

Changing Carbon Isotope Ratio of Atmospheric Carbon Dioxide: Implications For Food Authentication

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Carbon isotopes are often used to detect the addition of foreign sugars to foods. This technique takes advantage of the natural difference in carbon isotope ratio between C₃ and C₄ plants. Many foods are derived from C₃ plants, but the low-cost sweeteners corn and sugar cane are C₄ plants. Most adulteration studies do not take into account the secular shift of the carbon isotope ratio of atmospheric carbon dioxide caused by fossil fuel burning, a shift also seen in plant tissues. As a result statistical tests and threshold values that evaluate authenticity of foods based on carbon isotope ratios may need to be corrected for changing atmospheric isotope values. Literature and new data show that the atmospheric trend in carbon isotopes is seen in a 36-year data set of maple syrup analyses ($n = 246$), demonstrating that published thresholds for cane or corn sugar adulteration in maple syrup (and other foods) have become progressively more lenient over time.

KEYWORDS: Authenticity; adulteration; carbon dioxide; carbon isotopes; maple syrup

INTRODUCTION

Stable isotope methods for determining the authenticity of foods have proliferated in the last thirty years. This trend has accompanied the general growth of stable isotopes in geology, biology, ecology, and medicine and advances in mass spectrometry (1–3). The most commonly applied stable isotope technique used for determining food authenticity is carbon isotope analysis, which uses differences in photosynthetic discrimination of ¹²C vs ¹³C in different plants, primarily as a tool for determining the presence of exogenous sugars in food.

With the development of new analytical techniques for food chemistry comes the added complication of understanding the physiological and environmental controls on the parameter being measured. Here we highlight the importance of a changing environment as a strong control on plant carbon isotope ratios. In addition to responding to factors such as temperature, light, precipitation, and humidity (4), the carbon isotope ratio of plant material is strongly influenced by the isotope ratio of atmospheric CO₂. The carbon isotope ratio of atmospheric CO₂ has shifted appreciably in the last thirty years because of the burning of fossil fuels, which has important implications for food authentication studies.

The photosynthetic pathway used by plants has a first-order effect on the carbon isotope ratio of plant material (5). Carbon isotope ratios are expressed in parts per thousand (‰) relative to international reference standard calcium carbonate (Vienna Pee Dee Belemnite, VPDB):

$$\delta^{13}\text{C} = \left(\frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}} - {}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}}{({}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}})} \right) \times 1000 \quad (1)$$

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The average global $\delta^{13}\text{C}$ of atmospheric CO₂ is approximately -8‰ (5), which is fractionated during carbon uptake in plants. Most plants use the C₃ pathway for carbon fixation, which introduces a strong preference in favor of ¹²C over ¹³C. This results in C₃ plant $\delta^{13}\text{C}$ values of -22 to -30‰ (6). C₄ (Hatch–Slack pathway) plants such as corn and sugar cane have a distinct anatomy and biochemistry, which results in higher $\delta^{13}\text{C}$ values of -10 to -14‰ (6). Plants using crassulacean acid metabolism (CAM) are not commonly the focus of food adulteration studies, with a few exceptions (7). In biological studies, discrimination (Δ) is used to describe the uptake of carbon isotopes in plant material relative to atmospheric CO₂ (5):

$$\Delta = \delta^{13}\text{C}(\text{air}) - \delta^{13}\text{C}(\text{plant}) / (1 + \delta^{13}\text{C}(\text{plant})/1000) \quad (2)$$

Thus, discrimination for C₃ plants (14–23‰) is larger than for C₄ plants (2–6‰).

The difference in $\delta^{13}\text{C}$ between C₃ and C₄ plants forms the basis of using carbon isotopes in food authentication and adulteration detection, mainly in the detection of inexpensive C₄ sugars in foods derived from C₃ plants. Examples include the detection of cane and/or corn-derived sugars in fruit juices, honey, maple syrup, alcoholic beverages, and livestock feed (8–12).

Carbon isotope ratios of plants also depend on the carbon isotope composition of assimilated CO₂. In authentication studies where C₃ foodstuffs are compared to possible C₄ adulterants, possible differences in $\delta^{13}\text{C}(\text{AtmCO}_2)$ are not usually addressed. Atmospheric composition can be an important variable, however, when compared foods are grown under different conditions: either because of geographic or local differences in $\delta^{13}\text{C}(\text{AtmCO}_2)$, or because studies compare foods grown over many years, during which $\delta^{13}\text{C}(\text{AtmCO}_2)$ has changed. For the period covered by maple syrup samples in the study (1970–2006), this shift amounts

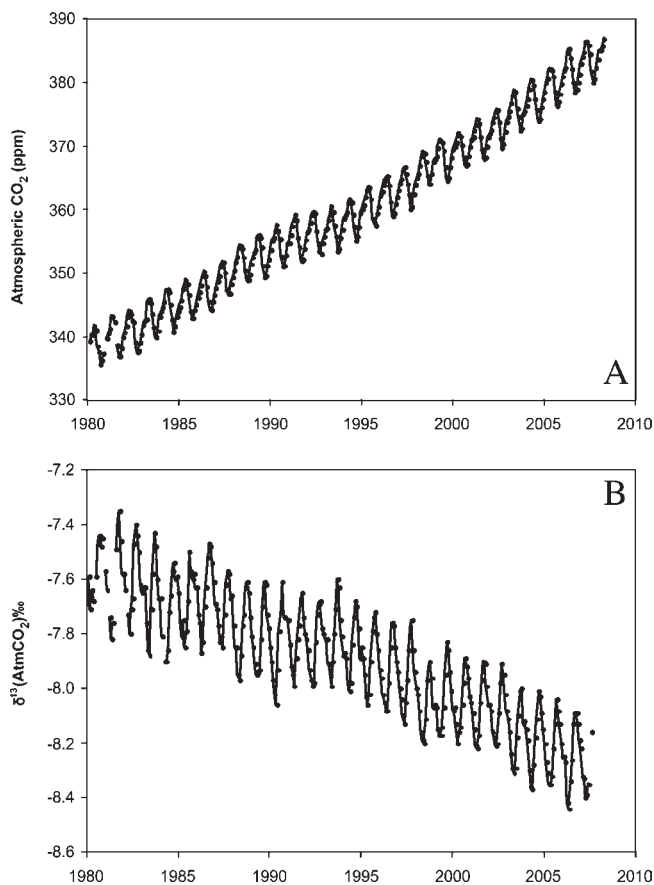


Figure 1. (A) Increasing atmospheric CO₂ concentrations and (B) decreasing $\delta^{13}\text{C}(\text{AtmCO}_2)$ values recorded at Mauna Loa, Hawaii. Both the anthropogenic trends toward higher CO₂ concentrations and lower $\delta^{13}\text{C}(\text{AtmCO}_2)$ also show yearly seasonal variation. Data from Keeling et al. (16).

to ca. 1.0‰ (13). Shifts of this magnitude are commonly seen in the literature for plant materials over similar time periods. A comparable shift over time is seen in a 30-year tree-ring sequence from a Quebec sugar maple (*Acer saccharum*) that shows decreases in $\delta^{13}\text{C}$ of ca. 1.0‰ (14), which is also similar to the overall shift in $\delta^{13}\text{C}$ of maple syrup seen in this study when historical samples and data are examined.

Besides the global shift in $\delta^{13}\text{C}(\text{AtmCO}_2)$, other factors can influence the $\delta^{13}\text{C}$ of plants. Regional differences in $\delta^{13}\text{C}(\text{AtmCO}_2)$ are small; for example in the northern hemisphere $\delta^{13}\text{C}(\text{AtmCO}_2)$ has been documented to be ca. 0.2‰ higher than in southern hemisphere because of more fossil fuel burning in the north (15). Plant responses to growth environments can have somewhat larger effects of carbon isotope fractionation, which probably overcome any local differences in the carbon isotope ratio of the atmosphere (8). One potentially important factor is the increasing CO₂ content of the atmosphere caused by fossil fuel burning (Figure 1A), which has been shown in some studies to cause physiological effects in C₃ plants resulting in lower $\delta^{13}\text{C}$ values. This factor has the potential to shift the $\delta^{13}\text{C}$ of plant materials up to ca. 0.5‰ for the sampling period of this study (17). C₄ plants do not show this effect and track $\delta^{13}\text{C}(\text{AtmCO}_2)$ well (18).

Comparison of carbon isotope ratios of foods produced over an extended period of years is thus problematic. Anthropogenic emissions of CO₂ (Figure 1A) may effect plant physiology and decrease plant $\delta^{13}\text{C}$, and anthropogenic CO₂ has directly decreased $\delta^{13}\text{C}(\text{AtmCO}_2)$ (Figure 1B), affecting the $\delta^{13}\text{C}$ of plants. Shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$ is routinely corrected for in

tree-ring studies, ecology, and archeology (3, 4, 19), but correcting for the physiological effect of increasing CO₂ is controversial because it is less well understood and plant response may be variable (4). A large data set of C₃ plants shows that > 90% of variability in plant $\delta^{13}\text{C}$ can be explained shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$, highlighting the minor role of physiological response to differences in atmospheric CO₂ concentration (20). In this study we address shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$ and not physiological factors because of these uncertainties and possible variability between growing regions.

MATERIALS AND METHODS

Twenty-three maple syrup samples were purchased in 2006 to provide good geographic coverage from New York State. Twenty-two Vermont samples were collected in 2006 as part of a study of commercial sugarbushes (21). Ninety-one samples were also analyzed from four years of production (1993, 1995, 2003, and 2005) from another Vermont sugarbush, and average yearly values are shown, in addition to a single 2006 sample. Three historic samples were obtained by email solicitation of New York maple syrup producers (1972, 1976, 1982). A few of the maple syrup samples were found to have partially crystallized or contain mold. Comparison of syrup and sugar crystals or syrup and mold yielded no measurable difference in carbon isotope ratio, thus these processes do not fractionate syrup $\delta^{13}\text{C}$. One New York sample of 1970 maple cream, a crystallized maple syrup product, was also analyzed. Ca. 0.4 mg samples were loaded into 3 × 5 mm tin capsules and heated overnight at 50 °C to remove water. Samples and standards were combusted using an elemental analyzer (ECS 4010, Costech Analytical Technologies, Valencia, CA) online with the stable isotope mass spectrometer (Delta Plus Advantage, Finnigan MAT, Bremen, Germany) at Colgate University in continuous-flow mode following the method previously described (22). Carbon isotope ratio was measured on masses 44, 45, and 46 of CO₂, and sample and standard signals were diluted with He for peak heights of ca. 2000–3000 mV on mass 46. Analytical conditions were monitored for this study using analysis of an internal laboratory standard that had an average daily precision of ± 0.20‰ (1σ SD). Analyses of USGS24 ($\delta^{13}\text{C} = -16.05\text{‰}$) during the analysis period averaged $-16.05 \pm 0.19\text{‰}$ ($n = 6$). Syrup samples were duplicated or triplicated with typical reproducibility of ± 0.15‰.

RESULTS AND DISCUSSION

The maple syrup literature provides excellent data to demonstrate the effects of shifting atmospheric values on food authentication. Figure 2 shows literature ($n = 193$) and new data ($n = 53$) for commercial maple syrup samples for the period 1970–2006. Maple syrup, a product made from the xylem sap of *Acer saccharum*, is produced primarily in the northeastern United States and Canada. Production areas for this data set include ten states and provinces, and are dominated by New York ($n = 32$), Vermont ($n = 59$), and Quebec ($n = 68$). A limited production area minimizes variability in $\delta^{13}\text{C}$ caused by differences in growing conditions, as does the averaging which occurs when sap from multiple trees is mixed in production. However, detailed study ($n = 91$) of four production years from a ca. 550 acre sugarbush in Vermont shows that 0.5 to 1.0‰ variability in $\delta^{13}\text{C}(\text{syrup})$ is typical in a single harvesting season (27). Although our preliminary data and the data of (28) suggest that maple sap varies ca. ≤ 0.5‰ for a single tree during one year, observed sugarbush-wide variability of 0.5–1.0‰ is likely the effect of other variables for the mixed tree population such as tree ages, health, position under the canopy, and other physiological factors (4).

Literature data for $\delta^{13}\text{C}(\text{syrup})$ and historical samples analyzed for this study from the oldest samples consistently have the highest

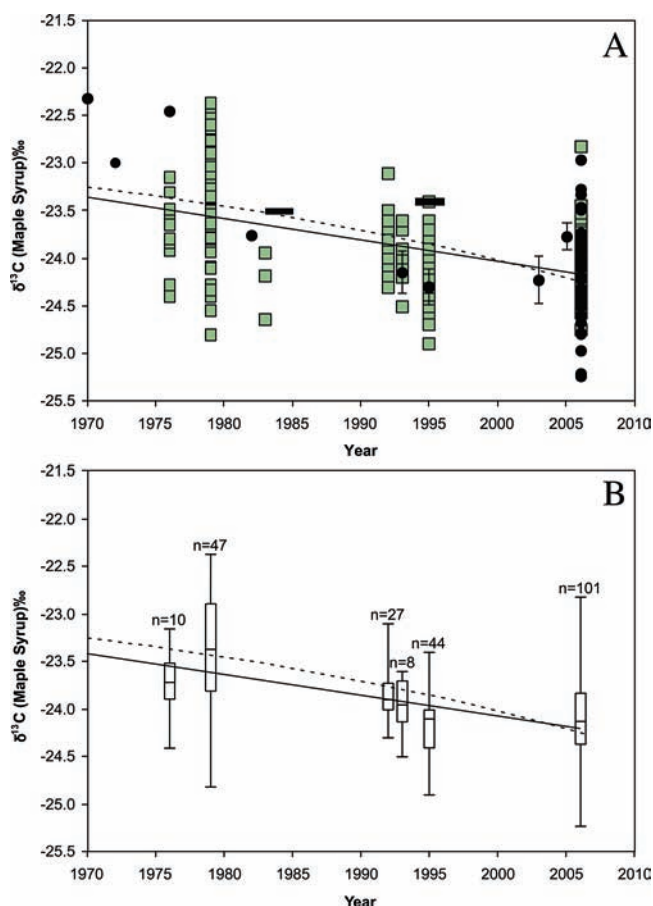


Figure 2. (A) Carbon isotope ratios of maple syrup. Literature data (10, 23–26) are shaded squares. Some analyses of alcohol produced by fermentation of maple syrup sugars have been corrected by 0.39‰, the average alcohol-sugar fractionation (see ref 25). Unless specified, production year is assumed to be the year before publication. New data are black circles. 1σ error bars are shown for the averages of 1993, 1995, 2003, and 2005 production from one Vermont sugarbush. Curved dashed line is the atmospheric $\delta^{13}\text{C}(\text{Atm CO}_2)$ from (13), displaced by an average CO_2 -maple syrup fractionation of 16‰. Straight line is a least-squares regression of the maple syrup data. Horizontal bars are the proposed upper cutoffs for adulteration by cane or corn sugar from refs 10, 25 at the years they were proposed. (B) Box and whiskers plot of the six years with eight or more analyses. Curved dashed line is the atmospheric $\delta^{13}\text{C}(\text{Atm CO}_2)$ from Figure 2A; straight line is a regression through the median maple syrup values.

$\delta^{13}\text{C}$ values (Figure 2). For example, samples from 1970 to 1983 average $\delta^{13}\text{C} = -23.48 \pm 0.65\text{‰}$ ($n = 64$), while samples from 1992 to 2006 average $\delta^{13}\text{C} = -24.07 \pm 0.38\text{‰}$ ($n = 182$), which are statistically distinct by t test. Even given scatter caused by different growing regions and within-season variability, the data set has a significant correlation between $\delta^{13}\text{C}$ and year of production ($r = -0.47$, $p < 0.0001$). The average decline in $\delta^{13}\text{C}(\text{syrup})$ for 1970–2006 is $0.023 \pm 0.003\text{‰/year}$. During this period $\delta^{13}\text{C}(\text{AtmCO}_2)$ declined by 0.028‰/year (24), which is within the 95% confidence interval of the maple syrup trend (Figure 2A). When the median values for years with ≥ 8 samples are regressed, the average decline in $\delta^{13}\text{C}(\text{syrup})$ is similar: 0.024‰/year ($r = -0.87$) for 1976 to 2006. Similar relationships are also seen in individual studies that examine multiple years of production, although none of these studies are for a very long time period and thus trends are not well constrained. Martin et al. (25) present maple syrup data from 1992 to 1995 that show an average

decline of $0.099 \pm 0.024\text{‰/year}$. During this period $\delta^{13}\text{C}(\text{AtmCO}_2)$ declined by 0.030‰/year (13), which is within the 95% confidence interval of this subset of the maple syrup data set. Pang et al. (29) present a summary of 20,888 analyses of Chinese commercial honeys from 1998 to 2004. Although average values are not given, their summary statistics can be modeled by yearly normal distributions of $\delta^{13}\text{C}(\text{honey})$ with $1\sigma = 1.6\text{--}2.1\text{‰}$ that decline by an average of ~ 0.05 to 0.15‰/year .

The carbon isotope ratios for different amounts of C_4 sugar adulteration of maple syrup have been determined by using comparisons of pure maple syrup, cane or corn syrup, and prepared adulterated samples (10, 23–26) (Figure 2). These threshold values are maximum allowable values because C_4 adulteration increases the $\delta^{13}\text{C}$ of maple products. However, the secular decline in atmospheric $\delta^{13}\text{C}$ has caused maple syrup $\delta^{13}\text{C}$ to move away from adulteration cutoffs. In essence, historic thresholds applied to modern maple syrups have become progressively too lenient, which could result in adulterated maple syrups being judged as authentic if old thresholds are applied. For example, the AOAC-approved method threshold (10) is -23.5‰ , the 95% confidence level at which 20% adulteration with C_4 sugars can be determined. Ca. 0.85‰ average change in $\delta^{13}\text{C}(\text{AtmCO}_2)$ since this study was published in 1984 could allow an additional $\sim 10\%$ adulteration with corn syrup until this threshold was met if this cutoff was used today, using data from ref 10.

For honey adulteration, the 1978 White and Donner (9) $\delta^{13}\text{C}$ value of -21.5‰ is often taken as a maximum permissible value for authentic honey, as it represents $+4\sigma$ for their 119 analyses of authentic material. Application of this cutoff to more recent samples (29, 30) can cause potential difficulties, since $\delta^{13}\text{C}(\text{AtmCO}_2)$ had shifted appreciably since the 1978 study. Use of this cutoff for 2009 honey, given that $\delta^{13}\text{C}(\text{AtmCO}_2)$ has shifted on average 1‰ since 1978, would in effect apply a $+3\sigma$ instead of a $+4\sigma$ cutoff based on the White and Donner data set.

Statistical examination of variability in food $\delta^{13}\text{C}$ needs to take into account atmospheric change if data sets or literature comparisons are from a significant span of years. One strategy for detecting adulteration is the use of comparison databases (31), but this method has the potential to be particularly problematic given shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$. For example, the normative database of compositional data for fruit juices and juice products maintained by the Technical Committee for Juice and Juice Products (32) contains carbon isotope analyses that are ten or more years old, and would be inappropriate for statistical determination of limits on authentic food products without correction. A more uncommon but similar situation is possible when historic, archived food material is compared with modern products (33).

Several approaches can be taken to minimize the effects of changing $\delta^{13}\text{C}(\text{AtmCO}_2)$ on food studies. The first possibility is that historical data or thresholds can be brought up-to-date by adding the amount of shift in $\delta^{13}\text{C}(\text{AtmCO}_2)$ to published values using an atmospheric model or tabulated atmosphere data (4, 13). This would in effect project data to the present (or to any year) along the dashed line in Figure 2 for comparison purposes. The second possibility is to use discrimination (Δ , formula 2), as is used in the biological sciences to normalize for shifting atmospheric values. This notation has the advantage of making the comparison of data from different years more straightforward, but is not commonly used in the food chemistry literature. Maple syrup samples from 1970–1983 and 1992–2006 have statistically distinct $\delta^{13}\text{C}$ values by t test, but are indistinguishable when $\delta^{13}\text{C}$ is corrected for shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$ (13) or by comparing Δ . Finally, so-called “internal standard” approaches can overcome problems of shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$. These authentication

strategies compare sugar $\delta^{13}\text{C}$ to nonsugar compounds from the same sample (26). Since all plant (or animal) compounds respond to shifting $\delta^{13}\text{C}(\text{AtmCO}_2)$, internal standard thresholds should still be valid.

If current trends in fossil fuel use continue, secular change in $\delta^{13}\text{C}(\text{AtmCO}_2)$ will only become more rapid over the next few decades, shifting ca. $\geq 0.6\%$ between 2009 and 2020. This change must be taken into account if adulteration thresholds established using literature data are to remain useful.

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