Maintaining consistent traceability in high-precision isotope measurements of CO\textsubscript{2}: a way to verify atmospheric trends of δ\textsuperscript{13}C and δ\textsuperscript{18}O

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Abstract. Maintaining consistent traceability of high-precision measurements of CO\textsubscript{2} isotopes is critical in order to obtain accurate atmospheric trends of δ\textsuperscript{13}C and δ\textsuperscript{18}O (in CO\textsubscript{2}). Although a number of laboratories/organizations around the world have been conducting baseline measurements of atmospheric CO\textsubscript{2} isotopes for several decades, reports on the traceability and maintenance are rare. In this paper, a principle and an approach for maintaining consistent traceability in high-precision isotope measurements (δ\textsuperscript{13}C and δ\textsuperscript{18}O) of atmospheric CO\textsubscript{2} are described. The concept of Big Delta is introduced and its role in maintaining traceability of the isotope measurements is described and discussed extensively. The uncertainties of the traceability have been estimated based on annual calibration records over the last 10 yr. The overall uncertainties of CO\textsubscript{2} isotope measurements for individual ambient samples analyzed by the program at Environment Canada have been estimated (excluding these associated with the sampling). The values are 0.02 and 0.05 %\textsubscript{o} in δ\textsuperscript{13}C and δ\textsuperscript{18}O, respectively, which are close to the World Meteorological Organization (WMO) targets for data compatibility. The annual rates of change in δ\textsuperscript{13}C and δ\textsuperscript{18}O of the primary anchor (which links the flask measurements back to the VPDB-CO\textsubscript{2} scale) are close to zero (−0.0016 ± 0.0012 %\textsubscript{o}, and −0.006 ± 0.003 %\textsubscript{o} per year, respectively) over a period of 10 yr (2001–2011). The average annual changes of δ\textsuperscript{13}C and δ\textsuperscript{18}O in air CO\textsubscript{2} at Alert GAW station over the period from 1999 to 2010 have been evaluated and confirmed; they are −0.025 ± 0.003 %\textsubscript{o} and 0.000 ± 0.010 %\textsubscript{o}, respectively. The results are consistent with a continuous contribution of fossil fuel CO\textsubscript{2} to the atmosphere, having a trend toward more negative in δ\textsuperscript{13}C, whereas the lack of change in δ\textsuperscript{18}O likely reflects the influence from the global hydrologic cycle. The total change of δ\textsuperscript{13}C and δ\textsuperscript{18}O during this period is ∼ −0.27 %\textsubscript{o} and ∼ 0.00 %\textsubscript{o}, respectively. Finally, the challenges and recommendations as strategies to maintain a consistent traceability are described.

1 Introduction

Precise determination of the isotope compositions of atmospheric CO\textsubscript{2} plays an important role in understanding the carbon cycle and, in turn, addresses the issue of the continuous increase of atmospheric CO\textsubscript{2} at regional and global scales. Numerous studies have been conducted to understand the exchanges of CO\textsubscript{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 at al., 1983; Francey et al., 1995; Bakwin et al., 1998; Ciais et al., 1995, 1997; Batté et al., 2000; Allison and Francey, 2007). From 1990 through 2010, the average annual global rate of change of carbon isotopic composition in atmospheric CO\textsubscript{2} is ∼ −0.026 ± 0.001 %\textsubscript{o} in δ\textsuperscript{13}C. This result was derived from annual averages of all surface marine boundary layer (MBL) references (http://www.esrl.noaa.gov/gmd/ccgg/about/global_means.html). “MBL” sites (Masarie and
The overall uncertainty of the ambient measurements). To precisely determine the uncertainties of CO₂ isotope measurements for ambient samples and derive long-term trends from those measurements, it is important to understand and quantify the uncertainties for the standards used for the measurements and the overall uncertainty through the traceability.

In this paper, we present our results from a period of decadal time and the approaches to obtain these results, including the following:

- The traceability used for high-precision CO₂ isotope measurements in our program at Environment Canada.
- The CO₂ isotope measurements and their trends at Alert station from 1999 to 2010.
- The entire records of annual calibrations of secondary standards (directly against NBS19-CO₂) to demonstrate the traceability implementation and maintenance.
- The uncertainties and the stability of the primary anchor, which helps to reveal the stability of NBS19 and to evaluate long-term trends of δ¹³C and δ¹⁸O in atmospheric CO₂ at Alert.
- The overall uncertainty of the ambient measurements (i.e., the uncertainty propagated from all different levels of standards used in the traceability chain, including the CO₂ evolved from NBS19).
- The challenges and recommendations.

2 Traceability

Metrological traceability is defined as “the 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 levels of standards are used for calibrations, CO₂
Fig. 1. (a) Evaluating the trend in $\delta^{13}\text{C}$ measurements of flask CO$_2$ at Alert (1998–2010) with the trend of the primary anchor. The top panel a: the individual flask measurements of $\delta^{13}\text{C}$ at Alert from 1998 to 2010 by Environment Canada; the middle panel b: the annual means of flask measurements in $\delta^{13}\text{C}$ from 1998 to 2010 (the range of “X” in the linear relationship: > 1999 and < 2011); the bottom panel c: the calibration results of the primary anchor (Cal2) in $\delta^{13}\text{C}$ from 2001 to 2011 (the range of “X” in the linear relationship: > 2001 and < 2012).

(b) Evaluating the trend in $\delta^{18}\text{O}$ measurements of flask CO$_2$ at Alert (1998–2010) with the trend of the primary anchor. The top panel a: the individual flask measurements of $\delta^{18}\text{O}$ at Alert from 1998 to 2010 by Environment Canada; the middle panel b: the annual means of flask measurements in $\delta^{18}\text{O}$ from 1998 to 2010 (the range of “X” in the linear relationship: > 1999 and < 2011); the bottom panel c: the calibration results of the primary anchor (Cal2) in $\delta^{18}\text{O}$ from 2001 to 2011 (the range of “X” in the linear relationship: > 2001 and < 2012).
isotope measurements should be traced back to the primary scale (VPDB) via the primary standard NBS19. It is known that VPDB is a hypothetical standard because the supply of PDB has been exhausted. The primary VPDB scale is established by adopting the isotopic compositions of NBS19 relative to VPDB as +1.95‰ for δ13C NBS19/VPDB and −2.2‰ for δ18O NBS19/VPDB (Friedman et al., 1982; Hut, 1987; Coplen et al., 2006a). However, NBS19 only defines one point on the primary scale. It is almost impossible to accurately calibrate other secondary standards by this one point scale. If we use a ruler as an analogy of the scale, then no units were defined on the primary ruler to account for scale contraction. In order to define the unit on the primary ruler, at least two standards are required (assuming instrument linearity). It would be even better to have three standards so that the linearity of the instrument can be taken into account. Following this principle, in establishing a secondary scale (i.e., a local scale for an individual program), at least two standards 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 CO2 isotope measurements back to the primary standard. One is the primary (i.e., NBS19) and the others are the secondary carbonate standards, including NBS18, Cal1 and Cal2. NBS19 and NBS 18 are international reference materials that were purchased from the International Atomic Energy Agency (IAEA) through the website (http://nucleus.iaea.org/rpst/ReferenceProducts/ ReferenceMaterials/Stable_Isotopes/13C18and7Li/index.htm; accessed on 22 March 2013). NBS19 was produced from limestone (mainly composed of CaCO3) with an unknown source, whereas NBS18 is a calcite (CaCO3) that originated from Fen, Norway (Friedman, et al., 1982; Hut, 1987; Stichler, 1995; Coplen et al., 2006a). NBS19 and NBS18 are both used to define the unit on the primary scale. Our Cal1 and Cal2 standards are calcium carbonates purchased from Aldrich Chemicals and Fisher Scientific, respectively. Cal1 and Cal2 are used to anchor the individual measurements on the primary scale and to evaluate the stability of the primary anchor (which will be discussed later). As shown on the schematic of the traceability pathway in Fig. 2, the implementation of the traceability in our program includes two operational steps: annual calibration and daily measurements.

2.1 Annual calibrations

The secondary standards (NBS18, Cal1 and Cal2) are calibrated to the primary standard (NBS19) by measuring them against the same aliquot of a pure CO2 gas, i.e., a working reference gas (WRG) within one day (the WRG preparation is described in Appendix C). This allows identical treatments for all standards in IRMS analysis procedures. The isotopic compositions of these standards are traced to the primary standard by the following equations.

\[
R_{\text{Lab-Std}}/R_{\text{VPDBCO2}} = \frac{R_{\text{Lab-Std}}}{R_{\text{WRG}}} = \frac{1}{(R_{\text{NBS19CO2}}/R_{\text{WRG}})} \\
= \left[ \frac{R_{\text{Lab-Std}}}{R_{\text{NBS19CO2}}} \right] \cdot \left( \frac{R_{\text{NBS19CO2}}/R_{\text{VPDBCO2}}}{} \right) \\
= \left[ \frac{\Delta_{\text{Lab-Std/NBS19CO2}} \times 10^{-3} + 1}{\Delta_{\text{NBS19CO2/VPDBCO2}} \times 10^{-3} + 1} \right].
\]

(1)

where \( R \) is either the ratio of [mass 45/mass 44] or [mass 46/mass 44] in CO2.

\[
\Delta_{\text{Lab-Std/NBS19CO2}} = \left( \frac{R_{\text{Lab-Std}} - R_{\text{NBS19CO2}}}{R_{\text{NBS19}}} \right)
\]

\[
\times 10^3 \% = \left( \delta_{\text{Lab-Std/WRG}} - \delta_{\text{NBS19CO2/WRG}} \right) / \left( \delta_{\text{NBS19CO2/WRG}} \times 10^{-3} + 1 \right) \%.
\]

This term \( \Delta_{45/46} \) is introduced as Big Delta. It is defined as the relative deviation of isotopic ratio (given in ‰) between two materials. It can also be expressed as \( \left( R_A/R_B \right) - 1 \times 10^3 \% \). In our case, A is a laboratory standard (Lab-Std) and B is NBS19-CO2. Although the expression of \( \Delta_{45/46} \) appears identical to the definition of the small delta between A and B (i.e., \( \delta_{45/46} = \left( R_A/R_B \right) - 1 \times 10^3 \% \)), the determination of Big Delta should not be obtained by a direct measurement against each other but from two raw measurements that are conducted separately against the same WRG for an identical treatment principle. Big Delta values used in this study are slightly different from those based on conventional definition (e.g., Hoefs, 1997). The latter are differences between two δ values.

By definition, a Big Delta value is independent of the WRG. It is, however, dependent on cross contaminations (CC) in the ion source due to the mixing of sample and reference gases (Meijer et al., 2000; Verkouteren et al., 2003a,b). Factors that impact the CC include ion source configuration, the material (that the source is made of), the pumping efficiency (source conductance and cleanliness) and the idle/integration time used for the analysis. Given a specific IRMS, although most of the factors could be kept unchanged, the extent of cleanliness of the ion source in an isotopic ratio mass spectrometer (IRMS) would vary with time. This affects CC and in turn, the Big Delta value will fluctuate. The extent of cleanliness is a relative status for each individual IRMS instrument. Theoretically, when the high vacuum reading is at its lowest, the readings of mass intensity (for masses 18, 28, 30, 32, 40 and 44) under background conditions are the lowest and the cleanest condition for an IRMS should be reached. Then, the extent of CC is the lowest and the largest Big Delta value should be observed. For a MAT252 instrument, the extent of cleanliness is indicated by “background count” and the electronic zero of the background count is 200 (Merritt and Hayes, 1994). Any physical
or configuration modifications to the ion source or changes in electronics (amplifiers) can either increase or decrease the Big Delta values due to their impacts on background count. Such modifications in turn impact the extent of cross contamination. Under ideal conditions (approaching the cleanest extent of an IRMS source), the Big Delta values between two CO2 samples should approach a constant that can be precisely determined. Using the Big Delta approach, the units on the primary scale can be defined/maintained and the issue of scale contraction can be addressed.

The first two terms on the right-hand side in Eq. (1) are measured during annual calibrations, and the last term is the constant recommended by the International Atomic Energy Agency (Craig, 1957; Allison et al., 1995). The annual calibrations determine the Big Delta values between the secondary laboratory standards and NBS19-CO2 (i.e., \([\Delta_{\text{Lab-Std/NBS19CO2}}]\)) that determine the unit of the primary scale. In each individual calibration, usually three sets of pure-CO2 ampoules are prepared (i.e., three separate extractions of evolved CO2) from the carbonate standards using acid digestion. The reaction is shown as follows:

\[
3\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + \text{Ca}_3(\text{PO}_4)_2.
\]  

(2)

Each calibration set includes NBS19-CO2, NBS18-CO2, Cal1-CO2 and Cal2-CO2. The corresponding Big Delta values (i.e., \(\Delta_{\text{NBS18/NBS19}}, \Delta_{\text{Cal1/NBS19}}, \Delta_{\text{Cal2/NBS19}}, \Delta_{\text{Cal2/Cal1}}\) etc.) have been determined (Tables 1–4). The measurement protocol is included in Table A1 (Appendix A). The Big Delta values of \(\Delta_{\text{NBS18/NBS19}}\) are used to validate the Big Delta values of \(\Delta_{\text{Cal1/NBS19}}, \Delta_{\text{Cal2/NBS19}}, \Delta_{\text{Cal2/Cal1}}\) since the NBS18 measured values can be compared with the literature values (Stichler, 1995; Verkouteren et al., 2004). The details for validating Big Delta values during annual calibrations are described in the caption of Fig. 2.
Table 1. Isotopic compositions of NBS18 in annual calibrations by MAT12 (2000–2011) and IRMS (2002–2011).

<table>
<thead>
<tr>
<th>Year</th>
<th>NBS18 (‰)</th>
<th>NBS19 (‰)</th>
<th>NBS18 (‰)</th>
<th>NBS19 (‰)</th>
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<td>2002</td>
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<td>8.045</td>
<td>-2.46</td>
</tr>
<tr>
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<td>8.046</td>
<td>-2.46</td>
<td>8.046</td>
<td>-2.46</td>
</tr>
<tr>
<td>2004</td>
<td>8.047</td>
<td>-2.46</td>
<td>8.047</td>
<td>-2.46</td>
</tr>
<tr>
<td>2005</td>
<td>8.048</td>
<td>-2.46</td>
<td>8.048</td>
<td>-2.46</td>
</tr>
<tr>
<td>2006</td>
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<td>-2.46</td>
<td>8.051</td>
<td>-2.46</td>
</tr>
<tr>
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<td>-2.46</td>
<td>8.052</td>
<td>-2.46</td>
</tr>
<tr>
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<td>-2.46</td>
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<td>-2.46</td>
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<tr>
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<td>8.054</td>
<td>-2.46</td>
<td>8.054</td>
<td>-2.46</td>
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</table>

Note: NBS18 and NBS19 are standard reference materials for CO2 isotope measurements.
Table 2. Isotopic compositions of Cal1 in annual calibrations by MAT252 (2001–2011) and IsoPrime (2002–2011).

<table>
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<tr>
<th>Year</th>
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<th>Pre-T °C</th>
<th>δ^45</th>
<th>s.d.</th>
<th>δ^18O</th>
<th>s.d.</th>
<th>δ^13C vs. VPDB</th>
<th>s.d.</th>
<th>Big Delta</th>
<th>σ (µ)</th>
<th>Big Delta</th>
<th>σ (µ)</th>
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<tr>
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<td>-12.327</td>
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<td>22.143</td>
<td>0.009</td>
<td>-45.235</td>
</tr>
<tr>
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<td>6</td>
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<td>0.016</td>
<td>-45.761</td>
<td>0.008</td>
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<tr>
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<td>0.015</td>
<td>-12.304</td>
<td>0.008</td>
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<td>0.016</td>
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<tr>
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<td>-45.349</td>
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</table>

Ave (n=45) | 46 | 0.046 | 0.075 | 0.046 | 0.075 | 0.032 | 0.023 |

Ave (n=33) | 33 | -45.820 | -21.969 | -45.290 | -19.889 | -38.350 | 0.742 |

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,

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<th>Date</th>
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<td>$-12.684$</td>
<td>0.020</td>
</tr>
</tbody>
</table>

**Ave (n = 45)**

| s.d. (1σ) | 42.632 | 9.816 |

**Ave (n = 45)**

| 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 | c $-32.261$ | 0.022 | $-12.291$ | 0.027 | 8.957 | 0.016 | $-2.678$ | 0.017 | 42.592 | 0.027 | 9.733 | 0.020 |
| 2004.27 | d $-32.074$ | 0.033 | $-12.410$ | 0.044 | 9.167 | 0.031 | $-2.816$ | 0.054 | 42.616 | 0.027 | 9.714 | 0.048 |
| 2005.15 | e $-32.047$ | 0.015 | $-12.410$ | 0.020 | 9.168 | 0.018 | $-2.858$ | 0.018 | 42.580 | 0.007 | 9.672 | 0.033 |
| 2006.22 | f $-32.148$ | 0.012 | $-12.536$ | 0.023 | 9.172 | 0.009 | $-2.898$ | 0.020 | 42.692 | 0.020 | 9.761 | 0.042 |
| 2007.18 | g $-32.141$ | 0.002 | $-12.503$ | 0.017 | 9.137 | 0.003 | $-2.941$ | 0.004 | 42.649 | 0.002 | 9.683 | 0.019 |
| 2008.24 | h $-32.170$ | 0.016 | $-12.581$ | 0.009 | 9.157 | 0.011 | $-2.969$ | 0.028 | 42.701 | 0.022 | 9.735 | 0.025 |
| 2009.15 | i $-32.112$ | 0.018 | $-12.516$ | 0.017 | 9.152 | 0.015 | $-2.938$ | 0.046 | 42.633 | 0.018 | 9.699 | 0.030 |
| 2010.17 | j $-32.145$ | 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)**

| s.d. (1σ) | 42.630 | 9.684 |

| s.d. (1σ) | 0.057 | 0.066 |

---


* BG count stands for background count, which is an indicator of 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.
2.2 Daily 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 within the period of a single day. A pair of Cal1 and Cal2 are analyzed at the beginning and a Cal2 is analyzed at the end of the suite. The measurement protocol is described in Table A2 (Appendix A). A Big Delta value is derived for every single daily measurement suite. The comparison of this value with the annually determined Big Delta value provides an important validation criterion for the daily prepared standards (Cal1 and Cal2). A second Cal2 analysis 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 linked to the primary standard.

\[
\frac{R_{\text{Sam}}}{R_{\text{VPDBCO}_2}} = \left( \frac{R_{\text{Lab-Std}}}{R_{\text{VPDBCO}_2}} \right) \cdot \left( \frac{R_{\text{Lab-Std}}}{R_{\text{VPDBCO}_2}} \right) \cdot \left( \frac{R_{\text{Lab-Std}}}{R_{\text{VPDBCO}_2}} \right) \cdot \left( \frac{R_{\text{Lab-Std}}}{R_{\text{VPDBCO}_2}} \right) = \left( \frac{\Delta_{\text{Sam/Lab-Std}} \times 10^{-3} + 1}{\Delta_{\text{Lab-Std/VPDBCO}_2} \times 10^{-3} + 1} \right),
\]

where \( R_{\text{Sam}} \) is either the ratio of mass 45 to 44 or mass 46 to 44 in a sample, \( \delta^{45}(\text{CO}_2)_{\text{Sam}}-\text{VPDBCO}_2 \) and \( \delta^{46}(\text{CO}_2)_{\text{Sam}}-\text{VPDBCO}_2 \) are defined as

\[
\delta^{45} \text{ or } 46(\text{CO}_2)_{\text{Sam}}-\text{VPDBCO}_2 = \left( \frac{R_{\text{Sam}}}{R_{\text{VPDBCO}_2}} - 1 \right) \times 10^3 \%	ext{. (4)}
\]

Equation (3) shows the documented traceability chain in CO_2 isotope measurements for individual CO_2 samples collected in the Environment Canada Greenhouse Gas Observation Network (Huang and Worthy, 2005). Here VPDB-CO_2 is the CO_2 gas that would be liberated from VPDB at 25°C if it existed, with a \( \delta^{13}\text{C}_{\text{VPDBCO}_2}/\text{VPDB} \) value equal to zero compared to a \( \delta^{18}\text{O}_{\text{VPDBCO}_2}/\text{VPDB} \) value of 10.25 ‰ (Gonfiantini et al., 1995). Using the results of Eq. (4), \( \delta^{13}\text{C}_{\text{VPDBCO}_2} \) and \( \delta^{18}\text{O}_{\text{VPDBCO}_2} \) of a sample are calculated by applying the \( \delta^{17}\text{O} \) correction used by Allison et al. (1995). This correction is very similar to the Craig correction (Craig, 1957).

It should also be noted that air samples have an additional N_2O correction as N_2O is an interference to masses 44, 45 and 46 in CO_2 isotopic ratio measurements. The equations used in our N_2O correction are based on the general equation by Mook and Van der Hoek (1983) and Mook and Jongma (1987):

\[
\delta^{13}\text{C}_{\text{corr}} = \delta^{13}\text{C}_{\text{meas}} + E \cdot \delta^{13}\text{N}_\text{2O} \cdot [N_2\text{O}/[\text{CO}_2]] \cdot 0.001 \quad (5a)
\]

\[
\delta^{18}\text{O}_{\text{corr}} = \delta^{18}\text{O}_{\text{meas}} + E \cdot \delta^{18}\text{N}_\text{2O} \cdot [N_2\text{O}/[\text{CO}_2]] - 0.001, \quad (5b)
\]

where \( E \) is the ratio of ionization efficiency (RIE) of N_2O related to CO_2, and 0.708 was determined using the MAT252 instrument (the only IRMS used for CO_2 isotopes measurements); \([N_2\text{O}]/[\text{CO}_2]\) are the mole fraction ratio of N_2O (ppb) and CO_2 (ppm) concentrations measured at Environment Canada. \( \delta^{13}\text{N}_\text{2O} \) and \( \delta^{18}\text{N}_\text{2O} \) are the delta values that would be obtained measuring N_2O as if it were CO_2 versus a CO_2 standard. Combining our measurements and the literature values (Mook and Van der Hoek, 1983; Friedli and Siegenthaler, 1988), the \( \delta^{13}\text{N}_\text{2O} \) and \( \delta^{18}\text{N}_\text{2O} \) used in the algorithm are \(-345\%e\) and \(-506\%e\), respectively. The uncertainties of the correction terms in Eq. (5a) and (5b), due to using various \( \delta^{13}\text{N}_\text{2O} \) or \( \delta^{18}\text{N}_\text{2O} \) (e.g., \( \pm 10\%e \) for \(-345\%e\) and \( \pm 10\%e \) for \(-506\%e\)) and different RIE (e.g., \(0.70\)–0.73), reported values of MAT252; Ghosh and Brand, 2004, and personal communication with C. Allison, March 2013), are negligible (\( \leq 0.01 \%e\)). \( \delta^{13}\text{C}_{\text{corr}} \) and \( \delta^{18}\text{O}_{\text{corr}} \) are N_2O corrected values of \( \delta^{13}\text{C}_{\text{meas}} \) and \( \delta^{18}\text{O}_{\text{meas}} \). The same correction algorithms for both \( ^{13}\text{C} \) and \( ^{18}\text{O} \) have been applied to the entire dataset to avoid any additional errors.

Big Delta values between the samples and the laboratory standards are also determined for daily measurements, which are used to anchor the individual measurements on the primary scale of VPDB-CO_2 (see Eq. 3). In general, a laboratory standard that has been calibrated directly or indirectly using NBS19-CO_2 and used in calculations of \( \delta^{13}\text{C}_{\text{VPDBCO}_2} \) and \( \delta^{18}\text{O}_{\text{VPDBCO}_2} \) to link the isotopic compositions of a sample to the primary scale is referred to as a primary anchor. The primary anchor adopted in our program is the pure CO_2 evolved from Cal2 carbonate. The overall uncertainties of \( \delta^{13}\text{C} \) and \( \delta^{18}\text{O} \) measurements can be estimated from Eq. (3) using error propagation for the two terms on the right (i.e., \( \Delta_{\text{Sam/Lab-Std}} \) and \( \Delta_{\text{Lab-Std/NBS19CO}_2} \)). One of the uncertainties is related to the primary anchor. The advantages of this approach for maintaining traceability include the following: (i) the units of the primary scale (accounting for scale contraction) are evaluated annually; (ii) individual isotopic measurements are firmly anchored to the primary scale; (iii) the uncertainty of the primary anchor can be characterized, monitored and minimized; and (iv) the overall uncertainty of individual ambient measurements can be explicitly estimated.

3 Uncertainty in traceability

In order to maintain the traceability for isotope measurements, two secondary carbonate standards (Cal1 and Cal2) with a significant difference in \( \delta^{13}\text{C} \) (~42.6 ‰) are used. They, along with NBS18, are directly calibrated by NBS19 on an annual basis during the periods (usually between February and April) when the relative humidity is typically the lowest of a year (so that the most stable \( \delta^{18}\text{O} \) values can be attained). The uncertainty of the traceability includes those from carbonate preparations, CO_2 extractions and IRMS analysis. Based on Eq. (3), the uncertainty of
$R_{\text{Sam}}/R_{\text{VPDBCO}}$ in the traceability is contributed only by two terms, i.e., $R_{\text{Sam}}/R_{\text{Lab-Std}}$ from daily measurements and $R_{\text{Lab-Std}}/R_{\text{NBS19-CO}_2}$ from annual calibrations.

The four carbonates (NBS19, NBS18, Cal1 and Cal2) are evolved into pure CO$_2$ via acid digestions using H$_2$PO$_4$ with mass percentage > 100 % and a specific gravity of 1.91–1.92 at 25 ± 0.1 °C. It is known that the amount of H$_2$O in H$_2$PO$_4$ impacts the precision of $\delta^{18}$O analysis because the oxygen isotopes in evolved CO$_2$ can easily exchange with those in liquid H$_2$O (e.g., McCrea, 1950; Clayton, 1959). Equation (2) shows that water would be released from the reaction along with the evolved CO$_2$. To minimize the impact of available liquid H$_2$O on the isotopic exchanges with CO$_2$, excess P$_2$O$_5$ is needed to absorb the H$_2$O that can potentially exist in the acid (Zachary, 2007). A solution of H$_2$PO$_4$ with a mass percentage greater than 100 % indicates excess P$_2$O$_5$ 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. This will also cause isotopic fractionations and affect the precision of the $\delta^{18}$O values.

The commercially available H$_2$PO$_4$ has mass percentages usually on the order of 85 % and is thus not suitable. H$_2$PO$_4$ with a mass percentage greater than 100 % can be only custom-made. The specific gravity of 100 % H$_2$PO$_4$ is approximately 1.86 g mL$^{-1}$. Based on our experiences, the ideal range of the specific gravity of H$_2$PO$_4$ is from 1.91 to 1.92 g mL$^{-1}$. The in-house procedure of making H$_2$PO$_4$ is attached as Appendix B. A recent report by Wendeberg et al. (2011) found that the $\delta^{18}$O of H$_2$PO$_4$ will likely affect the $\delta^{18}$O of CO$_2$ evolved from the acid digestion when the mass percentage of H$_2$PO$_4$ is < 102 %. This is due to isotopic exchange between H$_2$O and H$_2$PO$_4$. The specific gravity of H$_2$PO$_4$ 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 %. In each individual calibration event, at least three separate acid digestions are processed for each of the four carbonates, followed by cryogenic extractions of the evolved CO$_2$ and IRMS measurements. These data obtained from the annual calibrations (over the past decade) using two IRMSs, i.e., Finnigan MAT252 and Micromass IsoPrime, are shown in Tables 1–4, including the Big Delta values of $\Delta_{\text{Lab-Std/NBS19-CO}_2}$, the $\delta^{13}$C$_{\text{Lab-Std/VPDBCO}}$ and $\delta^{18}$O$_{\text{Lab-Std/VPDBCO}}$ values and the associated uncertainties (including those from carbonate preparations and IRMS analysis). The stability of the traceability and the overall uncertainty for individual measurements are estimated from these data.

The standard deviations of these corresponding Big Delta values range from 0.02–0.04 ‰ for $\Delta^{45}$ and 0.04–0.09 ‰ for $\Delta^{46}$, which are proportional to the absolute values of Big Delta (Fig. 3). It implies that the two samples with a larger Big Delta value would be more easily impacted by cross contaminations/scale contraction than the two with a smaller Big Delta value. This is also the reason why WMO experts recommended that the isotopic composition of the working reference gases should be as close as possible to that of CO$_2$ in ambient air (GAW Report No. 194). While the Big Delta value approaches zero, the cross contamination effect is the lowest, and thus a smaller standard deviation for the value would be obtained (Fig. 3). To minimize uncertainties due to the scale contraction introduced in both $\Delta_{\text{Sam/Lab-Std}}$ and $\Delta_{\text{Lab-Std/NBS19-CO}_2}$ (Fig. 3), it is suggested to use a laboratory standard with a $\delta^{13}$C value between the NBS19 (i.e., +1.95 ‰) and the ambient atmospheric CO$_2$ (∼ −8 ‰) as the primary anchor. Cal2 has been used as the primary anchor for all flask samples collected from the Environment Canada Greenhouse Gas Observation Network because it has the smallest Big Delta values related to NBS19 (i.e., $\Delta^{45}_{\text{Cal2/NBS19-CO}_2}$ and $\Delta^{46}_{\text{Cal2/NBS19-CO}_2}$) and the smallest standard deviations, showing the greatest stability over the period of 10 yr amongst all of the secondary standards (Tables 1–4).

The uncertainties related to the calibration of the primary anchor (one of the important uncertainties in the traceability) are < 0.02 ‰ in $\Delta^{45}_{\text{Cal2/NBS19-CO}_2}$ and ∼ 0.04 ‰ in $\Delta^{46}_{\text{Cal2/NBS19-CO}_2}$ (one standard deviation) measured using the MAT252 (the only IRMS used for flask $\delta^{13}$C and $\delta^{18}$O measurements of the program).

The uncertainty of the other term ($\Delta_{\text{Sam/Lab-Std}}$) in the traceability can be only determined by using an air-CO$_2$ cylinder because replicate analysis is required over many years. Flasks are not suitable due to the limitation of allowing only single analysis by our current procedure. A high-pressure aluminum cylinder of air CO$_2$, which can be very stable (Ghosh et al., 2005), was primarily used for quality control (QC) purposes and was treated in the same manner as air flask samples. The uncertainties of $\Delta_{\text{QC air-CO}_2}$/Lab-Std have been determined by repeated analysis over several years. The air-CO$_2$ tank used here for deriving the uncertainty of $\Delta_{\text{Sam/Lab-Std}}$ is designated as QC3 (which was filled with dry air at Alert GAW station in September 2000). As shown in Fig. 4, the one-sigma uncertainty of the measured $\Delta^{45}_{\text{QC3/Cal2}}$ and $\Delta^{46}_{\text{QC3/Cal2}}$ is 0.017 and 0.043 ‰, respectively. After applying the $\delta^{17}$O and N$_2$O corrections, the values of uncertainty in $\delta^{13}$C and $\delta^{18}$O are the same as those in $\Delta^{45}_{\text{QC3/Cal2}}$ and $\Delta^{46}_{\text{QC3/Cal2}}$. The uncertainties are primarily caused by carbonate preparations and IRMS measurements. Therefore, the uncertainty in Eq. (3) represents the uncertainty of the traceability (from $R_{\text{Sam}}/R_{\text{WGR}}$ to $R_{\text{Sam}}/R_{\text{VPDB-CO}_2}$). Using the uncertainties of $\Delta^{45/46}_{\text{Cal2/NBS19-CO}_2}$ (Table 3) and $\Delta^{45/46}_{\text{QC3/Cal2}}$ (Fig. 4), the overall uncertainties of $\Delta^{45/46}_{\text{Sam/VPDBCO}_2}$ (i.e., $\Delta^{45/46}_{\text{QC3/VPDBCO}_2}$) can be determined by applying the principle of error propagation to Eq. (3) as follows:

$$
\sigma \left( \Delta^{45/46}_{\text{QC3/Cal2}} \right) \approx \left[ \sigma \left( \Delta^{45/46}_{\text{Cal2/NBS19-CO}_2} \right)^2 + \sigma \left( \Delta^{45/46}_{\text{QC3/Cal2}} \right)^2 \right]^{1/2}.
$$
Fig. 3. There is a positive correlation between the absolute Big Delta values and the corresponding standard deviations in both carbon (top panel) and oxygen (bottom panel) isotopes. The coefficient of determination ($r^2$) is 0.94 and 0.63 for $\Delta^{45}$ and $\Delta^{46}$, respectively. The absolute Big Delta value of the primary anchor (Cal2) relative to NBS19 is $\sim 4.59$ ‰ in $\Delta^{45}$ (s.d.: 0.01 ‰) and $\sim 10.54$ ‰ in $\Delta^{46}$ (s.d.: 0.04 ‰).

The calculated uncertainty for $\delta^{45}$(CO$_2$)$_{QC3/VPDB}$ and $\delta^{46}$(CO$_2$)$_{QC3/VPDB}$ is 0.02 and 0.05 ‰, respectively. These are very close to the values shown in Fig. 4 that are based on statistical variations in the measurements. It is safe to conclude that the overall uncertainty of the traceability in CO$_2$ isotope measurements for individual flask samples from the Environment Canada network is on the order of $0.02%e$ for $\delta^{13}$C and $0.05%e$ for $\delta^{18}$O. No uncertainties in the $^{17}$O and N$_2$O corrections are considered here since the same parameters and algorithm have been applied since the inception of the program. As mentioned previously, the uncertainties due to using different values of the parameters in N$_2$O correction are negligible.

4 The roles of Big Delta

If two samples have intrinsic and distinguishable isotopic compositions, the relative deviation in isotope ratio should be constant and independent of the fluctuations of instrument response, as illustrated in Fig. 5. As introduced in Sect. 2, a Big Delta is a relative deviation of two isotopic ratios so that it can be precisely determined. The unique property of Big Delta has played two major roles in maintaining traceability of high-precision isotope measurements in our program over the last decade.

4.1 Linking to VPDB-CO$_2$ using Big Delta

The first role has been to link all individual measurements to the primary scale: VPDB as shown by Eq. (3). As described above the annual calibration and daily measurements are two independent rings in the chain of the traceability for our CO$_2$ isotope measurements, each expressed as a Big Delta value. The uncertainties of the two Big Delta terms helped determine the overall uncertainty along the traceability pathway. Over the 10 yr period, different batches (which were purchased in different years) of NBS19 and NBS18 were used, and parts were also changed on the IRMS. A new ion source that was installed in 2007 and the original voltage-to-frequency conversion (VFC) resistor was replaced in 2008 (noted in Tables 1–4). These changes could have potentially modified the Big Delta from the largest observable values and contributed 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 $\delta^{45}$ or $\delta^{46}$ values (raw data) fluctuate with time due to the use of various WRGs. This indicates that generally the procedures for carbonate preparations and the instruments analysis have been consistent over the entire 10 yr period. This consistency provides a solid foundation for evaluating and determining the long-term trends of $\delta^{13}$C and $\delta^{18}$O in atmospheric CO$_2$. 
likely that the cleanliness of the ion source of the MA T252 (as indicated by background count) has been a dominant factor for the small drift over the period, particularly for $\Delta^{45}$; as the ion source becomes cleaner, the $\Delta^{45}$ values get larger. Usually, the ion source would be cleaned by cycling the ion source (with 5.0 UHP grade from Praxair) through overnight.

A closer investigation of 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 (the largest and the most sensitive to procedure and/or instrument fluctuations). Based on results shown in Table 4, it is likely that the cleanliness of the ion source of the MAT252...
This cleaning procedure would be carried out when the reading of background count approached 220. The largest Big Delta values have been accepted as our benchmarks. Nevertheless, it is shown that the variations of $\Delta_{\text{Cal2/NBS19}}$ by MAT252 are very small, and its standard deviations (including all sources of errors) are within the ranges of $< 0.02\%e$ in $\delta^{13}C$ and $\sim 0.04\%e$ in $\delta^{18}O$ over this 10 yr period. These values are close to the WMO targets of 0.01 and 0.05\%e for data comparability in $\delta^{13}C$ and $\delta^{18}O$, providing the precision and the stability of Cal2 as the primary anchor. The results from IsoPrime analyses show very similar patterns for $\Delta_{45}^{\text{Cal2/NBS19}}$CO$_2$ but not for $\Delta_{46}^{\text{Cal2/NBS19}}$. This may suggest that the differences in the high vacuum and the water-content levels inside of ion source have larger impacts on $\delta^{18}O$ than those on $\delta^{13}C$ measurements. Usually, there is a lower vacuum and a higher level of water vapor in IsoPrime. Compared with those in MAT252, it is likely that more isotopic exchanges between CO$_2$ and H$_2$O would occur inside of IsoPrime’s ion source. This raises a serious issue of scale contraction regarding the $\delta^{18}O$ measurements by different types of instruments. However, we only used MAT252 for flask CO$_2$ isotope measurements. The MAT252 results indicate that as long as the Big Delta value is relatively small ($\sim 10\%e$ or less as shown in Fig. 3), even the fluctuations in cleanliness of the ion source would not have obvious impacts on the Big Delta value. Thus, the extent of scale contraction could be minimized. Therefore, it is concluded that using Cal2 as the primary anchor allows us to precisely and consistently link all of our isotopic measurements of atmospheric CO$_2$ samples to the VPDB-CO$_2$ scale.

4.2 Conducting QA/QC using Big Delta

The second role of Big Delta is to carry out quality assurance and quality control (QA/QC) procedures as a diagnostic tool, to monitor fluctuations in instruments and associated apparatuses. It also serves as a measure to track the stability of various levels of standards. It can be used to detect drifting of scales in time within one individual laboratory (Fig. 1a and b) or scale contractions between laboratories (Huang et al., 2011). A two-point scale normalization in carbon isotope measurements is recommended by Coplen et al. (2006b) in order to resolve the issues of scale contraction or shifting by normalizing the difference between $\delta^{13}C_{\text{NBS18/VPDB}}$ and $\Delta^{13}C_{\text{L-SVEC/VPDB}}$ obtained by 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 $\delta^{13}C_{\text{VPDB}}$ value ($-46.6 \pm 0.2\%e$), it was recommended to use NBS19 and L-SVEC together to implement a two-point calibration. However, to implement this recommendation, the Big Delta values (i.e., $\Delta^{45/46}_{L-SVEC/NBS19}$CO$_2$) between NBS19 and L-SVEC in individual labs should be determined annually to track scale contractions or shifts to ensure such consistency of the normalization over time. Instrument response and/or procedure fluctuations should be the major error sources causing the uncertainty in traceability, leading to non-consistency of the measurements over time even though the changes in the standards or references themselves are also possible. 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, and thus critical for verifying atmospheric trends of CO$_2$ isotopes (in both $\delta^{13}C$ and $\delta^{18}O$). Various combinations of Big Delta values derived amongst different standards and references have provided powerful tools to ensure the QA/QC procedures in our program. These include the following:

- The comparison of corresponding Big Delta values between two IRMSs (MAT252 and IsoPrime) has been used to assess the performance of instrumentations and provide the guidance of instrument usage, based on scientific requirements.

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

- The consistency of corresponding Big Delta values between two IRMSs (MAT252 and IsoPrime) ensures the consistency of the carbonate preparation procedures.

- The largest observed Big Delta values (the benchmarks) of $\Delta_{\text{Cal2/Cal1}}$ have been used as an indicator of cross contamination, which would be sensitively influenced by the cleanliness of the ion source. An obvious drift away from these values indicates that the ion source might need to be cleaned, and cleaning the ion source allows Big Delta values to return to the benchmarks. Keeping observed Big Delta values close to the benchmarks would minimize the effects of scale contraction.

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

- To ensure that the primary and secondary standard themselves have not drifted over time, a batch of uniformly pure-CO$_2$ samples was made by periodically taking a large aliquot of gas from a pure-CO$_2$ high-pressure cylinder (see Appendix C). The variation ranges of $\delta^{13}C$ and $\delta^{18}O$ are less than 0.02 and 0.04\%e, respectively. This batch of ampoules is only used for annual calibrations and referred to as “annual calibration WRG”. If carbonate preparations are consistent for
individual years, the raw Δ45 and Δ46 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 no differences between the calibrations in different years. The data presented in Tables 1 through 4 indicate that this is the case. It is shown that all the corresponding raw Δ45 and Δ46 values analyzed by MAT252 are very consistent from year to year with very small standard deviations (only ∼0.01 in Δ45 and ∼0.03 in Δ46) since the “annual calibration WRG” ampoules were used in 2008. This suggests that the four carbonate standards have not changed over the period and the fluctuations of Big Delta values are likely due to the impacts from external factors, i.e., instrument conditions or procedural variations.

In general, a small Big Delta can be used to minimize scale contraction (discussed in Sect. 4.1), whereas a large Big Delta can be used to monitor scale contraction (discussed in this section).

5 Verifying long-term trends in δ13C and δ18O at Alert

Determining accurate long-term trends of δ13C and δ18O in atmospheric CO2 is critical for understanding the changes in carbon emission sources and sinks with time. A long-term atmospheric trend in δ13C or δ18O can be precisely determined only if the stability of the primary anchor on the VPDB-CO2 scale is known. As shown in both panels c of Fig. 1a and b, the annual rate of change of the primary anchor (Cal2) over the last 10 yr (2001–2011) was essentially zero for both δ13C and δ18O (i.e., −0.0016 and −0.006‰, respectively). Those are much less than the uncertainties of the IRMS analysis just by itself (∼0.01 and 0.03 ‰), not including the additional uncertainties from carbonate preparations and cryogenic extraction etc.

In Fig. 4, we determine the annual drift rate of δ13C and δ18O for the QC3 air standard to be +0.003 and −0.007‰, respectively (which are close to zero too). It is evaluated and verified that the average annual change rate of the measured δ13C and δ18O in air CO2 at the Alert station is −0.025 ± 0.003‰ and 0.000 ± 0.010‰, respectively (Fig. 1a and b). This likely reflects real changes in relative contributions of sources and sinks to the atmospheric CO2, not due to drifts in the instrumentation and the isotope standards or analytical procedures applied. The total change of the observed δ13C in annual average value is ∼−0.27‰ from −8.22‰ in 1999 to −8.49‰ in 2010 (Fig. 1a), and the total corresponding change of δ18O is essentially zero (Fig. 1b). The results suggest that the trend of δ13C at Alert has been mainly influenced by the continuous contribution of fossil fuel CO2, whereas the pattern of δ18O was likely controlled by the global hydrologic cycle (Welp et al., 2011).

On the other hand, if a consistent traceability was not maintained, no conclusive results could be made regarding a trend in an atmospheric dataset as illustrated by recent discussions on the interhemispheric δ13CH4 trend. Kai et al. (2011) reported an interhemispheric trend in δ13CH4, whereas Levin et al. (2012) claimed no interhemispheric δ13CH4 trend observed. This debate has highlighted the importance of this issue in general for long-term atmospheric observations (Kai et al., 2011, 2012; Levin et al., 2012).

6 Summary: challenges and recommendations

Robust and traceable atmospheric CO2 isotope measurements require a stable primary anchor and consistent traceability, which are critical to assess the trends of atmospheric measurements. The primary anchor should be directly and regularly calibrated by NBS19-CO2 and linked to the VPDB scale firmly. However, all calibrations are based on the assumption that NBS19-CO2 has evolved from the NBS19 carbonate preparations properly with the isotopic composition of the assigned values passed on correctly over time. This assumption may not necessarily be valid due to the heterogeneity of NBS19 carbonate, which may vary between different batches purchased at various times and the inconsistency of carbonate preparations, which may be caused by having slightly different reaction temperatures and specific gravities of H3PO4 in acid digestions. Moreover, one factor that plays an important role in high-precision isotope measurements is instrument response, which could fluctuate due to variations in cleanliness of ion source and its physical configurations, consequently, leading to changes in cross contamination and scale contraction. The uncertainty caused by scale contraction might be trace back to calibrations using NBS19 and it could be passed on along the traceability chain. Ultimately all the uncertainties associated with the primary anchor would then impact on the uncertainties of individual isotope measurements.

As discussed, to obtain high-precision and traceable atmospheric CO2 isotope measurements over decadal time is very challenging. The challenges would include (1) identifying and verifying proper calibration materials, which should be homogenous and stable; (2) implementing consistent and proper procedures in carbonate preparations; and (3) quantifying and monitoring the response of individual instruments. In order to take on those challenges and to characterize and minimize the uncertainties of isotopic measurements (including both discrete flask and continuous 13C measurements, e.g., using cavity-ring-down techniques (Vogel et al., 2013) or other measurement techniques), the following recommendations, as strategies to maintain a consistent traceability, are devised:

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

www.atmos-meas-tech.net/6/1685/2013/
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.

Selecting at least two standards for each level (either air-CO$_2$ or pure CO$_2$ evolved from carbonates or commercially pressurized pure CO$_2$) with relatively large isotopic differences;

If possible, using two secondary laboratory standards with the largest Big Delta value, as a QA/QC tool, to monitor instrument and/or procedure fluctuations and to validate the stability of the primary anchor.

Selecting one of the secondary laboratory standards as the primary anchor. Ideally this anchor should have the $\delta^{13}$C value between NBS19-CO$_2$ and the ambient air, to minimize scale contraction in both calibrations and routine measurements.

Using the same working reference gas (stored batch-wise in glass ampules) during annual calibrations for a decadal time span to monitor the fluctuations in raw $\delta^{45}$ and $\delta^{46}$ values for NBS19-CO$_2$ and other standards to ensure the stability of the individual standards and validate carbonate 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 $\delta^{13}$C and $\delta^{18}$O, respectively. The type of pure CO$_2$ flame-sealed in ampoules (e.g., those named as “NARCIS” produced by Mukai et al., 2005) would be ideal for this purpose as “annual calibration WRG”;

Improving 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).

Using H$_3$PO$_4$ 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 recommendations are carefully taken, then the target of overall uncertainties for individual measurements (i.e., 0.02\% for $\delta^{13}$C and 0.05\% for $\delta^{18}$O) should be achievable, a stable primary anchor can be maintained and the atmospheric trends in $\delta^{13}$C can be evaluated, verified and confirmed.

Appendix A

Measurement protocols

A1 For annual calibrations

Usually, three sets of pure-CO$_2$ ampoules are prepared via acid digestion from carbonates. Each set includes NBS19, NBS18, Cal1 and Cal2. All ampoules are analyzed against the same working reference gas of pure CO$_2$ (i.e., APB2, the pure CO$_2$ from a high-pressure cylinder purchased from Air Products). A calibration event is completed within a period of 1 day. The measurement sequence is shown in Table A1.

A2 For daily measurements

Usually, there are a total of 12 samples measured for a period of one day by the dedicated IRMS (MAT252) together with laboratory 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$_3$PO$_4$)

B1 Apparatus

- hot plate with stirrer option
- an 800 mL Pyrex® beaker
- Teflon® coated magnetic stirrer
- Pyrex® spatula
- large metal beaker tongs

B2 Chemicals

- 85 % H$_3$PO$_4$ 400 mL (source: Aldrich cat# 21,510-4)
- P$_2$O$_5$ 300 g (source: Aldrich cat# 29,822-0)
- H$_2$O$_2$ 30 % 2 mL (source: Aldrich cat# 21,676-3)
- (H$_2$O$_2$ bp: 150.2 °C, mp: −0.41 °C) from CRC Handbook of Chemistry and Physics, 61st Edn. 1980–1981, B105.
- 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<sub>2</sub>O<sub>5</sub>.

3. Slowly add H<sub>2</sub>O<sub>2</sub> (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<sub>3</sub> to see if there is any excess H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub>O<sub>2</sub> is a reducing agent now and can be oxidized by CrO<sub>3</sub>). The solution may undergo a color change from yellow to light green (Cr<sup>6+</sup> to Cr<sup>3+</sup>).

5. Heat the acid to boiling and allow to boil for 2.5 h.

6. Cool slightly and transfer to Teflon® storage bottles 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 fully cooled down to room temperature. If the specific gravity 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 it. 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 preweighed 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 months before using it (according to our experience).

**Appendix C**

**Pure CO<sub>2</sub> working reference gas (WRG) ampoules preparation**

A pure-CO<sub>2</sub> high-pressure cylinder was purchased from Air Products Canada Ltd in 1998 (named as APB2). Two-liter flasks were preconditioned by cleaning, drying and evacuating–pressurizing several times before filling from the cylinder. Fifty to one hundred pure-CO<sub>2</sub> ampoules were...
## Table A2. Daily measurement\(^*\) sequence by IRMS (MAT252).

<table>
<thead>
<tr>
<th>Measurement order</th>
<th>Sample order</th>
<th>Reference sample</th>
<th>Description</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WRG</td>
<td>WRG</td>
<td><em>zero check</em> with both bellows connected to each other</td>
<td>to check if the crimps of both capillaries are evenly balanced</td>
</tr>
<tr>
<td>2</td>
<td>WRG</td>
<td>WRG</td>
<td><em>zero check</em> with both bellows disconnected from each other</td>
<td>to check any problems in running real samples (the related raw delta of this should close to 0 ‰)</td>
</tr>
<tr>
<td>3</td>
<td>Cal1</td>
<td>WRG</td>
<td>measuring a Lab-Std with (\delta^{13}C_{VPDB} \sim -45.8%)</td>
<td>to determine the Big Delta between two Lab-Stds for validation of the primary anchor (i.e., Cal2) and monitoring instrument’s variation.</td>
</tr>
<tr>
<td>4</td>
<td>Cal2</td>
<td>WRG</td>
<td>measuring a Lab-Std with (\delta^{13}C_{VPDB} \sim -2.6%)</td>
<td>to determine the Big Delta between two Lab-Stds 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 (otherwise a new Cal2 or Cal2 and Cal1 will be analyzed until the validation meets the criteria). The Cal2 will be valid as the primary anchor linking the samples to the primary scale.</td>
</tr>
<tr>
<td>5</td>
<td>Samp-1</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Samp-2</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Samp-3</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Samp-4</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Samp-5</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Samp-6</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Samp-7</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Samp-8</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Samp-9</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Samp-10</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Samp-11</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Samp-12</td>
<td>WRG</td>
<td>Sample measurement</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Cal2</td>
<td>WRG</td>
<td>measuring a Lab-Std with (\delta^{13}C_{VPDB} \sim -2.6%)</td>
<td>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 &lt; 0.02 ‰, it is assumed that the WRG was valid during the period of measuring 12 samples, and therefore all the sample measurements are assumed valid. Otherwise, another Cal2 will be measured until the validation meets the criterion.</td>
</tr>
</tbody>
</table>

\(^*\) Typical measurement conditions:  
- Measurement voltage: 3.5 V.  
- Idle time: 30 s.  
- Integration time: 8 s.  

made from an individual filled flask by freezing over and flame-sealing the glass, and only a dedicated flask would be used repeatedly for this purpose. The homogeneity of each batch was ensured by measuring the first and the last pairs of the batch against each other. The variation of \(\delta^{13}C\) and \(\delta^{18}O\) for each batch must be less than 0.02 and 0.04 ‰, respectively, otherwise the whole batch would be discarded. The isotopic compositions of the ampoules were linked to the primary VPDB-CO\(_2\) scale via the primary anchor (Cal2). The \(\delta^{13}C\) and \(\delta^{18}O\) records from the cylinder over a decade (1998–2011) are shown on Fig. C1. The total change in \(\delta^{13}C\) and \(\delta^{18}O\) is approximately 0.8 and 1 ‰, respectively, over the entire period. It is suggested that directly using pure CO\(_2\) from a high-pressure cylinder as a primary anchor and without frequent calibrations by NBS19-CO\(_2\) would not be proper because of changes in its isotopic compositions with time or cylinder pressure, particularly when a liquid phase of CO\(_2\) still exists in the cylinder.
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