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Maintaining consistent traceability in high precision isotope measurements of CO_2: verifying atmospheric trends of $\delta^{13}C$

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Abstract

Maintaining consistent traceability of high precision measurements of CO_2 isotopes is critical in being able to observe accurate atmospheric trends of $\delta^{13}C$ (CO_2). Although a number of laboratories/organizations around the world have been involved in baseline measurements of atmospheric CO_2 isotopes for several decades, the reports on their traceability measures are rare. In this paper, a principle and an approach for the traceability maintenance of high precision isotope measurements ($\delta^{13}C$ and $\delta^{18}O$) in atmospheric CO_2 is described. The uncertainties of the traceability have been estimated based on the history of annual calibrations over the last 10 yr. The overall uncertainties of CO_2 isotope measurements for individual ambient samples carried out by our program at Environment Canada are estimated (excluding the uncertainty associated with the sampling). The values are 0.02 ‰ and 0.05 ‰ in $\delta^{13}C$ and $\delta^{18}O$, respectively, close to the WMO targets for data compatibility. The annual rate of change in $\delta^{13}C$ of the primary anchor used in our program (which is the laboratory standard linking ambient measurements back to the primary VPDB scale) is close to zero (-0.0016 ± 0.0012 ‰ per year) over the period of 10 yr (2001–2011). The average annual decreasing rate of $\delta^{13}C$ in air CO_2 measurements at Alert over the period from 1999 to 2010 has been confirmed and verified, which is -0.025 ± 0.003 ‰ per year. The total change of $\delta^{13}C$ in the annual mean value during this period is ~ -0.27 ‰. The concept of "Big Delta" is introduced and its role in maintaining traceability of the isotope measurements is described and discussed extensively. Finally, the challenges and a strategy for maintaining traceability are also discussed and suggested.

1 Introduction

Precise determination of the isotope compositions of atmospheric CO_2 plays an important role in understanding carbon cycle, in turn, addressing the issue of the continuous increase of atmospheric CO_2 at regional and global scales. Numerous studies have been conducted to understand the exchanges of CO_2 between the atmosphere, the terrestrial biosphere and the oceans to quantify the relevant sources and sinks (Keeling 1960, 1961; Keeling et al., 1979, 1995; Mook et al., 1983; Francey et al., 1995; Bakwin et al., 1998; Ciais et al., 1995, 1997; Battle et al., 2000; Allison and Francey, 2007). From 1998 through 2010, an average annual global rate of change of carbon isotopic composition in atmospheric CO_2 is $\sim -0.026 \pm 0.001$ ‰ in δ^{13}C per year. The result is derived from annual averages of all surface mbl references. The mbl references are constructed (Masarie and Tans, 1995) using NOAA surface flask data from the Global Cooperative Air Sampling Network (http://www.esrl.noaa.gov/gmd/ccgg/about/global_means.html). The CO_2 isotope data from the network were analyzed by The Institute of Arctic and Alpine Research (INSTAAR) at University of Colorado (White and Vaughn, 2011). On a regional scale the corresponding value is very similar e.g. $\sim -0.025 \pm 0.003$ ‰ yr^{-1} from 1999 through 2010, obtained by Environment Canada, at Alert GAW station (Fig. 1a, b). The magnitudes of those changes, together with the corresponding CO_2 concentration changes, were driven by the contributions from various carbon sources and sinks (including natural and anthropogenic ones). Precisely identifying the magnitude of those changes will help us to understand the complicated mechanisms of carbon cycle and track the human-induced CO_2 in the atmosphere. This task is especially challenging as the gradients as well as the trends in atmospheric δ^{13}C are very small compared to the levels of analytical precision even by the most accurate measurement techniques applied (e.g. Isotope Ratio Mass Spectrometer, IRMS). That's why the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW) measurement community has strongly encouraged making high precision measurements in the order of 0.01 ‰ and 0.05 ‰ for δ^{13}C and δ^{18}O, respectively (Expert Group recommendations in GAW publications 161, 168, and 186: http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html). To precisely determine the small change of δ^{13}C in atmospheric CO_2, the corresponding changes in isotope standards, which link individual measurements to the primary scale, i.e., VBDB (Vienna PeeDee Belemnite), need to be taken into account to ensure that the annual changes of isotope standards are much less than 0.02 ‰. Isotope standards play an important role in maintaining consistent traceability (Huang et al., 2002). A consistent traceability is essential for the observed data being used to derive the trend. To implement a traceability for isotope measurements in flask air CO_2 samples, various forms of lab-standards are used, such as pure CO_2 in high pressure cylinders, air CO_2 and CO_2 produced from pure carbonates (Huang et al., 2002; Mukai et al., 2005; Allison and Francey, 2007; Brand, et al., 2009). Usually, more than one level (e.g. primary, secondary, etc.) and more than one form of standards are used in individual laboratories (Huang et al., 2002; Allison and Francey, 2007). It is very challenging, however, to ensure that the uncertainties of those standards are less than 0.02 ‰ in δ^{13}C (i.e., the standards are stable within the range of ~0.02 ‰) over a long time period. The time span should be comparable to this from which the atmospheric trend is derived. This is difficult because ensuring that a lower level standard is stable (or not drifting) within the range of ~0.02 ‰ requires a higher level standard with a better stability (i.e., <0.02 ‰). Usually, the higher level standard is used for the calibration of the lower level standard. Ultimately, it is imperative to ensure that the primary standard (i.e. NBS19) is stable over decadal time periods with an annual change rate significantly less than 0.02 ‰. The crucial questions arise therefore: Is this primary standard, NBS19 absolutely stable? How do we know? How well we know? And if not, how could we assess the uncertainty and stability of a standard? What is its impact on the uncertainties of CO_2 isotope measurements for individual ambient samples?

In this paper, we present our results obtained over the last 10 yr to illustrate how these questions are addressed, including:

- the traceability of high precision CO_2 isotope measurements for our program;
- the entire records in annual calibrations of secondary standards directly against NBS19-CO_2) over the period of 10 yr, which demonstrate the traceability implementation and maintenance in our program;

- the stability of the primary anchor (a secondary standard) which links the individual measurements back to the primary VPDB-CO_2 scale and implies the stability of NBS19. This can be used for verifying a long-term trend of $\delta^{13}C$ in atmospheric CO_2 at Alert;
- the uncertainty of the traceability (which is the overall uncertainty propagated from all different levels of standards used in the traceability chain, including NBS19-CO_2 production from carbonates) and the discussion;
- the challenges and recommendations based on the results, which can be used as a strategy to tackle these problems.

2 Traceability

Metrological traceability is defined as "property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty" (GAW Report No. 194). No matter what kind of and how many level of standards are used for calibrations, CO_2 isotope measurements must be finally traced back to the primary scale (VPDB) via the primary standard NBS19-CO_2. It is known that VPDB is a hypothetical standard. As the supply of PDB is exhausted, the primary VPDB scale is established by adopting the isotopic compositions of NBS19 relative to VPDB as: +1.95‰ for $\delta^{13}C_{NBS19/VPDB}$ and −2.2‰ for $\delta^{18}O_{NBS19/VPDB}$. However, NBS19-$CO_2$ only defines one point on the primary scale or ruler. It is almost impossible to accurately calibrate other secondary standards by the one point ruler with no unit defined. In order to define the unit on the primary ruler, at least two standards are required (assuming instrument liberality). It's better to have three standards, thus the linearity of the instrument can be assessed. Following this principle, establishing a secondary scale (i.e., a local scale for individual program), at least two standards (three are better) are needed and a large isotope difference should exist between the two. In our program, two levels of standards are used in the traceability chain to link the individual flask-air CO_2 isotope measurements back to the primary standard. One is the primary (i.e., NBS19) and the other is the secondary (i.e., lab carbonate standards), including NBS18, Cal1 and Cal2. NBS19 and NBS18 are international reference materials, which were purchased from the International Atomic Energy Agency (IAEA) through the web (http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/13C18and7Li/index.htm; last access: 26 May 2012). NBA19 was obtained from a limestone (mainly composed of $CaCO_3$) with an unknown source, whereas NBS18 is a calcite ($CaCO_3$) from Fen, Norway. NBS19 and NBS18 are used to define the unit on the primary scale. Both Cal1 and Cal2 are calcium carbonates purchased from Aldrich Chemicals and Fisher Scientific, respectively. Cal1 and Cal2 are used to build the link between the individual measurements and the primary standard and at the same time to ensure the stability of the primary anchor (discuss later). As shown the schematic of the traceability pathway in Fig. 2 the implementation of the traceability in our program includes two operational steps, i.e. annual calibration and routine measurement.

During the annual calibration periods, the secondary standards are calibrated by the primary standard, i.e. NBS19-CO_2. Each individual calibration period was conducted via measuring those secondary standards together with NBS19-CO_2 against the same Working Reference Gas (WRG) within one day time span (according to "the identical treatment" principle). The isotopic compositions of these standards are traced to the primary standard by the following equations.

$$\begin{aligned}
R_{\text{Lab-Std}}/R_{\text{VPDB-CO2}} &= [R_{\text{Lab-Std}}/R_{\text{WRG}}] \times [1/(R_{\text{NBS19-CO2}}/R_{\text{WRG}})] \times (R_{\text{NBS19-CO2}}/R_{\text{VPDB-CO2}}) \\
&= [R_{\text{Lab-Std}}/R_{\text{NBS19-CO2}}] \times (R_{\text{NBS19-CO2}}/R_{\text{VPDB-CO2}}) \\
&= [\Delta_{\text{Lab-Std/NBS19-CO2}} \times 10^{-3} + 1] \times [\Delta_{\text{NBS19-CO2/VPDB-CO2}} \times 10^{-3} + 1] \quad (1)
\end{aligned}$$

where R: the ratio of [mass 45/mass 44] or [mass 46/mass 44] in CO_2

$$\begin{aligned}
\Delta^{45\text{ or }46}_{\text{Lab-Std/NBS19-CO2}} &= [(R_{\text{Lab-Std}} - R_{\text{NBS19-CO2}})/R_{\text{NBS19-CO2}}] \times 10^{3}\,‰ \\
&= (\delta_{\text{Lab-Std/WRG}} - \delta_{\text{NBS19-CO2/WRG}})/(\delta_{\text{NBS19-CO2/WRG}} \times 10^{-3} + 1)\,‰
\end{aligned}$$

This term $\Delta^{45\text{ or }46}_{A/B}$ is introduced as Big Delta. It is the relative deviation of isotopic ratio (usually given in ‰) between two materials. It can also be expressed as $[(R_A/R_B)-1]\times 10^3$ ‰. For our case, A is the Lab-Std and B is NBS19-CO_2. Although the expression of $\Delta^{45\text{ or }46}_{A/B}$ appears identical as the definition of the small delta between A and B (i.e., $\delta^{45\text{ or }46}_{A/B}=[(R_A/R_B)-1]\times 10^3$) ‰, the determination of Big Delta should not be obtained by a direct measurement against each other because the identical treatment principle should be applied to both A and B. A Big Delta value should be derived from the two raw measurements which are conducted separately against the same WRG, as shown in Fig. 2.

By definition, a Big Delta value is independent of the WRG. It is, however, dependent on the configuration and the degree of cleanliness of the ion source in an IRMS, which determines the magnitude of possible cross-contaminations in the source (Meijer et al., 2000). Any physical or configuration modification to the ion-source or changes in electronics (amplifiers) can either increase or decrease the Big Delta values, due to decreases or increases the magnitude of cross-contamination (Meijer et al, 2000). Under ideal clean conditions of an IRMS, a Big Delta value is close to a constant, and thus can be precisely determined. Using Big Delta approach, the units on the primary scale can be defined.

The first two terms on the right side of Eq. (1) are measured during the annual calibration phase and the second term is the constant recommended by International Atomic Energy Agency (Craig, 1957; Allison et al. 1995). According to Eq. (1), the annual calibrations is to determine the Big Delta values between the secondary laboratory standards and NBS19-CO_2 (i.e., $[\Delta_{\text{Lab-Std/NBS19-CO2}}]$), which can be also considered as determining the units on the primary scale. During each individual calibration, three sets of pure CO_2 ampoules are prepared from acid digestions of carbonates as shown in the following reaction:

$$3CaCO_3 + 2H_3PO_4 \rightarrow 3CO_2 + 3H_2O + Ca_3(PO_4)_2 \qquad (2)$$

Each set includes NBS19-CO_2 (+1.95‰ in $\delta^{13}C_{VPDB\text{-}CO2}$ and −2.2‰ in $\delta^{18}O_{VPDB\text{-}CO2}$), NBS18-$CO_2$ (∼ −5 ‰ in $\delta^{13}C_{VPDB\text{-}CO2}$ and ∼ −23 ‰ in $\delta^{18}O_{VPDB\text{-}CO2}$), Cal1-$CO_2$ (∼ −46 ‰ in $\delta^{13}C_{VPDB\text{-}CO2}$ and ∼ −22 ‰ in $\delta^{18}O_{VPDB\text{-}CO2}$) and Cal2-$CO_2$ (∼ −2.6 ‰ in $\delta^{13}C_{VPDB\text{-}CO2}$ and ∼ −12.6 ‰ in $\delta^{18}O_{VPDB\text{-}CO2}$). The corresponding Big Delta values (i.e., $\Delta_{NBS18\text{-}CO2/NBS19\text{-}CO2}$, $\Delta_{Cal1/NBS19\text{-}CO2}$, $\Delta_{Cal2/NBS19\text{-}CO2}$, $\Delta_{Cal2/Cal1}$ and etc.) are determined. The measurement protocol is shown in Table A1. The Big Delta values of $\Delta_{NBS18\text{-}CO2/NBS19\text{-}CO2}$ are used as the criteria for the quality assurance/quality control (QAQC) of the Big Delta values of $\Delta_{Cal1/NBS19\text{-}CO2}$, $\Delta_{Cal2/NBS19\text{-}CO2}$, and $\Delta_{Cal2/Cal1}$ since the measurements of NBS18 can be compared with the literature values. The details for obtaining valid Big Delta values during annual calibrations are described in Fig. 2.

During routine measurements, individual flask CO_2 samples are analyzed in conjunction with the secondary standards against the same WRG. Usually, 12 samples are measured as a suite during a single day period. A pair of Cal1 and Cal2 are analyzed before and a Cal2 is analyzed after the suite. The measurement protocol is described in Table A2. The derivation of Big Delta is included in every single daily measurement suite. The comparison of this value with the annual determined Big Delta value provides an important validation measure of the secondary standard production. The second Cal2 analyses at the end of the daily measurement suite provides an additional measure of system stability over the entire measurement period and an important validation measure for the unknown samples in the suite. The isotopic composition of individual samples are determined using the following equation and traced back to the primary standard.

$$
\begin{aligned}
[R_{\text{Sam}}/R_{\text{VPDB-CO2}}] &= [R_{\text{Sam}}/R_{\text{WRG}}] \times [1/(R_{\text{Lab-Std}}/R_{\text{WRG}})] \times (R_{\text{Lab-Std}}/R_{\text{VPDB-CO2}}) \\
&= [R_{\text{Sam}}/R_{\text{Lab-Std}}] \times (R_{\text{Lab-Std}}/R_{\text{VPDB-CO2}}) \\
&= [R_{\text{Sam}}/R_{\text{Lab-Std}}] \times [R_{\text{Lab-Std}}/R_{\text{NBS19-CO2}}] \times (R_{\text{NBS19-CO2}}/R_{\text{VPDB-CO2}}) \\
&= [\Delta_{\text{Sam/Lab-Std}} \times 10^{-3} + 1] \times [\Delta_{\text{Lab-Std/NBS19-CO2}} \times 10^{-3} + 1] \\
&\quad \times [\Delta_{\text{NBS19-CO2/VPDB-CO2}} \times 10^{-3} + 1]
\end{aligned}
\tag{3}
$$

where R_{Sam}: the ratio of mass 45 to 44 or mass 46 to 44 in a sample. $\delta^{45}(\text{CO}_2)_{\text{Sam-VPDB-CO2}}$ and $\delta^{46}(\text{CO}_2)_{\text{Sam-VPDB-CO2}}$ are defined as:

$$
\delta^{45/\text{or }46}(\text{CO}_2)_{\text{Sam/VPDB-CO2}} = [(R_{\text{Sam}}/R_{\text{VPDB-CO2}}) - 1] \times 10^3 ‰ \tag{4}
$$

Equation (3) shows the documented traceability chain in CO_2 isotope measurements for individual CO_2 samples collected in Environment Canada Greenhouse Gas Observation Network (Huang and Worthy, 2005) back to the primary scale. Here VPDB-CO_2 represents the CO_2 evolved from VPDB (Vienna PeeDee Belemnite). Using the results of Eq. (4), $\delta^{13}\text{C}_{\text{Sam/VPDB-CO2}}$ and $\delta^{18}\text{O}_{\text{Sam/VPDB-CO2}}$ are calculated by applying the ^{17}O correction used by Allison et al. (1995). This correction is very similar to the Crag correction (Craig, 1957). It should be noted that air samples have an additional N_2O correction requirement as N_2O is an interference (also with masses 44, 45, 46) for CO_2 isotopic ratio measurements. The same correction algorithms for both ^{17}O and N_2O are applied to the entire dataset.

Based on Eq. (3), routine measurements is to determine the Big Delta value between the sample and the lab standards. Lab standards are used to anchor the unknown individual measurements to the primary scale (VPDB-CO_2). In general, a laboratory standard calibrated directly or indirectly using NBS19-CO_2 and used to determine $\delta^{13}\text{C}_{\text{Sam/VPDB-CO2}}$ and $\delta^{18}\text{O}_{\text{Sam/VPDB-CO2}}$ is referred to as a primary anchor. The primary anchor adopted in our program is the pure CO_2 evolved from Cal2 carbonate. The total uncertainties of the traceability in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ can be estimated from Eq. (3) via error propagations of the two terms on the right (i.e, $\Delta_{\text{Sam/Lab-Std}}$ and $\Delta_{\text{Lab-Std/NBS19-CO2}}$). One of the uncertainties is related to the primary anchor. Advantages of using this approach include:

i. the units of the primary scale are evaluated every year;

ii. individual isotopic measurements are firmly anchored to the primary scale;

iii. the uncertainty of the primary anchor can be characterized, monitored and minimized;

iv. and the overall uncertainty of individual ambient measurements can be explicitly estimated.

3 Uncertainty in traceability

To maintain a consistent traceability for isotope measurements in our program, two secondary standards (i.e., Cal1 and Cal2) are used with a significant isotopic difference (~ 42 ‰). They, along with NBS18, are directly calibrated by NBS19 on an annual basis. During the calibration periods (usually between February to April when the relative humidity is typically the lowest of a year and when the most stable δ^{18}O values can be attainable). NBS19, NBS18, Cal1 and Cal2 are evolved into pure CO_2 via acid digestions using the H_3PO_4(with mass percentage >100 % and the specific gravity of 1.91–1.92 at 25 ± 0.1 °C). It is known that the amount of H_2O in H_3PO_4 impacts the precision of δ^{18}O analysis because the oxygen isotopes in evolved CO_2 can easily exchange with those in liquid H_2O (e.g. McCrea 1950; Clayton, 1958). Equation (2) indicates that that some water will be released from the reaction together with the CO_2. To minimize the impact of available liquid H_2O on the isotopic exchanges between CO_2 and H_2O while the CO_2 is being evolved from the reaction, excess P_2O_5 is needed to absorb the H_2O which can potentially exist in the acid (Sharp, 2007). A solution of H_3PO_4 with a mass percentage of greater than 100 % indicates some excess P_2O_5 in the solution. If the mass percentage is too large, the solution tends to crystallize and makes the diffusion of CO_2 to the gas phase more difficult (Sharp, 2007). This will also cause isotopic fractionations and affect the precisions of the $\delta^{18}O$ values. Commercially available H_3PO_4 has mass percentages on the order of only 85 % and thus not suitable. H_3PO_4 with a mass percentage greater than 100 % can be only custom-made. The specific gravity of 100 % H_3PO_4 is approximately 1.86 g ml^{-1}. Based on our experiences, the ideal range of the specific gravity of H_3PO_4 is from 1.91 to 1.92 g ml^{-1}. Our in-house procedure of making the H_3PO_4 (>100 %) is attached as Appendix 2. A recent report by Wendeberg et al. (2011), found that the $\delta^{18}O$ of H_3PO_4 will likely affect the $\delta^{18}O$ of CO_2 evolved from the acid digestion when the mass percentage of H_3PO_4 is <102 %. This is likely due to isotopic exchanges between H_2O and H_3PO_4 and between H_2O and CO_2. Since it's important to use >100 % H_3PO_4, the specific gravity of H_3PO_4 used in our program over the past 10 yr ranges from 1.91 to 1.92 g ml^{-1} (corresponding to a mass percentage of 104 %–105 %). During individual calibration periods for each of the four carbonates, there are, at least, three separate acid digestion are processed, followed by cryogenic extractions (of the evolved CO_2) and IRMS measurements. The Big Delta values, i.e., [$\Delta_{\text{Lab-Std/NBS19-CO2}}$] between the secondary laboratory standards and NBS19 are obtained. $\delta^{13}C_{\text{Lab-Std/VPDB-CO2}}$ and $\delta^{18}O_{\text{Lab-Std/VPDB-CO2}}$ are determined, as described in Sect. 2. These data obtained from the calibration periods over the past decade (Tables 1–4) are sufficient for estimating the uncertainties and the stability of the primary anchor. In turns, theses results are used to assess the overall uncertainty of individual measurements and the stability of the traceability. To do this, the uncertainties of the two terms on the left side of Eq. (3) need to be estimated. The annual calibration data over last ten years (2001–2010) by using two different IRMSs (Finnegan MAT252 and Micromass, IsoPrime) are shown in Tables 1–4. The $\Delta_{\text{Lab-Std/NBS19-CO2}}$ and its associated uncertainties can be derived from these calibration data. The standard deviations of these corresponding Big Delta values range from 0.02–0.04 ‰ for Δ^{45} (the same as these for $\delta^{13}C$) and 0.04–0.09 ‰ for Δ^{46} (the same as these for δ^{18}O). One can see, that the standard deviation is proportional to the magnitude of absolute Big Delta value (Fig. 3). The smaller the absolute Big Delta value, the smaller its standard deviation, indicating that the cross contamination effect in the ion source has a larger impact on these Big Deltas with bigger absolute values than these Big Delta values with the smaller absolute values. The closer the absolute Big Delta value to zero, the smaller the cross contamination effect and thus obtaining the least possible standard deviations (Fig. 3). To minimize the cross contamination effect on both $\Delta_{\text{Sam/Lab-Std}}$ and $\Delta_{\text{Lab-Std/NBS19-CO2}}$, it is suggested to use a lab standard with its δ^{13}C value between the NBS19 (i.e., +1.95 ‰) and the ambient atmospheric CO_2 (~ −8 ‰) as the primary anchor. As mentioned, Cal2 is used as the primary anchor for all flask samples collected from Environment Canada Greenhouse Gas(GHG) sampling network because t has the smallest absolute Big Delta values with NBS19 (i.e., $\Delta^{45}_{\text{Cal2/NBS19}}$ and $\Delta^{46}_{\text{Cal2/NBS19}}$) as well as the smallest standard deviations in both $\Delta^{45}_{\text{Cal2/NBS19}}$ and $\Delta^{46}_{\text{Cal2/NBS19}}$. As shown in Table 3, the measured 1 sigma uncertainty of $\Delta^{45}_{\text{Cal2/NBS19-CO2}}$ and $\Delta^{46}_{\text{Cal2/NBS19-CO2}}$ is <0.02 ‰ and <0.04 ‰, respectively. It is also shown that Cal2 during the 10 yr period shows the greatest stability amongst all of the secondary standards (Fig. 1c), including NBS18. The uncertainty of the second term ($\Delta_{\text{Sam/Lab-Std}}$) can only be determined by using an air-CO_2 standard due to the need for replicate analysis over many years. Flasks are not suitable due to the limitation of having only single analyses with our measurement procedure. A high pressure air-CO_2 tank, which is used for the purpose of quality control (QC), is treated in exactly the same manner as air flasks. The uncertainties of $\Delta_{\text{QC air-CO2 tank/Lab-Std}}$ is determined by repeated analysis over several years. The QC air-CO_2 tank used here for deriving the uncertainty of $\Delta_{\text{Sam/Lab-Std}}$ is designated as QC3, and was filled at Alert, GAW station. As shown in Fig. 4, the measured 1 sigma uncertainty for $\Delta^{45}_{\text{QC3/Cal2}}$ and $\Delta^{46}_{\text{QC3/Cal2}}$ is 0.017 ‰ and 0.043 ‰, respectively. After applying the ^{17}O and N_2O corrections, the magnitude of the uncertainty in δ^{13}C and δ^{18}O are the same as those in $\Delta^{45}_{\text{QC3/Cal2}}$

and $\Delta^{46}_{QC3/Cal2}$, respectively, inferring that the uncertainties are primarily caused by the analytical procedures (i.e., acid digestions and IRMS measurements). Now that the uncertainties for $\Delta_{Lab\text{-}Std/NBS19\text{-}CO2}$ (i.e., $\Delta_{Cal2/NBS19\text{-}CO2}$) and $\Delta_{Sam/Lab\text{-}Std}$ (i.e., $\Delta_{QC3/Cal2}$) values have attained, the overall uncertainties in Eqs. (3) and (4) can be determined.

According to the principle of propagation of independent errors, the uncertainty of Eq. (3) can be calculated using Eq. (C2) in Appendix C, i.e.,

$$\sigma[\delta^{45/46}(CO_2)_{QC3/VPDB\text{-}CO2}]=[(\sigma\Delta^{45/46}_{QC3/Cal2})^2+(\sigma\Delta^{45/46}_{Cal2/NBS19\text{-}CO2})^2]^{1/2}$$

Using the results from Fig. 4 for σ ($\Delta^{45/46}_{QC3/Cal2}$) and Table 3 for σ ($\Delta^{45/46}_{Cal2/NBS19\text{-}CO2}$), the propagated uncertainty for $\delta^{45}R_{QC3/VPDB\text{-}CO2}$ and $\delta^{46}R_{QC3/VPDB\text{-}CO2}$ is 0.02 ‰ and 0.05 ‰, respectively. These are very close to the values shown in Fig. 4 which were based on statistical calculations of the individual measurements for $\delta^{13}C$ and $\delta^{18}O$. It is safe to conclude, that the overall uncertainty of the traceability in CO_2 isotope measurements for individual flask samples from our network is on the order 0.02 ‰ for $\delta^{13}C$ and 0.05 ‰ for $\delta^{18}O$. No uncertainties in the ^{17}O and N_2O corrections are considered since the same algorithm has been applied since the inception of the program.

4 Verifying a long-term trend of $\delta^{13}C$ at alert

Determining accurate long-term trends and mean annual change rates of $\delta^{13}C$ in atmospheric CO_2 is critical for understanding source and sink changes with time and as well as for assessing the effectiveness of carbon emission-control policies and mitigation measures. A long-term atmospheric trend in $\delta^{13}C$ can only be determined if the stability of the primary anchor on VPDB-CO_2 is known. As noted above, Cal2 has shown to be the most stable standard amongst the carbonate secondary standards. As shown in panel c of Fig. 1., the annual rate of change of the primary anchor (Cal2) in $\delta^{13}C$ over the period (from 2001 to 2011) was essentially zero (i.e., −0.0016 ‰). This is much less than the analytical uncertainties of the IRMS (~ 0.01 ‰). As shown in Fig. 4, the annual drift rate of δ^{13}C and δ^{18}O for the QC3 air standard is +0.003 ‰ and −0.007 ‰, respectively. Based on these results, it can be verified that the average annual change rate of the measured δ^{13}C in air CO_2 at the Alert station is −0.025 ± 0.003 ‰ per year. This likely reflects real changes in relative contributions of sources and sinks to the atmosphere CO_2, not due to drifts in the instrumentation and the isotope standards or analytical procedures applied. The total 10 yr change of the observed δ^{13}C in annual average value is ~ −0.27 ‰, from −8.22 ‰ in 1999 to −8.49 ‰ in 2010 (Fig. 1).

5 The roles of Big Delta

It is known that a measured isotopic ratio (by IRMS) varies with time as well as with different instruments. The latter is mainly due to different instrument design and operational conditions such as, physical configurations, material used, voltage applied, temperature, pressure or vacuum etc. To the best of our knowledge, current technologies and instruments are not able to measure the absolute isotope ratio of a sample but only the ratio of the isotopic ratio of the sample relative to another sample. If two samples have intrinsic and distinguishable isotopic compositions, the relative deviation in isotope ratio (in ‰) should be constant and independent on the fluctuations of instrument response, as illustrated in Fig. 5. A relative deviation of two isotope ratios, i.e., a Big Delta value, in principle, can be precisely measured on an IRMS. This allows Big Delta to play various roles in high precision isotopic measurements. Over the last decade, Big Delta has played two major roles in maintaining traceability of isotope measurements in our program.

The first role is to link all individual measurements to the primary scale (as shown by Eq. 3). As described in Sect. 2, the annual calibration and routine measurements are two independent steps in the chain of the traceability for our CO_2 isotope measurements, expressed as two Big Delta values. The uncertainties of the two Big Delta terms determine the overall uncertainty of the traceability pathway. Over the 10 yr period, different batches of NBS19 and NBS18 were used as well as a new ion source that was installed in 2007. In addition, the original voltage to frequency conversion (VFC) resistor was replaced in 2008 (noted in Tables 1–4). These changes can potentially modify the Big Delta values from the intrinsic values and contribute to their variations and uncertainties. However, as shown in Tables 1–4, Big Delta values are close to constant over the 10 yr period although the $\delta^{45/\text{or }46}$ values vary with time due to the use of various Working Reference Gases. This indicates that, generally, the procedures for acid digestion and the instruments for IRMS analysis have been consistent over the entire 10 yr period. A closer investigation at the Big Delta values (by MAT252) shows that the Big Delta values have also slightly varied or shifted, particularly for $\Delta_{\text{Cal2/Cal1}}$ values (i.e., the largest and the most sensitive to procedure/or instrument fluctuations). Based on Table 4, it is likely that the cleanliness of the ion source of the MAT252 (indicated by "BG count", i.e., background count) has been a dominant factor for the small drifting over the period, particularly for Δ^{45}. As the ion source gets cleaner, the corresponding Big Delta values get larger. The largest Big Delta values are the bench marks, which are the closest to the intrinsic/or true values. Usually, the bench mark values are obtained under the cleanest condition of an ion source. Nevertheless, it is shown that the variations of $\Delta_{\text{Cal2/NBS19-CO2}}$ by MAT252 are very small and its standard deviations (including all errors from the analytical procedures) are within the ranges of <0.02 ‰ in δ^{13}C and ~ 0.04 ‰ in δ^{18}O over this 10 yr period. These values are close to the WMO targets of 0.01 ‰ and 0.05 ‰ for data comparability in δ^{13}C and δ^{18}O, demonstrating a consistency in the precision and the stability of Cal2 as the primary anchor. The results on IsoPrime show very similar patterns for $\Delta^{45}_{\text{Cal2/NBS19-CO2}}$ but not for $\Delta^{46}_{\text{Cal2/NBS19-CO2}}$. This suggests that the difference in the high vacuum and the water-content levels inside of ion source may have larger impacts on δ^{18}O than δ^{13}C measurements. These results indicates that as long as the magnitude of a Big Delta value is relatively small (~10 ‰ or less as shown in Fig. 3), even the fluctuations in cleanliness of the ion source (i.e., the MAT252's) do not have obvious impacts on the Big Delta value. Thus, it is safe to conclude that Cal2, when used as the primary anchor, has precisely linked all of our isotopic measurements of atmospheric CO_2 samples to the VPDB-CO_2 scale.

The second role is to carry out quality assurance and quality control (QAQC), as a diagnostic tool, in monitoring fluctuations of instruments and associated apparatuses. It also serves as a measure to track the stability of various levels of standards. It can detect scale drifting in time within one individual laboratory or scale contractions between laboratories. A two-point-scale-normalization in carbon isotope measurements is recommended by Coplen et al. (2006) in order to resolve the issues of scale contraction or shifting via normalizing the difference between $\delta^{13}C_{NBS19/VPDB}$ and $\delta^{13}C_{L\text{-}SVEC/VPDB}$ obtained from individual laboratories to a fixed value (i.e., the recommended value). L-SVEC is a lithium carbonate prepared by H. Svec, Iowa State University, originally to be used as a reference material for lithium isotopic composition (Flesch et al., 1973). Due to its quite negative $\delta^{13}C$ value (-46.6 ± 0.2 ‰), it is recommended to use NBS19 and L-SVEC together to implement a two points calibration. However, to implement this recommendation, the Big Delta values (i.e., $\Delta^{45/46}_{L\text{-}SVEC/NBS19\text{-}CO2}$) between NBS19 and L-SVEC in individual labs should be determined annually to track the consistency of the normalization over time. The instrument and procedure fluctuations are major error sources causing the uncertainty in traceability, leading to non-consistency of the measurements over time. It is reasonably assumed that changes in standard or references themselves are also possible. This in turn can also cause changes in Big Delta values. However, distinguishing the fluctuations due to external factors from the changes due to standards themselves is not simple to answer, but very important to the traceability maintenance for high precision CO_2 isotope measurements, thus critical for verifying trends in the atmospheric $\delta^{13}C$. Various combinations of Big Delta values amongst different standards and references have provided powerful tools to ensure the QAQC procedures in our program. These are described as follows:

- The comparison of $\delta^{13}_{\text{NBS18/VPDB-CO2}}$ between our values and the IAEA recommended values ensures the quality of $\Delta_{\text{NBS18/NBS19-CO2}}$, $\Delta_{\text{Cal1/NBS19-CO2}}$, $\Delta_{\text{Cal2/NBS19-CO2}}$, $\Delta_{\text{Cal2/Cal1}}$ during annual calibrations.

- The comparison of corresponding Big Delta values on Δ^{45} between two IRMSs (MAT252 and IsoPrime) ensures the consistency of the acid digestion procedures (the comparison in $\Delta^{46}$is not valid due to the difference in high vacuum and water levels between the two instruments).

- The largest Big Delta values of $\Delta_{\text{Cal2/Cal1}}$ set the benchmark values of the ion source's cleanliness. An obvious drift away from these values indicates the degradation from the benchmark condition.

- The comparison in $\Delta_{\text{Cal2/Cal1}}$ between the daily measured values with these from annual calibrations validates the quality of the Cal1s and Cal2s used for daily measurements to ensure routine individual measurements firmly anchored to the primary scale.

- To ensure that the primary and secondary standards have not drifted over time, a batch of uniformly pure CO_2 samples has been made by freezing them into ampoules followed by flame sealing. The variation ranges of δ^{13}C and δ^{18}O are less than 0.02 ‰ and 0.04 ‰, respectively. This batch of ampoules are only used for annual calibrations, referred to as "annual calibration WRG". If the pure CO_2 preparation procedure is consistent for every year, the raw δ^{45} and δ^{46} values of the standards (e.g. NBS19, NBS18, Cal1 and Cal2) relative to the "WRG" should be close to constants for each calibration as well as between individual calibrations. As shown in Tables 1 to 3, the "annual calibration WRG" ampoules started being used in 2008 and all the corresponding raw δ^{45} and δ^{46} values by MAT252 are very consistent from year to year with very small standard deviations (only ~0.01 in δ^{45} and ~0.03 in δ^{46}). These results suggests that all the four carbonate standards have not changed over the period and the observed fluctuations of

Big Delta values are likely due to the impacts from external factor or instrument condition changes.

6 Challenges and recommendations

A primary anchor on the VPDB scale is required for atmospheric CO_2 isotope measurements. Primary anchors can be commercially purchased pure CO_2, pure CO_2 from carbonate or CO_2 from natural air. The primary anchors should be on the VPDB scale and must be calibrated relative to NBS19-CO_2. All calibrations are based on the assumption that NBS19-CO_2 has evolved from the NBS19 carbonate properly with the isotopic composition of the assigned values passe on correctly. This assumption is not necessarily valid due to the heterogeneity of NBS19 carbonate, which may vary between different batches purchased at various times, the uncertainties of pure CO_2 evolved from carbonates (which may be caused by having slightly different reaction temperatures and specific gravities of H_3PO_4 in acid digestions) and the variations in cleanliness of ion-source and physical configurations, which determines the degree of cross-contamination between samples and WRG during measurements. All of these factors will associate with the uncertainty of primary anchor, then, ultimately impact on the uncertainties of individual isotope measurements through a so-called traceability chain via error propagation. In order to characterize and minimize the uncertainties for isotopic measurements (including both discrete flask and continuous ^{13}C measurements, e.g. using Cavity-Ring-Down Techniques and other measurement techniques), the following strategy for maintaining traceability has been devised:

- Use different Big Delta values from multiple standards to establish a unique traceability pathway, as a documented chain in Eq. (3).

- Clearly identifying the number of levels through the traceability chain (i.e., how many levels of standards are needed to link ambient measurements to the primary scale) and the calibration frequency for each level.

- Select at least two standards for each level (could be air-CO_2, or pure CO_2 evolved from carbonates or commercially pressurized pure CO_2) with relatively large isotopic differences.

- If possible, using the lab standards with the largest Big Delta value, as a QAQC tool, to monitor instrument fluctuations. Using one of the secondary standards as the primary anchor, which should has the δ^{13}C value between NBS19 and the ambient air, and at the same time has a relative small Big Delta value (relative to NBS19-CO_2).

- Using the same Working Reference Gas during annual calibration periods for a decadal time span to monitor the fluctuations in raw δ^{45} and δ^{46} values for NBS19-CO_2 and other standards, ensuring the stability of the individual standards by valid acid preparation/extraction procedures. This kind of WRG has to be very homogenous and stable within an uncertainty range of <0.02 ‰ and <0.04 ‰ in δ^{13}C and δ^{18}O, respectively. The pure-CO_2 flame sealed in ampoules (e.g. "NARCIS"s type of samples, Mukai et al., 2005) should be ideally used as "annual calibration WRG".

- Improve the accuracy and precision of the reaction temperature during acid digestions of carbonates (e.g. thermometer calibration via a primary device, and temperature and humidity control of the surrounding environment of the whole reaction system).

- Use H_3PO_4 within a consistent range of specific gravity (i.e., 1.91–1.92 g cm^{-3}).

- If the primary anchor is air CO_2, it should be calibrated directly by NBS19-CO_2 at least once per year.

If these challenges and the recommendations are carefully taken care of, the target of overall uncertainties for individual measurements (i.e., 0.02 ‰ for δ^{13}C and 0.05 ‰ for δ^{18}O) should be achievable. A stable primary anchor and a consistent traceability can be maintained and the atmospheric trends in δ^{13}C can be constrained and verified.

Appendix A

Measurement protocols

A1 During annual calibrations

Usually, three sets of pure CO_2 ampoules are prepared via acid digestions from carbonates. Each set include NBS19, NBS18, Cal1 and Cal2. All ampoules are analyzed against the same working reference gas of pure CO_2 (e.g. APB2, a high pressure cylinder of pure CO_2 purchased from Air Products). A calibration event is completed within a time span of one day. The measurements sequence is shown in Table A1.

A2 During routine measurements

Usually, there are total 12 samples measured for a period of one day by the dedicated IRMS (MAT252) together with lab standards (i.e., Cal1 and Cal2). The measurement order and the reasons to carry out this order are shown in the Table A2.

Appendix B

Procedure for preparation of ~100 % phosphoric acid (H_3PO_4)

B1 Apparatus

Hot plate with stirrer option
800 ml pyrex beaker
Teflon coated magnetic stirrer
Pyrex spatula
Large metal beaker tongs

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B2 Chemicals

85 % H_3PO_4	400 ml (Source: Aldrich cat# 21,510-4)
P_2O_5	300 g (Source: Aldrich cat# 29,822-0)
H_2O_2 30 %	2 ml (Source: Aldrich cat# 21,676-3) (H_2O_2 bp: 150.2° C, mp: −0.43 °C)
CrO_3	10–20 mg (a few flakes) (Source: Aldrich cat#20,782-9)

B3 Procedures

1. Place 85 % phosphoric acid in an 800 ml beaker on the hot plate/with the stirrer in a fume hood and stir on very high speed with magnetic stirrer.
2. Very slowly add P_2O_5.
3. Slowly add H_2O_2 (to oxidize any possible organic compounds), turn on heat and slowly raise the temperature of the liquid.
4. As it heats, add a few flakes of CrO_3 to see if there is any excess H_2O_2 (H_2O_2 is a reducing agent now and can be oxidized by CrO_3). The solution may undergo a color change from yellow to light green (Cr^{6+} to Cr^{3+}).
5. Heat the acid to boiling and allow to boil for 2.5 h.
6. Cool slightly and transfer to Teflon storage bottle, while still hot so that it is still viscous, using the large tongs to hold the beaker.
7. Determine the specific Gravity of the acid once totally cooled down to room temperature. If the specific gravity (density) is relatively low (<1.91), reheat the batch of acid for a second time. If the specific gravity is relatively high (>1.92), add more 85 % phosphoric acid to the breaker. A specific gravity of 1.91–1.92 is ideal. Too high a specific gravity may result in precipitation of solute.

8. Specific gravity can be measured by pipetting 10 ml of room temperature acid into a volumetric flask that has been pre-weighed on a good quality balance (5 digits). Be careful not to get any acid on the walls of the flask above the volumetric line. Also ensure that the acid is homogenized by shaking the container before pipetting. Stratification of the acid may occur.

9. It is better to keep the phosphoric acid (~100 %) in the Teflon storage bottle for about two month before using it (according to our experience).

B4 Recommendations for the preparation

1. Transfer the pure H_3PO_4 to the storage bottle while still hot so that it is still viscous. Use rubber gloves, safety glasses and tongs. This step is dangerous.

2. Make sure that no water (also no vapor) comes into contact with the H_3PO_4 either during the preparation or after transferring to the Teflon storage bottles to ensure the quality of $\delta^{18}O$ values.

Appendix C

Uncertainty estimation of the traceability in CO_2 isotope measurements

Given:

$X = \Delta_{\text{Sam/Lab-Std}}$

$Y = \Delta_{\text{Lab-Std/NBS19-CO2}}$

$A = \Delta_{\text{NBS19-CO2/VPDB-CO2}} = \text{constant}$

$$
\begin{aligned}
f(X,Y) &= \delta^{45/46}(\mathrm{CO_2})_{\mathrm{Sam/VPDB\text{-}CO2}}(X,Y)\\
&= [(X\times10^{-3}+1)\times(Y\times10^{-3}+1)\times(A\times10^{-3}+1)-1]\times10^{3}\\
&= [A\times X\times Y\times10^{-6}+A\times X\times10^{-3}+A\times Y\times10^{-3}+X\times Y\times10^{-3}+A\ +X+Y]\\
&\approx [A\times X\times10^{-3}+A\times Y\times10^{-3}+X\times Y\times10^{-3}+A\ +X+Y] \qquad \text{(C1)}
\end{aligned}
$$

Given σX and σY, σf can be calculated as:

$$
\begin{aligned}
\sigma f = {} & [(\partial(A\times X\times10^{-3})/\partial X)^2\times(\sigma X)^2+(\partial(A\times Y\times10^{-3})/\partial Y)^2\times(\sigma Y)^2\\
&+(\partial(X\times Y\times10^{-3})/\partial X)^2\times(\sigma X)^2+(\partial(X\times Y\times10^{-3})/\partial Y)^2\times(\sigma Y)^2+(\sigma X)^2\\
&+(\sigma Y)^2]^{1/2} = [A^2\times10^{-6}\times(\sigma X)^2+A^2\times10^{-6}\times(\sigma Y)^2+Y^2\times10^{-6}\times(\sigma X)^2\\
&+X^2\times10^{-6}\times(\sigma Y)^2+(\sigma X)^2+(\sigma Y)^2]^{1/2}\\
&\approx[(\sigma X)^2+(\sigma Y)^2]^{1/2} \qquad \text{(C2)}
\end{aligned}
$$

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Table 1. Isotopic compositions of NBS18 in annual calibrations by MAT252 (2001–2011) and IsoPrime (2002–2011).

			NBS19				NBS18								Big Delta			
Decimal Year	Extra No.	Pre-T °C	δ45	s.d.	δ46	s.d.	δ45	s.d.	δ46	s.d.	δ^{13}C	s.d.	δ^{18}O	s.d.	Δ45	s.d.	Δ46	s.d.
			vs. Ref (raw)				vs. Ref (raw)				vs. VPDB-CO2				(NB18 vs.NB19)			
by IRMS: MAT252																		
2001.45[a]	4	25	13.560	0.008	7.894	0.014	6.281	0.013	–13.080	0.057	–5.023	0.012	–22.971	0.056	–7.181	0.012	–20.810	0.062
2001.54	6	25	13.568	0.010	7.904	0.026	6.280	0.013	–13.066	0.040	–5.033	0.014	–22.951	0.023	–7.192	0.015	–20.785	0.033
2002.33[b]	3	25	13.551	0.003	7.891	0.025	6.267	0.013	–13.012	0.017	–5.032	0.019	–22.900	0.011	–7.187	0.016	–20.739	0.030
2003.48	6	25	13.797	0.008	7.645	0.031	6.486	0.010	–13.335	0.018	–5.056	0.010	–22.976	0.018	–7.211	–0.014	–20.816	–0.033
2004.35[c]	3	25	13.799	0.014	7.638	0.039	6.500	0.014	–13.389	0.012	–5.041	0.015	–23.029	0.012	–7.200	0.010	–20.867	0.039
2005.20	3	25	13.797	0.008	7.685	0.027	6.478	0.007	–13.363	0.017	–5.061	0.007	–23.048	0.017	–7.219	0.014	–20.887	0.028
2006.54	3	25	13.807	0.003	7.634	0.020	6.486	0.011	–13.424	0.009	–5.063	0.012	–23.059	0.009	–7.221	0.008	–20.898	0.010
2007.20[d]	3	25	13.805	0.003	7.684	0.025	6.475	0.008	–13.488	0.026	–5.069	0.009	–23.171	0.026	–7.231	0.010	–21.010	0.034
2008.28[e]	3	25	13.844	0.006	7.751	0.008	6.521	0.003	–13.395	0.010	–5.062	0.004	–23.145	0.010	–7.223	0.007	–20.984	0.004
2009.22	3	25	13.840	0.003	7.692	0.052	6.523	0.022	–13.407	0.014	–5.057	0.023	–23.099	0.014	–7.217	0.022	–20.938	0.064
2010.20	3	25	13.843	0.007	7.753	0.019	6.513	0.021	–13.374	0.016	–5.070	0.022	–23.125	0.015	–7.230	0.022	–20.964	0.010
2011.28	3	25	13.846	0.003	7.706	0.017	6.513	0.019	–13.433	0.023	–5.073	0.019	–23.139	0.022	–7.233	0.016	–20.978	0.035
Ave ($n = 43$)											–5.053		–23.051		–7.212		–20.890	
s.d. (1σ)											0.017		0.088		0.018		0.088	
IAEA_1995* (mean)											–5.029		–23.035					
s.d. (1σ)											0.049		0.172					
NIST_2004* (mean)											–5.06		–23.01					
s.d. (1σ)											0.03		0.22					
by IRMS: IsoPrime																		
2002.74[b]	3	25	13.597	0.006	7.812	0.011	6.302	0.010	–12.773	0.057	–5.053	0.009	–22.587	0.056	–7.197	0.013	–20.425	0.065
2003.18	6	25	13.597	0.008	7.815	0.028	6.295	0.014	–13.010	0.034	–5.052	0.014	–22.824	0.033	–7.204	0.021	–20.663	0.047
2004.27[c]	3	25	13.778	0.008	7.522	0.036	6.471	0.010	–13.007	0.052	–5.066	0.009	–22.538	0.052	–7.208	0.008	–20.376	0.035
2005.15	3	25	13.830	0.007	7.622	0.033	6.499	0.009	–13.153	0.025	–5.083	0.009	–22.780	0.025	–7.231	0.010	–20.618	0.008
2006.22	3	25	13.821	0.006	7.622	0.037	6.517	0.009	–13.118	0.012	–5.056	0.010	–22.745	0.012	–7.205	0.011	–20.584	0.026
2007.18	3	25	13.827	0.002	7.677	0.005	6.511	0.012	–13.245	0.016	–5.063	0.012	–22.923	0.016	–7.217	0.012	–20.762	0.020
2008.24	3	25	13.819	0.014	7.551	0.052	6.503	0.007	–13.213	0.004	–5.067	0.007	–22.770	0.004	–7.216	0.019	–20.609	0.048
2009.15	3	25	13.828	0.006	7.598	0.039	6.513	0.011	–13.315	0.022	–5.062	0.011	–22.917	0.022	–7.216	0.015	–20.755	0.048
2010.17	3	25	13.832	0.014	7.600	0.010	6.494	0.004	–13.230	0.032	–5.088	0.004	–22.834	0.032	–7.237	0.018	–20.672	0.031
2011.24	3	25	13.831	0.008	7.644	0.060	6.500	0.005	–13.202	0.039	–5.080	0.006	–22.850	0.039	–7.231	0.005	–20.688	0.097
Ave ($n = 33$)											–5.067		–22.777		–7.216		–20.615	
s.d. (1σ)											0.013		0.128		0.013		0.128	

[a] NBS19 and NBS18 (purchased in 1995).

[b] NBS18 (purchased in 1998).

[c] NBS19 (purchased in 1998).

[d] A new ion source with Ta plates used in MAT25.

[e] changed VFC resistor for a brand new one from Ohmite in MAT25.

[*] ^{17}O correction algorithms used: Craig correction.

Table 2. Isotopic compositions of Cal1 in annual calibrations by MAT252 (2001–2011) and IsoPrime (2002–2011).

CAL1																		
Decimal Year	Extra No.	Pre-T °C	$\delta 45$	s.d.	$\delta 46$	s.d.	$\delta^{13}C$	s.d.	$\delta^{18}O$	s.d.	$\Delta 45$	s.d.	$\Delta 46$	s.d.	$\Delta 45$	s.d.	$\Delta 46$	s.d.
			vs. Ref (raw)				vs. VPDB-CO2				(Cal1 vs. NB19)				(Cal1 vs. NB18)			
by IRMS: MAT252											Big Delta				Big Delta			
2001.45[a]	4	25	–32.288	0.013	–12.327	0.010	–45.756	0.014	–22.143	0.009	–45.235	0.019	–20.063	0.015	–38.329	0.017	0.762	0.055
2001.54	6	25	–32.288	0.007	–12.324	0.016	–45.761	0.008	–22.149	0.015	–45.242	0.007	–20.070	0.020	–38.326	0.017	0.738	0.032
2002.33[b]	3	25	–32.277	0.015	–12.304	0.008	–45.736	0.016	–22.116	0.008	–45.215	0.014	–20.036	0.028	–38.303	0.028	0.718	0.018
2003.48	8	25	–32.087	0.015	–12.600	0.011	–45.781	0.016	–22.170	0.011	–45.258	0.015	–20.091	0.031	–38.321	0.021	0.748	0.021
2004.35[c]	3	25	–32.106	0.002	–12.671	0.021	–45.801	0.002	–22.234	0.021	–45.280	0.011	–20.155	0.046	–38.356	0.014	0.728	0.016
2005.20	3	25	–32.098	0.012	–12.640	0.009	–45.789	0.013	–22.249	0.009	–45.270	0.020	–20.170	0.018	–38.328	0.009	0.732	0.020
2006.54	3	25	–32.117	0.014	–12.648	0.028	–45.822	0.013	–22.207	0.028	–45.301	0.016	–20.119	0.044	–38.357	0.024	0.795	0.035
2007.20[d]	3	25	–32.146	0.002	–12.731	0.003	–45.846	0.002	–22.339	0.003	–45.325	0.003	–20.259	0.026	–38.372	0.009	0.767	0.024
2008.28[e]	3	25	–32.128	0.009	–12.643	0.027	–45.867	0.010	–22.316	0.027	–45.346	0.011	–20.222	0.031	–38.399	0.010	0.763	0.034
2009.22	3	25	–32.121	0.010	–12.633	0.004	–45.857	0.011	–22.250	0.004	–45.333	0.009	–20.171	0.055	–38.394	0.030	0.784	0.010
2010.20	3	25	–32.104	0.014	–12.625	0.016	–45.841	0.014	–22.293	0.016	–45.319	0.018	–20.222	0.008	–38.367	0.031	0.759	0.002
2011.28	3	25	–32.131	0.010	–12.684	0.020	–45.872	0.011	–22.314	0.020	–45.349	0.010	–20.234	0.008	–38.394	0.024	0.760	0.035
Ave ($n = 45$)	45						–45.811		–22.232		–45.290		–20.151		–38.354		0.754	
s.d. (1σ)							0.046		0.075		0.046		0.075		0.032		0.023	
by IRMS: IsoPrime																		
2002.74[b]	3	25	–32.267	0.018	–12.039	0.043	–45.782	0.020	–21.777	0.042	–45.248	0.022	–19.697	0.051	–38.327	0.025	0.743	0.014
2003.18	6	25	–32.261	0.022	–12.291	0.027	–45.768	0.022	–22.030	0.027	–45.243	0.028	–19.950	0.039	–38.315	0.012	0.728	0.008
2004.27[c]	3	25	–32.013	0.012	–12.263	0.021	–45.699	0.012	–21.718	0.021	–45.169	0.019	–19.638	0.049	–38.237	0.019	0.753	0.073
2005.15	3	25	–32.074	0.033	–12.410	0.044	–45.807	0.034	–21.961	0.044	–45.278	0.036	–19.881	0.017	–38.324	0.026	0.753	0.025
2006.22	3	25	–32.047	0.015	–12.410	0.020	–45.771	0.017	–21.961	0.020	–45.243	0.013	–19.881	0.033	–38.314	0.009	0.717	0.025
2007.18	3	25	–32.148	0.012	–12.536	0.023	–45.877	0.012	–22.139	0.022	–45.348	0.013	–20.059	0.023	–38.408	0.023	0.718	0.037
2008.24	3	25	–32.141	0.002	–12.503	0.017	–45.867	0.002	–21.983	0.017	–45.334	0.012	–19.904	0.045	–38.394	0.007	0.720	0.013
2009.15	3	25	–32.170	0.016	–12.581	0.009	–45.903	0.017	–22.107	0.009	–45.371	0.017	–20.027	0.047	–38.433	0.025	0.744	0.022
2010.17	3	25	–32.112	0.018	–12.516	0.017	–45.846	0.019	–22.044	0.017	–45.316	0.027	–19.964	0.019	–38.357	0.015	0.723	0.049
2011.24	3	25	–32.145	0.009	–12.395	0.080	–45.884	0.007	–21.967	0.079	–45.349	0.012	–19.887	0.107	–38.396	0.013	0.818	0.090
Ave ($n = 33$)							–45.820		–21.969		–45.290		–19.889		–38.350		0.742	
s.d. (1σ)							0.065		0.132		0.064		0.132		0.059		0.030	

[a] NBS19 and NBS18 (purchased in 1995).

[b] NBS18 (purchased in 1998).

[c] NBS19 (purchased in 1998).

[d] A new ion source with Ta plates used in MAT252.

[e] changed VFC resistor for a brand new one from Ohmite in MAT252.

Table 3. Isotopic compositions of Cal2 in annual calibrations by MAT252 (2001–2011) and IsoPrime (2002–2011).

CAL2																		
Decimal Year	Extra No.	Pre-T °C	δ45	s.d.	δ46	s.d.	δ^{13}C	s.d.	δ^{18}O	s.d.	Δ45	s.d.	Δ46	s.d.	Δ45	s.d.	Δ46	s.d.
				vs. Ref (raw)				vs. VPDB-CO2				(Cal2 vs. NB19)				(Cal2 vs. NB18)		
by IRMS: MAT252												Big Delta				Big Delta		
2001.45[a]	4	25	8.920	0.015	−2.694	0.042	−2.590	0.015	−12.683	0.040	−4.578	0.019	−10.505	0.044	2.622	0.012	10.524	0.054
2001.54	6	25	8.926	0.017	−2.705	0.055	−2.589	0.016	−12.701	0.054	−4.578	0.023	−10.523	0.067	2.632	0.023	10.484	0.057
2002.33[b]	3	25	8.918	0.015	−2.666	0.033	−2.584	0.015	−12.653	0.033	−4.571	0.011	−10.474	0.037	2.634	0.013	10.482	0.025
2003.48	8	25	9.159	0.019	−2.931	0.013	−2.588	0.020	−12.673	0.013	−4.573	0.023	−10.486	0.027	2.657	0.016	10.548	0.016
2004.35[c]	3	25	9.143	0.018	−2.988	0.015	−2.604	0.019	−12.724	0.015	−4.592	0.009	−10.545	0.022	2.622	0.023	10.540	0.003
2005.20	3	25	9.144	0.018	−2.921	0.021	−2.601	0.019	−12.703	0.021	−4.589	0.022	−10.525	0.035	2.649	0.012	10.583	0.007
2006.54	3	25	9.150	0.017	−3.011	0.007	−2.618	0.029	−12.758	0.032	−4.606	0.027	−10.585	0.021	2.636	0.028	10.536	0.027
2007.20[d]	3	25	9.123	0.019	−2.998	0.022	−2.631	0.019	−12.778	0.021	−4.619	0.020	−10.600	0.043	2.631	0.022	10.634	0.045
2008.28[e]	3	25	9.195	0.012	−2.887	0.015	−2.597	0.012	−12.735	0.014	−4.586	0.007	−10.556	0.008	2.656	0.014	10.651	0.011
2009.22	3	25	9.183	0.004	−2.900	0.008	−2.607	0.004	−12.690	0.008	−4.594	0.007	−10.511	0.059	2.642	0.024	10.650	0.008
2010.20	3	25	9.189	0.005	−2.899	0.008	−2.602	0.005	−12.741	0.008	−4.591	0.005	−10.570	0.027	2.658	0.018	10.617	0.024
2011.28	3	25	9.202	0.024	−2.919	0.032	−2.592	0.025	−12.723	0.031	−4.581	0.026	−10.544	0.020	2.672	0.032	10.657	0.042
Ave ($n = 45$)	45					−2.600		−12.713		−4.588		−10.535		2.643		10.576		
s.d. (1σ)						0.014		0.036		0.014		0.039		0.016		0.065		
by IRMS: IsoPrime																		
2002.74[b]	3	25	8.958	0.013	−2.603	0.032	−2.594	0.013	−12.512	0.032	−4.576	0.018	−10.334	0.023	2.640	0.011	10.302	0.078
2003.18	6	25	8.957	0.016	−2.678	0.017	−2.593	0.017	−12.590	0.017	−4.578	0.015	−10.411	0.020	2.645	0.025	10.468	0.028
2004.27[c]	3	25	9.159	0.011	−2.792	0.025	−2.576	0.011	−12.416	0.025	−4.556	0.019	−10.237	0.060	2.671	0.016	10.349	0.069
2005.15	3	25	9.176	0.031	−2.816	0.054	−2.609	0.031	−12.538	0.054	−4.591	0.028	−10.360	0.034	2.659	0.022	10.474	0.034
2006.22	3	25	9.168	0.018	−2.858	0.018	−2.606	0.018	−12.579	0.017	−4.589	0.014	−10.401	0.030	2.635	0.015	10.397	0.009
2007.18	3	25	9.172	0.009	−2.898	0.020	−2.606	0.009	−12.672	0.020	−4.592	0.007	−10.494	0.023	2.644	0.012	10.486	0.004
2008.24	3	25	9.137	0.003	−2.941	0.004	−2.636	0.003	−12.592	0.004	−4.618	0.014	−10.414	0.049	2.617	0.005	10.409	0.006
2009.15	3	25	9.157	0.011	−2.969	0.028	−2.623	0.012	−12.666	0.028	−4.608	0.016	−10.487	0.056	2.627	0.008	10.486	0.047
2010.17	3	25	9.152	0.015	−2.938	0.046	−2.629	0.014	−12.635	0.046	−4.616	0.015	−10.459	0.048	2.641	0.016	10.429	0.080
2011.24	3	25	9.186	0.015	−2.813	0.049	−2.599	0.014	−12.557	0.048	−4.582	0.022	−10.378	0.107	2.668	0.018	10.528	0.011
Ave ($n = 33$)							−2.607		−12.576		−4.590		−10.397		2.645		10.433	
s.d. (1σ)							0.018		0.077		0.019		0.077		0.017		0.070	

[a] NBS19 and NBS18 (purchased in 1995).

[b] NBS18 (purchased in 1998).

[c] NBS19 (purchased in 1998).

[d] A new ion source with Ta plates used in MAT252.

[e] changed VFC resistor for a brand new one from Ohmite in MAT252.

Table 4. Isotopic compositions of the Big Delta (Cal2 vs. Cal1) in annual calibrations by MAT252 (2001–2011) and IsoPrime (2002–2011).

Decimal Year	CAL1 vs. Ref (raw) δ45	s.d.	δ46	s.d.	CAL2 vs. Ref (raw) δ45	s.d.	δ46	s.d.	Big Delta (Cal2 vs. Cal1) Δ45	s.d.	Δ46	s.d.	Cleanliness indicator of IRMS BG Count[*]	s.d.
by IRMS: MAT252														
2001.45[a]	−32.288	0.013	−12.327	0.010	8.920	0.015	−2.694	0.042	42.584	0.009	9.754	0.033	208.14	1.16
2001.54	−32.288	0.007	−12.324	0.016	8.926	0.017	−2.705	0.055	42.589	0.021	9.739	0.059	206.74	1.79
2002.33[b]	−32.277	0.015	−12.304	0.008	8.918	0.015	−2.666	0.033	42.568	0.020	9.758	0.042	212.07	2.49
2003.48	−32.087	0.015	−12.600	0.011	9.159	0.019	−2.931	0.013	42.619	0.027	9.795	0.020	207.76	1.25
2004.35[c]	−32.106	0.002	−12.671	0.021	9.143	0.018	−2.988	0.015	42.618	0.020	9.807	0.035	205.53	1.10
2005.20	−32.098	0.012	−12.640	0.009	9.144	0.018	−2.921	0.021	42.610	0.019	9.844	0.026	208.71	1.00
2006.54	−32.117	0.014	−12.648	0.028	9.150	0.017	−3.011	0.007	42.623	0.032	9.740	0.057	208.71	2.00
2007.20[d]	−32.146	0.002	−12.731	0.003	9.123	0.019	−2.998	0.022	42.639	0.018	9.859	0.022	201.76	0.40
2008.28[e]	−32.128	0.009	−12.643	0.027	9.195	0.012	−2.887	0.015	42.699	0.011	9.890	0.043	201.11	0.23
2009.22	−32.121	0.010	−12.633	0.004	9.183	0.004	−2.900	0.008	42.674	0.012	9.858	0.008	200.41	0.22
2010.20	−32.104	0.014	−12.625	0.016	9.189	0.005	−2.899	0.008	42.662	0.020	9.851	0.024	202.10	0.61
2011.28	−32.131	0.010	−12.684	0.020	9.202	0.024	−2.919	0.032	42.705	0.036	9.890	0.013	199.91	0.86
Ave ($n = 45$)									42.632		9.815			
s.d. (1σ)									0.044		0.057			
by IRMS: IsoPrime														
2002.74[b]	−32.267	0.018	−12.039	0.043	8.958	0.013	−2.603	0.032	42.600	0.020	9.552	0.065		
2003.18	−32.261	0.022	−12.291	0.027	8.957	0.016	−2.678	0.017	42.592	0.027	9.733	0.020		
2004.27[c]	−32.013	0.012	−12.263	0.021	9.159	0.011	−2.792	0.025	42.533	0.007	9.589	0.031		
2005.15	−32.074	0.033	−12.410	0.044	9.176	0.031	−2.816	0.054	42.616	0.027	9.714	0.048		
2006.22	−32.047	0.015	−12.410	0.020	9.168	0.018	−2.858	0.018	42.580	0.007	9.672	0.033		
2007.18	−32.148	0.012	−12.536	0.023	9.172	0.009	−2.898	0.020	42.692	0.020	9.761	0.042		
2008.24	−32.141	0.002	−12.503	0.017	9.137	0.003	−2.941	0.004	42.649	0.002	9.683	0.019		
2009.15	−32.170	0.016	−12.581	0.009	9.157	0.011	−2.969	0.028	42.701	0.022	9.735	0.025		
2010.17	−32.112	0.018	−12.516	0.017	9.152	0.015	−2.938	0.046	42.633	0.018	9.699	0.030		
2011.24	−32.145	0.009	−12.395	0.080	9.186	0.015	−2.813	0.049	42.704	0.019	9.702	0.100		
Ave ($n = 33$)									42.630		9.684			
s.d. (1σ)									0.057		0.066			

[a] NBS19 and NBS18 (purchased in 1995).

[b] NBS18 (purchased in 1998).

[c] NBS19 (purchased in 1998).

[d] A new ion source with Ta plates used in MAT252.

[e] changed VFC resistor for a brand new one from Ohmite in MAT252.

[*] BG count: stands for background count which is an indicator for the degree of cleanliness of the ion source in MAT252 IRMS. The smaller the number, the cleaner the ion source. ~200 is the electronic zero.

Table A1. Annual calibration sequence by IRMS (MAT252).

Measurement order	Sample bellow	Reference bellow	Description	Purpose
1	WRG[*]	WRG	Zero check with both bellows connected to each other.	To check if the crimps for both capillaries at sample and reference sides are evenly balanced (the related raw delta of sample to reference should be close 0 ‰).
2	WRG	WRG	Zero check with both bellows dis-connected to each other.	To check if all the conditions in both sample and reference sides are identical when real samples are running (the related raw delta of this should be close 0 ‰).
3	Cal1	WR	Measuring a lab-std (i.e., Cal1) with $\delta^{13}C_{VPDB\text{-}CO2}$ ~ −45 ‰.	To obtain the Big Delta values between the lab-standard and NBS19 and to anchor Cal1 on the primary scale via NBS19.
4	Cal2	WR	Measuring a lab-std (i.e., Cal2) with $\delta^{13}C_{VPDB\text{-}CO2}$ ~ −2 ‰.	To obtain the Big Delta values between the lab-standard and NBS19 and to anchor Cal2 on the primary scale via NBS19.
5	NBS18	WR	Measuring an international reference (i.e., NBS18) with $\delta^{13}C_{VPDB\text{-}CO2}$ ~ −5 ‰.	To obtain the Big Delta values between NBS18 and NBS19, and and to anchor NBS18 on the primary scale via NBS19.
6	NBS19	WR	Measuring an international standard (i.e., the anchor on the primary scale: VPDB-CO2) with $\delta^{13}C_{VPDB\text{-}CO2}$: +1.95 ‰.	To obtain $\delta^{13}C_{NBS18/VPDB\text{-}CO2}$, $\delta^{13}C_{Cal1/VPDB\text{-}CO2}$, $\delta^{13}C_{Cal2/VPDB\text{-}CO2}$ via measuring the Big Deltas between NBS19 and those samples.
7	Cal1	WR	The same as the previous Cal.	The same as above.
8	Cal2	WR	The same as the previous Cal.	The same as above.
9	NBS18	WR	The same as the previous NBS18.	The same as above.
10	NBS19	WR	The same as the previous NBS19.	The same as above.
11	Cal1	WR	The same as the previous Cal.	The same as above.
12	Cal2	WR	The same as the previous Cal.	The same as above.
13	NBS18	WR	The same as the previous NBS18.	The same as above.
14	NBS19	WR	The same as the previous NBS19.	The same as above.

[*] Starting with 2008, the WRG ampoules used for annual calibrations were from the same batch of APB2 (i.e., all the ampoules were produced at the same time and very homogenous). It is expected that the raw data (i.e., δ^{45} and δ^{45}) between NBS19, NBS18, Cal1, Cal2 and WRG are very close within one annual calibration as well as between these annual calibrations (2008–2011) if these samples are propoerly made via acid diagestion. It is shown in Table 1 through 4 that the results are very close to each others.

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Table A2. Daily measurement sequence by IRMS (MAT252).

Measurement order	Sample bellow	Reference bellow	Description	Purpose
1	WRG	WRG	Zero check with both bellows connected to each other	To check if the crimps of both capillaries are evenly balanced.
2	WRG	WRG	Zero check with both bellows dis-connected to each other	To check any problems in running real samples (the related raw delta of this should close 0 ‰).
3	Cal1	WRG	Measuring a lab-std with $\delta^{13}C_{VPDB\text{-}CO2} \sim -4$ ‰	To determine the Big Delta between two lab-standards for validation of the primary anchor (i.e., Cal2) and monitoring instrument's variation.
4	Cal2	WRG	Measuring a lab-std with $\delta^{13}C_{VPDB\text{-}CO2} \sim -2$ ‰	To determine the Big Delta between two lab-standards for validation of the primary anchor (i.e., Cal2) and monitoring instrument's variation. If the Big Delta values are within a two-standard-deviation range (respect to the mean of annual calibrations), it is assumed that the Cal1 and Cal2 are valid during the preparation process. The Cal2 will be valid as the primary anchor linking the samples to the primary scale.
5	Samp-1	WRG	Sample measurement	
6	Samp-2	WRG	Sample measurement	
7	Samp-3	WRG	Sample measurement	
8	Samp-4	WRG	Sample measurement	
9	Samp-5	WRG	Sample measurement	
10	Samp-6	WRG	Sample measurement	
11	Samp-7	WRG	Sample measurement	
12	Samp-8	WRG	Sample measurement	
13	Samp-9	WRG	Sample measurement	
14	Samp-10	WRG	Sample measurement	
15	Samp-11	WRG	Sample measurement	
16	Samp-12	WRG	Sample measurement	
17	Cal2	WRG	Measuring a lab-std with $\delta^{13}C_{VPDB\text{-}CO2} \sim -2$ ‰	To evaluate how much WRG has changed during the period of running 12 samples. If the change of the raw delta for carbon between the first Cal2 and the second Cal2 is <0.0 ‰, it is assumed that the WRG was valid during the period of measuring 12 samples and therefore, all the sample measurements are assumed valid.

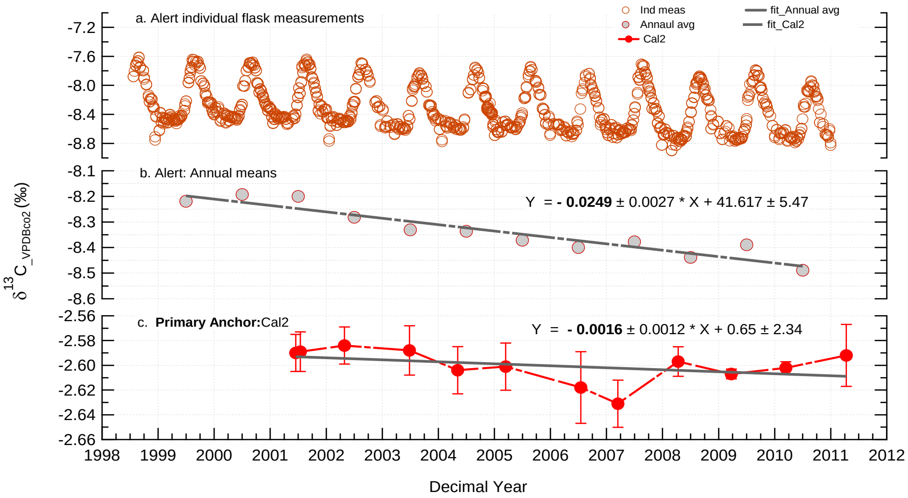

Fig. 1. Verifying the trend in δ^{13}C measurements of flask CO_2 at Alert (1998–2010) with the trend of the primary anchor on the VPDB-CO_2 scale. The top panel **(a)**: the individual flask measurements of δ^{13}C at Alert from 1998 to 2010 by Environment Canada; the middle panel **(b)**: the annual means of flask measurements in δ^{13}C from 1998 to 2010; the bottom panel **(c)**: the calibration results of the primary anchor (Cal2) in δ^{13}C from 2001 to 2011.

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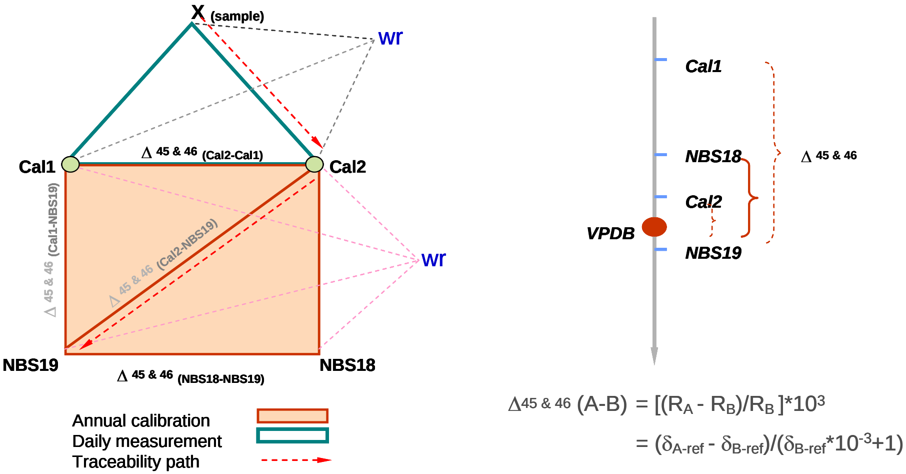

Fig. 2. Caption on next page.

Fig. 2. A schematic (on the left panel) of traceability in high precision isotopic measurements via multi-carbonates, at the Stable Isotope Research Lab (SIRL), CRD, Environment Canada, and the relative positions of $\delta^{13}C_{\text{VPDB-CO2}}$ on the primary scale (on the right panel). The direction of the arrow is towards more positive values (in VPDB scale). NBS19, NBS18, Cal1 and Cal2 are calcium carbonates (NBS19 and NBS18 are international reference materials, whereas Cal1 and Cal2 are lab- standards). NBS19 has assigned values (+1.95‰ in $\delta^{13}C$ and −2.2‰ in $\delta^{18}O$) on the primary VPDB scale. Based on various international inter-comparison results, NBS18 has recommended values of −5.029 ± 0.049‰ and −23.035 ± 0.172 for $\delta^{13}C$ and $\delta^{18}O$, respectively (Gonfiantini et al., 1995). In 2004, NBS18 were reported as −5.06 ± 0.03‰ and −23.01 ± 0.22‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively in NIST Special Publication 260-149, 2004 Edition (Verkouteren and Klinedinst, 2004). Craig ^{17}O correction has been applied to both datasets. The three carbonates (i.e. NBS18, Cal1 and Cla2) are calibrated by NBS19 during individual annual calibration events. Big Delta values (i.e. Δ^{45} or Δ^{46}) are independent on working reference gases and can be precisely determined by IRMS measurements. The Big Delta values between NBS18 and NBS19 have been used as the quality control criteria for obtaining other Big Delta values (e.g. $\Delta_{\text{Cal1/NBS19-CO2}}$, $\Delta_{\text{Cal2/NBS19-CO2}}$, & $\Delta_{\text{Cal2/Cal1}}$) during annual calibrations. When the $\delta^{13}C_{\text{NBS18-CO2/VPDP-CO2}}$ and $\delta^{18}O_{\text{NBS18-CO2/VPDP-CO2}}$ match with the recommended values by IAEA (via using the $\Delta_{\text{NBS18/NBS19-CO2}}$ value in calculations), the other Big Delta values are considered valid. Cal2 and Cal1 are also measured together with air-CO_2 ambient samples during daily measurements. The Big Delta values between Cal2 and Cal1 are used as the quality control criteria for daily measurements, via comparing the values with the corresponding values from annual calibrations. Once the two sets (annual calibration vs. daily measurements) of Big Delta values are comparable, the quality of this Cal2 sample is verified. Thus, the specific Cal2 sample can be used as the primary anchor for isotopic measurements of flask air samples during the day. Finally, the $\delta^{13}C$ and $\delta^{18}O$ values are derived from Eq. (2), using the two Big Delta (i.e., $\Delta_{\text{Sam/Cal2}}$ and $\Delta_{\text{Cal2/NBS19-CO2}}$) values. Then, the overall uncertainty of the ambient sample measurements simply depends on the uncertainties of the two Big Delta values, which are obtained from both daily measurements and annual calibrations.

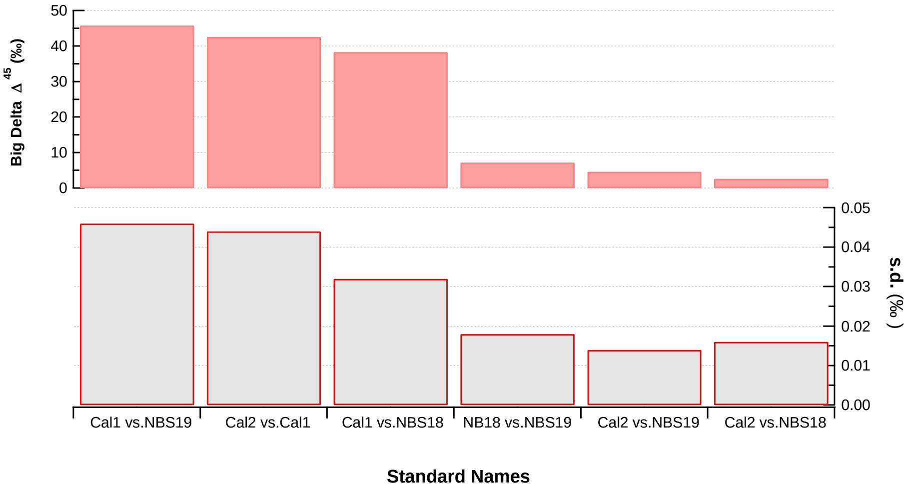

Fig. 3. There is a positive correlation between the Big Delta values (top panel) and the corresponding standard deviations (bottom panel). The Coefficient of determination (r^2) is 0.94. The Big Delta value between the primary anchor (Cal2) and NBS19 is ∼ −4.6 ‰ (with a smallest standard deviation of 0.014 ‰).

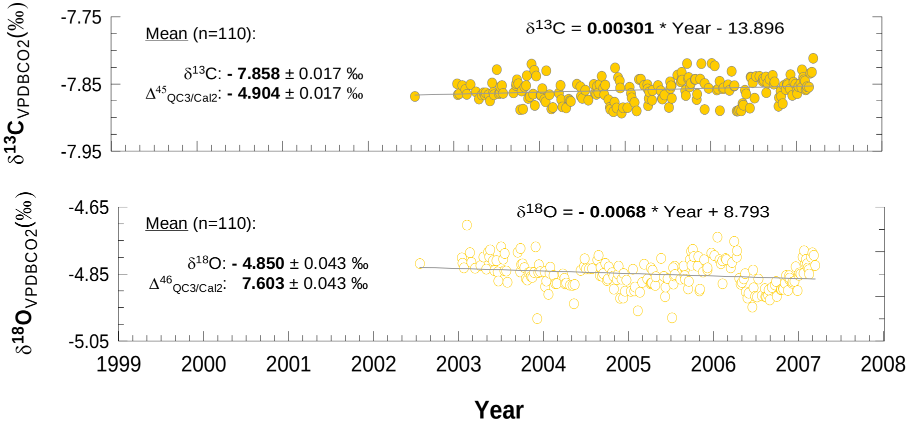

Fig. 4. Uncertainty and stability of isotopic composition of QC3 (a QC air-CO_2 tank) over 4 yr (2003 to 2007).

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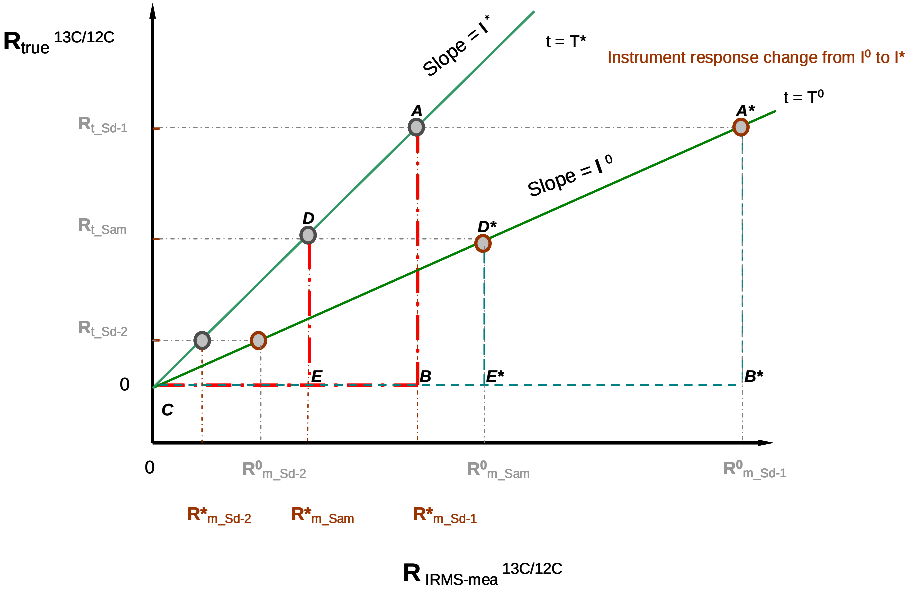

Fig. 5. Schematic of the relationship between the intrinsic/or true isotopic ratio (i.e., $R = {}^{13}C/{}^{12}C$) and the isotopic ratio measured by IRMS. There are two standards (Sd-1 and Std-2) and one sample shown in the diagram. Their intrinsic/or true isotopic compositions are distinguishable as $R^0_{\mathrm{t\_Sd\text{-}1}}$, $R^0_{\mathrm{t\_Sd\text{-}2}}$, and $R^0_{\mathrm{t\_Sam}}$. If the instrument response changes from I^0 (at $t = T^0$) to I^* (at $t = T^*$), the measured isotopic ratios for two standards and the sample would change from $R^0_{\mathrm{m\_Sd\text{-}1}}$, $R^0_{\mathrm{m\_Sd\text{-}2}}$, $R^0_{\mathrm{m\_Sam}}$ to $R^*_{\mathrm{m\_Sd\text{-}1}}$, $R^*_{\mathrm{m\_Sd\text{-}2}}$, $R^*_{\mathrm{m\_Sam}}$. However, the ratios (i.e., $[R^0_{\mathrm{m\_Sam}}/R^0_{\mathrm{m\_Sd\text{-}1}}]$, $[R^0_{\mathrm{m\_Sd\text{-}2}}/R^0_{\mathrm{m\_Sd\text{-}1}}]$) would not change and they are always equal to the corresponding intrinsic/true ratios $[R^0_{\mathrm{t\_Sam}}/R^0_{\mathrm{t\_Sd\text{-}1}}]$, $[R^0_{\mathrm{t\_Sd\text{-}2}}/R^0_{\mathrm{t\_Sd\text{-}1}}]$), respectively, since triangle *ABC* similar to triangle *DEC* and triangle *A*B*C** similar to triangle *D*E*C** illustrated in above schematic.

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