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Reassessment of the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ isotopic fractionation ratio and its impact on high-precision radiocarbon dating

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Abstract

The vast majority of radiocarbon measurement results ($^{14}C/^{12}C$ isotopic ratios or sample activities) are corrected for isotopic fractionation processes (measured as $^{13}C/^{12}C$ isotopic ratios) that occur in nature, in sample preparation and measurement. In 1954 Harmon Craig suggested a value of 2.0 for the fractionation ratio b that is used to correct $^{14}C/^{12}C$ ratios for shifts in the $^{13}C/^{12}C$ ratios and this value has been applied by the radiocarbon community ever since. While theoretical considerations suggest moderate deviations of b from 2.0, some measurements have suggested larger differences (e.g. $b = 2.3$, measured by Saliège and Fontes in 1984). With the high precision attained in radiocarbon measurements today (±2‰), even a relatively small deviation of b from 2.0 can impact the accuracy of radiocarbon data, and it is, therefore, of interest to re-evaluate the fractionation corrections. In the present study, the fractionation ratio b was determined by independent experiments on the chemical reduction of carbon dioxide (CO_2) to elemental carbon (graphitization reaction) and on the photosynthetic uptake of CO_2 by C_3 and C_4 plants. The results yielded $b = 1.882 \pm 0.019$ for the reduction of CO_2 to solid graphite and $b = 1.953 \pm 0.025$ for the weighted mean of measurements involving C_3 and C_4 photosynthesis pathways. In addition, the analysis of over 9600 full-sized OX-I and OX-II normalizing standards measured between 2002 and 2012 confirms b values lower than 2.0. The obtained values are in good agreement with quantum mechanical estimates of the equilibrium fractionation and classic kinetic fractionation as well as with results from other light three-isotope systems (oxygen, magnesium, silicon and sulfur). While the value of the fractionation ratio varies with the relative importance of kinetic and equilibrium fractionation, the values obtained in the present study cluster around $b = 1.9$. Our findings suggest that a significant fraction of all samples (“unknowns”) would be shifted by 2‰ (16 radiocarbon years) or more due to this effect: for example, for $b = 1.882$, between 16.8% and 25.9% of almost 60,000 radiocarbon values measured at the Keck Carbon Cycle AMS facility between 2002 and 2012 would be affected. The implications for radiocarbon dating and its accuracy are discussed.

Keywords: Photosynthesis; Radiocarbon; ^{14}C; AMS; High-precision measurement; Three-isotope system; Isotopic fractionation; Fractionation correction

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1. INTRODUCTION

1.1. Radiocarbon fractionation corrections

By convention (Stuiver and Polach, 1977), radiocarbon (^{14}C) data for dating and other applications is corrected for isotopic fractionation by normalizing samples to a $\delta^{13}C$ value of −25‰ (for a definition of the $\delta^{13}C$ notation see Eq. (14)) with respect to the Pee Dee Belemnite (PDB) reference material (Craig, 1957). The objective of this fractionation correction is the decoupling of ^{14}C sample activities (or $^{14}C/^{12}C$ isotopic ratios) from fractionation processes so that activities or isotopic ratios are a function of the sample's age or composition rather than isotopic fractionation. The correction accounts for any isotopic fractionation occurring in natural processes as well as during sample preparation and measurement, and is fundamental for the accuracy of radiocarbon dating. The nature of underlying kinetic and equilibrium fractionation processes are described in more detail in the discussion (Section 4). A general algebraic derivation of the fractionation correction has been given by Bigeleisen and Mayer (1947) and has been discussed in detail for the carbon three-isotope system by Southon (2011) as well as by Wigley and Muller (1981). According to the terminology used by Southon (2011) and Wigley and Muller (1981), the fractionation factor α_{14} of a $^{14}C/^{12}C$ ratio corresponds to a fractionation factor α_{13} of a $^{13}C/^{12}C$ ratio to the power of b[1]:

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

where b is the fractionation ratio and the fractionation factor α denotes a ratio R_A/R_B; R_A being the initial isotopic ratio and R_B being the ratio after a fractionation process, hence:

$$\alpha_{14} = \frac{R_{A,14}}{R_{B,14}} = \frac{\left(\frac{^{14}C}{^{12}C}\right)_A}{\left(\frac{^{14}C}{^{12}C}\right)_B} \text{ and } \alpha_{13} = \frac{R_{A,13}}{R_{B,13}} = \frac{\left(\frac{^{13}C}{^{12}C}\right)_A}{\left(\frac{^{13}C}{^{12}C}\right)_B} \tag{2}$$

By rewriting Eq. (1) with $\varepsilon = \alpha - 1$ and $\ln(1 + x) \approx x$ for $x \ll 1$ one obtains the often-used approximation:

$$b = \frac{\ln(1+\varepsilon_{14})}{\ln(1+\varepsilon_{13})} \approx \frac{\varepsilon_{14}}{\varepsilon_{13}} \text{ or } \varepsilon_{14} \approx b \cdot \varepsilon_{13} \tag{3}$$

While isotopic ratios are consistently used when dealing with stable isotopes, radiocarbon values were historically reported as specific activities due to the measurement method of decay counting. The radiocarbon reporting conventions (Stuiver and Polach, 1977) were established in the era of decay counting and are thus using activities rather than isotopic ratios. It is therefore important to understand how isotopic ratios and sample activities are linked: Specific sample activities A_S and the corresponding $^{14}C/^{12}C$ ratios R_S are closely proportional to each other. The only deviation from proportionality arises from omitting the $1 + (\delta^{13}C/1000)$ term in the denominator of Eq. (4):

$$A_S \propto \frac{^{14}C}{C} = \frac{^{14}C}{^{12}C + ^{13}C} = \frac{\frac{^{14}C}{^{12}C}}{1 + \frac{^{13}C}{^{12}C_{PDB}}\left(1 + \frac{\delta^{13}C}{1000}\right)} \approx \frac{\frac{^{14}C}{^{12}C}}{1 + \frac{^{13}C}{^{12}C}_{PDB}} \propto \frac{^{14}C}{^{12}C} \tag{4}$$

where $^{13}C/^{12}C_{PDB}$ is the $^{13}C/^{12}C$ isotopic ratio of the Pee Dee Belemnite (PDB) reference material (Craig, 1957). The discrepancy between specific activities and isotopic ratios arising from this simplification is on the order of 0.28‰ for a common $\delta^{13}C$ value of −25‰ in nature. However, normalization (Eqs. (9) and (10)) of activities (A_S and A_{SN}) or isotopic ratios (R_S and R_{SN}) with the activity or isotopic ratio of a measured standard (A_{ON} or R_{ON}, Eqs. (9) and (10)) will reduce this error as the difference in $\delta^{13}C$ values of standards and samples ($\Delta\delta^{13}C$) is much less than 25‰ in most cases. Therefore, activities and isotopic ratios are used interchangeably in the radiocarbon community and throughout this paper.

In radiocarbon fractionation corrections, b is always set to 2 by convention and a sample specific activity A_S is corrected to a $\delta^{13}C$ value of −25‰ to give the normalized sample activity A_{SN} (Stuiver and Robinson, 1974):

$$A_{SN} = A_S \frac{\left(1 + \frac{-25}{1000}\right)^b}{\left(1 + \frac{\delta^{13}C_S}{1000}\right)^b} = A_S \frac{0.975^b}{\left(1 + \frac{\delta^{13}C_S}{1000}\right)^b} \tag{5}$$

Or as a commonly used approximation (Stuiver and Polach, 1977):

$$A_{SN} = A_S\left(1 - \frac{b(25 + \delta^{13}C_S)}{1000}\right) \tag{6}$$

where $\delta^{13}C_S$ is the measured sample $\delta^{13}C$ value. With a fractionation ratio of 2, the measured $^{14}C/^{12}C$ ratio is corrected for exactly twice the difference between the $\delta^{13}C$ value of the sample and the $\delta^{13}C$ value of −25‰.

Similarly, the isotopic ratio or activity A_{OX} of a NIST oxalic acid I (SRM 4990B, OX-I) normalizing standard is fractionation-corrected to −19‰ $\delta^{13}C$ with respect to PDB, using a fractionation ratio of 2. By convention, the obtained value is then multiplied with a factor of 0.95 in order to obtain the normalized isotopic ratio or activity A_{ON}:

$$A_{ON} = 0.95 \cdot A_{OX} \frac{\left(1 + \frac{-19}{1000}\right)^b}{\left(1 + \frac{\delta^{13}C_{OX}}{1000}\right)^b} = 0.95 \cdot A_{OX} \frac{0.981^b}{\left(1 + \frac{\delta^{13}C_{OX}}{1000}\right)^b} \tag{7}$$

where $\delta^{13}C_{OX}$ is the measured $\delta^{13}C$ value of the OX-I normalizing standard. Accordingly, when using a different standard for normalization, Eq. (7) can be written as:

$$A_{ON} = \frac{0.95}{Ratio_{Std/OX}} \cdot A_{Std} \cdot \frac{\left(1 + \frac{\delta^{13}C_{StdNorm}}{1000}\right)^b}{\left(1 + \frac{\delta^{13}C_{Std}}{1000}\right)^b} \tag{8}$$

where $Ratio_{Std/OX}$ is 1.2736 for NIST oxalic acid II (OX-II, SRM 4990C) when OX-I is normalized to −19‰ and OX-II to −25‰ (Mann, 1983). A_{std} is the measured activity of the standard and $\delta^{13}C_{StdNorm}$ is −25‰ for all standards, except

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[1] The fractionation ratio b is widely used in the radiocarbon community. In studies on other three-isotope systems, however, the inverse value denoted β or λ is more commonly used. Hence, with $b = \beta^{-1} = \lambda^{-1}$, the equation $\alpha_{14} = \alpha_{13}{}^{b}$ corresponds to $\alpha_{13} = \alpha_{14}{}^{\beta}$.

for NIST (or NBS) OX-I, which is defined to be −19‰. $\delta^{13}C_{Std}$ corresponds to the measured $\delta^{13}C$ value of the standard.

Finally, the reported fraction modern ($F^{14}C$) values are obtained by dividing the fractionation-corrected isotopic ratio or specific sample activity A_{SN} by the fractionation-corrected isotopic ratio or specific activity of the oxalic acid normalizing standard A_{ON}. This is summarized in Eq. (9) and the resulting value corresponds to the fractionation-corrected fraction modern F_m (Donahue et al., 1990), which was redefined by Reimer et al. (2004) as $F^{14}C$:

$$F^{14}C = F_m = \frac{A_{SN}}{A_{ON}} = \frac{A_S}{0.95 \cdot A_{OX}} \cdot \left(\frac{0.975}{0.981}\right)^b \cdot \left(\frac{1 + \frac{\delta^{13}C_{OX}}{1000}}{1 + \frac{\delta^{13}C_S}{1000}}\right)^b \tag{9}$$

Accordingly, Eq. (9) can be written in a more general manner to include any standard material:

$$F^{14}C = F_m = \frac{A_{SN}}{A_{ON}} = \frac{A_S}{\frac{0.95}{Ratio_{Std/OX}} \cdot A_{Std}} \cdot \left(\frac{0.975}{1 + \frac{\delta^{13}C_{StdNorm}}{1000}}\right)^b \cdot \left(\frac{1 + \frac{\delta^{13}C_{Std}}{1000}}{1 + \frac{\delta^{13}C_S}{1000}}\right)^b \tag{10}$$

Other corrections may apply depending on the nature of the sample and there are cases where the fractionation correction is not applied to the sample activity but only to the normalizing standard (e.g. $d^{14}C$ and $\delta^{14}C$, Stuiver and Polach, 1977; Mook and Van der Plicht, 1999). However, the vast majority of reported ^{14}C values including radiocarbon ages are corrected for fractionation as shown in Eqs. (9) and (10).

It becomes clear from the above considerations that the accuracy of the fractionation correction critically depends on the fractionation ratio b, which is difficult to determine experimentally and for which the first order approximation of 2.0 has been used. Even though theoretical frameworks for the treatment of three-isotope systems including carbon exist, the fractionation ratio can vary depending on the relative contributions of kinetic and equilibrium fractionation (see Section 4.2.). While theoretical considerations of the kinetic and equilibrium fractionation suggest the value of b should be smaller than 2, many early studies have indicated values larger than 2 (Section 1.2 and Fig. 1). The goal of this work is to reassess the fractionation ratio and to experimentally determine a more accurate value. Moreover, the consequences on radiocarbon data of any deviation from 2.0 shall be discussed.

1.2. Previous determinations of the fractionation ratio

In 1954, Harmon Craig concluded that the use of a fractionation ratio of 2.0 was the most appropriate practice to correct $^{14}C/^{12}C$ values for differences in $^{13}C/^{12}C$ values (Craig, 1954). This choice was based partly on quantum mechanical calculations by Bigeleisen and Mayer (1947) that predicted b to be on the order of 1.9 (Bigeleisen, 1952), and Craig also considered an analogous isotopic fractionation ratio of the stable sulfur isotope ratios $^{32}S/^{34}S$ vs. $^{32}S/^{33}S$ that showed the expected fractionation ratio close to 2 ($b = 2.047 \pm 0.091$) in an experimental study by Thode et al. (1949). At the time, the precision of radiocarbon measurements was relatively low and the effects on ^{14}C ages of inaccuracies in fractionation corrections due to small deviations of b from 2 were not significant. The value for b was not well-constrained by early attempts to measure the carbon three-isotope system itself, since the experimental data showed a very large spread

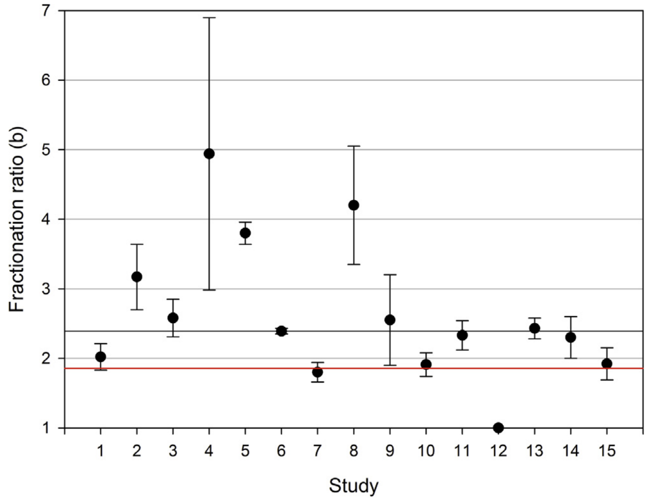


Fig. 1. Summary of all experimental studies on the carbon fractionation ratio b, sorted by year of publication and author's last names: (1) Fry and Calvin (1952); (2) Schmitt et al. (1952); (3) Stevens et al. (1952); (4) Van Norman and Brown (1952); (5) Yankwich et al. (1952); (6) Buchanan et al. (1953); (7) Schmitt and Daniels (1953); (8) Yankwich and Stivers (1953); (9) Attree et al. (1954); (10) Yankwich et al. (1954); (11) Rafter (1955); (12) Frey et al. (1956) and Stevenson et al. (1948); (13) Radnell (1980); (14) Saliège and Fontes (1984); (15) Meijer et al. (2006). The error weighted mean of all values (except for study 12) is shown as a black line ($b = 2.39$). The red line shows the equilibrium fractionation ratio of 1.857 for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 1). This could have been caused by the use of heavily ^{14}C-labeled compounds that were required to attain high sensitivity from decay-counting, or simultaneous mass spectrometric measurements of all three carbon isotopes. Moreover, results produced from tracer tests would have been more susceptive to ^{14}C contamination issues.

In 1975 and 1977, Saliège and Fontes (1984) carried out the first experiment to measure the fractionation ratio using natural levels of ^{14}C, in a study of photosynthesis of C_3 and C_4 plants. In spite of the care that was taken in the planning and execution of this pioneering effort, the results were compromised by contamination with "old" carbon from an unknown source. The authors attempted to correct for the effect of ^{14}C-free carbon on their data, but their reported value of $b = 2.3 \pm 0.3$ was still strongly depended on assumptions made concerning the uniformity of this contamination across different plant species and photosynthetic pathways (Southon, 2011). In the same publication, Saliège and Fontes (1984) calculated a value of 2.05 for the fractionation ratio based on the Morse potential (Richet et al., 1977) employing spectroscopic factors from Jobard and Chedin (1975), rather than the harmonic oscillator model that had been used previously. This result of $b = 2.05$ disagrees with calculations based on the approach of Bigeleisen and Mayer (1947) and Bigeleisen and Ishida (1968): under that scheme the first order approximation for equilibrium fractionation yields $b = 1.857$ (Eq. (19)) and the temperature dependent values derived by Stern and Vogel (1971) are $b_{min} = 1.84$ at 20 K and, $b_{max} = 1.98$ at 2000 K.

The most recent study on the fractionation ratio (Meijer et al., 2006) was performed on OX-I and IAEA C6 sucrose (Rozanski et al., 1992) reference materials by correlating $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios of multiple aliquots of these standards that exhibited different isotopic fractionations. The resulting value of $b = 1.92 \pm 0.23$ from this study is in good agreement with the theoretical considerations described above, and disagrees with the higher values from some of the early experiments (Fig. 1). However, the experiment performed by Meijer et al. (2006) still left the true value for b relatively poorly constrained as values of $b = 2$ or even $b > 2$ still lie within the $1 - \sigma$ interval due to the small fractionation effects induced in the experiment.

1.3. Motivation for the present work

The lack of agreement between results obtained with different theoretical frameworks as well as the large uncertainties and widely varying results from experimental work indicate that a re-assessment of the fractionation ratio is necessary. Empirically, the isotopic fractionation effects associated with sample preparation or measurement seem to be properly corrected for with a fractionation ratio of $b = 2.0$. I.e. measurements of a reference material undergoing different isotopic fractionation will yield the same $^{14}C/^{12}C$ ratio (within errors) after the isotopic correction with Eq. (9) or Eq. (10). However, the high precision of radiocarbon measurements achieved by many laboratories today and the growing number of samples and applications substantiate the importance of a more accurate fractionation ratio. Moreover, it would be of great general interest to confirm or disprove any anomaly in the fractionation behavior of the carbon isotopes, as suggested by the studies that found $b > 2.0$.

2. METHODS

2.1. General overview

While the experimental determination of α_{13} of a fractionation process is relatively simple, the simultaneous, precise and accurate determination of α_{14} has proven to be much more difficult. This is mainly due to the very low abundance of ^{14}C in nature, which limits the achievable measurement precision (the ratio of $^{14}C/C$ in so-called modern carbon, $F^{14}C = 1$, is $1.18 \cdot 10^{-12}$, Olsson, 1968). In addition, while ^{14}C owes its usefulness for dating applications to its radioactive nature, the same property makes the determination of the fractionation ratio more difficult as the radiocarbon content in a sample is not only a function of isotopic fractionation but also of the sample age or the mixing of old and modern carbon. Therefore, samples of the same original material but of different fractionation must be compared to assess the fraction ratio b.

An experimental design without ^{14}C-labeling was chosen for the determination of the fractionation ratio b, to avoid the risk of contaminating equipment or other samples. In order to increase the measurable effects of any potential deviation of b from 2.0, reference materials with well-defined $^{13}C/^{12}C$ and $^{14}C/^{12}C$ values had to be subjected to reactions and processes that induce strong isotopic fractionation. Two fundamentally different processes that play an important role in ^{14}C applications were investigated for their fractionation ratios: the conversion of CO_2 to graphite by means of a reduction with hydrogen (Section 2.2) and the photosynthetic uptake of CO_2 by C_3 as well as C_4 plants (Section 2.3). The latter process is much more difficult to characterize theoretically as it involves many steps such as gaseous diffusion through the stomata ($\alpha_{13} = 1.0044$, Craig, 1954) and the carbon fixation by the enzyme RuBisCo ($\alpha_{13} = 1.0196$ up to 1.0303, Guy et al., 1993).

2.2. The fractionation ratio in the incomplete graphitization reaction

The reduction of CO_2 with hydrogen over a metal catalyst to produce graphite (Vogel et al., 1984) is a standard procedure in ^{14}C sample preparation for Accelerator Mass Spectrometry (AMS) measurements. The formed graphite/metal mixture can be readily measured by AMS to determine $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios from the same graphite target. The main reaction can be summarized as:

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

and

$$CO + H_2 \xrightarrow{\Delta,\ catalyst} C(s) + H_2O$$

where iron (Walker et al., 1959) or other metals such as cobalt serve as a catalyst for the graphite reduction reaction. It is known that the maximum CO (carbon monoxide) concentration is reached long before completion of the reaction (McNichol et al., 1992); hence the reduction of CO to elemental carbon is the rate limiting step. With a major lack of hydrogen, the reduction does not reach completion and significant isotopic fractionation occurs (Vogel et al., 1987), depleting the graphite in the heavier carbon isotopes. This effect was used for the deliberate fractionation of OX-I and OX-II (NIST SRM 4990C) standard materials (hereinafter referred to as "fractionation samples" or "fractionated samples"). Approximately 60 mg of OX-I or OX-II materials (as oxalic acid dihydrate) were combusted at 900 °C for 3 h in sealed quartz tubes with ~180 mg prebaked cupric oxide (CuO). Upon cracking the quartz tubes in a vacuum line, the produced CO_2 was split into several graphitization reactors (Santos et al., 2007): Fractionation samples (~1.75 mg C each as CO_2 at the start, and ~0.3 mg C of graphite in the end; graphite carbon mass determined by elemental analyzer) and fully reacted, non-fractionated comparative samples (~0.3 mg C each, matching the sample size of fractionated samples after graphitization) were produced as graphite. For normalization and quality control purposes, OX-I graphite targets of ~0.75 mg C each were produced by our standard procedure (Santos et al., 2004). A stoichiometric amount of H_2 gas was added to the reactors for the normalizing standards and non-fractionated comparative samples to allow a complete reduction of the CO_2, but only 25% of the H_2 necessary for a complete reduction was added to the fractionation samples. In order to minimize oxidation of the iron with excess CO_2 (Gibbs et al., 1973), the graphitization reaction of the fractionation samples was conducted at 450 °C (instead of the conventional 550 °C). Consequently, the non-fractionated comparative samples were graphitized at the same temperature to keep the sample treatments comparable. The amount of iron catalyst was kept constant at 5.0 ± 0.2 mg for all reactors and the water produced in the reduction reaction was trapped with fresh magnesium perchlorate ($Mg(ClO_4)_2$), as described in Santos et al. (2004). After a graphitization reaction time of 3 h, the heating was stopped and residual gas was pumped away. By analogy with the preconditioning of the iron powder for surface carbon removal (e.g. Vogel et al., 1987), the partly oxidized iron in the iron/graphite mixture was reduced with 200 Torr of H_2 for 20 min at 400 °C in the presence of the graphite in both fractionated and non-fractionated comparative samples. This minimized the abundance of oxygen and its negative effects (a lower efficiency for production of C^- due to the competition for electrons, Fahrni et al., 2013) and ensured that the ionization efficiencies of both fractionated and non-fractionated comparative samples were similar. After this reduction step, the graphite samples were pressed into 1 mm diameter bore hole aluminum target holders. Finally, two separate batches of OX-I and OX-II samples consisting of fractionated and non-fractionated comparative samples and OX-I normalizing standards were measured by ^{14}C-AMS at the KCCAMS facility at UC Irvine (see Table 1 for results). Fractionated and non-fractionated samples were randomized throughout the sample wheel in order to cancel out potential systematic effects during the measurement.

2.3. The fractionation ratio in photosynthesis

To measure the fractionation ratio b in photosynthesis, the isotopic composition of CO_2 in a gas cylinder of compressed air was compared to the biomass that was grown in the same atmosphere. Seeds of Alfalfa (*Medicago sativa*, C_3), Basil (*Ocimum basilicum*, C_3) as well as Amaranth (*Amaranthus caudatus*, C_4) were grown in a desiccator that was used as an airtight greenhouse (Fig. 2). These plant species were chosen for their fast germination and growth as

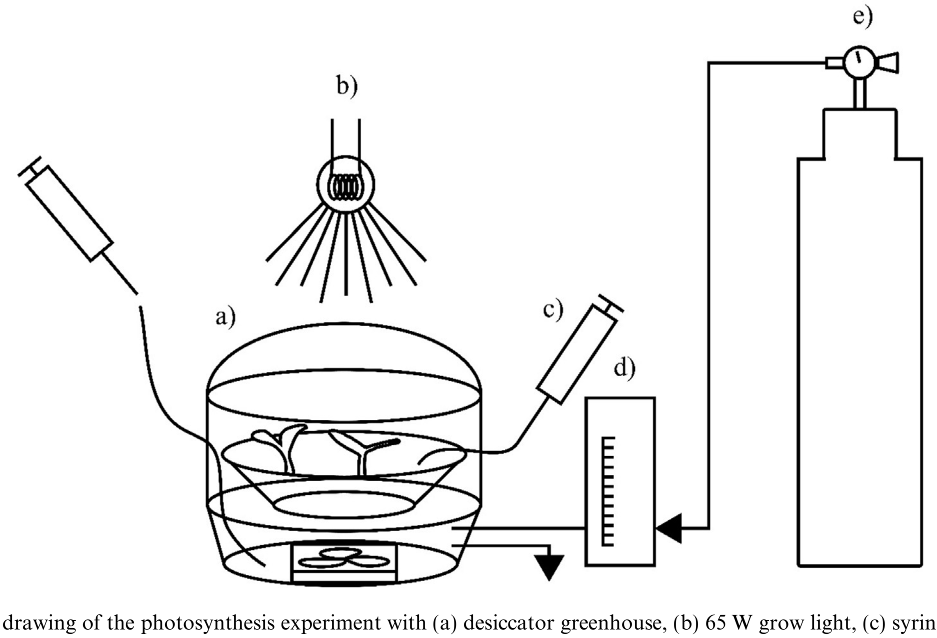


Fig. 2. Schematic drawing of the photosynthesis experiment with (a) desiccator greenhouse, (b) 65 W grow light, (c) syringe with long needle for irrigation, (d) flow meter, (e) gas cylinder with a mixture of breathing air and CO_2 from OX-I.

well as for their small seeds, which contained minimal amounts of stored carbon.

In order to obtain a carbon-free "soil" substrate, ca. 600 ml of sand was acidified overnight with 0.1 M HCl to hydrolyze any $CaCO_3$ originally present. Thereafter, the sand was rinsed and brought to a pH between 5 and 6, dried at 120 °C and baked at 900 °C for 3 h in a porcelain dish of 21.5 cm diameter. Upon cooling, the sand was watered with Mili-Q water with a very low total organic carbon content of $\leq$2 μg carbon L^{-1}. The porcelain dish containing the wet sand was placed on an elevated, perforated plate in a clear polycarbonate desiccator (10 3/4″ O.D., 12 1/8″ height, McMaster-Carr, USA). An electric fan was installed below the ceramic dish to provide sufficient mixing of the air during the experiment. The fan was powered via two stainless steel capillaries that also served as inlet and closable sampling outlet for the gas. A 25 ml gastight instrument syringe (Hamilton, Reno, USA) with a stainless steel needle allowed injection and straightforward dosing of water through a rubber septum. A carbon-free fertilizer was prepared according to Hewitt and Smith (1975): 8 mM KNO_3, 8 mM $Ca(NO_3)_2$, 3 mM $MgSO_4$ and 2.7 mM NaH_2PO_4 were dissolved in 1 L degassed Milli-Q water. The fertilizer was added roughly every 2 days using the 25 ml syringe. Water that condensed on the walls was collected on the bottom of the desiccator, and a closable drain was installed through which the water could be drawn out with a syringe without any gas exchange. A schematic drawing of the setup is shown in Fig. 2.

All seeds were soaked in Milli-Q water for 5 days before they were sowed into the wet sand. Compressed artificial air mixed from pure oxygen, nitrogen and 373 ppm of CO_2 derived from OX-I was used to provide a ^{14}C isotopic composition similar to contemporary atmosphere but with a well-known and well-defined isotopic composition. The gas was delivered to the greenhouse at increasing flow rates of 4 L/hr to 12 L/hr over the course of the experiment, with higher flow rates at the end when more biomass was present, thus avoiding excessive photosynthetic drawdown and fractionation of the desiccator CO_2 pool, and ensuring that the atmosphere retained a well-defined isotopic content. The desiccator was kept at slight overpressure at all times to ensure that ambient air (with its different isotopic composition) could not contaminate the plant carbon growing within the desiccator. Aliquots of the gas inside the desiccator were sampled at the gas outlet with evacuated 6 L canisters before, during and after the experiment to serve as comparative samples for the produced biomass. The extraction of CO_2 from sampled air was performed with the vacuum line described by Xu et al. (2007).

Under constant illumination with a growing light (Spot-Gro, 65 W, Sylvania, USA), the germinated seeds grew to seedlings 1–4 days after sowing. With the seedlings being less prone to drying out than the germinating seeds, a second lamp was installed to provide enough light for all seedlings to grow. 20 days after sowing, the seedlings were harvested in dim light to minimize photosynthetic uptake of ambient CO_2. The plants were vacuum dried immediately (5 min after harvesting) at 50 °C. Pairs of true leaves (leaves that are growing from newly photosynthesized biomass, not the "seed leaves" or cotyledons) were cut off from every dried plant and combusted with ~60 mg CuO in evacuated and sealed quartz tubes. The CO_2 from those combustions as well the CO_2 extracts from the compressed air feeding the plants were graphitized over 5.0 ± 0.2 mg Fe catalyst with stoichiometric amounts of H_2 at 550 °C (Santos et al., 2007). The graphite targets produced from leaves of C_3 and C_4 plants, comparative gas extracts and normalizing OX-I standards were all measured in a single AMS run to prevent potential offsets between different runs (see Table 1 for results).

A second experiment was run with the same setup but with pressured air containing 398 ppm of radiocarbon-free (fossil, $F^{14}C = 0$) CO_2 (Airgas, USA). This experiment was performed to confirm that the selected leaves (true leaves) were indeed free of contamination from ambient air or seed carbon, which would bias the determination of the fractionation ratio b. ^{14}C signatures of seeds were measured prior to the experiment and the plants were harvested after 26 days from sowing. Sample preparation and measurements were performed as described above, results are summarized in Table 2.

2.4. Determining the fractionation ratio from experimental data

The new fractionation ratio b_{new} can be calculated directly from isotopic ratios or specific activities with Eq. (1). However, it is not common to refer to such "raw" $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios and ^{14}C data in publications or report files are usually normalized relative to a standard and fractionation-corrected (Eqs. (9) and (10)). Therefore, the following discussion will focus on the calculation of b_{new} from $F^{14}C$ and $\delta^{13}C$ values. AMS $\delta^{13}C$ values (measured online with ^{14}C) were used for this calculation, rather than $\delta^{13}C$ values from a more precise isotope ratio mass spectrometer (IRMS) because IRMS $\delta^{13}C$ values cannot account for isotopic fractionation occurring in the sputter ion source or other parts of the AMS instrument (Santos et al., 2007).

In order to calculate the new fractionation ratio values, all samples (fractionated and non-fractionated comparative samples) were treated as unknown samples according to well-established radiocarbon conventions (Stuiver and Polach, 1977). $F^{14}C$ values were calculated according to Eqs. (9) and (10) with b = 2 using the Lawrence Livermore (LLNL) Fudger code (Version 5.3) by T. Ognibene and as described in Santos et al., 2007.

In order to use fractionation-corrected ^{14}C values, the numerator of the known Eq. (1) is rewritten as:

$$ln\left(\frac{R_{A,14}}{R_{B,14}}\right) = ln\left(\frac{A_{S_A}}{A_{S_B}}\right) = ln\left(\frac{\frac{A_{SN_A}}{A_{ON}}}{\frac{A_{SN_B}}{A_{ON}}} \cdot \frac{\frac{\left(1+\frac{\delta^{13}C_A}{1000}\right)^b}{0.975^b}}{\frac{\left(1+\frac{\delta^{13}C_B}{1000}\right)^b}{0.975^b}}\right) \qquad (11)$$

where the last term in brackets cancels the previously applied fractionation correction with b = 2. Because the same normalizing standards were used for both sample sets,

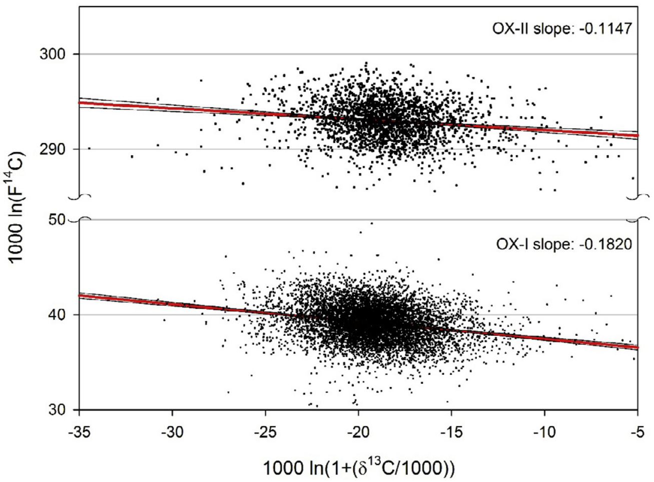


Fig. 3. Three-isotope plot of all normalizing OX-I and OX-II standards measured at the KCCAMS facility between 2002 and 2012. The least squares fits are shown as red lines and the 95% confidence intervals are indicated with black lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

their corrections cancel out and are not shown in Eq. (11). With the denominators 0.975^b cancelling out and with $A_{SN}/A_{ON} = F^{14}C$ (Eq. (9)), Eq. (11) becomes:

$$ln\left(\frac{R_{A,14}}{R_{B,14}}\right) = ln\left(\frac{F^{14}C_A}{F^{14}C_B}\cdot\left(\frac{1+\frac{\delta^{13}C_A}{1000}}{1+\frac{\delta^{13}C_B}{1000}}\right)^b\right) \tag{12}$$

After further simplification, the numerator can be written as:

$$ln\left(\frac{R_{A,14}}{R_{B,14}}\right) = ln\left(\frac{F^{14}C_A}{F^{14}C_B}\right) + b\cdot ln\left(\frac{\delta^{13}C_A+1000}{\delta^{13}C_B+1000}\right) \tag{13}$$

In order to obtain the isotopic ratio for the denominator of Eq. (1), the delta notation:

$$\delta^{13}C_S = \frac{R_{S,13}-R_{PDB}}{R_{PDB}}\cdot 1000 \tag{14}$$

is converted to an isotopic ratio:

$$R_{S,13} = \delta^{13}C_S\cdot\frac{R_{PDB}}{1000} + R_{PDB} = (\delta^{13}C_S+1000)\cdot\frac{R_{PDB}}{1000} \tag{15}$$

The denominator of Eq. (1) can thus be written as:

$$ln\left(\frac{R_{A,13}}{R_{B,13}}\right) = ln\left(\frac{(\delta^{13}C_A+1000)\cdot\frac{R_{PDB}}{1000}}{(\delta^{13}C_B+1000)\cdot\frac{R_{PDB}}{1000}}\right) = ln\left(\frac{\delta^{13}C_A+1000}{\delta^{13}C_B+1000}\right) \tag{16}$$

Inserting Eqs. (13) and (16) in Eq. (1) and further simplification yields the equation for the new fractionation ratio b_{new}:

$$b_{new} = \frac{ln\left(\frac{F^{14}C_A}{F^{14}C_B}\right)}{ln\left(\frac{\delta^{13}C_A+1000}{\delta^{13}C_B+1000}\right)} + b \tag{17}$$

where $F^{14}C_A$ and $\delta^{13}C_A$ are error weighted mean values of the non-fractionated samples and $F^{14}C_B$ as well as $\delta^{13}C_B$ are the error weighted means of the fractionated samples. Because a fractionation ratio of 2 is used by convention for the normalization of sample $F^{14}C$ values, the summand b (=2) in Eq. (17) accounts for the previously applied fractionation correction. It should be noted that Eq. (17) does not contain any approximations other than equating activities with isotopic ratios and thereby neglecting the 1 + (δ^{13}C/1000) term in Eq. (4). This approximation will lead to an error on the order of 10% of the error caused by using a fractionation ratio of 2 instead of the "true" fractionation ratio.

Alternatively to Eq. (17), the difference ($b_{new} - 2$) between the new fractionation ratio values (b_{new}) and the old fractionation ratio ($b = 2$) can be obtained from the slope of a linear regression of all fractionated and unfractionated samples in a three-isotope plot (Fig. 3). However, while plotting isotopic ratios in the δ-notation would correspond to a simplification equivalent to Eq. (3), plotting isotopic ratios according to Eq. (17) ($\ln(\delta^{13}C_S + 1000)$ versus $\ln(F^{14}C_S)$) would lead to meaningless axis scales. In order to illustrate the mathematically correct logarithmic scales of Eq. (17) while keeping a scale that closely corresponds to the δ-notation, Miller (2002) introduced an axis scale that can be written as $1000\cdot\ln(1 + (\delta^{13}C_S/1000))$ versus $1000\cdot\ln(F^{14}C)$ for the carbon isotopes.

3. RESULTS

3.1. Results and error estimation

The results of the fractionation experiments and the values for the fractionation ratio b_{new} are summarized in Table 1. The fractionation ratios in Table 1 were calculated as error-weighted means according to Olive et al. (2014). 1σ errors of b_{new} in Table 1 were calculated by error propagation (Bevington and Robinson, 2002) based on Eq. (17), with uncertainties obtained by dividing the standard deviation of each set of fractionated and non-fractionated samples by the square root of n, the number of measurements.

Table 1
Summary of the fractionation experiments. Δ-values were calculated using error weighted means of fractionated and non-fractionated sample sets. Uncertainties of Δ-values were obtained by pooling standard errors of the means of fractionated and non-fractionated samples. b_{new} values were calculated according to Eq. (17) and uncertainties were estimated by error propagation. b^*_{new} values and their errors were derived from slopes in three-isotope plots. The means of all measurements were error weighed. The number of measurements n are indicated as fractionated + non-fractioned samples. The non-fractionated samples in the photosynthesis experiment were the same for C_3 and C_4 comparisons.

Experiment	$\Delta\delta^{13}C$	$\Delta\delta^{13}C\pm$	$\Delta F^{14}C/F^{14}C$	$\Delta F^{14}C/F^{14}C\pm$	b_{new}	$b_{new}\pm$	b^*_{new}	$b^*_{new}\pm$	n
OX-I (graphitization)	29.2	0.4	−0.00154	0.00155	1.949	0.052	1.938	0.051	9 + 9
OX-II (graphitization)	32.1	0.8	−0.00424	0.00067	1.872	0.021	1.887	0.020	11 + 11
					1.882	0.019	1.894	0.019	40
C3 (photosynthesis)	24.9	0.7	−0.00127	0.00070	1.952	0.026	1.951	0.026	21 + 16
C4 (photosynthesis)	7.2	0.8	0.00024	0.00094	1.968	0.123	1.977	0.107	7 + 16
					1.953	0.025	1.952	0.025	44

Table 2
Summary of the results from the second photosynthetic experiment for the evaluation of background levels. The propagation of seed carbon in the growing leaves is given in percent.

	Basil (C_3)	Alfalfa (C_3)	Amaranth (C_4)
Seeds ($F^{14}C$)	1.0507 ± 0.0014	1.0610 ± 0.0016	1.0681 ± 0.0014
Cotyledon (% seed C)	19.2	8.1	14.7
1st true leaves (% seed C)	1.0	3.8	0.4
2nd true leaves (% seed C)	0.7	2.1	0.3
3rd true leaves (% seed C)	0.7	2.0	N/A
4th true leaves (% seed C)	N/A	2.1	N/A

Results from Miller-type plots (b^*_{new}) are given in Table 1 for comparison with the values of the error-weighted means and the data of Fig. 3 is illustrated in a Miller-type plot. The small difference between b values calculated by Eq. (17) and the three-isotope plot are explained by the error weighting of the data when Eq. (17) was used versus an unweighted linear regression for the three-isotope plots.

3.2. The fractionation ratio in the incomplete graphitization reaction

The fractionation ratio of the graphitization experiments was $b = 1.882 \pm 0.019$ ($n_{total} = 40$). Precision differences between the OX-I and OX-II fractionation results shown in Table 1 are due to poorer AMS system performance during the OX-I run, which resulted in a more pronounced scatter of the OX-I ^{14}C results and, consequently, increased the uncertainty of the OX-I fractionation data.

3.3. The fractionation ratio in photosynthesis

The fractionation ratio of the photosynthesis experiments was 1.953 ± 0.025 ($n_{total} = 44$). The comparatively large uncertainty of b in the C_4 plant experiment is explained mostly by the small fractionation that was induced by the C_4 photosynthesis and the sensitivity of the error propagation of Eq. (17) to small differences in $\Delta\delta^{13}C$ values. Nevertheless, the value of C_4 plants is in good agreement with the values obtained with C_3 plants. Calculating the fractionation ratio b by comparing C_3 and C_4 biomass yielded a fractionation ratio ($b = 1.946 \pm 0.048$) comparable to the fractionation ratio obtained when comparing C_3 or C_4 biomass to gas extracts of OX-I CO_2 air (Table 1). The consistency of biomass vs. biomass and biomass vs. gas extracts largely rules out an artifact through different treatments of gas and biomass samples.

Results of the photosynthesis experiment with ^{14}C-free (fossil) CO_2 in air are shown in Table 2. The results demonstrate that the fraction of the measured biomass derived from seed carbon was very small and that contamination by ambient carbon from outside the desiccator was negligible. The seeds used in the photosynthesis experiment (Section 2.3, Table 1) with OX-I CO_2 had $F^{14}C$ values of 1.044 (basil), 1.0563 (alfalfa) and 1.0644 (amaranth). All of those $F^{14}C$ values are very close to the value of the OX-I in the desiccator air of the first experiment and hence the effect of seed carbon on the calculated b values was negligible.

3.4. The fractionation ratio in normalizing standards

In addition to the deliberately introduced fractionation in the experiments described in this work, standard materials that were measured over the course of 10 years at the KCCAMS laboratory were analyzed for deviations in b (Fig. 3). Even though these samples have well-known and well-defined $\delta^{13}C$ values in the bulk material, their AMS $\delta^{13}C$ values vary due to fractionation during the measurement in the accelerator mass spectrometer and to a lesser degree in the graphitization reaction. If fractionation corrections with a value of $b = 2.0$ led to an absolute independence ($R^2 \approx 0$) of ^{14}C and ^{13}C values as well as a linear regression with a slope of 0 in the three-isotope plots, 2.0 could be considered the true fractionation ratio. However, that was not found from the analysis of 7241 OX-I and 2386 OX-II measurements (all normalizing or secondary standards larger than 0.5 mg C to minimize effects of size dependence). A linear regression of the three-isotope plots of OX-I and OX-II yielded $b = 1.818 \pm 0.009$ ($2–0.1820 = 1.8180$) and $b = 1.885 \pm 0.014$ ($2–0.1147 = 1.8853$), respectively (Fig. 3). Errors were calculated from uncertainties of the regression. It is unclear why the OX-I values are not in better agreement with those obtained from the OX-II standards and the results from the deliberate fractionation experiment produced in this study. However, an important difference is that the deliberately fractionated samples show a much higher degree of isotopic fractionation than the regular OX-I and OX-II samples produced by standard procedures. Hence, the fractionation ratios measured in the deliberate fractionation experiments can be determined more precisely with Eq. (17) and with a relatively small number of measurements, while the errors of the slope determination may be underestimating the true uncertainty. Furthermore, the isotopic fractionation induced by any AMS instrument can be significant and may not be strictly mass dependent *per se* (Steier et al., 2004), e.g. if ion optical effects lead to disproportionate beam losses of the three carbon isotopes. However, for samples of similar size and similar negative ion currents measured in a single measurement run, any such machine-induced isotopic fractionation effects should be constant and hence will largely cancel in direct comparisons of fractionated and non-fractionated samples. Negative ion currents of fractionated and non-fractionated OX-I and OX-II samples in Table 1 were kept within a range of 5% to minimize any such mass-independent effects. Furthermore, the photosynthesis samples were all full-sized graphite targets (>0.65 mg C) and hence all produced very similar negative ion beam currents.

4. DISCUSSION

4.1. General aspects

The values found from the incomplete reduction reaction (Section 2.2) and the photosynthetic conversion of CO_2 into plant biomass (Section 2.3) yielded fractionation ratios that are in agreement with the predicted values between 1.857 and 2 based on the Bigeleisen and Mayer (1947) approach. In the following, the plausibility of the new data, comparisons to other three-isotope systems and the consequences of a deviation of the true fractionation ratio from the conventional value of 2 are discussed.

4.2. Theoretical considerations of the equilibrium and kinetic fractionation

The fractionation ratio b in any process or sequence of processes can vary with the relative importance of equilibrium and kinetic fractionation. In the latter case, the resulting fractionation ratio also depends on the mass of the atoms bonded to the isotope of interest. In contrast to the kinetic fractionation, fractionation that occurs in chemical equilibrium is nearly independent of chemical bonding and depends mostly on isotopic masses (and to a lesser degree on temperature). The theoretical framework for this fractionation process was developed by Bigeleisen and Mayer (1947) and derivations of the resulting value for b were given in Young et al. (2002) and Southon (2011). In its simplest form (to first order only and neglecting temperature effects), the fractionation ratio in chemical equilibrium is given by:

$$b_{equ} = \frac{\frac{1}{m} - \frac{1}{m+2}}{\frac{1}{m} - \frac{1}{m+1}} \tag{18}$$

where m is the mass of the lightest isotope of the triplet. This equation can be further simplified to:

$$b_{equ} = 2\frac{m+1}{m+2} \tag{19}$$

Which results in a value of $b = 1.857$ for $m = 12$.

Kinetic fractionation (e.g. diffusion, evaporation, irreversible bond dissociations) on the other hand can be described by classical mechanics and depends on the mass of the atoms bonded to the isotopes of interest. The kinetic fractionation ratio b_{kin} can be calculated as (Young et al., 2002):

$$\beta_{kin} = \frac{\ln\left(\frac{\mu_1}{\mu_2}\right)}{\ln\left(\frac{\mu_1}{\mu_3}\right)} \tag{20}$$

and since $b = \beta^{-1}$

$$b_{kin} = \frac{\ln\left(\frac{\mu_1}{\mu_3}\right)}{\ln\left(\frac{\mu_1}{\mu_2}\right)} \tag{21}$$

where in the simplest case of breaking a C-C bond, the reduced masses μ_1, μ_2, and μ_3 are calculated directly from the isotopic masses $m = 12$, $m + 1 = 13$, and $m + 2 = 14$:

$$\mu_1 = \frac{1}{\frac{1}{m} + \frac{1}{m}}, \quad \mu_2 = \frac{1}{\frac{1}{m+1} + \frac{1}{m}}, \quad \mu_3 = \frac{1}{\frac{1}{m+2} + \frac{1}{m}} \tag{22}$$

when interactions with other atoms are neglected and the second atom is assumed to be ^{12}C, thereby neglecting the 1.1% of ^{13}C in any sample.

For the diffusion of the isotopologues of CO_2 ($^{12}CO_2$ ($m = 44$), $^{13}CO_2$ ($m + 1 = 45$), $^{14}CO_2$ ($m + 2 = 46$)) in air, Eq. (21) can be written as:

$$b_{kin} = \frac{\ln\left(\frac{\frac{1}{\frac{1}{m}+\frac{1}{m_{Air}}}}{\frac{1}{\frac{1}{m+2}+\frac{1}{m_{Air}}}}\right)}{\ln\left(\frac{\frac{1}{\frac{1}{m}+\frac{1}{m_{Air}}}}{\frac{1}{\frac{1}{m+1}+\frac{1}{m_{Air}}}}\right)} = \frac{\ln\left(\frac{m((m+2)+m_{Air})}{(m+2)(m+m_{Air})}\right)}{\ln\left(\frac{m((m+1)+m_{Air})}{(m+1)(m+m_{Air})}\right)} \tag{23}$$

Breaking of the C-C bond in the first-order approximation (neglecting the interaction with masses of the atoms bonded to the carbon atoms in question) using Eqs. (21) and (22) results in a fractionation ratio of $b = 1.890$ and the diffusion of the isotopologues of CO_2 in air (Eq. (23)) yields $b = 1.965$ with an average mass for air molecules m_{Air} of 28.8 amu. It can be shown that the upper limit of b, calculated with Eq. (21), is 2. However, $b = 2$ would correspond to the consideration of e.g. the diffusion of high-molecular weight isotopologues, which will be a rare process and will not greatly influence the overall fractionation ratio in most radiocarbon samples.

4.3. Relative importance of equilibrium and kinetic fractionation

Both equilibrium and kinetic fractionation are likely to occur in any complex fractionation process. Indeed, the measured fractionation ratio of $b = 1.882 \pm 0.019$ for the reduction of CO_2 to graphite lies between the theoretical value of 1.857 for equilibrium fractionation and the theoretical kinetic fractionation values of 1.890 for C-C bond breaking, or 1.965 for the diffusion of CO_2 in air. The relatively low value of 1.882 found in the graphitization fractionation can be interpreted as a consequence of a large contribution from equilibrium fractionation, and if kinetic fractionation is involved in the process, it involves molecules of low molecular weight, thus also contributing to a low fractionation ratio. Hence, the low value for b in the graphite reaction appears to be the logical consequence of a slow high-temperature reaction of small molecules. In contrast, photosynthetic uptake is strongly influenced by processes involving kinetic fractionation, such as the diffusion of CO_2 through the stomata and the enzymatically controlled carboxylation reactions that actually fix CO_2 (O'Leary, 1988). Therefore, while the reactions involved in photosynthesis are much more complex than for graphitization, the measured fractionation ratio of 1.953 ± 0.025 also seems plausible.

4.4. Comparison to other three-isotope systems

Since the theoretical framework discussed above will also apply to other three-isotope systems, a comparison of theoretical fractionation ratios and experimentally determined values for those systems provides another basis for the verification of the fractionation ratios determined in the present study. The fractionation ratios measured for low-mass, stable three-isotope systems are compared to the carbon fractionation ratio in Fig. 4.

High precision studies on the fractionation ratio of the stable isotopes of oxygen (O^{16}, O^{17}, and O^{18}), magnesium (Mg^{24}, Mg^{25}, Mg^{26}), silicon (Si^{28}, Si^{29}, Si^{30}), and sulfur (S^{32}, S^{33}, S^{34}) have been published in recent years. Rather than measuring the isotopic composition before and after a number of fractionation processes in an experiment, these studies compared the isotopic composition of a variety of samples found in nature. Similarly to the method described earlier, the slopes of the linear regressions of these three-isotope plots yielded the fractionation exponents variously quoted as β or λ, which are inverse to the fractionation ratio b (Eqs. (20) and (21)). This method simplifies the determination of b for stable isotope triplets, as no cumbersome fractionation experiments are necessary.

Mass-wise, oxygen is the closest stable three-isotope system to carbon. The $^{17}O/^{16}O$ to $^{18}O/^{16}O$ fractionation ratio has been determined in an experiment on electrolysis of water employing IRMS. From their high precision measurements Meijer and Li (1998) reported $\alpha_{17} = \alpha_{18}^{\lambda}$ with $\lambda = 0.5281 \pm 0.0015$ for a wide range of natural waters. This corresponds to $\alpha_{18} = \alpha_{17}^{b}$ with $b = 1.8936 \pm 0.0054$, which is in good agreement with the theoretical value of 1.888 according to Eq. (19) with $m = 16$. After correcting data from Miller et al. (1999), Miller (2002) reported $\lambda = 0.5247 \pm 0.0007$ ($b = 1.9059 \pm 0.0025$) for terrestrial rocks and minerals. Thus, only small differences in the fractionation ratios were found from different oxygen sample types such as waters and minerals and fractionation ratios are close to the value for equilibrium fractionation.

Neon and its isotopic ratios (Ne^{20}, Ne^{21}, Ne^{22}) are not only influenced by isotopic fractionation but also their origins (primordial vs. nucleogenic). Isotopic ratios may vary in different reservoirs depending on the origin and the exposure to radiation (Caffee et al., 1999). Therefore, the frac-

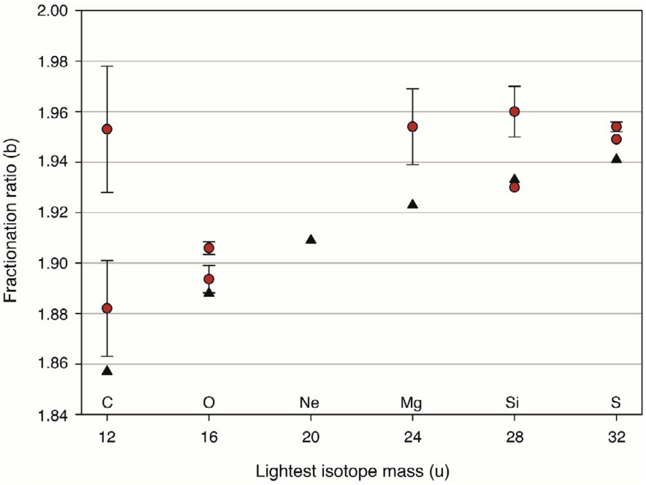


Fig. 4. Comparison of carbon fractionation ratios found in the present study with fractionation ratios from other low-mass three-isotope systems. The ordinate values correspond to the mass of the lightest of three isotopes. Black triangles indicate the theoretical values for equilibrium fractionation ratios as calculated with Eq. (19) and red circles represent the experimentally determined fractionation lines from the literature and the present study. Error bars are only shown where errors were reported.

tionation ratio of the three stable neon isotopes is not readily determined from natural samples.

The Mg^{25}/Mg^{24} vs. Mg^{26}/Mg^{24} fractionation ratio was determined by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) for 9 terrestrial samples by Galy et al. (2001) to $\beta = 0.5118 \pm 0.0038$ ($b = 1.954 \pm 0.015$). This value is relatively high compared to the equilibrium fractionation according to Eq. (19) ($b = 1.923$) and may indicate a larger contribution of kinetic fractionation in the analyzed samples.

Also, the fractionation ratio of the isotope triplet Si^{28}, Si^{29}, Si^{30} has been described in the literature. De La Rocha (2002) found $b = 1.93$ ($R^2 = 0.99$) while Engstrom et al. (2006), Reynolds et al. (2006) and Van Den Boorn et al. (2006) measured a value of 1.96 as opposed to $b = 1.933$ for pure equilibrium fractionation. Although silicon and carbon are homologs, the two elements have quite different chemical properties and undergo very different processes in nature. A relatively high apparent contribution of kinetic fractionation in silicon should therefore not be over-interpreted.

The experimental data obtained by Thode et al. (1949) for $^{33}S/^{32}S$ vs. $^{34}S/^{32}S$ ($b = 2.047 \pm 0.091$) is in agreement (2σ) with a value of $b = 1.941$ from Eq. (19), but the uncertainty in the measured value is large. A more recent and much more precise set of experiments on the reduction of sulfate by bacteria (*Archaeoglobus fulgidus*) was conducted by Farquhar et al. (2003) and yielded $\lambda = 0.5117 \pm 0.0005$ ($b = 1.954 \pm 0.0019$). Rumble et al. (1993) found $\lambda = 0.513$ ($b = 1.949$) with laser fluorination of 209 sulfide minerals.

The comparison with other low-mass three-isotope systems shows that all of these systems including carbon follow the theoretical values with $b \leq 2$ (Fig. 4), thus supporting the feasibility of our newly determined carbon fractionation ratios. Most values for other three-isotope systems are close to the theoretical lower limit of the equilibrium fractionation and it seems that the fractionation ratio of photosynthesis is an exception to this general trend. However, given the processes involved this is plausible, as discussed above. Overall, our results with b consistently lower than 2.0 show that the fractionation behavior of the carbon isotopes is not anomalous. The large deviations from the theoretical values of experimentally determined fractionation ratios reported in early studies (summarized in Fig. 1) were likely due to problems with experimental design, contamination issues, small isotopic fractionation factors and insufficient measurement accuracy.

4.5. Implications for radiocarbon measurements

The implications of $b \neq 2$ are complicated by the fact, that OX-I is corrected to −19‰ wrt. PDB by definition (Eq. (9)), while any other normalizing standard is corrected to −25‰ wrt. PDB (Eq. (10)). By inserting the nominal $\delta^{13}C$ value of OX-I (−19.2‰ wrt. PDB) into $\delta^{13}C_{OX}$ in Eq. (9), it becomes clear that the denominator 0.981 and the numerator $1 + (\delta^{13}C_{OX}/1000)$ will almost perfectly cancel out. The deviation of $b \neq 2$ will then only have an effect on samples with a $\delta^{13}C_S$ value different from −25‰ wrt. PDB. In the case of todays most-used normalizing material (OX-II), samples are affected differently: By inserting the nominal $\delta^{13}C$ value of OX-II (−17.8‰ wrt. PDB) into the term $\delta^{13}C_{Std}$ and −25‰ into $\delta^{13}C_{StdNorm}$, the effects of $b \neq 2$ will become more pronounced for samples with a $\delta^{13}C_S$ value further from −17.8‰ wrt. PDB. Similarly, the effects of a fractionation correction with $b = 2$ with other normalizing standards will be more pronounced, the further away the $\delta^{13}C_S$ value is from the $\delta^{13}C_{Std}$ value. Hence, the discussion on effects will not only depend on the fractionation processes that yield different fractionation ratios, but also on which normalizing standard has been used. For simplicity, the case of OX-I shall be discussed in this paragraph with values for OX-II given in brackets.

The fractionation ratios of 1.882 ± 0.019 and 1.953 ± 0.025 determined here are close to the value of 2.0 adopted by the radiocarbon community. Our results, the comparison to other three-isotope systems as well as theoretical considerations indicate that the continued use of the Saliège and Fontes (1984) value of $b = 2.3$ in some speleothem and hydrology modeling studies (e.g. Fohlmeister et al., 2011; Rudzka et al., 2011; Hodge et al., 2011) is not justified, and will deliver ^{14}C ages that are too old in most cases (when $\delta^{13}C > -25‰$ wrt. PDB for OX-I and $\delta^{13}C > -17.8‰$ wrt. PDB for OX-II). On the other hand, the varying nature of isotopic fractionation process and the relative importance of equilibrium and kinetic fractionation will produce a range of fractionation ratios, not a single value (see Section 4.3).

For the high percentage of samples that have $\delta^{13}C$ values close to −25‰, the effects of using $b = 2$ rather than $b = 1.882 \pm 0.019$ or 1.953 ± 0.025 are negligible. For $\delta^{13}C$ values differing greatly from −25‰ wrt. PDB (−17.8‰ wrt. PDB for OX-II), the effects of $b \neq 2$ on ^{14}C ages become more pronounced. For instance, in the case where the true b value is 1.882, a dating deviation of roughly 1 radiocarbon year for each per mil in $\delta^{13}C$ will result. Fig. 5 depicts the dating errors that arise from employing $b = 2.0$ rather than $b = 1.882$ or 1.953. For comparison, the deviations arising from the use of $b = 2.3$ are also shown. In order to obtain high precision and high accuracy in AMS radiocarbon dates, it is, therefore, important to reach completeness of the graphitization reaction, and that sample preparation processes are highly reproducible. Clearly, consistency in sample preparation is also important for other reasons, such as ensuring that process blanks are accurately determined and reproducible.

Fig. 6 depicts the $\delta^{13}C$ distribution of some 59,881 unknown samples measured by AMS at the KCCAMS facility between 2002 and 2012. Normalizing and secondary standards as well as test and background measurements were excluded from Fig. 6 in order to show the $\delta^{13}C$ signature of “real” (unknown) samples only. It is clear from Fig. 6 that a large number of analyzed samples have $\delta^{13}C$ values significantly different from −25‰ wrt. PDB (or from −17.8‰ wrt. PDB for OX-II) and are therefore subject to offsets induced by the correction with $b = 2$ instead of b_{new} obtained in the present study: for OX-I normalization the accuracy of a total of 25.9% of samples would we off by

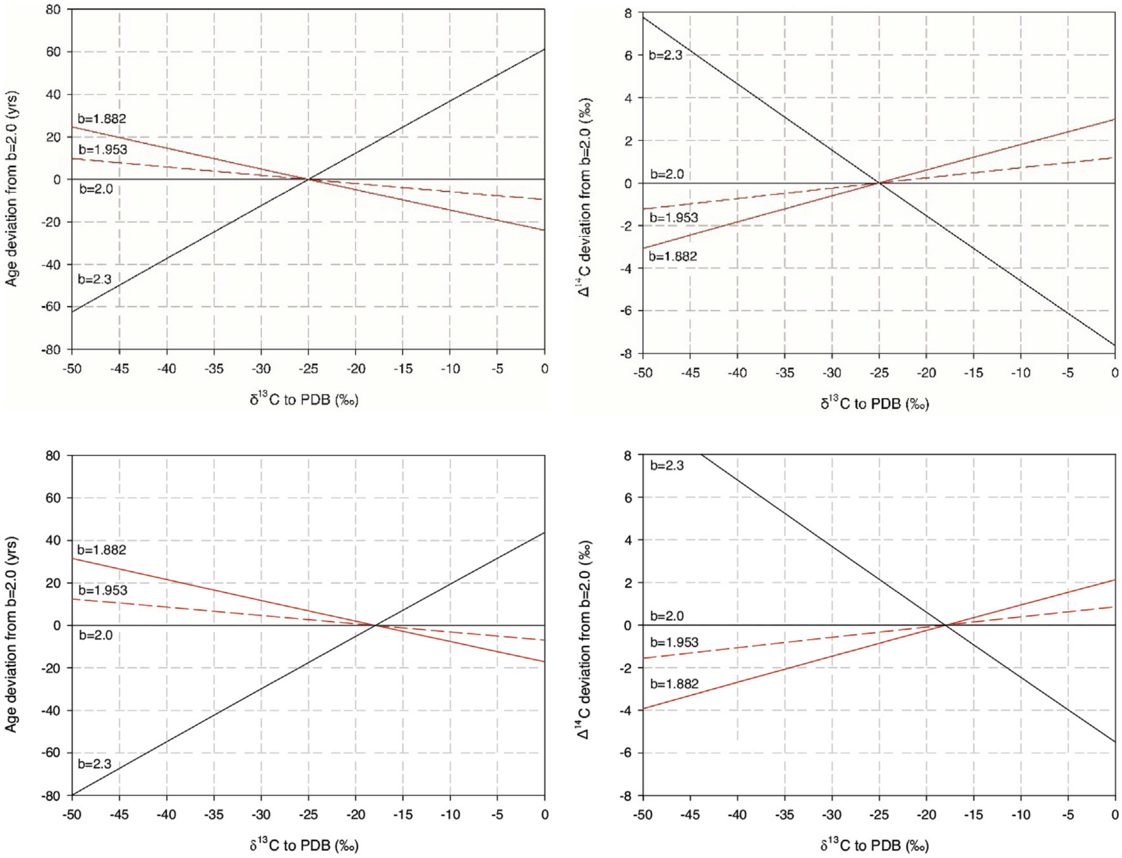
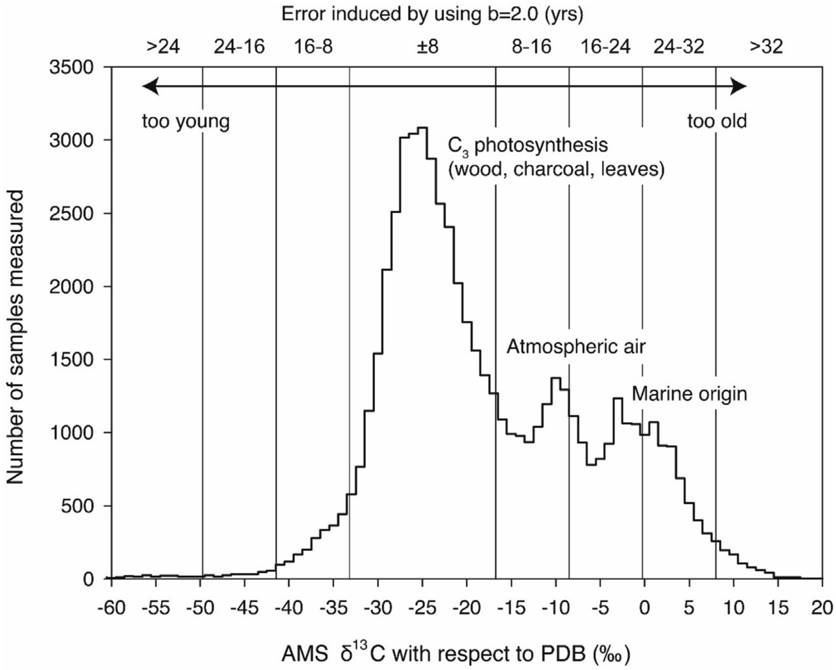


Fig. 5. ^{14}C age shifts for OX-I normalization and OX-II normalization (top and bottom left) and Δ^{14}C shifts for OX-I normalization and OX-II normalization (top and bottom right) introduced by the new fractionation ratio shown as a function of the δ^{13}C value of a sample (red). The value of 2.3 obtained by Saliège and Fontes (1984) is shown for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2‰ or more and in the case of OX-II normalization 16.8% of all samples would be inaccurately dated. As a precision of 2‰ is now common for high precision measurements in many radiocarbon laboratories, offsets on the same scale are no longer negligible. However, when comparing samples of the same origin and with a consistent offset from −25‰ wrt. PDB (or −17.8‰ wrt. PDB for OX-II) in δ^{13}C (such as atmospheric air, C_4 vegetation, as well as marine and speleothem carbonate) it is often the relative difference between samples that is of interest. Since such samples are affected very similarly, the fractionation error will be irrelevant to relative comparisons. Moreover, comparisons of samples of very different δ^{13}C values (e.g. marine or speleothem carbonate versus a terrestrial calibration record of C_3 plants) often involve corrections for a marine reservoir offset (foraminifera, corals, etc.) or a dead carbon fraction (speleothems). These corrections usually introduce uncertainties that are much larger than the error of using $b = 2$. On the other hand, a more significant problem arises when the sample preparation induces large isotopic fractionation, or when samples display extreme isotopic fractionation such as methane and CO_2 from microbial decomposition processes (e.g. Palstra and Meijer, 2014; maximum $\Delta\delta^{13}$C value: 84.09‰). In these cases, the offsets due to the use of $b = 2$ rather than b_{new} can become important. As Meijer et al. (2006) pointed out, even the nominal values of homogeneous reference materials such as the IAEA C6 sucrose (−10.8‰ in δ^{13}C) may change significantly when applying an incorrect fractionation correction. With the fractionation ratio of $b = 1.882$ and OX-I normalization, the IAEA C6 F^{14}C value of 1.5061 (obtained with $b = 2$) would increase by ~1.7‰, yielding a F^{14}C of 1.5087. However, if the fractionation ratio for photosynthesis of 1.953 is used to correct the IAEA C6 sucrose (produced from C_4 sugarcane), the offset effect on F^{14}C results would be reduced to ~0.68‰.

While more accurate dates may be obtained with the new fractionation ratio of $b = 1.882$ or $b = 1.953$, the net effect would be very small in many cases, particularly where a marine reservoir correction or dead carbon fraction correction is applied to the data, dominating the overall errors. However, in extreme cases where the δ^{13}C values of samples differ significantly from −25‰ wrt. PDB (or from −17.8‰ wrt. PDB for OX-II), the high precision of results may not be indicative of the accuracy of dates. This limitation is not associated with other typical sources of low accuracy, such as poor sample collection, sample preparation procedures or background corrections.

We deduce that a fractionation ratio value of $b = 1.9$ would better represent most biogeochemical processes than the accepted value of 2.0. Nevertheless, a change in the practice of fractionation correction would lead to inconsistencies



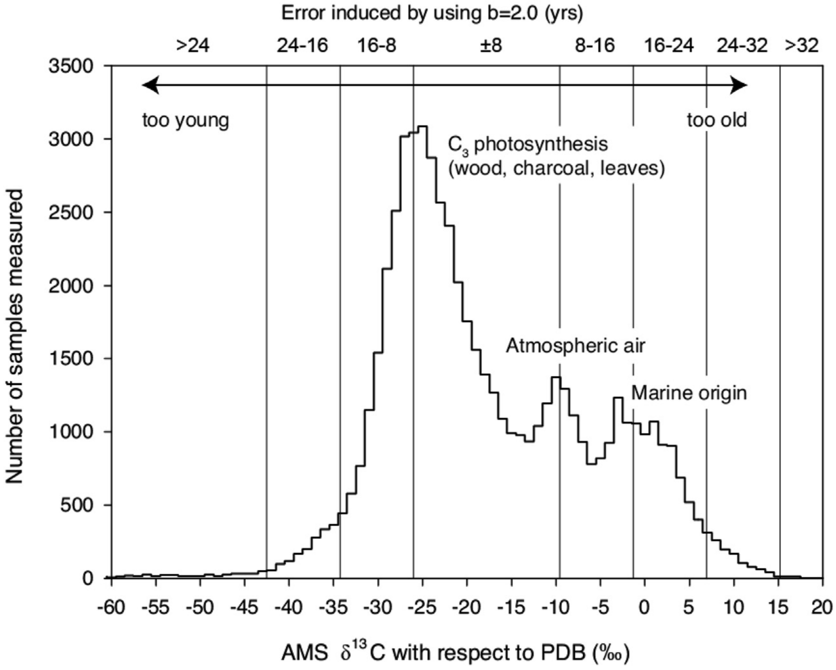


Fig. 6. The $\delta^{13}C$ distribution of 59,881 unknown samples measured at the KCCAMS facility within 10 years. The secondary abscissa (on top) indicates the error (loss of accuracy) in radiocarbon years by using b = 2.0 rather than b = 1.882. The top figure depicts OX-I normalization and the bottom figure OX-II normalization.

in the reported data and is therefore not advisable. While we do not suggest to change the fractionation correction, further improvements of the repeatability and measurement precision in radiocarbon laboratories should not obscure the fact that the accuracy of radiocarbon dates may not keep up with the reported precision.

4.6. Calculating errors and true values with the new fractionation ratios

To calculate the fractionation correction with the new fractionation ratio from uncorrected sample and standard activities the following equation is used:

$$F^{14}C_{b_{new}} = \frac{A_S}{\frac{0.95}{Ratio_{Std/OX}} \cdot A_{Std}} \cdot \left(\frac{0.975}{1+\frac{\delta^{13}C_{StdNorm}}{1000}}\right)^{b_{new}} \cdot \left(\frac{1+\frac{\delta^{13}C_{Std}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^{b_{new}} \tag{24}$$

If a $F^{14}C$ value corrected with a fractionation ratio of 2.0 is to be corrected with b_{new} in retrospect, the following equation applies:

$$F^{14}C_{b_{new}} = F^{14}C_{b=2.0}\left(\frac{0.975}{1+\frac{\delta^{13}C_{StdNorm}}{1000}}\right)^{b_{new}-2} \cdot \left(\frac{1+\frac{\delta^{13}C_{Std}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^{b_{new}-2} \tag{25}$$

where $\delta^{13}C_{Std}$ may be approximated with the nominal $\delta^{13}C$ value for that particular standard ($\delta^{13}C_{StdNomin}$, e.g. −19.2‰ for OX-I, −17.8‰ for OX-II, etc.) if the measured value $\delta^{13}C_{Std}$ is not known. For OX-I with a normalization value of −19‰, Eq. (25) can then be approximated with:

$$F^{14}C_{b_{new}} = F^{14}C_{b=2.0}\left(\frac{0.975}{1+\frac{\delta^{13}C_S}{1000}}\right)^{b_{new}-2} \tag{26}$$

while for all other standard materials (where $\delta^{13}C_{StdNorm} = -25‰$), Eq. (25) becomes:

$$F^{14}C_{b_{new}} = F^{14}C_{b=2.0}\left(\frac{1+\frac{\delta^{13}C_{StdNomin}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^{b_{new}-2} \tag{27}$$

if $\delta^{13}C_{Std}$ is not known.

In order to determine the error induced by the use of $b = 2$ instead of the true fractionation ratio b_{new}, the following equations are used:

$$\begin{aligned} absolute\ error(F^{14}C) &= F^{14}C_{b=2} - F^{14}C_{b_{new}} \\ &= F^{14}C_{b=2.0} \cdot \left(1 - \left(\frac{0.975}{1+\frac{\delta^{13}C_{StdNorm}}{1000}}\right)^{b_{new}-2} \cdot \left(\frac{1+\frac{\delta^{13}C_{Std}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^{b_{new}-2}\right) \\ &= \frac{A_S}{\frac{0.95}{Ratio_{Std/OX}} \cdot A_{Std}}\left(\left(\frac{0.975}{1+\frac{\delta^{13}C_{StdNorm}}{1000}} \cdot \frac{1+\frac{\delta^{13}C_{Std}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^2 \right. \\ &\quad \left. - \left(\frac{0.975}{1+\frac{\delta^{13}C_{StdNorm}}{1000}} \cdot \frac{1+\frac{\delta^{13}C_{Std}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^{b_{new}}\right) \end{aligned} \tag{28}$$

and

$$\begin{aligned} relative\ error\ (‰) &= \frac{F^{14}C_{b=2} - F^{14}C_{b_{new}}}{F^{14}C_{b_{new}}} \cdot 1000 \\ &= \left(\left(\frac{0.975}{1+\frac{\delta^{13}C_{StdNorm}}{1000}}\right)^{2-b_{new}} \cdot \left(\frac{1+\frac{\delta^{13}C_{Std}}{1000}}{1+\frac{\delta^{13}C_S}{1000}}\right)^{2-b_{new}} - 1\right) \cdot 1000 \end{aligned} \tag{29}$$

5. CONCLUSION

Experimental results of the present study indicate that isotopic fractionation in carbon isotopes does not show anomalous behavior compared to other light elements, as some previous studies suggested. Our findings are based on 84 high-precision radiocarbon results from two experimental approaches: the chemical reduction of CO_2 to elemental carbon (graphitization reaction) and the photosynthetic uptake of CO_2 by C_3 and C_4 plants. Moreover, the analysis of 9627 standards has confirmed the trend towards a fractionation ratio $b < 2$.

In extreme cases the fractionation ratio of carbon may be as low as the equilibrium fractionation ($b = 1.857$) or as high as the upper limit of the kinetic fractionation ($b = 2$). However, the results of this study show that a fractionation ratio of 1.882 ± 0.015 is the best estimate for the average fractionation factor of the reduction of CO_2 and 1.953 ± 0.025 is the best estimate for the fractionation ratio in photosynthesis. As many fractionation processes involve both equilibrium and kinetic fractionation, we deduce that carbon fractionation ratios for a wide variety of biogeochemical processes will be close to a value of 1.9. This assumption is supported by the relatively small variations of fractionation ratios found in other three-isotope studies.

The difference of the newly determined fractionation ratios and the $b = 2$ fractionation ratio used by convention may lead to significant shifts in measured ages for samples with $\delta^{13}C$ values very different from −25‰ wrt. PDB for OX-I normalization (or from −17.8‰ wrt. PDB for OX-II normalization): Roughly 1 radiocarbon year offset for every 1‰ of $\delta^{13}C$ apart from −25‰/−17.8‰ with $b = 1.882$. In many cases, the resulting offsets will be marginal compared to other errors induced by necessary corrections (e.g. marine reservoir offset or dead carbon correction). Applying fractionation corrections with $b = 2$ will thus have little effect on the measurement accuracy. In order to keep radiocarbon values comparable, we advise against the adoption of a new fractionation ratio ($b \neq 2$) for fractionation corrections. However, we suggest that isotopic fractionation during any part of the sample preparation or measurement be kept to a minimum, and treatment of unknowns and standards should be as consistent as possible to maximize the cancellation of these effects in the normalization of the results.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2017.05.038.

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