy is unknown, but the uncertainties shown for the measured ^{14}C-specific activities in SF84 Table 4 and 5 are unusually small—equivalent to just ±2‰. An even lower value of ±1.5‰ is quoted in the text, but probably refers to the error from counting statistics alone. For comparison, Pearson (1979) showed that errors of ±2.5‰ could be justified for the Belfast calibration work, which was widely regarded as state of the art for LSC in the mid-1970s, when the SF84 measurements were performed. One possibility is that a laboratory error multiplier was used in the SF84 calculations, though no mention of this appears in the text. Substituting uncertainties of ±0.027 cpm/g (i.e. about ±2.7‰, close to the Pearson values) in Table 1 and propagating the results produces final errors that are close to those of SF84 Table 6 (not shown). However, since this interpretation is spec-

ulative and impossible to verify, the smaller errors of ±0.02 cpm/g are retained here and propagated in Tables 1 and 2.

As expected, when values of 0.6% and 0.8% for the dead-carbon fraction of the biomass produced in 1975 and 1977 are assumed as in the original paper, the SF84 [14]C-^{13}C fractionation ratios are reproduced to within ~1% (with small differences due to roundoff). The initial highly elevated results are sharply reduced and the corrected fractionation ratios cluster closely around a value of 2.3 (Table 2, Figure 1).

However, when the uncertainties are taken into account, the picture becomes considerably less clear. Because the isotopic shifts between CO_2 and C_4 plant tissue are small, the effects of the ^{14}C uncertainties are magnified and the errors for the fractionation ratios are very large. Regardless of whether the uncertainties are back-calculated from the errors in SF84 Table 6 or are based on the propagated ^{14}C and ^{13}C measurement errors from SF84 Tables 4 and 5, all of the [14]C-^{13}C fractionation ratios calculated from the corrected C_4 data lie well within one standard deviation of 2.0. Furthermore, the C_3-based values are all within 2σ of 2.0 even when the smaller error set is applied (Figure 1).

Moreover, as is also shown in Table 2, if slightly larger dead-carbon contributions of 0.8% and 1.0% are assumed for 1975 and 1977, respectively, the corrected results are reduced still further. When the smaller error set is used, 4 of the 5 corrected [14]C-^{13}C fractionation ratios are at or within 1 standard deviation of 2.0 and the fifth is at 1.2σ (Figure 1). If the larger errors based on SF84 Table 6 are used, all of the corrected ratios lie well within 1 standard deviation of 2.0. In the absence of any reason for preferring one set of dead-carbon corrections over another, an obvious conclusion is that these results provide no basis for rejecting the null hypothesis. The SF84 data for C_3 and C_4 photosynthesis must therefore be considered consistent with the commonly used [14]C-^{13}C fractionation ratio of 2.0, and they cannot be used to infer that the standard value is incorrect.

CONCLUSION

A study by Saliege and Fontes (1984) produced values for the fractionation ratio for ^{14}C/^{12}C versus ^{13}C/^{12}C in photosynthesis that appeared significantly different from the commonly used value of 2.0. However, although the experiments were carefully planned and executed, they were apparently compromised by ^{14}C-dead carbon from an unknown source that depressed ^{14}C in the measured plant tissues. Regardless of the origin of that contamination, the initial results can only be corrected if the dead-carbon contributions to the total biomass of all of the plants in the study are precisely known. Since there is no justification for the assumption of a constant dead-carbon fraction across different plant species and photosynthetic pathways, no meaningful corrections are possible. Furthermore, even if this fundamental problem is ignored, the application of slightly larger dead-carbon corrections than those used in the original paper produces a set of corrected [14]C-^{13}C fractionation ratios that are indistinguishable from 2.0.

In summary, the Saliege and Fontes (1984) experiments provide no basis for abandoning the use of 2.0 for the [14]C-^{13}C fractionation ratio in ^{14}C calculations, and use of their value of 2.3 cannot be justified. However, a significant body of theoretical work suggests that the true value for the fractionation ratio in many chemical reactions may be slightly smaller than 2.0, though different studies have produced computed values ranging from ~1.85 to 2.05. Given the high precisions that are now achievable in ^{14}C measurements, these deviations could significantly impact the accuracy of ^{14}C dates, and this topic clearly deserves further attention from the ^{14}C community.

REFERENCES

Amiro BD, Ewing LL. 1992. Physiological conditions and uptake if inorganic carbon-14 by plant roots. *Environmental and Experimental Botany* 42(3):203–11.

Amos B, Arkebauer TJ, Doran JW. 2005. Soil surface fluxes of greenhouse gases in an irrigated maize-based agroecosystem. *Soil Society of America Journal* 69:387–95.

Bigeleisen J, Ishida T. 1968. Applications of finite orthogonal polynomials to the thermal functions of harmonic oscillators. *Journal of Chemical Physics* 48(3):1311–30.

Bigeleisen J, Mayer MG. 1947. Calculation of equilibrium constants for isotopic exchange reactions. *Journal of Chemical Physics* 15:261–7.

Bond-Lamberty B, Wang C, Gower ST. 2004. A global relationship between the heterotrophic and autotrophic components of soil respiration? *Global Change Biology* 10(10):1756–66.

Craig H. 1954. Carbon 13 in plants and the relationships between carbon 13 and carbon 14 in nature. *Journal of Geology* 62(2):115–49.

Ding L, Wang KJ, Jiang GM, Li YG, Jiang CD, Liu M, Niu SL, Peng Y. 2004. Diurnal variation of gas exchange, chlorophyll fluorescence and xanthophylls cycle components of maize hybrids released in different years. 2006. *Photosynthetica* 44(1):26–31.

Eisberg RM. 1961. *Fundamentals of Modern Physics*. New York: Wiley and Sons.

Enoch HZ, Olesen JM. 1993. Plant response to irrigation with water enriched with carbon dioxide. *New Phytolologist* 125:249–58.

Fohlmeister J, Kromer B, Mangini A. 2011. The influence of soil organic matter age spectrum on the reconstruction of atmospheric ^{14}C levels via stalagmites. *Radiocarbon* 53(1):99–115.

Fontes JC. 1992. Chemical and isotopic constraints on ^{14}C dating of groundwater. In: Taylor RE, Long A, Kra RS. *Radiocarbon After Four Decades*. Berlin: Springer. p 242–61.

Ford CR, Wurzburger N, Hendrick RL, Teskey RO. 2007. Soil DIC uptake and fixation in *Pinus taeda* seedlings and its C contribution to plant tissues and ectomycorrhizal fungi. *Tree Physiology* 27:375–83.

Genty D, Massault M. 1999. Carbon transfer dynamics from bomb ^{14}C and δ^{13}C vs time series of a laminated stalagmite from SW France – modeling and comparison with other stalagmite records. *Geochimica et Cosmochimica Acta* 63(10):1537–48.

Hartshorn SR, Shiner Jr VJ. 1972. Calculation of H/D carbon-12/carbon-13, and carbon-12/carbon-14 fractionation factors from valence force fields derived for a series of simple organics molecules. *Journal of the American Chemical Society* 94(26):9002–12.

Hodge E, McDonald J, Fischer M, Redwood D, Hua Q, Levchenko V, Drysdale R, Waring C, Fink D. 2011.

Using the ^{14}C bomb pulse to date young speleothems. *Radiocarbon* 53(2):345–57.

Ishida T. 2002. Isotope effect and isotope separation: a chemist's view. *Journal of Nuclear Science and Technology* 39:407–12.

Jobard I, Chedin A. 1975. Critical analysis of the series expansion of the potential energy function of CO_2. *Journal of Molecular Spectroscopy* 57:464–79.

Kalt-Torres W, Kerr PS, Usuda H, Huber SC. 1987. Diurnal changes in maize leaf photosynthesis. *Plant Physiology* 83:283–8.

Kang S, Shi W, Zhang J. 2000. An improved water-use efficiency for maize grown under regulated deficit irrigation. *Field Crops Research* 67:207–14.

Levin I, Kromer B, Scoch-Fisher H, Bruns M, Munnich M, Berdau D, Vogel JC, Munnich KO. 1985. 25 years of tropospheric ^{14}C observations in central Europe. *Radiocarbon* 27(1):1–19.

Levin I, Hammer S, Kromer B, Meinharrdt F. 2008. Radiocarbon observations in atmospheric CO_2: determining fossil fuel CO_2 over Europe using Jungfraujoch observations as background. *Science of the Total Environment* 391(2–3):211–6.

Liu S, Liang XH. 2009. Observed diurnal cycle climatology of planetary boundary layer height. *Journal of Climate* 23:5790–809.

Long SP, Humphries S, Falkowski PG. 1994. Photoinhibition of photosynthesis in nature. *Annual Reviews of Plant Physiology and Plant Molecular Biology* 45:633–62.

Melander L. 1960. *Isotope Effects on Reaction Rates*. New York: Ronald Press Co.

O'Leary MH. 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20(4):353–67.

Olsson IU, Klasson M, Abd-el-Mageed A. 1972. Uppsala natural radiocarbon measurements XI. *Radiocarbon* 14(1):237–69.

Pearson GW. 1979. Precise ^{14}C measurements by liquid scintillation counting. *Radiocarbon* 21(1):1–21.

Power JF, Prasad R. 1997. *Soil Fertility Management for Sustainable Agriculture*. Boca Raton: CRC Press.

Reimer PJ, Brown TA, Reimer RW. 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3):1299–304.

Richet P, Bottinga Y, Javoy M. 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Annual Review of Earth and Planetary Science* 5:65–110.

Riley WJ, Hsueh DY, Randerson JT, Fischer ML, Hatch JG, Pataki DE, Wang W, Guolden MJ. 2008. Where do fossil fuel carbon dioxide emissions from California go? *Journal of Geophysical Research* 113: G04002, doi:10.1029/2007JG000625.

Rudzka D, McDermott F, Baldini LM, Fleitmann D, Moreno A, Stoll H. 2011. The coupled δ^{13}C-radiocar-

bon systematics of three late Glacial/early Holocene speleothems; insights into soil and cave processes at climatic transitions. *Geochimica et Cosmochimica Acta* 75(15):4321–39.

Saliege JF, Fontes JC. 1984. Essai de détermination expérimentale du fractionnement des isotopes ^{13}C et ^{14}C du carbone au cours de processus naturels. *International Journal of Applied Radiation and Isotopes* 35(1):55–62.

Stern MJ, Vogel PC. 1971. Relative ^{14}C-^{13}C kinetic isotope effects. *Journal of Chemical Physics* 55(5): 2007–13.

Stuiver M, Polach HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Stuiver M, Robinson SW. 1974. University of Washington GEOSECS North Atlantic carbon-14 results.

Earth and Planetary Science Letters 23(1):87–90.

Tcherkez G, Farquhar GD 2005. Carbon isotope effect predictions for enzymes involved in the primary carbon metabolism of plant leaves. *Functional Plant Biology* 32:277–91.

Van der Laan S, Karstens U, Neubert REM, Van der Laan-Luijkx IT, Meijer HAJ. 2010. Observation-based estimates of fossil fuel-derived CO_2 emissions in the Netherlands using $\Delta^{14}C$, CO and ^{222}Radon. *Tellus B* 62(5):389–402.

Wigley TML, Muller AB. 1981. Fractionation corrections in radiocarbon dating. *Radiocarbon* 23(2):173–90.

Wolfsberg M. 1972. Theoretical evaluation of experimentally observed isotope effects. *Accounts of Chemical Research* 7:225–33.

APPENDIX A: ISOTOPIC FRACTIONATION IN CHEMICAL EQUILIBRIA AND DIFFUSION PROCESSES

The following outline of isotopic fractionation for single-atom isotopic substitution in equilibrium chemical reactions is based on Bigeleisen and Mayer (1947) and is included to show the basis for predictions that the fractionation ratio for $^{14}C/^{12}C$ and $^{13}C/^{12}C$ is ~1.9. It should be noted that extrapolating from this value to complex processes such as photosynthesis is difficult. Major contributions to overall fractionation factors arise from diffusion of CO_2 through plant stomata (see Appendix A.2), carboxylation of the Rubisco enzyme (Tcherkez and Farquhar 2005), and in C_4 plants, leakage during internal transport of CO_2 from the initial site of fixation in PEP-carboxylase to the bundle sheath cells where decarboxylation and final fixation takes place (O'Leary 1981). Equilibrium and kinetic (non-equilibrium) fractionation effects from many other chemical reactions are also involved, as well as contributions from $CO_{2(gas)}$-$CO_{2(aq)}$ equilibria. The resulting mathematical expressions for overall fractionation factors become very complicated, and at least some of the fractionation factors and reaction constants for contributing processes are poorly characterized (O'Leary 1981; Tcherchez and Farquhar 2005).

A.1 Chemical Equilibria

In statistical mechanics, the probability that a single particle within an ensemble of identical particles of absolute temperature *T* will occupy an energy state *E* is given by

$$p(E) = (1/Q)e^{-E/kT}$$

where *k* is Boltzmann's constant and *Q* is the partition function. Since $\sum p(E) = 1$,

$$Q = \sum e^{-Ei/kT}$$

Hence, *Q* is a measure of the total number of states that can be populated in the molecular system at a given temperature: in a figurative sense it gives the "capacity" of the molecule as a container (Ishida 2002). Since the overall balance of an equilibrium chemical system depends on the number of states available for population by the reaction constituents, the equilibrium constant *K* for a single-atom isotopic substitution reaction AX + BX* = AX* + BX is simply

$$K = Q_{AX*}Q_{BX}/(Q_{AX}Q_{BX*}) \tag{A1}$$

where X and X* are the substituted atoms, with * indicating the heavy isotope.

As a first approximation, the partition function can be split into a product of translational, rotational, and vibrational factors. Furthermore, it can be shown that at ambient temperatures the translational and rotational contributions have their classical values (Eisberg 1961):

$$Q_{tr} = (2\pi MkT/h^2)^{3/2} \, V$$

$$Q_{rot} = \pi^{1/2} \, (8\pi^2 kT)^{3/2} (I_a I_b I_c)^{1/2}/sh^3$$

where V is the volume in which the molecule is free to move, M is the molecular weight, h is Planck's constant, I_a is the moment of inertia of the molecule about axis a, and s are symmetry numbers that give the number of equivalent ways of rotationally orienting the molecule in space. Then,

$$Q_{AX*}/Q_{AX} = (s/s_*)_{AX} \, (Q_{vib \, AX*}/Q_{vib \, AX})(M_{AX*}/(M_{AX}))^{3/2}(I_a I_b I_{c \, AX*}/I_a I_b I_{c \, AX})^{1/2} \qquad (A2)$$

The Teller-Redlich product rule relates the mass and geometry of a molecule undergoing isotopic substitution to the energy of vibrational states u and the mass of the substituted atom m:

$$\Pi(u^*_i/u_i) = (m/m^*)^{3/2} \, (M^*/(M))^{3/2}[I^*_a I^*_b I^*_c/(I_a I_b I_c)]^{1/2}$$

where the product runs over all vibrational degrees of freedom in the molecule.

Substituting in Equation A2 yields

$$Q_{AX*}/Q_{AX} = (s/s_*)_{AX} \, (Q_{vib \, AX*}/Q_{vib \, AX})(m^*/m)^{3/2}\Pi(u^*_i/u_i) \qquad (A3)$$

Substituting in Equation A1 and noting that the masses of the substituted atom m, m^* are the same in Q_{AX*}/Q_{AX} and Q_{BX*}/Q_{BX} so that the $(m^*/m)^{3/2}$ terms cancel:

$$K = [(s/s^*)_{AX}/(s/s^*)_{BX}][\Pi(u_i^*/u_i)_{AX}/\Pi(u_i^*/u_i)_{BX}][(Q_{vib \, AX*}/Q_{vib \, AX})/(Q_{vib \, BX*}/Q_{vib \, BX})] \quad (A4)$$

The vibrational partition functions are calculated by approximating the interactions between atoms by harmonic oscillators. The allowed energies for a quantum mechanical oscillator are

$$E_n = (n+1/2)h\upsilon \quad n = 0,1,2,\ldots$$

where υ is the classical harmonic oscillator frequency $\upsilon = 1/2[a/\mu]^{1/2}$, h is Planck's constant, a is a force constant, and μ a reduced mass (Eisberg 1961). Then, for a diatomic molecule

$$Q_{vib} = \sum e^{-(n+1/2) \, h\upsilon/kT}$$

$$= e^{-h\upsilon/2kT}(1 + e^{-h\upsilon/kT} + e^{-2h\upsilon/kT} + e^{-3h\upsilon/kT} + \ldots.)$$

$$= e^{-ui/2}/(1 - e^{-ui})$$

where $u_i = h\upsilon_i/kT$. For polyatomic molecules, each vibrational mode can be treated as an independent harmonic oscillator, and the full vibrational partition function for the molecule is

$$Q_{vib} = \Pi e^{-ui/2}/(1 - e^{-ui}) \qquad (A5)$$

where the product runs over all vibrational degrees of freedom.

It is convenient to define the reduced partition function ratio (RPFR), typically written $(s^*/s)f$:

$$(s^*/s)f_{AX} = (s^*/s)_{AX}(Q_{AX*}/Q_{AX})(m/m^*)^{3/2}$$

From Equations A3 and A5,

$$(s^*/s)f_{AX} = (Q_{\text{vib AX}*}/Q_{\text{vib AX}})\Pi(u^*_i/u_i) \tag{A6}$$

$$= \Pi u^*_i e^{-ui^*/2}/(1-e^{-ui^*})/\Pi u_i e^{-ui/2}/(1-e^{-ui})$$

Hence, $$\ln(s^*/sf)_{AX} = \Sigma\{\ln(u^*_i/u_i) + (u_i-u^*_i)/2 - \ln[(1-e^{-ui^*})/(1-e^{-ui})]\}$$

$$= \Sigma\{\ln(1-\Delta u_i/u_i) + \Delta u_i/2 - \ln[1+e^{-ui}(1-e^{\Delta ui})/(1-e^{-ui})]\}$$

where $\Delta u_i = u_i - u^*_i$. For small Δu_i, $1-e^{\Delta ui} - \Delta u_i$ and the third term reduces to $\ln[1-\Delta u_i/(e^{ui}-1)]$.

Using $\ln(1+x) \approx x$ for $x \ll 1$,

$$\ln(s^*/sf)_{AX} = \Sigma[-1/u_i+1/2+1/(e^{ui}-1)]\Delta u_i \tag{A7}$$

Expanding e^{ui} as a power series in u_i gives

$$1/(e^{ui}-1) = [u_i + u_i^2/2! + u_i^3/3! + u_i^4/4! +\ldots]^{-1}$$

$$= (1/u_i)[1 + (u_i/2! + u_i^2/3! + u_i^3/4! +\ldots)]^{-1}$$

$$= (1/u_i)[1 - (u_i/2! + u_i^2/3! + u_i^3/4! +\ldots) + (u_i/2! + u_i^2/3! + u_i^3/4! +\ldots)^2 - (\ )^3 +\ldots]$$

$$= 1/u_i - 1/2 - u_i/6 + u_i/4 \text{ to first order}$$

Then, from Equation A7, $\ln(s^*/sf)_{AX} = \Sigma(u_i/12)\Delta u_i = 1/24\Sigma\Delta(u_i^2)$.

The fractionation factor $\alpha_{B-A} = (X^*/X)_{AX}/(X^*/X)_{BX}$ is a ratio of isotope ratios for the molecular species AX and BX, and is clearly related to the reaction constant K for the isotopic substitution reaction, because by definition

$$K = [AX^*]/[AX]/([BX^*]/[BX]) \text{ where } [\ ] \text{ indicate concentrations.}$$

The classical value for K is simply the symmetry number factor in Equation A4:

$$K_{cl} = (s^*/s)_{AX}/(s^*/s)_{BX}$$

which represents the relative probabilities of forming symmetrical and unsymmetrical molecules with a completely random distribution of isotopes between the molecular species. In order to determine the fractionation factor α arising from a preference by the isotopic atoms for one or other of the reaction constituents, the molecular concentrations for the reactants and products must be normalized to remove that factor, so that

$$\alpha_{B-A} = K/K_{cl}$$

Therefore, from Equations A6 and A4:

$$\alpha_{B-A} = (s^*/s)f_{AX}/(s^*/s)f_{BX}$$

i.e. the fractionation factor is just the ratio of the RPFRs for the molecules AX and BX. Therefore,

$$\ln \alpha = \ln(s^*/sf)_{AX} - \ln(s^*/sf)_{BX} = 1/24\Sigma(\Delta(u_i^2)_{AX}-\Delta(u_i^2)_{BX}) \tag{A8}$$

For harmonic oscillator states, $u_i = h/(2\pi kT)(a_i/\mu)^{1/2}$ where a is a force constant and μ is a reduced mass given by $1/\mu = 1/m + 1/M$, with M representing other masses in the molecule that interact with the substituted atom. In the Born-Oppenheimer approximation, the motion of electrons can be treated separately from nuclei, which implies that the force constants do not change under isotopic substitution. Therefore, the changes $\Delta(u_i^2)$ are due to changes in the reduced masses, and Equation A8 can be rewritten as

$$\ln\alpha = 1/24[h/(2\pi kT)]^2[(1/\mu_{AX} - 1/\mu^*_{AX})\Sigma a_{iAX} - (1/\mu_{BX} - 1/\mu^*_{BX})\Sigma a_{iBX})]$$

and since the non-substituted masses M cancel in the differences of the reduced masses

$$\ln\alpha = 1/24[h/(2\pi kT)]^2(1/m - 1/m^*)\Sigma(a_{iAX} - a_{iBX}) \tag{A9}$$

It follows that
$$\ln\alpha_{m+2}/\ln\alpha_{m+1} = [1/m - 1/(m+2)]/[1/m - 1/(m+1)]$$

$$= 2(m+1)/(m+2) \tag{A10}$$

and therefore for $m = 12$, $\qquad b = \ln\alpha_{14}/\ln\alpha_{13} = 2(13/14) = 1.86$.

Note that based on Equation A10, the equality $\ln\alpha_{m+2}/\ln\alpha_{m+1} \approx 2.0$ (Craig 1954) is a poor approximation for elements as light as carbon.

This derivation of $\ln\alpha$—the so-called first quantum correction (Wolfsberg 1972)—is valid only when the vibrational energies are small, but the treatment has been extended to cover a much larger range of energies (Bigeleisen and Ishida 1968) and gives an almost identical functional form for $\ln\alpha$. Detailed calculations for individual equilibrium reactions, taking higher order effects into account, show most ^{14}C-^{13}C fractionation ratios clustering around 1.85–1.9 (Stern and Vogel 1971; Hartshorn and Shiner 1972). Furthermore, expressions similar to Equation A9 can be derived for kinetic fractionation for non-equilibrium reactions (Melander 1960; Wolfsberg 1972), implying similar mass dependence. However, Saliege and Fontes (1984) used spectroscopic factors from Jobard and Chedin (1975) in an alternative theoretical framework based on the use of Morse potentials rather than harmonic oscillator potentials (Richet et al. 1977) to derive ^{14}C-^{13}C fractionation ratios of 2.05 for reactions involving CO_2. Clearly, the theoretical basis for fractionation ratios remains unresolved.

A2. Gaseous Diffusion in Air

It can be shown from classical diffusion theory (Craig 1954) that the fractionation factor for CO_2 in air is given by

$$\alpha = [\mu/\mu^*]^{1/2}$$

where μ is a reduced mass for CO_2 in air given by

$$1/\mu = 1/M_{CO2} + 1/M_{air}$$

with $M_{CO2} = 44,45,46$ and taking $M_{air} \approx 28.8$, this yields $\alpha = 0.99559$ for ^{13}C/^{12}C and 0.99136 for ^{14}C/^{12}C, for a fractionation ratio of 1.96.