



Maintaining consistent traceability in high-precision isotope measurements of CO₂: a way to verify atmospheric trends of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

L. Huang¹, A. Chivulescu¹, D. Ernst¹, W. Zhang¹, A.-L. Norman², and Y.-S. Lee^{1,*}

¹Climate Research Division (CRD), Atmospheric Science & Technology Directorate (ASTD), Science and Technology Branch (STB), Environment Canada (EC) 4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

²Department of Physics & Astronomy, University of Calgary, Calgary, Canada

*currently at: Korea Astronomy and Space Science Institute (KASI), 776 Daedeokdae-ro, Yuseong-gu, Daejeon, Korea

Correspondence to: L. Huang (lin.huang@ec.gc.ca)

Received: 12 March 2012 – Published in Atmos. Meas. Tech. Discuss.: 6 June 2012

Revised: 15 May 2013 – Accepted: 29 May 2013 – Published: 17 July 2013

Abstract. Maintaining consistent traceability of high-precision measurements of CO₂ isotopes is critical in order to obtain accurate atmospheric trends of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (in CO₂). Although a number of laboratories/organizations around the world have been conducting baseline measurements of atmospheric CO₂ 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 ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of atmospheric CO₂ 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 CO₂ isotope measurements for individual ambient samples analyzed by the program at Environment Canada have been estimated (excluding those associated with the sampling). The values are 0.02 and 0.05 ‰ in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively, which are close to the World Meteorological Organization (WMO) targets for data compatibility. The annual rates of change in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the primary anchor (which links the flask measurements back to the VPDB-CO₂ scale) are close to zero (-0.0016 ± 0.0012 ‰, and -0.006 ± 0.003 ‰ per year, respectively) over a period of 10 yr (2001–2011). The average annual changes of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in air CO₂ at Alert GAW station over the period from 1999 to 2010 have been evaluated and confirmed; they are -0.025 ± 0.003 ‰ and

0.000 ± 0.010 ‰, respectively. The results are consistent with a continuous contribution of fossil fuel CO₂ to the atmosphere, having a trend toward more negative in $\delta^{13}\text{C}$, whereas the lack of change in $\delta^{18}\text{O}$ likely reflects the influence from the global hydrologic cycle. The total change of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during this period is ~ -0.27 ‰ and ~ 0.00 ‰, 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 CO₂ plays an important role in understanding the carbon cycle and, in turn, addresses the issue of the continuous increase of atmospheric CO₂ at regional and global scales. Numerous studies have been conducted to understand the exchanges of CO₂ 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 1990 through 2010, the average annual global rate of change of carbon isotopic composition in atmospheric CO₂ is $\sim -0.026 \pm 0.001$ ‰ in $\delta^{13}\text{C}$. 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

Tans, 1995) are a subset of the global cooperative air sampling network sites operated by National Oceanic and Atmospheric Administration (NOAA), where samples are predominantly representative of a large volume of the atmosphere. These sites are typically at remote marine sea level locations with prevailing onshore winds. The use of MBL data results in a low-noise representation of the global trend and allows us to make the estimate directly from the data without the need for an atmospheric transport model.

The CO₂ isotope data obtained from the “MBL” sites were measured by the Institute of Arctic and Alpine Research (INSTAAR) at University of Colorado (White and Vaughn, 2011; Vaughn et al., 2010; Masarie et al., 2001; Trolier et al., 1996). In the Northern Hemisphere, corresponding values were derived from measurements (Fig. 1a and b) made by Environment Canada at the Alert GAW station (82°27' N, 62°31' W). The average annual rate of change in $\delta^{13}\text{C}$ (i.e., $\sim -0.025 \pm 0.003 \text{‰ yr}^{-1}$ from 1999 through 2010) is very similar to that derived by NOAA ($-0.026 \pm 0.001 \text{‰ yr}^{-1}$). The extent of the observed change was driven by the contributions from natural and anthropogenic carbon sources and sinks. Precisely determining the magnitude of those changes will help us to understand the complicated mechanisms of carbon cycle and track the human-induced CO₂ increase in the atmosphere. This task is especially challenging as the spatial gradients as well as the trends in atmospheric $\delta^{13}\text{C}$ are very small in comparison to the levels of analytical precision even when the most accurate measurement techniques are applied (e.g., isotope ratio mass spectrometry – IRMS). That is the reason why the World Meteorological Organization/Global Atmosphere Watch (WMO/GAW) measurement community has strongly encouraged making high-precision measurements at the level of 0.01 and 0.05 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively, to meet the targets for data compatibility (Expert Group recommendations in GAW publications 161, 168, 186, 194 and 206: <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>). To precisely determine small changes in isotopic compositions of atmospheric CO₂, any changes in standards that link the individual measurements to the primary scale, i.e., VPDB (Vienna PeeDee Belemnite), need to be taken into account. In other words, determining an accurate atmospheric trend over a period of time requires a stable analytical standard over the same period.

Standards play an important role in maintaining traceable isotopic measurements (Huang et al., 2002). Consistent traceability is essential for deriving trends from the observed data. To implement traceability for isotope measurements in flask air CO₂ samples, various forms of laboratory standards are used, including pure CO₂, air CO₂ contained in high-pressure cylinders and CO₂ produced from pure carbonates (Trolier et al., 1996; Huang et al., 2002; Mukai et al., 2005; Allison and Francey, 2007; Brand et al., 2009; Vaughn et al., 2010). More than one level (e.g., primary, secondary, tertiary etc.) and more than one form of standards are generally used in individual analytical laboratories. Differences in the

isotope compositions of these standards can be exploited to ensure that long-term reproducibility and precision are maintained (Huang et al., 2002; Allison and Francey, 2007). Here, the concepts behind best practices for ensuring consistent traceability (standardization) in long-term isotope measurements of atmospheric CO₂ using differences in standards is explored.

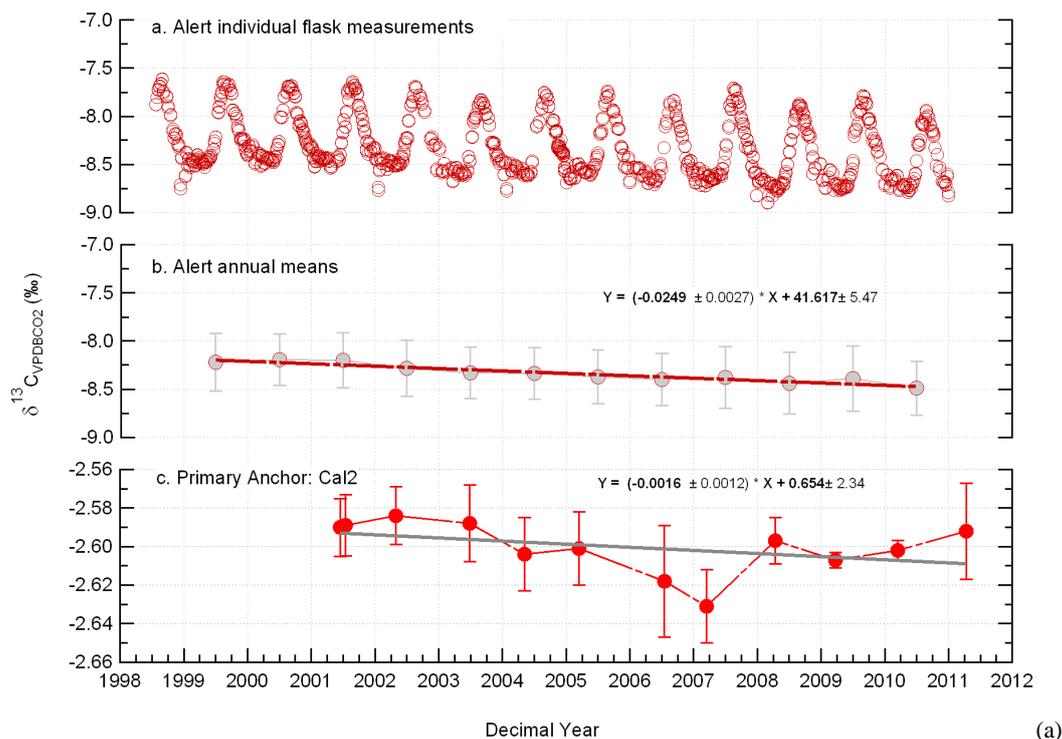
It is very challenging to ensure low uncertainty in the determination of a singular standard (for example, less than 0.02 ‰ for $\delta^{13}\text{C}$ as pure CO₂ gas over decades). This difficulty is exacerbated because in order to ensure a lower level standard (e.g., a secondary or tertiary) is stable within the range of $\sim 0.02 \text{‰}$, better stability ($< 0.02 \text{‰}$) is required for a higher level standard (e.g., the primary or secondary). Ultimately, it is imperative to ensure that the primary standard (NBS19) is stable over long periods of time with an annual change rate significantly less than 0.02 ‰. In order to quantify 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:

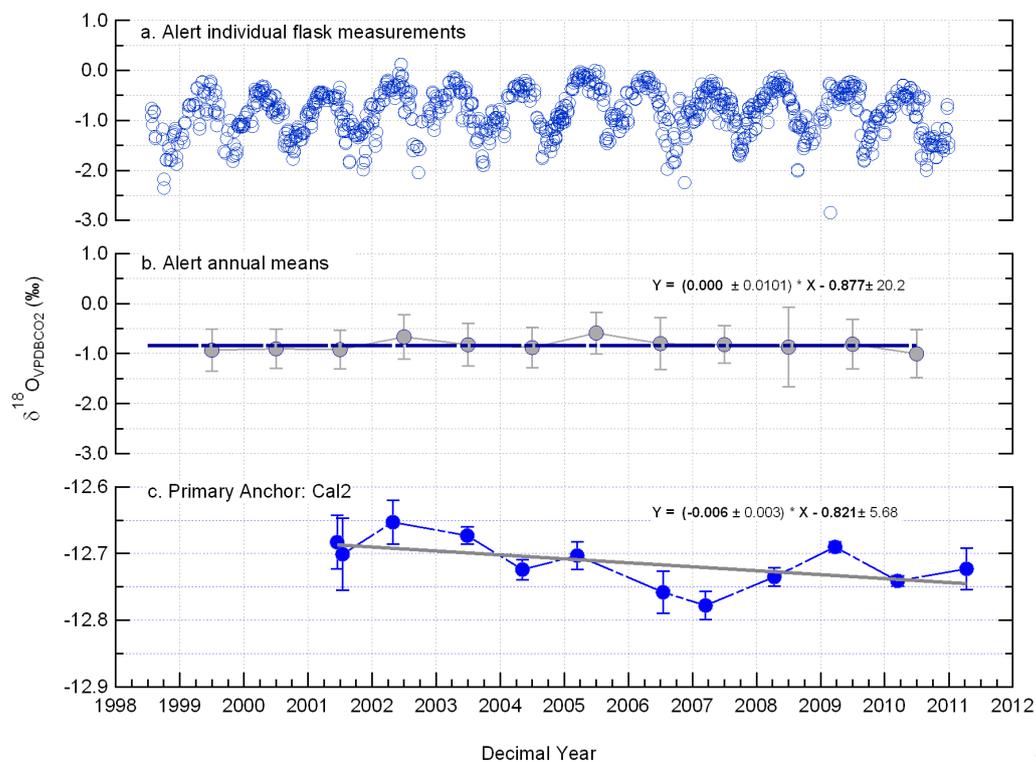
- The traceability used for high-precision CO₂ isotope measurements in our program at Environment Canada.
- The CO₂ isotope measurements and their trends at Alert station from 1999 to 2010.
- The entire records of annual calibrations of secondary standards (directly against NBS19-CO₂) to demonstrate 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ 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



(a)



(b)

Fig. 1. (a) Evaluating the trend in $\delta^{13}\text{C}$ measurements of flask CO₂ 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 CO₂ 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 $\delta^{13}\text{C}_{\text{NBS19/VPDB}}$ and -2.2 ‰ for $\delta^{18}\text{O}_{\text{NBS19/VPDB}}$ (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.

$$\begin{aligned} R_{\text{Lab-Std}/R_{\text{VPDBCO}_2}} &= [R_{\text{Lab-Std}}/R_{\text{WRG}}] \\ &\cdot [1/(R_{\text{NBS19CO}_2}/R_{\text{WRG}})] \cdot (R_{\text{NBS19CO}_2}/R_{\text{VPDBCO}_2}) \\ &= [R_{\text{Lab-Std}}/R_{\text{NBS19CO}_2}] \cdot (R_{\text{NBS19CO}_2}/R_{\text{VPDBCO}_2}) \\ &= [\Delta_{\text{Lab-Std/NBS19CO}_2} \times 10^{-3} + 1] \\ &\cdot [\Delta_{\text{NBS19CO}_2/\text{VPDBCO}_2} \times 10^{-3} + 1], \end{aligned} \quad (1)$$

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

$$\begin{aligned} \Delta_{\text{Lab-Std/NBS19CO}_2}^{45 \text{ or } 46} &= [(R_{\text{Lab-Std}} - R_{\text{NBS19CO}_2})/R_{\text{NBS19CO}_2}] \\ &\times 10^3 \text{ ‰} = (\delta_{\text{Lab-Std/WRG}} - \delta_{\text{NBS19CO}_2/\text{WRG}}) / \\ &(\delta_{\text{NBS19CO}_2/\text{WRG}} \times 10^{-3} + 1) \text{ ‰}. \end{aligned}$$

This term $\Delta_{\text{A/B}}^{45 \text{ or } 46}$ 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 $[(R_{\text{A}}/R_{\text{B}}) - 1] \times 10^3 \text{ ‰}$. In our case, A is a laboratory standard (Lab-Std) and B is NBS19-CO₂. Although the expression of $\Delta_{\text{A/B}}^{45 \text{ or } 46}$ appears identical to the definition of the small delta between A and B (i.e., $\delta_{\text{A/B}}^{45 \text{ or } 46} = [(R_{\text{A}}/R_{\text{B}}) - 1] \times 10^3 \text{ ‰}$), 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

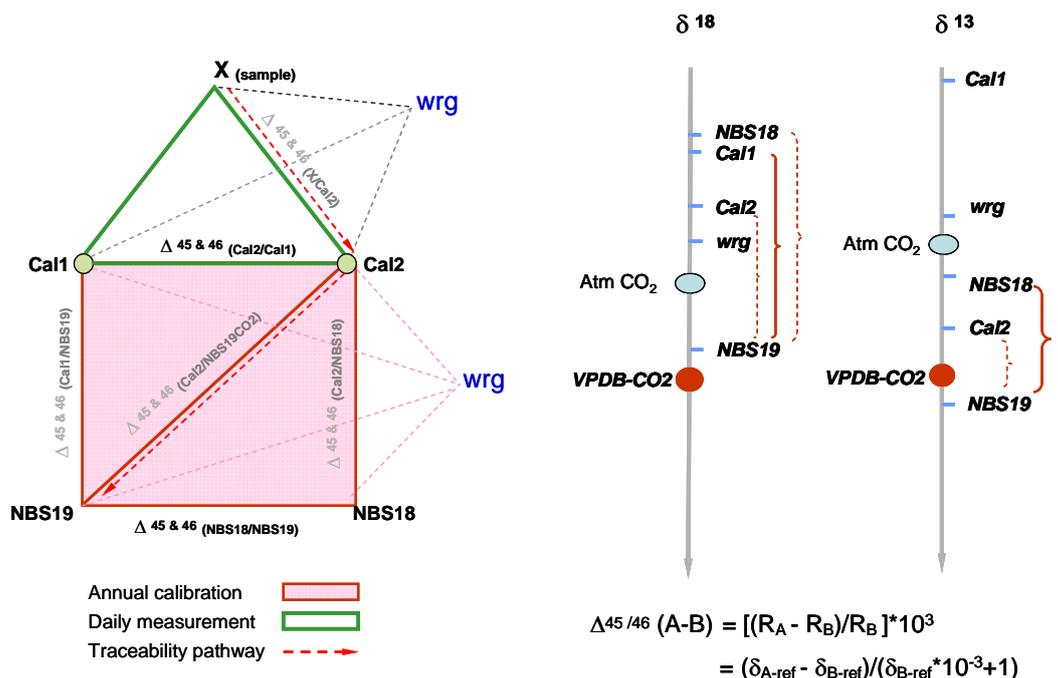
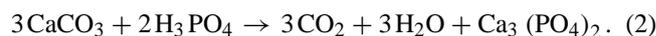


Fig. 2. On the left panel: a schematic of traceability in high-precision isotopic measurements using multiple carbonates, at the Stable Isotope Research Laboratory (SIRL), CRD/ASTD, Environment Canada. Where the pink square links the standards measured in annual calibrations and the green triangle links the standards and the sample X in daily measurements. The dotted lines (pink or gray) representing the pathways by that raw $\delta^{45/46}$ values are measured, and the solid lines (dark red or green) link the standards or sample from which *Big Delta* values can be derived; the red dotted lines with arrows indicate the traceability pathway, i.e., having the sample anchored on VPDB-CO₂ scale through two *Big Delta* values ($\Delta_{X/Cal2}$ and $\Delta_{Cal2/NBS19CO_2}$). In the right-hand panel, a schematic of relative positions on the primary VPDB-CO₂ scale (in $\delta^{13}C_{VPDBCO_2}$ and $\delta^{18}O_{VPDBCO_2}$) for the standards, the WRG and atmospheric CO₂. The arrow heads of gray lines are towards more positive values on VPDB-CO₂ scale. The *Big Delta* values relating NBS18 and NBS19 have been used as the quality control criteria for obtaining other *Big Delta* values (e.g., $\Delta_{Cal1/NBS19CO_2}$, $\Delta_{Cal2/NBS19CO_2}$ and $\Delta_{Cal2/Cal1}$) during annual calibrations. When the $\delta^{13}C_{NBS18CO_2/VPDBCO_2}$ and $\delta^{18}O_{NBS18CO_2/VPDBCO_2}$ match with the recommended values by IAEA, the other *Big Delta* values are considered valid. $\Delta_{Cal2/Cal1}$ is measured on both annual calibrations and daily measurements (see the left panel), and has been used as the quality control criteria for daily measurements. Comparing the $\Delta_{Cal2/Cal1}$ values with these obtained from annual calibrations, the quality of the primary anchor (Cal2) value is ensured and validated. Therefore, the traceability and quality of samples in daily measurements have been guaranteed.

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., $[\Delta_{Lab-Std/NBS19CO_2}]$) 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:



Each calibration set includes NBS19-CO₂, NBS18-CO₂, Cal1-CO₂ and Cal2-CO₂. The corresponding *Big Delta* values (i.e., $\Delta_{NBS18/NBS19}$, $\Delta_{Cal1/NBS19}$, $\Delta_{Cal2/NBS19}$, $\Delta_{Cal2/Cal1}$ etc.) have been determined (Tables 1–4). The measurement protocol is included in Table A1 (Appendix A). The *Big Delta* values of $\Delta_{NBS18/NBS19}$ are used to validate the *Big Delta* values of $\Delta_{Cal1/NBS19}$, $\Delta_{Cal2/NBS19}$ and $\Delta_{Cal2/Cal1}$ 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 MAT252 (2001–2011) and IsoPrime (2002–2011).

Decimal year	Extra. No.**	Pre-T °C	NBS19			NBS18			Big Delta											
			δ ⁴⁵ vs. Ref (raw)	δ ⁴⁶ vs. Ref (raw)	δ ⁴⁵ vs. Ref (raw)	δ ⁴⁶ vs. Ref (raw)	13C vs. VPDBCO ₂	18O vs. VPDBCO ₂	Δ ⁴⁵ (NBS18 vs. NBS19)	Δ ⁴⁶ (NBS18 vs. NBS19)	s.d.									
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	6.278	0.013	-13.053	0.023	-5.033	0.014	-22.951	0.023	-7.192	0.015	-20.792	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	-20.821	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	0.003	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)																				
s.d. (1σ)																				
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)																				
s.d. (1σ)																				
IAEA.1995* (mean)																				
s.d. (1σ)																				
NIST.2004* (mean)																				
s.d. (1σ)																				

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.
 * 17O correction algorithms used: Craig correction, ** Extra. No.: extraction number.

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

		CALI																	
Extra. No. **	Pre-T °C	δ^{45} s.d. vs. Ref (raw)	δ^{46} s.d.	$\delta^{13}\text{C}$ s.d. vs. VPDBCO ₂	^{18}O s.d.	Δ^{45} s.d. (CalI vs. NBS19)	Δ^{46} s.d. (CalI vs. NBS19)	Δ^{45} s.d. (CalI vs. NBS18)	Δ^{46} s.d. (CalI vs. NBS18)	Big Delta									
										δ^{45} s.d.	δ^{46} s.d.								
by IRMS: MAT252																			
	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
		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
	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
		9	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
	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
		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
		3	25	-32.117	0.013	-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
	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
		3	25	-32.128	0.009	-12.643	0.027	-45.867	0.010	-22.316	0.027	-45.346	0.011	-20.224	0.030	-38.399	0.010	0.763	0.034
	e	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
		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
		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 ($n = 45$)	46						-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																			
	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
		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
	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
		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
		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
		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
		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
		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
		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
		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, ** Extra. No.: extraction number.

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

Decimal year	Extra No.**	Pre-T °C	CAL2																
			δ^{45}	s.d.	δ^{46}	s.d.	¹³ C	s.d.	¹⁸ O	s.d.	Δ^{45}	s.d.	Δ^{46}	s.d.	Δ^{45}	s.d.	Δ^{46}	s.d.	
			vs. Ref (raw)		vs. VDPBCO ₂		vs. NBS19)		vs. NBS18)		Big Delta		Big Delta		Big Delta		Big Delta		
by IRMS: MAT252																			
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		7	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		4	25	9.137	0.029	-3.027	0.032	-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	-10.536	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)																			
						-2.600		-2.600		-12.713		-4.588		-10.535		2.643		10.576	
						s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)	
						0.014		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		-2.607		-12.576		-4.590		-10.397		2.645		10.433	
						s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)		s.d. (1 σ)	
						0.018		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.
 ** Extra. No.: extraction number.

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			CAL2			<i>Big Delta</i>			Cleanliness indicator of IRMS				
	δ^{45}	s.d. vs. Ref (raw)	s.d.	δ^{45}	s.d. vs. Ref (raw)	s.d.	Δ^{45}	s.d. (Cal2 vs. Cal1)	Δ^{46}	s.d.	BG count*	s.d.		
by IRMS: MAT252														
2001.45	-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	-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	-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	9.137	0.029	-3.027	0.032	42.623	0.032	9.744	0.060	208.71	2.00
2007.20	-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	-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		9.816			
s.d. (1σ)									0.044		0.057			
by IRMS: IsoPrime														
2002.74	-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	-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 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 CO₂ 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.

$$\begin{aligned} [R_{\text{Sam}}/R_{\text{VPDBCO}_2}] &= [R_{\text{Sam}}/R_{\text{WRG}}] \cdot [1/(R_{\text{Lab-Std}}/R_{\text{WRG}})] \\ &\cdot (R_{\text{Lab-Std}}/R_{\text{VPDBCO}_2}) = [R_{\text{Sam}}/R_{\text{Lab-Std}}] \\ &\cdot (R_{\text{Lab-Std}}/R_{\text{VPDBCO}_2}) = [R_{\text{Sam}}/R_{\text{Lab-Std}}] \\ &\cdot [R_{\text{Lab-Std}}/R_{\text{NBS19CO}_2}] \cdot (R_{\text{NBS19CO}_2}/R_{\text{VPDBCO}_2}) \\ &= [\Delta_{\text{Sam/Lab-Std}} \times 10^{-3} + 1] \\ &\cdot [\Delta_{\text{Lab-Std/NBS19CO}_2} \times 10^{-3} + 1] \\ &\cdot [\Delta_{\text{NBS19CO}_2/\text{VPDBCO}_2} \times 10^{-3} + 1], \quad (3) \end{aligned}$$

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

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

Equation (3) shows the documented traceability chain in CO₂ isotope measurements for individual CO₂ samples collected in the Environment Canada Greenhouse Gas Observation Network (Huang and Worthy, 2005). Here VPDB-CO₂ is the CO₂ 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 ¹⁷O 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 N₂O correction as N₂O is an interference to masses 44, 45 and 46 in CO₂ isotopic ratio measurements. The equations used in our N₂O correction are based on the general equation by Mook and Van der Hoek (1983) and Mook and Jongsma (1987):

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

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

where E is the ratio of ionization efficiency (RIE) of N₂O related to CO₂, and 0.708 was determined using the MAT252 instrument (the only IRMS used for CO₂ isotopes measurements); $[\text{N}_2\text{O}]/[\text{CO}_2]$ are the mole fraction ratio of N₂O (ppb) and CO₂ (ppm) concentrations measured at Environment Canada. $\delta_{\text{N}_2\text{O}}^{13}$ and $\delta_{\text{N}_2\text{O}}^{18}$ are the delta values that would be obtained measuring N₂O as if it were CO₂ versus a CO₂ standard. Combining our measurements and the literature values (Mook and Van der Hoek, 1983; Friedli and Siegenthaler, 1988), the $\delta_{\text{N}_2\text{O}}^{13}$ and $\delta_{\text{N}_2\text{O}}^{18}$ used in the algorithm are −345 ‰ and −506 ‰, respectively. The uncertainties of the correction terms in Eq. (5a) and (5b), due to using various $\delta_{\text{N}_2\text{O}}^{13}$ or $\delta_{\text{N}_2\text{O}}^{18}$ (e.g., ±10 ‰ for −345 ‰ and ±10 ‰ for −506 ‰) 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 (≤0.01 ‰). $\delta^{13}\text{C}_{\text{corr}}$ and $\delta^{18}\text{O}_{\text{corr}}$ are N₂O corrected values of $\delta^{13}\text{C}_{\text{meas}}$ and $\delta^{18}\text{O}_{\text{meas}}$. The same correction algorithms for both ¹⁷O and N₂O 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-CO₂ (see Eq. 3). In general, a *laboratory standard that has been calibrated directly or indirectly using NBS19-CO₂ 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 CO₂ 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, CO₂ extractions and IRMS analysis. Based on Eq. (3), the uncertainty of

$R_{\text{Sam}}/R_{\text{VPDBCO}_2}$ 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 CO₂ via acid digestions using H₃PO₄ 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 H₂O in H₃PO₄ impacts the precision of δ¹⁸O analysis because the oxygen isotopes in evolved CO₂ can easily exchange with those in liquid H₂O (e.g., McCrea, 1950; Clayton, 1959). Equation (2) shows that water would be released from the reaction along with the evolved CO₂. To minimize the impact of available liquid H₂O on the isotopic exchanges with CO₂, excess P₂O₅ is needed to absorb the H₂O that can potentially exist in the acid (Zachary, 2007). A solution of H₃PO₄ with a mass percentage greater than 100 % indicates excess P₂O₅ in the solution. If the mass percentage is too large, the solution tends to crystallize and makes the diffusion of CO₂ to the gas phase more difficult. This will also cause isotopic fractionations and affect the precision of the δ¹⁸O values. The commercially available H₃PO₄ has mass percentages usually on the order of 85 % and is thus not suitable. H₃PO₄ with a mass percentage greater than 100 % can be only custom-made. The specific gravity of 100 % H₃PO₄ is approximately 1.86 g mL⁻¹. Based on our experiences, the ideal range of the specific gravity of H₃PO₄ is from 1.91 to 1.92 g mL⁻¹. The in-house procedure of making H₃PO₄ is attached as Appendix B. A recent report by Wendeborg et al. (2011) found that the δ¹⁸O of H₃PO₄ will likely affect the δ¹⁸O of CO₂ evolved from the acid digestion when the mass percentage of H₃PO₄ is < 102 %. This is due to isotopic exchange between H₂O and H₃PO₄. The specific gravity of H₃PO₄ 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 CO₂ 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 Δ_{Lab-Std/NBS19CO₂}, the δ¹³C_{Lab-Std/VPDBCO₂} and δ¹⁸O_{Lab-Std/VPDBCO₂} 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 Δ⁴⁵ and 0.04–0.09 ‰ for Δ⁴⁶, 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 CO₂ 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 Δ_{Sam/Lab-Std} and Δ_{Lab-Std/NBS19CO₂} (Fig. 3), it is suggested to use a laboratory standard with a δ¹³C value between the NBS19 (i.e., +1.95 ‰) and the ambient atmospheric CO₂ (~ -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., Δ_{Cal2/NBS19CO₂}⁴⁵ and Δ_{Cal2/NBS19CO₂}⁴⁶) 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 Δ_{Cal2/NBS19CO₂}⁴⁵ and ~ 0.04 ‰ in Δ_{Cal2/NBS19CO₂}⁴⁶ (one standard deviation) measured using the MAT252 (the only IRMS used for flask δ¹³C and δ¹⁸O measurements of the program).

The uncertainty of the other term (Δ_{Sam/Lab-Std}) in the traceability can be only determined by using an air-CO₂ 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 CO₂, 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 Δ_{QC air-CO₂tank/Lab-Std} have been determined by repeated analysis over several years. The air-CO₂ tank used here for deriving the uncertainty of Δ_{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 Δ_{QC3/Cal2}⁴⁵ and Δ_{QC3/Cal2}⁴⁶ is 0.017 and 0.043 ‰, respectively. After applying the ¹⁷O and N₂O corrections, the values of uncertainty in δ¹³C and δ¹⁸O are the same as those in Δ_{QC3/Cal2}⁴⁵ and Δ_{QC3/Cal2}⁴⁶, inferring that 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 $R_{\text{Sam}}/R_{\text{VPDBCO}_2}$). Using the uncertainties of Δ_{Cal2/NBS19CO₂}^{45/46} (Table 3) and Δ_{QC3/Cal2}^{45/46} (Fig. 4), the overall uncertainties of Δ_{Sam/VPDBCO₂}^{45/46} (i.e., Δ_{QC3/VPDBCO₂}^{45/46}) can be determined by applying the principle of error propagation to Eq. (3) as follows:

$$\begin{aligned} \sigma \left(\delta^{45/46} (\text{CO}_2)_{\text{QC3/VPDBCO}_2} \right) \\ \cong \left[\sigma \left(\Delta_{\text{QC3/Cal2}}^{45/46} \right)^2 + \sigma \left(\Delta_{\text{Cal2/NBS19CO}_2}^{45/46} \right)^2 \right]^{1/2}. \end{aligned}$$

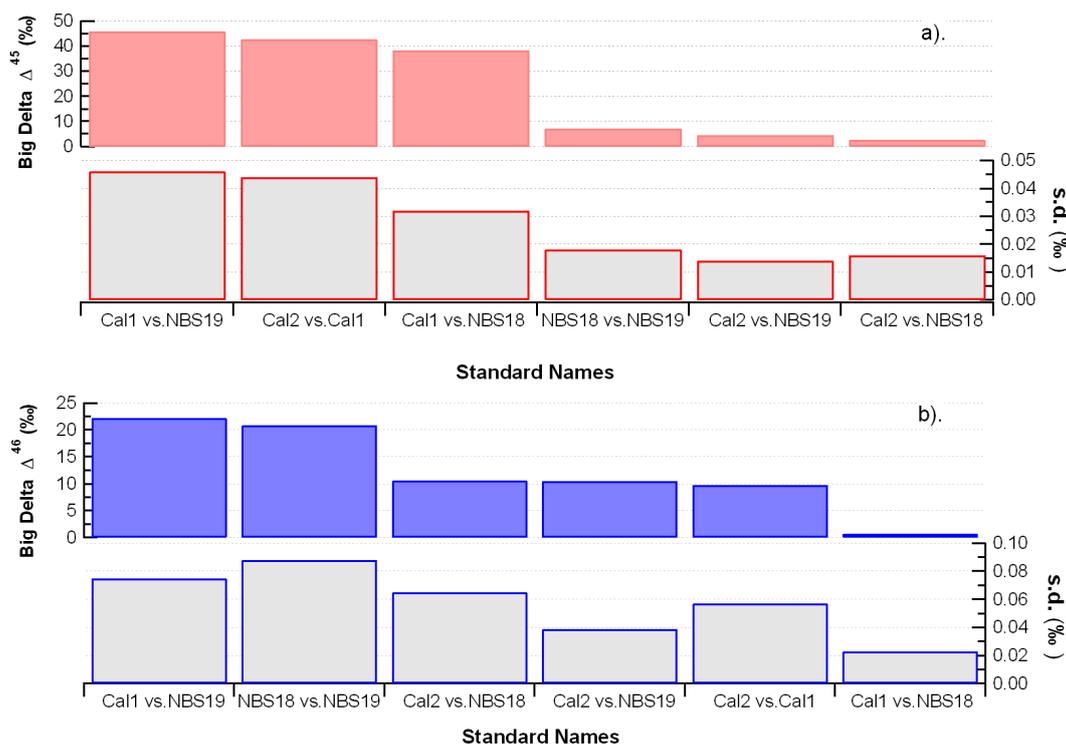


Fig. 3. There is a positive correlation between the absolute *Big Delta* values and the corresponding standard deviations in both carbon (top panel) and oxygen (bottom panel) isotopes. The coefficient of determination (r^2) is 0.94 and 0.63 for Δ^{45} and Δ^{46} , respectively. The absolute *Big Delta* value of the primary anchor (Cal2) relative to NBS19 is ~ 4.59 ‰ in Δ^{45} (s.d.: 0.01 ‰) and ~ 10.54 ‰ in Δ^{46} (s.d.: 0.04 ‰).

The calculated uncertainty for $\delta^{45}(\text{CO}_2)_{\text{QC3/VPDBCO}_2}$ and $\delta^{46}(\text{CO}_2)_{\text{QC3/VPDBCO}_2}$ 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 CO₂ isotope measurements for individual flask samples from the Environment Canada network is on the order 0.02 ‰ for $\delta^{13}\text{C}$ and 0.05 ‰ for $\delta^{18}\text{O}$. No uncertainties in the ^{17}O and N_2O 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_2O 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-CO₂ 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 CO₂ 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 δ^{45} or δ^{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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in atmospheric CO₂.

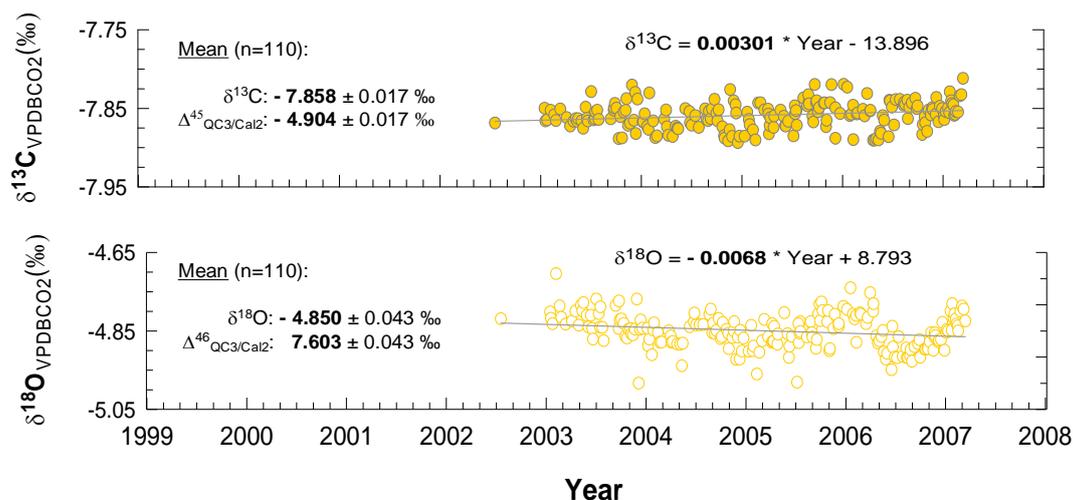


Fig. 4. Isotopic measurements of QC3 from 2003 to 2008 (QC3 is an aluminum high-pressure air-CO₂ tank that was filled with dry air at Alert in Sept. 2000). Top panel is for $\delta^{13}\text{C}$ and the bottom panel for $\delta^{18}\text{O}$ (the range of “Year” in the linear relationship: > 2002 and < 2008).

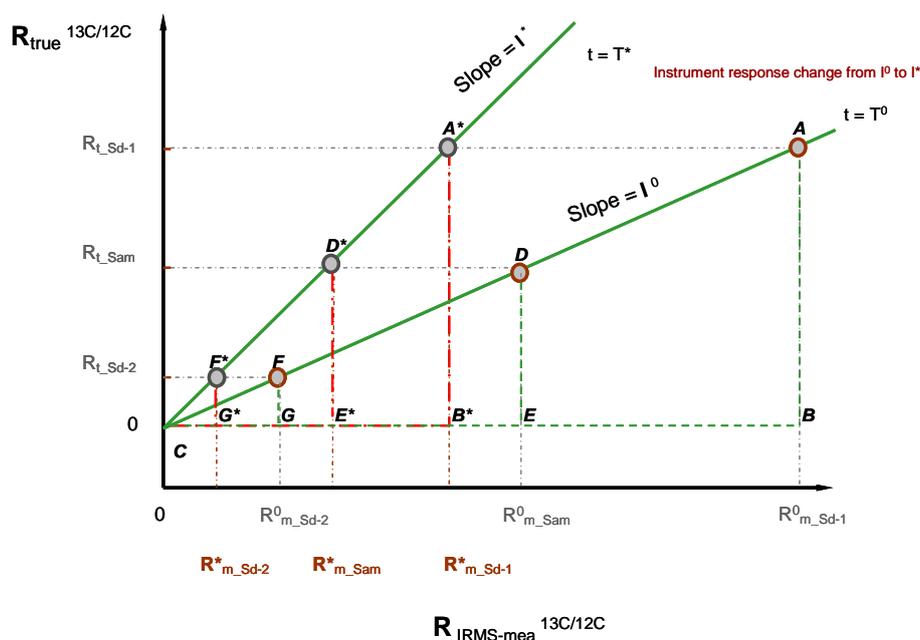


Fig. 5. Schematic of the relationship between the intrinsic/true isotopic ratio (i.e., $R = {}^{13}\text{C}/{}^{12}\text{C}$) and the isotopic ratio measured by IRMS. There are two standards (Std-1 and Std-2) and one sample shown in the diagram. Their intrinsic/true isotopic compositions are distinguishable as $R_{\text{t_Sd-1}}$, $R_{\text{t_Sd-2}}$, and $R_{\text{t_Sam}}$ on the y-axis and the corresponding measured isotopic compositions are shown on the x-axis. 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 $R_{\text{m_Sd-1}}^0$, $R_{\text{m_Sd-2}}^0$, $R_{\text{m_Sam}}^0$ to $R_{\text{m_Sd-1}}^*$, $R_{\text{m_Sd-2}}^*$, $R_{\text{m_Sam}}^*$. However, the ratios (i.e., $[R_{\text{m_Sam}}^0/R_{\text{m_Sd-1}}^0]$, $[R_{\text{m_Sd-2}}^0/R_{\text{m_Sd-1}}^0]$) would not change and they are always equal to the corresponding intrinsic/true ratios $[R_{\text{t_Sam}}/R_{\text{t_Sd-1}}]$, $[R_{\text{t_Sd-2}}/R_{\text{t_Sd-1}}]$, respectively, since triangle ABC is similar to triangles DEC and FGC, and triangle A^*B^*C is similar to triangle D^*E^*C and F^*G^*C , as illustrated in the above schematic.

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

(as indicated by background count) has been a dominant factor for the small drift over the period, particularly for Δ^{45} ; as the ion source becomes cleaner, the *Big Delta* values get larger. Usually, the ion source would be cleaned by baking at $\sim 100^\circ\text{C}$ for > 24 h while bleeding pure hydrogen (with 5.0 UHP grade from Praxair) through overnight.

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 $\Delta_{\text{Cal2/NBS19CO}_2}$ by MAT252 are very small, and its standard deviations (including all sources of errors) are within the ranges of $< 0.02\%$ in $\delta^{13}\text{C}$ and $\sim 0.04\%$ in $\delta^{18}\text{O}$ over this 10 yr period. These values are close to the WMO targets of 0.01 and 0.05% for data comparability in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, providing the precision and the stability of Cal2 as the primary anchor. The results from IsoPrime analyses show very similar patterns for $\Delta_{\text{Cal2/NBS19CO}_2}^{45}$ but not for $\Delta_{\text{Cal2/NBS19CO}_2}^{46}$. This may suggest that the differences in the high vacuum and the water-content levels inside of ion source have larger impacts on $\delta^{18}\text{O}$ than those on $\delta^{13}\text{C}$ 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 CO₂ and H₂O would occur inside of IsoPrime's ion source. This raises a serious issue of scale contraction regarding the $\delta^{18}\text{O}$ measurements by different types of instruments. However, we only used MAT252 for flask CO₂ isotope measurements. The MAT252 results indicate that as long as the *Big Delta* value is relatively small ($\sim 10\%$ 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 CO₂ samples to the VPDB-CO₂ 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 $\delta^{13}\text{C}_{\text{NBS19/VPDB}}$ and $\delta^{13}\text{C}_{\text{L-SVEC/VPDB}}$ 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 $\delta^{13}\text{C}_{\text{VPDB}}$ value ($-46.6 \pm 0.2\%$), 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., $\Delta_{\text{L-SVEC/NBS19CO}_2}^{45/46}$) 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 CO₂ isotope measurements, and thus critical for verifying atmospheric trends of CO₂ isotopes (in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). 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 $\delta^{13}\text{C}_{\text{NBS18/VPDBCO}_2}$ 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-CO₂ samples was made by periodically taking a large aliquot of gas from a pure-CO₂ high-pressure cylinder (see Appendix C). The variation ranges of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are less than 0.02 and 0.04%, 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 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 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 δ^{45} and δ^{46} values analyzed 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}) 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ at Alert

Determining accurate long-term trends of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in atmospheric CO₂ is critical for understanding the changes in carbon emission sources and sinks with time. A long-term atmospheric trend in $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{18}\text{O}$ is essentially zero (Fig. 1b). The results suggest that the trend of $\delta^{13}\text{C}$ at Alert has been mainly influenced by the continuous contribution of fossil fuel CO₂, whereas the pattern of $\delta^{18}\text{O}$ 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 $\delta^{13}\text{CH}_4$ trend. Kai et al. (2011) reported an interhemispheric trend in $\delta^{13}\text{CH}_4$, whereas Levin et al. (2012) claimed no interhemispheric $\delta^{13}\text{CH}_4$ 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 requires 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 traced 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).

- 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-CO₂ or pure CO₂ evolved from carbonates or commercially pressurized pure CO₂) 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 $\delta^{13}\text{C}$ value between NBS19-CO₂ 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 ampoules) during annual calibrations for a decadal time span to monitor the fluctuations in raw δ^{45} and δ^{46} values for NBS19-CO₂ 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. The type of pure CO₂ 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 H₃PO₄ within a consistent range of specific gravity (i.e., 1.91–1.92 g cm⁻³).
- If the primary anchor is air CO₂, it should be calibrated directly by NBS19-CO₂ 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 $\delta^{13}\text{C}$ and 0.05 ‰ for $\delta^{18}\text{O}$) should be achievable, a stable primary anchor can be maintained and the atmospheric trends in $\delta^{13}\text{C}$ can be evaluated, verified and confirmed.

Appendix A

Measurement protocols

A1 For annual calibrations

Usually, three sets of pure-CO₂ 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 CO₂ (i.e., APB2, the pure CO₂ 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 (H₃PO₄)

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 % H₃PO₄ 400 mL (source: Aldrich cat# 21,510-4)
- P₂O₅ 300 g (source: Aldrich cat# 29,822-0)
- H₂O₂ 30 % 2 mL (source: Aldrich cat# 21,676-3)
- (H₂O₂ bp: 150.2 °C, mp: -0.41 °C) from CRC Handbook of Chemistry and Physics, 61st Edn. 1980–1981, B105.
- CrO₃ 10–20 mg (a few flakes) (source: Aldrich cat# 20,782-9)

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

Measurement order	Sample bellow	Reference bellow	Description	Purpose
1	WRG	WRG	<i>zero check</i> 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 to 0 ‰)
2	WRG	WRG	<i>zero check</i> with both bellows disconnected from 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 to 0 ‰)
3	Cal1	WRG	measuring a <i>Lab-Std</i> (i.e., Cal1) with $\delta^{13}\text{C}_{\text{VPDB-CO}_2} \sim -45.8\text{‰}$	to obtain the <i>Big Delta</i> values between the Lab-Std and NBS19 and to anchor Cal1 on the primary scale via NBS19.
4	Cal2	WRG	measuring a <i>Lab-Std</i> (i.e., Cal2) with $\delta^{13}\text{C}_{\text{VPDB-CO}_2} \sim -2.6\text{‰}$	to obtain the <i>Big Delta</i> values between the Lab-Std and NBS19 and to anchor Cal2 on the primary scale via NBS19.
5	NBS18	WRG	measuring an <i>international reference</i> (i.e., NBS18) with $\delta^{13}\text{C}_{\text{VPDB-CO}_2} \sim -5\text{‰}$	to obtain the <i>Big Delta</i> values between NBS18 and NBS19, and and to anchor NBS18 on the primary scale via NBS19.
6	NBS19	WRG	measuring an <i>international standard</i> (i.e., the anchor on the primary scale: VPDB-CO ₂) with $\delta^{13}\text{C}_{\text{VPDB-CO}_2} : +1.95\text{‰}$	to obtain $\delta^{13}\text{C}_{\text{NBS18/VPDB-CO}_2}$, $\delta^{13}\text{C}_{\text{Cal1/VPDB-CO}_2}$ and $\delta^{13}\text{C}_{\text{Cal2/VPDB-CO}_2}$ via measuring the <i>Big Delta</i> values between NBS19 and those samples.
7	Cal1	WRG	the same as the previous Cal1	the same as above
8	Cal2	WRG	the same as the previous Cal2	the same as above
9	NBS18	WRG	the same as the previous NBS18	the same as above
10	NBS19	WRG	the same as the previous NBS19	the same as above
11	Cal1	WRG	the same as the previous Cal1	the same as above
12	Cal2	WRG	the same as the previous Cal2	the same as above
13	NBS18	WRG	the same as the previous NBS18	the same as above
14	NBS19	WRG	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., ⁴⁵ and 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 properly produced via acid digestion. The data presented in Tables 1 through 4 indicate that this is the case.

B3 Procedures

- 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.
- Very slowly add P₂O₅.
- Slowly add H₂O₂ (to oxidize any possible organic compounds), turn on heat and slowly raise the temperature of the liquid.
- As it heats, add a few flakes of CrO₃ to see if there is any excess H₂O₂ (H₂O₂ is a reducing agent now and can be oxidized by CrO₃). The solution may undergo a color change from yellow to light green (Cr⁶⁺ to Cr³⁺).
- Heat the acid to boiling and allow to boil for 2.5 h.
- 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.
- 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.

- 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.
- 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 CO₂ working reference gas (WRG) ampoules preparation

A pure-CO₂ 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-CO₂ ampoules were

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

Measurement order	Sample bellow	Reference bellow	Description	Purpose
1	WRG	WRG	<i>zero check</i> with both bellows connected to each other	to check if the crimps of both capillaries are evenly balanced
2	WRG	WRG	<i>zero check</i> with both bellows disconnected from each other	to check any problems in running real samples (the related raw delta of this should close to 0‰)
3	Cal1	WRG	measuring a <i>Lab-Std</i> with $\delta^{13}\text{C}_{\text{VPDBCO}_2} \sim -45.8\text{‰}$	to determine the <i>Big Delta</i> between two Lab-Stds for validation of the primary anchor (i.e., Cal2) and monitoring instrument's variation.
4	Cal2	WRG	measuring a <i>Lab-Std</i> with $\delta^{13}\text{C}_{\text{VPDBCO}_2} \sim -2.6\text{‰}$	to determine the <i>Big Delta</i> between two Lab-Stds for validation of the <i>primary anchor</i> (i.e., Cal2) and monitoring instrument's variation. If the <i>Big Delta</i> 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 Cal1 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.
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 <i>Lab-Std</i> with $\delta^{13}\text{C}_{\text{VPDBCO}_2} \sim -2.6\text{‰}$	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 $< 0.02\text{‰}$, 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.

* 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ 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-CO₂ scale via the primary anchor (Cal2). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records from the cylinder over a decade (1998–2011) are shown on Fig. C1. The total change in $\delta^{13}\text{C}$

and $\delta^{18}\text{O}$ is approximately 0.8 and 1‰, respectively, over the entire period. It is suggested that directly using pure CO₂ from a high-pressure cylinder as a primary anchor and without frequent calibrations by NBS19-CO₂ would not be proper because of changes in its isotopic compositions with time or cylinder pressure, particularly when a liquid phase of CO₂ still exists in the cylinder.

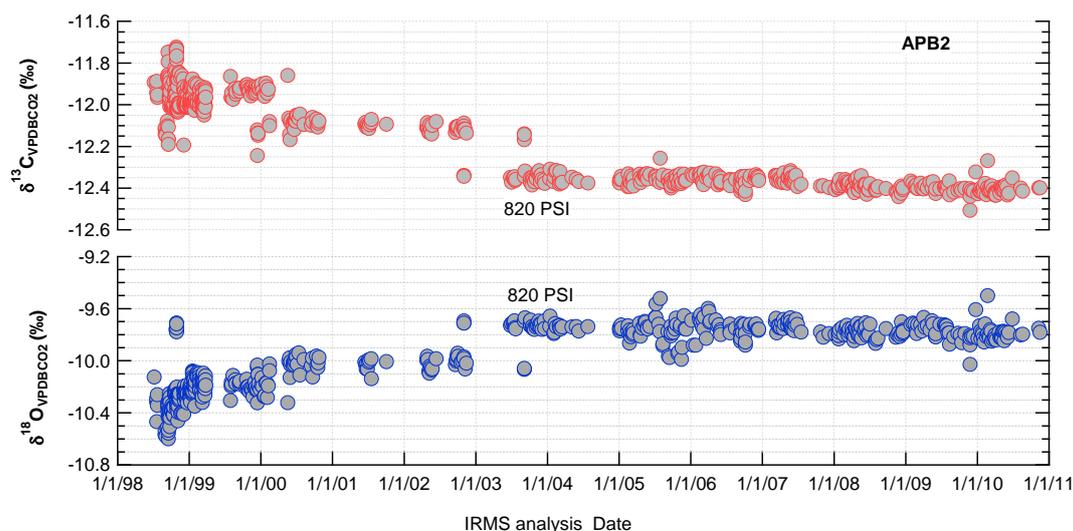


Fig. C1. Isotopic compositions of pure CO₂ in a high-pressure cylinder (APB2) over a period of time of more than 10 yr (1998–2011). Top panel: $\delta^{13}\text{C}_{\text{VPDB-CO}_2}$, bottom panel: $\delta^{18}\text{O}_{\text{VPDB-CO}_2}$. The numbers indicate the pressure readings at the time of IRMS analysis. The results show that the isotopic compositions were more stable below the pressure of ~ 800 PSI, when all CO₂ becomes gaseous phase.

Acknowledgements. This work has been supported by Environment Canada (EC) A-base funding (related to climate research) over the last 10 yr. The authors sincerely thank those research managers from Environment Canada for their understanding and for supporting the fundamental work in carbon-cycle-related atmospheric measurements; colleagues from the Global Monitoring Division (GMD) of the Earth System Research Laboratory (ESRL), the National Oceanic Atmospheric Administration (NOAA), USA, and the Institute of Arctic and Alpine Research (INSTAAR) at the University of Colorado for the accessibility of the global $\delta^{13}\text{C}$ (CO₂) data; and colleagues from the Commonwealth Scientific and Industrial Research Organization (CSIRO) for valuable advice during the early stage of the program. The authors also thank the World Meteorological Organization (WMO) and the International Atomic Energy Agency (IAEA) for providing a platform for scientific discussions and inspiration in the WMO/IAEA Expert meetings over the last 10 yr, as well as Pieter Tans, Felix Vogel, Douglas Chan, Doug Worthy and two anonymous referees for their detailed comments on improving the manuscript.

Edited by: O. Tarasova

References

- Allison, C. E. and Francey, R. J.: Verifying Southern Hemisphere trends in atmospheric carbon dioxide stable isotopes, *J. Geophys. Res.-Atmos.*, 112, D21304, doi:10.1029/2006JD007345, 2007.
- Allison, C. E., Francey, R. J., and Meijer, H. A. J.: Recommendations for reporting stable isotope measurements of carbon and oxygen in CO₂ gas, IAEA TECDOC, 825, 155–162, 1995.
- Bakwin, P. S., Tans, P. P., White, J. W. C., and Andres, R. J.: Determination of the isotopic ($^{13}\text{C}/^{12}\text{C}$) discrimination by terrestrial biology from a global network of observations, *Global Biogeochem. Cy.*, 12, 555–562, 1998.
- Battle, M., Bender, M. L., Tans, P. P., White, J. W. C., Ellis, J. T., Conway, T., and Francey, R. J.: Global carbon sinks and their variability inferred from atmospheric O₂ and $\delta^{13}\text{C}$, *Science*, 287, 2467–2470, 2000.
- Brand, W. A., Huang, L., Mukai, L., Chivulescu, A., Richter, J. M., and Rothe, M.: How well do we know VPDB? Variability of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO₂ generated from NBS19-calcite, *Rapid Commun. Mass. Spectrom.*, 23, 915–926, 2009.
- Ciais, P., Tans, P. P., Trolier, M., White, J. W. C., and Francey, R. J.: A large northern hemisphere terrestrial CO₂ sink indicated by the $^{13}\text{C}/^{12}\text{C}$ Ratio of atmospheric CO₂, *Science*, 269, 1098–1102, 1995.
- Ciais, P., Denning, D., Tans, P. P., Berry, J. A., Randall, D. A., Colatz, G. J., Sellers, P. J., White, J. W. C., Trolier, M., Meijer, H. A. J., Francey, R. J., Monfray, P., and Heimann, M.: A three-dimensional synthesis study of $\delta^{18}\text{O}$ in atmospheric CO₂ I. Surface fluxes, *J. Geophys. Res.*, 102, 5857–5872, 1997.
- Clayton, R. N.: Oxygen Isotope Fraction in the system calcium carbonate-water, *J. Chem. Phys.*, 30, 1246–1250, 1959.
- Coplen, T. B., Brand, W. A., Gehre, M., Gröning, M., Meijer, H. A. J., Toman, B., and Verkouteren, R. M.: New Guidelines for ^{13}C Measurements, *Anal. Chem.*, 78, 2439–2441, 2006a.
- Coplen, T. B., Brand, W. A., Gehre, M., Gröning, M., and Meijer, H. A. J.: After two decades a second anchor for the VPDB $\delta^{13}\text{C}$ scale, *Rapid Commun. Mass. Spectrom.*, 20, 3165–3166, 2006b.
- Craig, H.: Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta*, 12, 133–149, 1957.
- CRC Handbook of Chemistry and Physics: 61st Edn., B105, 1980–1981.
- Flesch, G. D., Anderson Jr., A. R., and Svec, H. J.: A secondary isotopic standard for $^6\text{Li}/^7\text{Li}$ determinations, *Int. J. Mass. Spectrom. Ion Phys.*, 12, 265–272, 1973.

- Francey, R. J., Tans, P. P., Allison, C. E., Enting, I. G., White, J. W. C., and Troler, M.: Changes in oceanic and terrestrial carbon uptake since 1982, *Nature*, 373, 326–330, 1995.
- Friedli, H. and Siegenthaler, U.: Influence of N₂O on isotope analyses in CO₂ and mass-spectrometric determination of N₂O in air samples, *Tellus B*, 40, 129–133, 1988.
- Friedman, I., O’Neil, J., and Cebula, G.: Two New Carbonate Stable Isotope Standards, *Geostand. Newslett.*, 6, 11–12, 1982.
- GAW Report No. 161: the Expert Group Recommendation in: Report of the 12th WMO/IAEA Meeting of Experts on carbon dioxide and related tracers measurement techniques, 15–18 September 2003, edited by: Worthy, D. and Huang, L., Toronto, Canada, 2005.
- GAW Report No. 168: the Expert Group Recommendation in: Report of the 13th WMO/IAEA Meeting of Experts on carbon dioxide and related tracers measurement techniques, 19–22 September 2005, edited by: Miller, J., Boulder, Colorado, USA, 2006.
- GAW Report No. 186: the Expert Group Recommendation in: Report of the 14th WMO/IAEA Meeting of Experts on carbon dioxide, other Greenhouse Gases and related tracers measurement techniques, 10–13 September 2007, edited by: Laurila, T., Helsinki, Finland, 2009.
- GAW Report No. 194: the Expert Group Recommendation in: Report of the 15th WMO/IAEA Meeting of Experts on carbon dioxide, other greenhouse gases and related tracers measurement techniques, 7–10 September 2009, edited by: Brand, W. A., Jena, Germany, 2011.
- GAW Report No. 206: the Expert Group Recommendation in: Report of the 16th WMO/IAEA Meeting on carbon dioxide, other greenhouse gases and related tracers measurement techniques (GGMT-2011), 25–28 October 2011, edited by: Brailsford, G., Wellington, New Zealand, 2012.
- Ghosh, P. and Brand, W. A.: The effect of N₂O on the isotopic composition of air-CO₂ samples, *Rapid Commun. Mass. Spectrom.*, 18, 1830–1838, 2004.
- Ghosh, P., Patecki, M., Rothe, M., and Brand, W. A.: Calcite-CO₂ mixed into CO₂-free air: a new CO₂-in-air stable isotope reference material for the VPDB scale, *Rapid Commun. Mass. Spectrom.*, 19, 1097–1119, 2005.
- Gonfiantini, R., Stichler, W., and Rozanski, K.: Standards and Intercomparison Materials Distributed by the International Atomic Energy Agency for Stable Isotope Measurements, Proceedings of a consultants meeting held in Vienna, 1–3 December 1993, IAEA-TECDOC-825, Vienna, 13–29, 1995.
- Hoefs, J.: Chapter 1: Theoretical and experimental principles, in: *Stable Isotope Geochemistry*, Springer-Verlag, Berlin, Heidelberg, 1–26, 1997.
- Huang, L. and Worthy, D.: Flask Sampling Strategy by MSC for Atmospheric Observations of Greenhouse Gases and CO₂ Isotopes over Canada: Status & Plan, in: Report of the 12th WMO/IAEA Meeting of Experts on CO₂ Concentration and Related Tracer Measurement Techniques, September 2003, GAW publication 161, Toronto, 94–100, 2005.
- Huang, L., Norman, A. L., Allison, C. E., Francey, R. J., Ernst, D., Chivulescu, A., and Higuchi, K.: Traceability – maintenance for high precision stable isotope measurement ($\delta^{13}\text{C}$ & $\delta^{18}\text{O}$) of Air-CO₂ by Lab-Carbonate-Standards at MSC: Application to the Inter-Comparison Program (Alert, Canada) with CSIRO, in: Report of the 11th WMO/IAEA Meeting of Experts on CO₂ Concentration and Related Tracer Measurement Techniques, September 2001, WMO publication, No. 148, Tokyo, 9–16, 2002.
- Huang, L., Chivulescu, A., Allison, C. E., Brailsford, G., Brand, W. A., Wendeberg, M., Bollenbacher, A., Keeling, R., Levin, I., Sabasch, M., Leuenberger, M., Mukai, H., Nakazawa, T., Aoki, S., Neubert, R., Aerts-Bijma, A., Verkouteren, M., White, J. W. C., Vaughn, B., Michel, S., Zhou, L., and Liu L. X.: A Report of $\delta^{13}\text{C}$ & $\delta^{18}\text{O}$ Measurements in NBS19 and NBS18 pure CO₂: Uncertainty in Traceability of CO₂ Isotope Measurements, in: the proceeding of Report to the 15th WMO/IAEA CO₂ Expert Meeting, September 2009, WMO Report No. 194, Jena, 220–225, 2011.
- Hut, G.: Consultants’ group meeting on stable isotope reference samples for geochemical and hydrological investigations, Report to the Director General, International Atomic Energy Agency, Vienna, April 1987.
- Kai, F. M., Tylor, S. C., Randerson, J. T., and Blake, D. R.: Reduced methane growth rate explained by decreased Northern Hemisphere microbial sources, *Nature*, 476, 194–197, 2011.
- Kai, F. M., Tylor, S. C., Randerson, J. T., and Blake, D. R.: Replying to Levin et al., *Nature*, 486, E4, 2012.
- Keeling, C. D.: The concentration and isotopic abundances of carbon dioxide in the atmosphere, *Tellus*, 12, 200–203, 1960.
- Keeling, C. D.: The concentration and isotopic abundance of carbon dioxide in rural and marine air, *Geochim. Cosmochim. Acta*, 24, 277–208, 1961.
- Keeling, C. D., Mook, W. G., and Tans, P. P.: Recent trend in the ¹³C/¹²C ratio of atmospheric carbon dioxide, *Nature*, 277, 121–122, 1979.
- Keeling, C. D., Whorf, T. P., Wahlen, M., and van der Plicht, J.: Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980, *Nature*, 375, 666–670, 1995.
- Levin, I., Veidt, C., Vaughn, B. H., Brailsford, G., Bromley, T., Heinz, R., Lowe, D., Miller, J. B., Poß, C., and White, J. W. C.: No inter-hemispheric $\delta^{13}\text{C}\text{CH}_4$ trend observed, *Nature*, 486, E3–E4, 2012.
- Masarie, K. A. and Tans, P. P.: Extension and integration of atmospheric carbon dioxide data into a globally consistent measurement record, *J. Geophys. Res.-Atmos.*, 100, 11593–11610, 1995.
- Masarie, K. A., Allison, C. E., Conway, T. J., Dlugokencky, E. J., Francey, R. J., Langenfeld, R. L., Novelli, P. C., Steele, L. P., Tans, P. P., Vaughn, B. H., and White, J. W. C.: The NOAA/CSIRO Flask-Air Intercomparison Program: A strategy for directly assessing consistency among measurements derived from independent laboratories, *J. Geophys. Res.*, 106, 20445–20464, 2001.
- McCrea, J. M.: On the isotopic chemistry of carbonates and a paleotemperature scale, *J. Chem. Phys.*, 18, 849–857, 1950.
- Meijer, H. A. J., Neubert, R. E. M., Visser, G. H.: Cross contamination in dual inlet isotope ratio mass spectrometers, *Int. J. Mass. Spectrom.*, 198, 45–61, 2000.
- Merritt, D. A. and Hayes, J. M.: Factors controlling precision and accuracy in isotope-ratio-monitoring mass spectrometry, *Anal. Chem.*, 66, 2336–2347, 1994.
- Mook, W. G. and Jongsma, J.: Measurement of the N₂O correction for ¹³C/¹²C ratios of atmospheric CO₂ by removal of N₂O, *Tellus B*, 39, 96–99, 1987.

- Mook, W. G., and Koopmans, M., Carter, A. F., and Keeling, C. D.: Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric carbon dioxide 1. results from land stations, *J. Geophys. Res.*, 88, 10915–10933, 1983.
- Mook, W. G. and Van der Hoek, S.: The N₂O correction in the carbon and oxygen isotopic analysis of atmospheric CO₂, *Isot. Geosci.*, 1, 237–242, 1983.
- Mukai, H., Nakazawa, T., Brand, W. A., Huang, L., Levin, I., Allison, C. E., White, J. W. C., Leuenberger, M., and Assonov, S. S.: About disagreements in inter-comparison activities of isotope ratio measurements for CO₂, in: Report of the 13th IAEA/WMO Meeting of CO₂ experts, edited by: Miller, J. and Conway, T., vol. WMO/GAW, No. 68, Boulder, 41–48, 2005.
- Stichler, W.: Interlaboratory Comparison of new materials for carbon and oxygen isotope ratio measurements. Proceedings of a consultants meeting held in Vienna, 1–3 December 1993, IAEA-TECDOC-825, Vienna, 67–74, 1995.
- Trolier, M., White, J. W. C., Tans, P. P., Masarie, K. A., and Gemery, P. A.: Monitoring the isotopic composition of atmospheric CO₂: Measurements from the NOAA Global Air Sampling Network, *J. Geophys. Res.*, 101, 25897–25916, 1996.
- Vaughn, B. H., Evans, C. U., White, J. W. C., Still, C. J., Masarie, K. A., and Turnbull, J.: Global network measurements of atmospheric trace gas isotopes, in: *Isoscapes*, edited by: West, J. B., Bowen, G. J., Dawson, T. E., and Tu, K. P., 1st Edn., Hardcover, Springer, XXIV, p. 487, 2010.
- Verkouteren, R. M. and Klinedinst, D. B.: Value assignment and uncertainty estimation of selected light stable isotope reference materials: RMs 8543–8545, RMs 8562–8564, and RM 8566, in: NIST Special Publication 260-149, 2004 Edn., 2004.
- Verkouteren, R. M., Allison, C. E., Studley, S. A., and Leckrone, K. J.: Isotopic metrology of carbon dioxide, I. Interlaboratory comparison and empirical modeling of inlet equilibration time, inlet pressure, and ion source conductance, *Rapid Commun. Mass. Spectrom.*, 17, 771–776, doi:10.1002/rcm.905, 2003a.
- Verkouteren, R. M., Assonov, S., Klinedinst, D. B., and Brand, W. A.: Isotopic metrology of carbon dioxide, II. Effects of ion source materials, conductance, emission, and accelerating voltage on dual-inlet cross contamination, *Rapid Commun. Mass. Spectrom.*, 17, 777–782, doi:10.1002/rcm.906, 2003b.
- Vogel, F. R., Huang, L., Ernst, D., Giroux, L., Racki, S., and Worthy, D. E. J.: Evaluation of a cavity ring-down spectrometer for in situ observations of ¹³CO₂, *Atmos. Meas. Tech.*, 6, 301–308, doi:10.5194/amt-6-301-2013, 2013.
- Welp, L. R., Keeling, R. F., Meijer, H. A. J., Bollenbacher, A. F., Piper, S. C., Yoshimura, K., Francey, R. J., Allison, C. E., and Wahlen, M.: Interannual variability in the oxygen isotopes of atmospheric CO₂ driven by El Niño, *Nature*, 477, 579–582, 2011.
- Wendeberg, M., Richter, J. M., and Rothe, M., and Brand, W. A.: ¹⁸O anchoring to VPDB: Calcite digestion with ¹⁸O adjusted ortho-phosphoric acid, *Rapid Commun. Mass. Spectrom.*, 25, 851–860, doi:10.1002/rcm.4933, 2011.
- White, J. W. C. and Vaughn, B. H.: University of Colorado, Institute of Arctic and Alpine Research (INSTAAR), Stable Isotopic Composition of Atmospheric Carbon Dioxide (¹³C and ¹⁸O) from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1990–2010, Version: 2011-11-08, <ftp://ftp.cmdl.noaa.gov/ccg/co2c13/flask/event/> (last access: 16 April 2012) 2011.
- Zachary, S.: The Phosphoric Acid Method, in: Chapter 6 of *Principles of Stable Isotope Geochemistry*, Pearson Prentice Hall, 121–122, 2007.