

# Abundances of isotopologues and calibration of CO<sub>2</sub> greenhouse gas measurements

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## Abstract

We have developed a method to calculate the fractional distribution of CO<sub>2</sub> across all of its component isotopologues based on measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. The fractional distribution can be used with known total CO<sub>2</sub> to calculate ~~the amount of substance fraction (mole fraction) abundance of~~ each component isotopologue ~~in air~~ individually, ~~in units of mole fraction~~. The technique is applicable to any molecule where isotopologue-specific values are desired. We used it with a new CO<sub>2</sub> calibration system to account for isotopic differences among the primary CO<sub>2</sub> standards that define the WMO X2007 CO<sub>2</sub> in air calibration scale and between the primary standards and standards in subsequent levels of the calibration hierarchy. The new calibration system uses multiple laser spectroscopic techniques to measure ~~mole fractions amount of substance fractions (in mole fractions units)~~ of the three major CO<sub>2</sub> isotopologues (<sup>16</sup>O<sup>12</sup>C<sup>16</sup>O, <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O, and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O<sup>18</sup>O) individually. The three measured values are then combined into total CO<sub>2</sub> (accounting for the rare unmeasured isotopologues),  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  values. The new calibration system significantly improves our ability to transfer the WMO CO<sub>2</sub> calibration scale with low uncertainty through our role as the World Meteorological Organization Global Atmosphere Watch Central Calibration Laboratory for CO<sub>2</sub>. Our current estimates for reproducibility of the new calibration system are  $\pm 0.01$   $\mu\text{mol mol}^{-1}$  CO<sub>2</sub>,  $\pm 0.2$  ‰  $\delta^{13}\text{C}$ , and  $\pm 0.2$  ‰  $\delta^{18}\text{O}$ , all at 68 % confidence interval (CI).

## 1 Introduction

Long-term atmospheric monitoring of the greenhouse gases relies on a stable calibration scale to be able to quantify small spatial gradients and temporal trends. Small changes in trends and spatial gradients result from realignments in the strengths of emissions (“sources”) and removals (“sinks”) of the greenhouse gases. Inconsistent scale propagation to atmospheric measurements would give biased results from one monitoring station or network to the next that would be attributed incorrectly to sources/sinks by atmospheric transport models. Preventing biased results from various national monitoring networks enables improved understanding of the carbon cycle and its response to

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human intervention and climate change. It has now become even more important as countries have pledged emissions reductions. The capability to independently and transparently verify emission reductions could be helpful for creating trust in the agreements.

The World Meteorological Organization Global Atmosphere Watch (WMO GAW) program facilitates cooperation and data sharing among participating national monitoring programs. Atmospheric data collected over small regional scales is difficult to interpret without global coverage that provides boundary conditions and also insight into influences outside of the region. WMO GAW sets stringent compatibility goals so that measurements from independent laboratories can be combined in scientific studies. This greatly enhances the value of the individual data sets since it allows processes occurring within the region to be better distinguished from processes external to that region. In combining data sets it is imperative that systematic biases between the monitoring networks be small enough that they do not influence scientific interpretation of patterns and strengths of sources and sinks. For CO<sub>2</sub>, the consensus of the scientific community is that network biases should be below 0.1 μmol mol<sup>-1</sup> in the Northern Hemisphere but less than 0.05 μmol mol<sup>-1</sup> in the Southern Hemisphere where atmospheric gradients are smaller (WMO, 2016). One initial requirement to accomplishing this network compatibility goal is that measurements are comparable, that is each independent laboratory uses a single common calibration scale. The use of a single calibration scale makes spatial gradients and temporal changes insensitive to large components in the full uncertainty budget of the scale itself. The calibration scale must be maintained indefinitely to ensure that measurements from various organizations are compatible and that measurements over long time scales can be directly compared to infer rates of changes. The WMO GAW has designated a single laboratory as the Central Calibration Laboratory (CCL) whose mission is to maintain a stable reference scale over time and to disseminate it to other organizations with very low uncertainty (WMO, 2016). The WMO GAW program has two ways to help individual laboratories maintain close ties to the WMO scale. One is a “round-robin” comparison where calibrated cylinders are sent from the CCL to individual laboratories. The values assigned by the CCL are unknown to the laboratories, and they measure them as unknowns. At the end all values are compared with the values assigned by the CCL. This occurs once every few years. The second method is the establishment of several World Calibration Centers (WCC). Each of them provides assistance in their own region with general quality control of air measurements and calibrations.

The WMO X2007 CO<sub>2</sub> in air calibration scale is maintained and propagated by the National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division (NOAA) in its role as the WMO GAW CCL for CO<sub>2</sub>. The scale is defined by 15 primary standards covering the range 250 – 520 μmol mol<sup>-1</sup>. The primary standards are modified real air standards made in the early 1990's by filling cylinders with dried (H<sub>2</sub>O < 2 μmol mol<sup>-1</sup>) natural air at Niwot Ridge, CO, USA, a remote site at approximately 3040 masl in the Rocky Mountains. It typically is exposed to clean tropospheric air and is only occasionally influenced by local sources. CO<sub>2</sub> abundances of the primary standards were adjusted either by scrubbing CO<sub>2</sub> from a portion of the natural air using a trap with sodium hydroxide coated silica to lower the CO<sub>2</sub> or by spiking with a mixture of CO<sub>2</sub> in air (approximately 10%) to raise it. This differs slightly from the current practice of targeting lower than local ambient CO<sub>2</sub> by diluting

with ~~ultra-high-purity-zero~~ultrapure air, CO<sub>2</sub> nominally < 1 μmol mol<sup>-1</sup> (Scott Marrin Inc., Riverside CA, USA) (Kitzis, 2009).

The assigned values of the primary standards come from repeated (approximately every two years) manometric determinations of the primary standards. The manometer, ~~an absolute measurement method~~, described fully in Zhao et al. (1997), essentially measures the CO<sub>2</sub> ~~amount of substance fraction (mole fraction) in units of mole fraction (X<sub>CO2</sub>)~~ by accurate measurement of pressure and temperature (~~both traceable to SI~~) of a whole air sample and then of pure CO<sub>2</sub> extracted from the whole air sample in fixed volumes. The manometer is enclosed in an oven capable of maintaining a constant temperature (within ±0.01 °C). A 6 L volume borosilicate glass bulb (the large volume) is flushed with the dried whole air sample (dew point < -70 °C) and the pressure and temperature are measured after the large volume temperature equilibrates with the oven. CO<sub>2</sub> plus N<sub>2</sub>O and trace amounts of H<sub>2</sub>O are cryogenically extracted from the whole air sample using two liquid nitrogen cold traps. CO<sub>2</sub> and N<sub>2</sub>O are then cryogenically distilled from H<sub>2</sub>O and transferred to a ~10 mL cylindrical glass vessel (the small volume). Pressure and temperature of the small volume are measured after the oven temperature has stabilized following the transfer. ~~The volume ratio of the small to large volumes, determined by an off-line sequential volume expansion experiment, is used with the measured temperatures and pressures to calculate the ratio of moles CO<sub>2</sub> (corrected for the N<sub>2</sub>O) to total moles of air in the sample using the virial equation of state. Uncertainty of the method is approximately ±0.1 μmol mol<sup>-1</sup> (68 % CI) at 400 μmol mol<sup>-1</sup> (Zhao et al., 2006, Brad-Hall, et al., in preparation-personal communication).~~

~~The subject of this paper is the transfer of the scale to lower level standards and its uncertainty. We do not discuss the total uncertainty of the primary scale itself. It is described in a separate paper (Hall et al., in preparation).~~ The transfer of the scale from primary to secondary standards and hence to tertiary standards (which are used as working standards by NOAA and delivered to other organizations) has been done historically using nondispersive infrared absorption spectroscopy (NDIR). The secondary standards are used to prolong the lifetime of the primary standards. The current primary standards have been in use for nearly 25 years and provide a consistent scale over that time period. All measurements by NOAA and WMO GAW contributing programs are directly traceable to this single set of primary standards through a strict hierarchy of calibration.

The transfer of the scale from primary to secondary standards has typically been done using a subset of 3 or 4 primary standards rather than the entire set of 15 primary standards. This was done because we wanted to perform a local curve fit of the non-linear NDIR response while also minimizing use of the primary standards. The subset of primary standards chosen was a function of the expected CO<sub>2</sub> ~~abundance~~ in the secondary standards and was designed to closely bracket the expected values with a small range of CO<sub>2</sub> in the primary standards. The relatively large uncertainty of the individual manometric assigned values would potentially introduce significant biases due to the use of subsets of primary standards. To prevent these biases, the individual manometrically assigned values of the primary standards were corrected based on the residuals to a consistency fit of almost all primary standards (usually without the highest and the lowest primary) run on the NDIR. The re-assigned values (average manometer value minus the residual) were assumed to be the best assigned value for the primary standards. This in theory

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**Comment [AMC2]:** Pieter, check this wording and change if you think it should be different. This is a correct description. The equation of state, with known pressures, temperatures, and a volume ratio, results in a ratio of number of moles of gas in the large and in the small volume.

**Comment [pt3]:** We need to state this clearly up front. There was some confusion among reviewers about it.

should allow the use of subsets of the primary standards when transferring the scale from primary to secondary. In practice, as will be shown, there are still possible biases due to the grouping of primary standards based on expected CO<sub>2</sub> of the secondary standards. Tertiary standards were calibrated similarly against closely spaced subsets of secondary standards that bracketed the expected values of the tertiary standards.

5 New analytical methods developed over the last several years have greatly improved the ability of monitoring stations to measure CO<sub>2</sub>. These new analytical techniques and improved diligence of monitoring network staff are pushing the uncertainties of measurements lower and improving the network compatibility. Current [scale](#) reproducibility [of standards](#) using the NDIR calibration system is 0.03 μmol mol<sup>-1</sup> (68% CI) ("Carbon Dioxide WMO Scale", 2017). This is a significant component of the targeted 0.1 μmol mol<sup>-1</sup> (or 0.05 μmol mol<sup>-1</sup> in the 10 Southern Hemisphere) network compatibility goal (WMO, 2016). Improvements in the scale propagation uncertainty would help monitoring programs achieve the compatibility goals. We have therefore undertaken to improve our calibration capabilities and to address key uncertainty components of the scale transfer. These key components are the reproducibility of the scale transfer, the potential for mole fraction dependent biases, and [of](#) ~~most importance to this paper~~ the potential issues [we describe in this paper](#) relating to the isotopic composition of 15 the primary standards and subsequent standards in the calibration hierarchy.

## 2 Isotopic influence on CO<sub>2</sub> measurement

The WMO CO<sub>2</sub> mole fraction scale is defined as the number of molecules of CO<sub>2</sub> per mole of dry air, without regard to its isotopic composition. An isotopologue of CO<sub>2</sub> has a specific isotopic composition. The five most abundant 20 CO<sub>2</sub> isotopologues, in order of abundance, are: <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O, <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O, <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O, <sup>16</sup>O<sup>12</sup>C<sup>17</sup>O, and <sup>18</sup>O<sup>12</sup>C<sup>18</sup>O (referred to in equations in this work by [the HITRAN \(Rothman, 2013\) shorthand notations](#) 626, 636, ~~826628~~, ~~726627~~, and ~~836-638~~ respectively). For CO<sub>2</sub> the two oxygen positions are equivalent due to the symmetry of the molecule so the position of the oxygen isotopes does not matter. The abundance of the radioactive <sup>14</sup>C relative to <sup>12</sup>C is ~10<sup>-12</sup>; which is too small to be of significance in this context. Analysts need to take 25 into account differences in the relative sensitivity of their analyzers to different isotopologues (or isotopomers, see below) as well as differences in the isotopic composition of sample and standard gases.

Isotopic composition is typically measured by isotope ratio mass spectroscopy (IRMS) and is reported as the difference in the minor isotope to major isotope ratio (i.e. <sup>13</sup>C/<sup>12</sup>C) from the ratio of an accepted standard reference material, ~~typically in units of per mil (‰)~~. For example, the <sup>13</sup>C ~~isotopic isotope delta~~ value (δ<sup>13</sup>C) is defined as:

$$\delta^{13}\text{C} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Standard}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Standard}}} + 1000$$

(1)

Where  $(^{13}\text{C}/^{12}\text{C})_{\text{sample}}$  and  $(^{13}\text{C}/^{12}\text{C})_{\text{standard}}$  are the  $^{13}\text{C}$  to  $^{12}\text{C}$  isotope abundance ratios for the sample and the standard reference material respectively. The international accepted scale for  $^{13}\text{C}$  is the Vienna Pee Dee Bellemnite (VPDB) scale, realized as calcium carbonate. Oxygen isotopic ratios ( $^{18}\text{O}/^{16}\text{O}$  or  $^{17}\text{O}/^{16}\text{O}$ ) in  $\text{CO}_2$  are described with a similar isotope delta notation relative to an accepted reference material. Isotope delta values for carbon and oxygen are typically reported in units of per mil (‰) by multiplying Eq. (1) by 1000. For many applications, the  $^{17}\text{O}$  isotope is not actually measured but is assumed to follow a mass dependent relationship with  $^{18}\text{O}$  where  $\delta^{17}\text{O} \approx 0.528 * \delta^{18}\text{O}$ . This approximation is adequate for the purpose of defining the oxygen isotopic effects on atmospheric  $\text{CO}_2$  measurements. For more detailed descriptions of this relationship see Santrock et al. (1985), Assonov and Brenninkmeijer (2003), Brand et al. (2010) and references therein. Oxygen isotopes can be related to either Vienna Standard Mean Ocean Water (VSMOW) or to VPDB- $\text{CO}_2$ , with the latter commonly used in the atmospheric  $\text{CO}_2$  community. The VPDB- $\text{CO}_2$  scale relates to the  $\text{CO}_2$  gas evolved from the calcium carbonate material itself during the reaction with phosphoric acid and accounts for oxygen fractionation that occurs during the reaction (Swart et al., 1991). In this paper all oxygen isotope values are referenced to the VPDB- $\text{CO}_2$  scale unless otherwise noted.

$\text{CO}_2$  analysers are not equally sensitive to the isotopologues of  $\text{CO}_2$ . For example, gas chromatography where  $\text{CO}_2$  is reduced to  $\text{CH}_4$  and detected with a flame ionization detector (GC-FID) (Weiss, 1981) is equally sensitive to all isotopologues whereas laser based absorption techniques that measure an absorption line from the single major  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  isotopologue are blind to all of the minor isotopologues. NDIR instruments are much more complicated in their response to the various minor isotopologues of  $\text{CO}_2$ . Most NDIR analyzers use an optical band pass filter to limit the wavelengths of light reaching the detectors. These filters often exclude part of the absorption bands of the minor isotopologues (e.g. Tohjima et al. 2009), but are more sensitive to the  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$  lines within the pass band because absorption of the much stronger  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  lines is partially saturated. The width and shape of the transmission window of the filter is generally not identical between instruments. Tohjima et al. (2009) found significant differences in the sensitivity to the minor isotopologues between three different LI-COR NDIR analyzers. In addition, Lee et al. (2006) found the response of a Siemens ULTRAMAT 6E NDIR analyzer to be almost completely insensitive to the minor isotopologues.

The range of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  encountered in the background atmosphere ( $\sim -7.0$  to  $-9.0$  ‰  $\delta^{13}\text{C}$  and  $2$  to  $-2$  ‰  $\delta^{18}\text{O}$ ) is too small to cause a significant bias on the total  $\text{CO}_2$  measurements with any of these techniques. At  $400 \mu\text{mol mol}^{-1}$  total  $\text{CO}_2$ , neglecting  $\delta^{13}\text{C}$  values leads to errors of  $0.0044 \mu\text{mol mol}^{-1}$  per 1 ‰, and neglecting  $\delta^{18}\text{O}$  values leads to errors of  $0.0018 \mu\text{mol mol}^{-1}$  per 1 ‰. A problem arises however when standards with significantly different isotopic

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Comment [pt5]: Good. Coplen's notation guidelines say that the space needs to be there.

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compositions from the atmosphere are used to calibrate instruments that have partial or no sensitivity to the minor isotopologues. This occurs when standards are made from fossil fuel sourced CO<sub>2</sub> (~~such as often~~ from combustion of oil or natural gas) which results in significant depletion in <sup>13</sup>C and <sup>18</sup>O (Andres et al., 2000; Schumacher et al., 2011).

In the past we have neglected the dependency of the NDIR response to isotopic composition during scale transfer. The manometer measurement of the primary standards is not sensitive to isotopic composition, all isotopologues are included in the total. However, the primary standards have a range of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values (-7 ‰ to -18 ‰  $\delta^{13}\text{C}$  and 0 to -15 ‰  $\delta^{18}\text{O}$ ) with higher CO<sub>2</sub> standards being more depleted due to the use in the early 1990's of a spike gas that was isotopically depleted. This probably introduced a slight bias in the results when the scale was transferred to secondary standards (often with ambient isotopic values) via NDIR measurements. It was assumed that the bias was small relative to the measurement noise in the NDIR analysis.

We intend to provide standards to the atmospheric monitoring community with isotopic values similar to the background atmosphere by using natural air whenever possible. To adjust the CO<sub>2</sub> content in the natural air standards, the current practice is to dilute using essentially CO<sub>2</sub> free natural air (~~ultra high purity~~ ultrapure air, Scott Marrin, Inc. Riverside CA, USA) or enrich using high CO<sub>2</sub> (10 – 20 %) spike gases with  $\delta^{13}\text{C} \approx -9 \text{ ‰}$  and  $\delta^{18}\text{O} \approx -30 \text{ ‰}$ . The  $\delta^{13}\text{C}$  isotopic composition of the resulting mixture is not significantly different from ambient background air. Currently, urban air highly enriched in CO<sub>2</sub> would have  $\delta^{13}\text{C}$  values ~~significantly~~ lower than the spiked standards of similar CO<sub>2</sub> made by us. However, the WMO scale is designed to track the slow isotopic depletion of background air as the global burden of CO<sub>2</sub> increases over the next decades due to burning of fossil fuels rather than approximate the composition of air influenced by local emission sources. We started using the isotopically correct spike gases in November 2011, ~~prior to this the spike gas was fossil fuel sourced and was depleted in  $\delta^{13}\text{C}$ .~~ Background atmospheric  $\delta^{18}\text{O}$  is not well matched with the current spike gases or the historical spike gases ( $\delta^{18}\text{O} \approx -30$  to  $-40 \text{ ‰}$ ) and does result in depleted  $\delta^{18}\text{O}$  values in cylinders that are spiked to targeted values above local ambient values. It is also our goal to provide calibration results that incorporate a characterization of the main isotopologues and accounts for isotopic differences among the primary standards and between the primary standards and measured cylinders through the calibration hierarchy as proposed by Loh et al. (2011). ~~This will ensure that the transfer of the WMO scale by distributing calibrated cylinders is not biased by isotopic differences and will provide users of the distributed cylinders the information required to account for isotopic effects on their own measurement systems. Doing this will ensure that the transfer of the WMO scale by distributing calibrated cylinders is not biased by isotopic differences and will provide the users of the distributed standards the information required to properly address isotopic issues when making ambient air measurements.~~

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### 3 Two different ways to define isotopic ratios and notation conventions

In order to estimate the influence of isotopic composition differences on CO<sub>2</sub> measurements and to develop a precise method for calibration transfer that takes isotopic composition into account we first introduce the “mole fraction”

notation for isotopic ratios in molecules. The conventional definitions of atomic isotopic ratios ( $r$ ) are:

$$^{13}r \stackrel{\text{def}}{=} \frac{^{13}\text{C}}{^{12}\text{C}} \quad ^{18}r \stackrel{\text{def}}{=} \frac{^{18}\text{O}}{^{16}\text{O}} \quad \text{etc.}$$

As used here the symbols  $^{13}\text{C}$ ,  $^{18}\text{O}$ , etc. stand for amounts/bundances. It will simplify derivations below if we ~~re-~~  
~~define~~use isotopic ratios as amount/bundance ratios relative to all carbon, oxygen, etc., similar to mole fractions in air. We give these re-defined-isotope-amount fractions/ratios the symbol “ $x$ ” instead of “ $r$ ”.

$$^{13}x \stackrel{\text{def}}{=} \frac{^{13}\text{C}}{^{12}\text{C} + ^{13}\text{C}} \quad ^{18}x \stackrel{\text{def}}{=} \frac{^{18}\text{O}}{^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O}} \quad ==> \quad ^{16}x = 1 - \frac{^{17}\text{O} + ^{18}\text{O}}{^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O}}$$

These definitions lead to the following relationships:

$$^{13}x = \frac{^{13}r}{1 + ^{13}r} \quad ^{13}r = \frac{^{13}x}{1 - ^{13}x} \quad (2)$$

The equivalents for oxygen are:

$$^{17}x = \frac{^{17}r}{1 + ^{17}r + ^{18}r} \quad ^{17}r = \frac{^{17}\text{O}}{^{16}\text{O}} = \frac{^{17}\text{O}/(^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O})}{^{16}\text{O}/(^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O})} = \frac{^{17}x}{1 - ^{17}x - ^{18}x} \quad (3)$$

and similarly for  $^{18}x$  and  $^{18}r$ .

From here on we will abbreviate ~~VPDB and~~ VPDB-CO<sub>2</sub> as VPDB to keep the notation manageable. Using Table 1 and these conventions gives us

$$^{13}x_{\text{VPDB}} = 0.0110564 \quad (4a)$$

$$^{17}x_{\text{VPDB}} = 395.11 \cdot 10^{-6} / (1 + 2088.35 \cdot 10^{-6} + 395.11 \cdot 10^{-6}) = 394.1 \cdot 10^{-6} \quad (4b)$$

$$^{18}x_{\text{VPDB}} = 2088.35 \cdot 10^{-6} / (1 + 2088.35 \cdot 10^{-6} + 395.11 \cdot 10^{-6}) = 2083.2 \cdot 10^{-6} \quad (4c)$$

Isotopic ratio measurements have always been expressed in terms of their (typically) small difference from the standard reference materials, in the so-called delta notation:

$$^{13}\delta \stackrel{\text{def}}{=} (^{13}r - ^{13}r_{\text{VPDB}}) / ^{13}r_{\text{VPDB}} = ^{13}r / ^{13}r_{\text{VPDB}} - 1, \text{ so that } ^{13}r - ^{13}r_{\text{VPDB}} = ^{13}r_{\text{VPDB}} \cdot ^{13}\delta \quad (5)$$

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**Comment [pt11]:** Now we are following Not sure if we should use a new definition for VPDB

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and similarly for  $^{17}\delta$  and  $^{18}\delta$

By analogy we define for the amount fractions ratios R:

$$^{13}\Delta \stackrel{\text{def}}{=} (^{13}x - ^{13}x_{\text{VPDB}})/^{13}x_{\text{VPDB}} = ^{13}x/^{13}x_{\text{VPDB}} - 1, \text{ so that } ^{13}x - ^{13}x_{\text{VPDB}} = ^{13}x_{\text{VPDB}} ^{13}\Delta \quad (6)$$

and similarly for  $^{17}\Delta$  and  $^{18}\Delta$

In the above (Eqs. (5) and (6)) and the rest of this work we will express  $\delta$  and  $\Delta$  as small numbers, not in the “permil” (‰) notation, in which every delta value is multiplied by 1000. For example  $\delta=0.020$  would normally be written as 20 permil or 20 ‰. To keep the notation economical and the paper more readable we introduced simplified notations such as  $^{13}r$  and  $^{13}\delta$  instead of  $r(^{13}\text{C}/^{12}\text{C})$  and  $\delta^{13}\text{C}$  in equations. This produces no ambiguities. In addition, in this paper we need to distinguish between isotope-amount fractions *within*  $\text{CO}_2$  (denoted “ $x$ ” above in accordance with Coplen (2011)) of isotopes (and isotopologues) from mole fraction in air. We normally denote mole fraction in air by “ $x$ ” or “ $X$ ”, but here we use “ $y$ ” (in accordance with notation recommendations for gas mixtures (IUPAC, 2006)) to distinguish mole fraction in air from isotope or isotopologue amount fraction. For example,  $x(636)$  is the amount fraction of  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$  to all isotopologues of  $\text{CO}_2$  whereas  $y(636)$  is the mole fraction of the  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$  isotopologue in air.

#### 4 Fractional abundances of isotopologues in molecules.

Converting measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values into  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$  (~~denoted as 636~~) and  $^{18}\text{O}^{13}\text{C}^{16}\text{O}$  (~~826~~) isotopologue abundances is not straightforward due to the rare  $^{17}\text{O}^{12}\text{C}^{16}\text{O}$  (~~726~~) and doubly substituted isotopologues. Isotope ratio mass spectrometry (IRMS) determines  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values by measuring molecular mass 45/44 and ~~mass~~ 46/44 ratios, with appropriate corrections for interfering masses, relative to a standard reference material. These mass ratios can be used with the accepted isotopic ratios of the standard reference materials to approximate the abundance as amount mole-fraction ( ~~$xX$~~ ) of the three main isotopologues in  $\text{CO}_2$  using:

$$x(636) \cong ^{13}x, \quad x(628) \cong 2 \cdot ^{18}x, \quad x(626) \cong 1 - x(636) - x(628) \quad (7)$$

The oxygen abundance ratio is multiplied by a factor of two in Eq. (~~87~~) to convert the amount fractions isotopic ratios from atomic abundance (i.e.  $^{18}\text{O}/^{16}\text{O}$ ) into molecular abundance. The approximations in Eqs. (7) (~~9~~) ignore the contribution of the oxygen isotopes to  ~~$xX(636)$~~  and of  $^{13}\text{C}$  to  ~~$xX(826628)$~~ , as well as the portion of the total composed of the rare isotopologues. Depending on the level of uncertainty desired this may or may not be acceptable. As the WMO GAW CCL for  $\text{CO}_2$ , NOAA is obligated to minimize biases in the  $\text{CO}_2$  calibration scale, and therefore we will correctly account for the apportionment of  $\text{CO}_2$  through all isotopologues. The same technique was developed independently by Flores et al. (2017) for use in calibrating spectroscopic instruments for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements. Here our focus is on total  $\text{CO}_2$  measurements that account for isotopic differences between standards.

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Comment [AMC13]: I think we may want to include that  $13x$  needs to be multiplied by  $y_{\text{CO}_2}$ . So  $x(636) \sim 13x \cdot y_{\text{CO}_2}$ . Not here, because we are talking about amount fractions within total  $\text{CO}_2$ .

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We start by assuming a purely statistical distribution of  $^{13}\text{C}$ ,  $^{18}\text{O}$ , and other atoms when putting together a molecule starting from atomic ~~amount fractions~~ ~~abundance ratios~~ as given ~~for standard reference materials in~~ (Table 1), namely, that the probability of picking a particular isotope is not affected by what is picked before or later. In general the other picks can affect the probability a little (called “clumped” isotopes), so that the thermodynamic abundances are slightly different from the statistical distribution. We will ignore that ~~for now~~, and construct a purely statistical baseline distribution ~~for the reference~~. ~~It is important to note that thermodynamic and kinetic fractionation effects are reflected in actual measured delta values and fractionation factors relative to the agreed upon reference material that standard.~~ Thus the probability of picking a  $^{13}\text{C}$  atom for a carbon position is defined as simply  $x_a$  ~~(the abundance ratio of  $^{13}\text{C}$  to total carbon)~~. However, a molecule may have more than one position for C, O, N, etc. For example, suppose there are N chemical positions for a particular atom in a molecule and we want to define the probability of M of those positions being filled with one particular isotope (denoted isotope a). If the locations of the M, as a subset of N, do not matter, as is the case for symmetrical molecules like  $\text{CO}_2$  and  $\text{CH}_4$ , we could call the N positions equivalent. In that case the probability is

$$P = \binom{N}{M} * x_a^M * x_b^{N-M} \quad (408)$$

$x_a$  is the ~~amount fraction~~ of isotope a,  $x_b$  is the ~~amount fraction abundance ratio~~ of other isotopes ( $x_b = 1 - x_a$ ). The first term in ~~equation 10-Eq. (8)~~ is the statistical weight which equals the number of combinations (a statistical term, the order of picking the M does not matter) of M out of N, given as

$$\frac{N!}{M!(N-M)!} \stackrel{\text{def}}{=} \binom{N}{M} \quad (449)$$

$N!$  is the factorial notation,  $N! \stackrel{\text{def}}{=} 1 * 2 * 3 * \dots * (N-1) * N$ , with the special case  $0! \stackrel{\text{def}}{=} 1$

Example: there are two equivalent positions for a single  $^{18}\text{O}$  in  $\text{CO}_2$ , namely  $^{18}\text{O}^{12}\text{C}^{16}\text{O}$  and  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ , jointly denoted as “~~826628~~” (one  $^{18}\text{O}^{16}\text{O}$ , one  $^{12}\text{C}$ , one  $^{16}\text{O}^{18}\text{O}$ ), so that the statistical weight is

$$\binom{2}{1} = \frac{2!}{1! * (2-1)!} = 2.$$

Or for methane, a single or double substitution of deuterium ( $^2\text{H}$  ~~or D~~) for  $^1\text{H}$  has respective statistical weights:

$$\binom{4}{1} = \frac{4!}{1! * (4-1)!} = 4 \quad \binom{4}{2} = \frac{4!}{2! * (4-2)!} = 6$$

It should be noted that whether positions can be considered equivalent depends on the symmetry of the molecule and the measurement method. For example for nitrous oxide the two positions for N in NNO would be equivalent when mass 45 (one  $^{14}\text{N}$ , one  $^{15}\text{N}$ , one  $^{16}\text{O}$ ) is measured in a mass spectrometer but they are not when an optical absorption method is used because the spectrum of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  is different from  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ . In the latter case we need to keep

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separate track of the probabilities, denoted below as “P”, of these two isotopomers. Isotopomers have the same number of specific isotopes, but they differ in their position in the molecule.

The probability for any particular CO<sub>2</sub> isotopologue is the product of the probability of picking the carbon isotope and the probability of picking the oxygen isotopes. Each of these probabilities is determined using Eq. (408). For example, the probability for the <sup>18</sup>O<sup>13</sup>C<sup>16</sup>O isotopologue is the probability of picking one <sup>13</sup>C isotope for one carbon position times the probability of picking one <sup>18</sup>O isotope for one of the two oxygen positions and one <sup>16</sup>O for the other.

The equations below give the probabilities for individual CO<sub>2</sub> isotopologues. When the isotopic compositions of the standard reference materials (VPDB in Table 1) are filled in we obtain the numbers after the “=>” sign.

$$P(626) = (1 - x^{13}) * (1 - x^{17} - x^{18})^2 \Rightarrow 0.98404985 = 1 - 0.01595015 \quad (410)$$

$$P(636) = x^{13} * (1 - x^{17} - x^{18})^2 \Rightarrow 0.011001688 \quad (411)$$

$$P(82628) = (1 - x^{13}) * 2 * x^{18} * (1 - x^{17} - x^{18}) \Rightarrow 0.0041101273 \quad (412)$$

The sum of the above three major abundances is  $0.99916166 = 1 - 0.00083834$

$$P(72627) = (1 - x^{13}) * 2 * x^{17} * (1 - x^{17} - x^{18}) \Rightarrow 0.000777554 \quad (413)$$

The sum of the above four major abundances is  $0.99993922 = 1 - 0.00006078$

$$P(83638) = x^{13} * 2 * x^{18} * (1 - x^{17} - x^{18}) \Rightarrow 4.59513 \cdot 10^{-5}$$

and so on, with progressively smaller probabilities. The sum of all probabilities equals 1, which was verified digitally in double precision. This example was for VPDB, but in any population of CO<sub>2</sub> molecules, (i.e. in a sample or standard cylinder) probabilities determined from the isotope-amount fractions of the population equate to the amount fraction-fractional abundance of each isotopologue.

## 5 An expression for potential effects of isotopic mismatches on measurements of CO<sub>2</sub>

In this section we derive some practical expressions for errors/biases, and corrections, resulting from isotopic mismatches if they are ignored, for the case of CO<sub>2</sub>. Similar considerations apply to other greenhouse gases such as CH<sub>4</sub>, N<sub>2</sub>O, etc. Such corrections can be generally applied to CO<sub>2</sub> measurements if desired. The unknown quantity of CO<sub>2</sub>-in-air that we intend to measure is called “measurand”. It can be a real air sample or an intermediate transfer standard. The errors/biases typically depend on the instrument used because an instrument may be sensitive to just

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Comment [pt14]: We have mentioned this already, we don't need to repeat it.

one isotopologue, or equally sensitive to all isotopologues, or something in between. Here we give an example for an instrument that quantifies the mole fraction of total CO<sub>2</sub> in air, denoted  $x_{\text{CO}_2}$ , by measuring only one isotopologue, namely <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O. We normally denote the species mole fraction or number fraction by “ $x$ ” or “ $X$ ”, but here we want to distinguish it from isotope amount fractions by using the symbol “ $x$ ” which is in accordance with notation recommendations for gas mixtures. We assume that the instrument is calibrated by a CO<sub>2</sub> standard with amount fractions or abundances  $^{13}\text{R}_{\text{PDB}}$ ,  $^{13}\text{x}_{\text{VPDB}}$  and  $^{18}\text{R}_{\text{PDB}}$ ,  $^{18}\text{x}_{\text{VPDB}}$  of the two main isotopologues, corresponding to the international VPDB reference points for <sup>13</sup>C and <sup>18</sup>O. In almost all cases deviations of  $^{17}\text{R}$ ,  $^{17}\text{x}$  from VPDB are tightly correlated with deviations of  $^{18}\text{R}$ ,  $^{18}\text{x}$  from VPDB. The deviation of total CO<sub>2</sub> from being proportional to P(626) due to inconsistencies of  $^{13}\text{R}$ ,  $^{13}\text{x}$ ,  $^{17}\text{R}$ ,  $^{17}\text{x}$ ,  $^{18}\text{R}$ ,  $^{18}\text{x}$  between the measurand and VPDB, using Eq. (429810), is

$$\Delta P(626) \stackrel{\text{def}}{=} P(626) - P_{\text{VPDB}}(626) =$$

$$\frac{\partial P(626)}{\partial ^{13}\text{R}} (^{13}\text{R} - ^{13}\text{R}_{\text{VPDB}}) + \frac{\partial P(626)}{\partial ^{17}\text{R}} (^{17}\text{R} - ^{17}\text{R}_{\text{VPDB}}) + \frac{\partial P(626)}{\partial ^{18}\text{R}} (^{18}\text{R} - ^{18}\text{R}_{\text{VPDB}})$$

(14)

The above are the first terms of a Taylor expansion around  $P_{\text{VPDB}}(626)$ . Inserting the first derivatives and using Eq. (6) gives:

$$\Delta P(626) = -(1 - ^{17}\text{R}_{\text{VPDB}} - ^{18}\text{R}_{\text{VPDB}})^2 (^{13}\text{R}_{\text{VPDB}} ^{13}\Delta) +$$

$$-2(1 - ^{13}\text{R}_{\text{VPDB}})(1 - ^{17}\text{R}_{\text{VPDB}} - ^{18}\text{R}_{\text{VPDB}}) (^{17}\text{R}_{\text{VPDB}} ^{17}\Delta + ^{18}\text{R}_{\text{VPDB}} ^{18}\Delta)$$

(15)

If <sup>13</sup>Δ is positive the air to be measured has a higher <sup>13</sup>C/<sup>12</sup>C ratio than VPDB. Therefore P(626) is slightly lower than it is for VPDB, and the relative correction in the mole fraction assigned to the measured air will have to be positive, of opposite sign to the relative error of P(626):

$$\frac{\Delta x_{\text{CO}_2}}{x_{\text{CO}_2}} = -\frac{\Delta P(626)}{P(626)} = \frac{^{13}\text{R}_{\text{VPDB}} ^{13}\Delta}{(1 - ^{13}\text{R}_{\text{VPDB}})} + \frac{2(^{17}\text{R}_{\text{VPDB}} ^{17}\Delta + ^{18}\text{R}_{\text{VPDB}} ^{18}\Delta)}{(1 - ^{17}\text{R}_{\text{VPDB}} - ^{18}\text{R}_{\text{VPDB}})}$$

(16)

We note here that we could have used a <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O line for quantifying  $x_{\text{CO}_2}$ , but an analogous derivation for ΔP(636)/P(636) shows that it is 90 times more sensitive to isotopic errors or mismatches.

Using Eqs. (2) and (3) gives

$$\frac{\Delta x_{\text{CO}_2}}{x_{\text{CO}_2}} = ^{13}\text{r}_{\text{VPDB}} ^{13}\Delta + 2(^{17}\text{r}_{\text{VPDB}} ^{17}\Delta + ^{18}\text{r}_{\text{VPDB}} ^{18}\Delta)$$

(176)

Generally, one is not making atmospheric CO<sub>2</sub> measurements with standards that have isotopic abundances for C and O exactly like VPDB. Because the linear Eq. (4617) applies to the measurement of a transfer standard itself as well as to an air sample, we can give an expression for corrections to be made when the standard (subscript “st”) has an isotopic composition different from air but not equal to VPDB:

**Comment [pt15]:** Reference: IUPAC, Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”) (1997)

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$$\frac{\Delta \chi_{\text{CO}_2}}{\chi_{\text{CO}_2}} = {}^{13}\text{r}_{\text{VPDB}}({}^{13}\Delta_{\text{air}} - {}^{13}\Delta_{\text{st}}) + 2({}^{17}\text{r}_{\text{VPDB}}({}^{17}\Delta_{\text{air}} - {}^{17}\Delta_{\text{st}}) + {}^{18}\text{r}_{\text{VPDB}}({}^{18}\Delta_{\text{air}} - {}^{18}\Delta_{\text{st}}))$$

(187)

In the Appendix we derive the following very close approximation to Eq. (187) in which the  $\Delta$  values have been replaced by the familiar  $\delta$  values:

$$\Delta \chi_{\text{CO}_2} = \chi_{\text{CO}_2} [0.0110644({}^{13}\delta_{\text{air}} - {}^{13}\delta_{\text{st}}) + 2 * 0.0023({}^{18}\delta_{\text{air}} - {}^{18}\delta_{\text{st}})]$$

(198)

This is an expression for  $\text{CO}_2$  corrections when only the  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  isotopologue is used to measure  $\chi_{\text{CO}_2}$ , and we are using VPDB scales. As an example, if we use a standard with  $\text{CO}_2$  made from natural gas, it could have  ${}^{13}\delta_{\text{st}} = -0.045$  and  ${}^{18}\delta_{\text{st}} = -0.017$  on the VPDB scales, whereas air has  ${}^{13}\delta_{\text{air}} \cong -0.008$  and  ${}^{18}\delta_{\text{air}} \cong 0.000$ . Assuming  $\chi_{\text{CO}_2} = 400 \mu\text{mol mol}^{-1}$ , then  $\Delta \chi_{\text{CO}_2} = 0.164 + 0.031 = 0.194 + 0.195 \mu\text{mol mol}^{-1}$ .  ${}^{13}\delta_{\text{air}}$  is higher than  ${}^{13}\delta_{\text{st}}$ , so that the  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  abundance of the standard is higher than assumed, resulting in the air measurement being too low. Therefore an upward correction is needed for  $^{13}\text{C}$  and likewise for  $^{18}\text{O}$ .

## 6 Practical calculations for definition and propagation of the $\text{CO}_2$ calibration scale

Equations (18) and (19) gives the correction required when only the  $^{16}\text{O}^{12}\text{C}^{16}\text{O}$  isotopologue is used to determine  $\chi_{\text{CO}_2}$  as a function of the isotopic differences between the sample and a single standard. However, most  $\text{CO}_2$  measurements are made vs a suite of standards that may have various isotopic compositions and the isotopic compositions may be a function of  $\text{CO}_2$  (as is the case for the primary  $\text{CO}_2$  standards used by the WMO GAW CCL). In this case the calibration curve that defines the response of the analyser may incorporate a systematic error making the idea of a simple “correction” impractical. Equations (18) and (19) can best be used to quickly estimate the potential offsets due to sample/standard isotopic differences but is not practical for making corrections when multiple standards are used. Therefore, we must instead use a calibration approach that fully accounts for the isotopic composition of the standards rather than using a post measurement correction.

A great advantage of our method is that it uses multiple standards covering a range of values to create a scale. “Scale contraction” can result from having a single standard reference, and mass spectrometer measurements have suffered from that. We do not have such “contraction” because we have a real scale over the full range of interest instead of a single point so that we can create a response curve for any analyzer. Secondly, having such isotopologue specific response curves over a large range also opens the possibility to make a new determination of the value of  $\epsilon^{13}\text{C}$  and  $\epsilon^{18}\text{O}$ . One could make for example 400 ppm and 800 ppm  $\text{CO}_2$  in air mixtures with their isotopic ratios

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~~close to the VPDB values. Then a small and well known amount of pure  $^{12}\text{C}$   $\text{CO}_2$  could be added to the 400 ppm standard so that its  $^{636}$  isotopologue mole fraction in air ends up close to, say, that of the 800 ppm mixture.~~

We have taken the approach of decomposing the total  $\text{CO}_2$  in the primary standards, as defined by manometric measurements, into individual isotopologue mole fractions in air based on measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are determined by IRMS by the Stable Isotope Laboratory, Institute of Arctic and Alpine Research, University of Colorado, Boulder (INSTAAR) on their own realization of the VPDB scales. The current scales used by INSTAAR were set using NBS-19 and NBS-20 (carbonates) and VSMOW, GISP and SLAP (waters) (Troler et al., 1996). These isotopologue specific mole fractions in air of the standards are used to calibrate laser-based spectroscopic instruments for the three major  $\text{CO}_2$  isotopologues ( $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ ,  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ , and  $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ ) individually. The three major isotopologues in unknown cylinders are measured relative to these isotopologue specific calibration curves. The isotopologue mole fractions in air of the unknowns are then recombined into total  $\text{CO}_2$  and conventional  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  values while properly accounting for the non-measured rare isotopologues.

~~A great advantage of our method is that it uses multiple standards covering a range of values to create a scale. "Scale contraction" can result from having extrapolating from a single standard reference, and mass spectrometer measurements have suffered from that. We do not have such "contraction" because we have a real scale calibrate with multiple standards over the full range of interest instead of using a single point so that we can create a response curve for any analyzer. Having such isotopologue specific response curves over a large range also opens the intriguing possibilities of making  $\text{CO}_2$  isotopic scales that are traceable to SI and improving our understanding of VPDB and its relation with LSVEC. This may be beyond the scope of our laboratory but we offer it as an interesting aside. Secondly, having such isotopologue specific response curves over a large range also opens the possibility to make a new determination of the value of  $(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}$ . One could make for example 400 ppm and 800 ppm  $\text{CO}_2$  in air mixtures with their isotopic ratios close to the VPDB values. Then a small and well known amount of pure  $^{12}\text{C}$   $\text{CO}_2$  could be added to the 400 ppm standard so that its  $^{636}$  isotopologue mole fraction in air ends up close to, say, that of the 800 ppm mixture. added needed to double the amount of 636 that corresponds to VPDB provides a measure of VPDB itself.~~

Suppose we have one or more instruments measuring each isotopologue ( $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ ,  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ ,  $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ ,  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  and perhaps also  $^{18}\text{O}^{13}\text{C}^{16}\text{O}$ ) individually. The response of the instrument(s) for each of the isotopologues needs to be calibrated separately. How often such calibrations need to be repeated depends on the instrument. For this purpose we need to have a series of reference gas standards with well defined total  $\text{CO}_2$  ( $x_{\text{CO}_2}$ ) and with known conventional  $\delta$ -values for the isotopic ratios. Equations (1210)-(1513) can be used to convert that information to the fractional abundances of the isotopologues, by first writing them in terms of conventional delta values by using relations (2) and (3) and by writing  $f_{\text{sample}}$  as  $f_{\text{VPDB}}(1+\delta)$  (see Eq. (5)).

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$$P(626) = \frac{1}{1 + {}^{13}r_{VPDB}(1 + {}^{13}\delta)} \frac{1}{[1 + {}^{17}r_{VPDB}(1 + {}^{17}\delta) + {}^{18}r_{VPDB}(1 + {}^{18}\delta)]^2}$$

(2049)

$$P(636) = \frac{{}^{13}r_{VPDB}(1 + {}^{13}\delta)}{1 + {}^{13}r_{VPDB}(1 + {}^{13}\delta)} \frac{1}{[1 + {}^{17}r_{VPDB}(1 + {}^{17}\delta) + {}^{18}r_{VPDB}(1 + {}^{18}\delta)]^2}$$

(219)

$$P(826628) = \frac{1}{1 + {}^{13}r_{VPDB}(1 + {}^{13}\delta)} \frac{2 * {}^{18}r_{VPDB}(1 + {}^{18}\delta)}{[1 + {}^{17}r_{VPDB}(1 + {}^{17}\delta) + {}^{18}r_{VPDB}(1 + {}^{18}\delta)]^2}$$

(224)

$$P(726627) = \frac{1}{1 + {}^{13}r_{VPDB}(1 + {}^{13}\delta)} \frac{2 * {}^{17}r_{VPDB}(1 + {}^{17}\delta)}{[1 + {}^{17}r_{VPDB}(1 + {}^{17}\delta) + {}^{18}r_{VPDB}(1 + {}^{18}\delta)]^2}$$

(232)

If  $\delta^{17}\text{O}$  has not been measured, we approximate  $\delta^{17}\text{O} = 0.528 * \delta^{18}\text{O}$  to determine the fractional abundances above.

10 The fractional abundances (Eqs. (2049)-(232)) are converted into mole fractions in dry air by multiplying with the total mole fraction of  $\text{CO}_2$  in dry air ( $X_{\text{CO}_2\text{CO}_2}$ ). The isotopologue mole fractions in air are written as  $X_y(626)$ , etc. In other words, we have  $X_y(626) = X_{\text{CO}_2\text{CO}_2} * P(626)$  and similar for all isotopologues.

A series of standards can in this way be used to calibrate the instrument response for each isotopologue individually. With these response functions we can then assign mole fractions in air to the isotopologues of the unknown gas mixtures that are being measured,  $X_y(626)_{\text{unk}}$ , etc.

Then we need to convert the measured isotopologue abundances—mole fractions of the unknown ( $X_y(626)_{\text{unk}}$ ,  $X_y(636)_{\text{unk}}$ , and  $X_y(628)_{\text{unk}}$ ) back to standard delta-notation using Eqs. (4920)-(2223) as follows:

$$\frac{X_y(636)_{\text{unk}}}{X_y(626)_{\text{unk}}} = \frac{P(636)}{P(626)} = {}^{13}r_{VPDB}(1 + {}^{13}\delta) \Rightarrow {}^{13}\delta = \frac{X_y(636)_{\text{unk}}}{{}^{13}r_{VPDB} * X_y(626)_{\text{unk}}} - 1$$

(243)

$$\text{and } \frac{X(826)_{\text{unk}}}{X(626)_{\text{unk}}} = \frac{P(826)}{P(626)} = 2 * \frac{{}^{18}r_{VPDB}(1 + {}^{18}\delta)}{[1 + {}^{17}r_{VPDB}(1 + {}^{17}\delta) + {}^{18}r_{VPDB}(1 + {}^{18}\delta)]} \quad (24)$$

$$\frac{X_y(826)_{\text{unk}}}{X_y(626)_{\text{unk}}} = \frac{P(826)}{P(626)} = 2 * {}^{18}r_{VPDB}(1 + {}^{18}\delta) \Rightarrow {}^{18}\delta = \frac{X_y(826)_{\text{unk}}}{2 * {}^{18}r_{VPDB} * X_y(626)_{\text{unk}}} - 1$$

(254)

and similarly for  $\delta^{17}\text{O}$ . If  $\delta^{17}\text{O}$  has not been measured we assume that  $\delta^{17}\text{O} = 0.528 * \delta^{18}\text{O}$ . Equation (24) is (weakly) non-linear. We re-arrange it as

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$$\frac{X(826)_{\text{unk}}}{2 + {}^{18}\text{r}_{\text{PDB}} + X(626)_{\text{unk}}} = 1 + [\dots] + {}^{18}\delta (1 + [\dots])$$

in which we defined  $[\dots] = {}^{17}\text{r}_{\text{PDB}}(1 + {}^{17}\delta) + {}^{18}\text{r}_{\text{PDB}}(1 + {}^{18}\delta)$

and rearrange it further into:

$${}^{18}\delta = \left[ \frac{X(826)_{\text{unk}}}{2 + {}^{18}\text{r}_{\text{PDB}} + X(626)_{\text{unk}}} - 1 \right] \frac{1}{[(1 + {}^{18}\delta)({}^{17}\text{r}_{\text{PDB}}(1 + {}^{17}\delta) + {}^{18}\text{r}_{\text{PDB}}(1 + {}^{18}\delta))]} \quad (25)$$

The first approximation to  ${}^{18}\delta$  is to assume  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O} = 0$  on the right hand side, i.e. equal to the standard reference material:

$${}^{18}\delta = \left[ \frac{X(826)_{\text{unk}}}{2 + {}^{18}\text{r}_{\text{PDB}} + X(626)_{\text{unk}}} - 1 \right] \frac{1}{{}^{17}\text{r}_{\text{PDB}} + {}^{18}\text{r}_{\text{PDB}}}$$

Then we substitute this first approximation into Eq. (25), with the assumption of  $\delta^{17}\text{O} = 0.528 * \delta^{18}\text{O}$ , and iterate the solution for  ${}^{18}\delta$  by continuing to substitute it in the right hand side of Eq. (25). The approximation is extremely close to the full solution unless the sample is highly depleted in  $\delta^{18}\text{O}$ .

If  $X(726)_{\text{unk}}$  has been measured, an equation similar to Eq. (25) applies:

$${}^{17}\delta = \left[ \frac{X(726)_{\text{unk}}}{2 + {}^{17}\text{r}_{\text{PDB}} + X(626)_{\text{unk}}} - 1 \right] \frac{1}{[(1 + {}^{17}\delta)({}^{17}\text{r}_{\text{PDB}}(1 + {}^{17}\delta) + {}^{18}\text{r}_{\text{PDB}}(1 + {}^{18}\delta))]} \quad (26)$$

In this case Eqs. (25) and (26) can be iterated together substituting updated values for both  ${}^{18}\delta$  and  ${}^{17}\delta$ .

The total  $\text{CO}_2$  in dry air is given by

$$X_{\text{CO}_2, \text{unk}} = \frac{Xy(626)_{\text{unk}} + Xy(636)_{\text{unk}} + Xy(826628)_{\text{unk}} + Xy(726627)_{\text{unk}}}{P(626)_{\text{unk}} + P(636)_{\text{unk}} + P(826628)_{\text{unk}} + P(726627)_{\text{unk}}} \quad (2667)$$

Dividing by the sum of the probabilities (fractional abundances P) corrects the sum of the measured isotopologues for the unmeasured rare isotopologues. The sum of the probabilities in Eq (26) which would be equal to 0.99993894 99993922 if the isotopic ratios are equal to the standard reference materials for carbon and oxygen. This would add 0.024  $\mu\text{mol mol}^{-1}$  to the sum of the measured isotopologues  $X_{\text{CO}_2}$ , assuming  $X_{\text{CO}_2} \sim 400 \mu\text{mol mol}^{-1}$ . This small difference accounts for the rare isotopologues with multiple isotopic substitutions that are not being measured. The correction in Eq. (2667) that applies for actual the unknowns will in general be very slightly different from 1-0.00006106099993932 (see above, the sum of the four major molecular abundances assuming VPDB values). We calculate actual P values for the unknown using Eqs. (4920)-(2223) with the  $\delta$ -values from Eqs. (2324)-(2556)

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and then use those in Eq. (2667) instead of the standard reference material values to account for this small discrepancy, but it is not necessary in most cases.

## 7 Analytical methods

NOAA's new CO<sub>2</sub> calibration system is based on multiple laser spectroscopic techniques. It uses a combination of cavity ring-down spectroscopy (CRDS, Picarro, Inc. CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>O analyzer, model number G2301) (O'Keefe and Deacon, 1988; Crosson, 2008), off-axis integrated cavity output spectroscopy (ICOS, Los Gatos Research, Inc., carbon dioxide isotope analyzer, CCIA-46-EP, model number 913-0033-0000) (Paul et al., 2001; Baer et al., 2002), and quantum cascade tunable infrared laser differential absorption spectroscopy (QC-TILDAS, Aerodyne Research, Inc., carbon dioxide isotope analyzer, model QCTILDAS-CS) (Tuzson et al., 2008; McManus et al., 2015).

The CRDS instrument measures a single absorption line from the <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O isotopologue at 1603 nm (Crosson, 2008). For most of the data presented here, the instrument operated in an enhanced CO<sub>2</sub> mode where it did not measure CH<sub>4</sub> and instead focussed exclusively on the CO<sub>2</sub> absorption line with periodic measurements of H<sub>2</sub>O as a diagnostic. However, we have since determined this enhanced CO<sub>2</sub> mode does not improve the reproducibility of CO<sub>2</sub> measurements. We are currently testing the ability to do CH<sub>4</sub> calibrations at the same time as the CO<sub>2</sub> calibrations using the standard operating mode of the CRDS.

The ICOS and QC-TILDAS analyzers both measure absorption lines of <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O, <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O, and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O isotopologues individually (using lines in the at 23090 cm<sup>-1</sup> CO<sub>2</sub> absorption bands). Both analyzers also measure the <sup>17</sup>O<sup>12</sup>C<sup>16</sup>O isotopologue but we cannot independently calibrate this measurement because our standards have not been measured for <sup>17</sup>O. We assume that <sup>17</sup>O follows the mass dependent fractionation relative to <sup>18</sup>O. Deviations from this relationship would be small and be insignificant when calculating total CO<sub>2</sub>.

The two analyzers have comparable performance and serve as backups for each other since only one is installed and used at a time. In the following discussion they are designated collectively as the CO<sub>2</sub> isotope analyzer. The <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O measurement in the isotope analyzers uses a weak absorption line to match the measured absorption with the low abundance minor isotopologues. They are therefore not as precise as the measurement on the CRDS. The internal <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O measurement from the isotope analyzer is not used to calculate total CO<sub>2</sub> but is used as  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (see Eqs. (2324) and (2525) in the discussion above). Using this "internal"  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurement gives slightly more precise  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  results than using the "external"  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurement from the CRDS system-instrument since it accounts for some instrument bias common to both the <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O and the <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O and <sup>18</sup>O<sup>12</sup>C<sup>16</sup>O isotopologue measurements.  $\delta^{13}\text{C}$  from the CRDS system is used in Eq. (2726) to calculate total CO<sub>2</sub>.

Figure 1 is a plumbing diagram for the CO<sub>2</sub> calibration system. The system uses the CRDS analyzer plus one of the CO<sub>2</sub> isotope analyzers. All measurements on the system are relative to a reference tank of compressed, unmodified natural air. A 4-port, 2-position switching valve (Valco Instruments Co, Inc. (VICI), model EUDA-24UWE) is used

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to send sample/standard gas to one analyzer while the other analyzer simultaneously measures the reference tank. Sample and standard tanks are introduced to the system via two identical sample manifolds composed of 16-port multi-position selection valves (VICI, model EUTA-2CSD16MWE). A 4-port multi-position stream selection valve (VICI, model EUTA-2SD4MWE) is used to select either manifold A, B, or, optionally, for expansion to a third manifold C. A plugged port on the manifold selection valve is used as a safe off port during shutdown. Sample/standard and reference gas pressures are controlled at 760  $\pm$ 1 Torr by two electronic pressure controllers with integrated mass flow meters (MKS Instruments, type 649B electronic pressure controller, model number 649B00813T13C2MR). The analyzers themselves control their internal cell pressures. However, controlling the inlet pressure prevents large inlet pressure swings due to inconsistent cylinder regulator set points and allows the internal pressure control to be more consistent. All three instruments are continuous flow instruments so an idle gas is provided through a 3-way solenoid valve (Parker, model 009-0143-900) just upstream of the instrument inlet. ~~The solenoid valve fails to the idle gas during power outages to prevent loss of cylinders.~~ This idle gas is partially dried room air drawn through a Nafion drier (Perma Pure LLC.) for extended system idle time (e.g. on weekends) but is a cylinder of dried ambient natural air (dew point  $\sim$  -80 °C) for short idle times during and just prior to actual calibrations. This cylinder ensures that the system downstream of the water traps does not get exposed to elevated levels of water vapor during short idle times between analyses. Each analyzer has a H<sub>2</sub>O trap up-stream of the inlet that normalizes any differences in water content among cylinders analyzed. These traps are 3.2 mm OD stainless steel tubing loops immersed in a -78 °C ethanol bath (SP Scientific Inc., MultiCool, model number MC480A). Both analyzers have individual sampling pumps to pull gas through the sample cell at partial vacuum. All tubing in the system is 3.2 mm or 1.6 mm OD stainless steel.

The flow rates are set to 130 - 150 mL min<sup>-1</sup> by using a critical flow orifice downstream of the isotope analyzer cell or by partially closing the upstream solenoid valve in the CRDS instrument and relying on a stable pressure at the instrument inlet. The analysis sequence starts with a 4 minute flush of the sample/standard regulator (and sample/standard electronic pressure controller) and then alternates reference and sample through the two analyzers for 8 cycles before moving to the next sample or standard. Each measurement cycle is 2.5 minutes of flushing and a 30 second signal average.

## 8 Calibration and system performance

Analyzers are calibrated approximately every two weeks in an offline calibration mode using a suite of 14 secondary standards, covering the range 250 to 600  $\mu$ mol mol<sup>-1</sup> total CO<sub>2</sub>. The system is calibrated routinely to 600  $\mu$ mol mol<sup>-1</sup> in expectation of a scale expansion in 2017. Each isotopologue is calibrated independently after decomposing the standard's total CO<sub>2</sub> into its component isotopologue mole fractions using the method discussed above. The secondary standards have assigned total CO<sub>2</sub> values by calibration against the entire set of primary standards (plus two additional standards that will extend the scale to 600  $\mu$ mol mol<sup>-1</sup>) in an analogous manner as described here. This is a significant change from our previous NDIR [calibration](#) system where subsets of standards were used. It

makes the new calibration system less likely to have CO<sub>2</sub> dependent biases. The secondary standard's  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values were assigned by IRMS measurement at INSTAAR. Primary standards also have  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values assigned by INSTAAR, which we use when primary standards are used to calibrate secondary standards. The use of INSTAAR  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  assigned values on the secondary standards rather than the values from measurement versus the primary standards, shortens the traceability of the delta measurements to a true IRMS measurement. A comparison of the INSTAAR assignments with the NOAA measured isotopic values for the secondary standards is discussed below.

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As mentioned in section 6, INSTAAR  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements are relative to their own realization of the VPBD scales rather than on the WMO GAW scale for isotopic measurements of CO<sub>2</sub> (Jena Reference Air Set (JRAS-06) maintained by the Max Planck Institute for Biogeochemistry, Jena Germany) (Wendeberg et al., 2013). INSTAAR has scale contraction issues relative to JRAS. The relationships between INSTAAR and JRAS published by Wendeberg et al. (2013) indicate that while the offsets are significant for isotopic studies, the use of the INSTAAR realization for accounting for isotopic differences when determining total CO<sub>2</sub> will not add significant bias. When we use primary standards to calibrate secondary standards, the apportionment of the total CO<sub>2</sub> into component isotopologues will be slightly off. However, this is partially corrected when we recombine the resulting measured isotopologue mole fractions of the secondary standards into total CO<sub>2</sub>. Using approximate JRAS values for our primary standards based on the Wendeberg et al. (2013) relationships, we see changes in the apportionment of the <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O isotopologues on the order of 0.000 to 0.004  $\mu\text{mol mol}^{-1}$  with corresponding but opposite sign changes in the other isotopologues.

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The instrument readings are absorption measurements corrected for cell pressure and temperature and converted into nominal mole fraction units. However, we treat them purely as an instrument response in arbitrary units. They could also be a voltage or a current. The responses from the analyzers are subsequently used in an offline calibration of each instrument. We do not use the internal calibration capabilities of the instruments; this ensures that the measurements are directly traceable to the WMO primary standards and can be reprocessed for future scale revisions. Each standard is measured relative to a reference cylinder to correct for slow drift of the analyzers. For the CRDS and ICOS analyzers the instrument response to each standard is divided by the average instrument response of the bracketing reference aliquots. For the QC-TILDAS, the difference between the response to the standard and the reference is used. In both cases we term the resulting values "response ratios". The choice of division vs subtraction is made due to the characteristics of the drift in each analyser. For example, the division operation does a better job when there is a slow span drift (perhaps due to variations in cell temperature and pressure) causing relative changes that are proportional to  $X_{\text{CO}_2}\text{CO}_2$ , whereas the difference operation is more appropriate when the majority of the drift is caused by a uniform shift in the output that ~~does not depend on  $X_{\text{CO}_2}$  is not proportional to CO<sub>2</sub>~~. Rather

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than characterize the source of drift in each analyzer we use the reproducibility of target tank measurements to empirically determine which method gives more consistent results between calibration episodes.

The calibration curves are CO<sub>2</sub> isotopologue mole fractions as a function of response ratios. The CRDS instrument response is linear within the uncertainty of the standards (typical uncertainty of the primary standards is  $\pm 0.1 \mu\text{mol mol}^{-1}$  68 % CI). However, both isotope analyzers are slightly non-linear in their response and are fit with a quadratic polynomial. Non-linearity in the isotope analyzers may be partially due to incomplete flushing of the sample cell, caused by un-swept dead volumes, as the system switches from reference to standard. Memory of the Residual reference gas (ambient air from Niwot Ridge,  $\sim 400 \mu\text{mol mol}^{-1}$  CO<sub>2</sub>) in the sample cell influences the standards on the ends of the scale more than those close to the reference gas value potentially leading to a slight non-linear response. The difference in <sup>16</sup>O<sup>13</sup>C<sup>16</sup>O calibration curve residuals at 600  $\mu\text{mol/mol}$  using a quadratic fit (0.0005  $\mu\text{mol/mol}$ ) and a linear fit (0.003  $\mu\text{mol/mol}$ ) indicate the memory effect is small in terms of total CO<sub>2</sub>. Since all standards and all samples are treated identically and measured against the same reference gas, small memory effects should cancel out. Longer flushing times would reduce the memory effect but would decrease the lifetime of the standards.

Sample measurements are made relative to the same reference tank to account for drift in the analyzers between calibration episodes. The sample response ratios are used with the isotopologue specific calibration curves to determine isotopologue mole fractions for the sample cylinder which are combined into total CO<sub>2</sub>,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  values using the method discussed above. These values (total CO<sub>2</sub>,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$ ) are stored in the NOAA database and are reported to the user via certificates and the web interface. Isotopologue specific mole fractions are not provided, however the equations described in this paper can be used to regenerate them.

Performance of the new calibration system has been evaluated over approximately one year by repeated measurements of target tanks (cylinders repeatedly measured as a diagnostic of system performance). Figure 2 shows the time series of total CO<sub>2</sub> measured for 4 target tanks with CO<sub>2</sub> ranging from 357 to 456  $\mu\text{mol mol}^{-1}$ . Standard deviations of the measurements are approximately  $\pm 0.007 \mu\text{mol mol}^{-1}$ . Reproducibility of the target tanks close to the reference tank (typically  $\sim 400 \mu\text{mol mol}^{-1}$  CO<sub>2</sub>) are a little better than those farther out on the ends of the calibration range but the difference is small. While one year is not a long enough time series to fully quantify the reproducibility of the system, we estimate it to be  $\pm 0.01 \mu\text{mol mol}^{-1}$  (68 % CI) based on these target tank measurements. This is a significant improvement over the NDIR system where reproducibility is  $\pm 0.03 \mu\text{mol mol}^{-1}$  (68 % CI) ("Carbon Dioxide WMO Scale", 2017).

Prior to this new CO<sub>2</sub> calibration system, NOAA provided informational isotopic values for tertiary standards delivered to outside organizations by taking discrete samples from cylinders in flasks and having them measured by INSTAAR. This continued during the 6 months period when both calibration systems were run in parallel. Comparisons of these measurements with the isotopic results from the new calibration system are shown in Figs. 3 and 4. The top plot in each figure is differences of measured delta values (NOAA – INSTAAR) vs INSTAAR values and the bottom plot in each figure is differences as a function of total CO<sub>2</sub> measured by NOAA. There is no

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systematic bias between the NOAA and INSTAAR measurements for either species, except for highly depleted cylinders ( $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  less than  $-20\text{‰}$ , shown by open symbols in both figures) and  $\delta^{18}\text{O}$  in very high  $\text{CO}_2$  cylinders ( $> 490\text{ }\mu\text{mol mol}^{-1}$ ). The average offset (NOAA – INSTAAR) of non-depleted tanks is  $0.0 \pm 0.1\text{‰}$   $\delta^{13}\text{C}$  and  $0.0 \pm 0.2\text{‰}$   $\delta^{18}\text{O}$ . The offset in the highly depleted cylinders most likely occurs as a result of the large extrapolation in the INSTAAR IRMS measurements from the working standard at ambient  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . These offsets are roughly consistent with the INSTAAR JRAS offsets (Wendeberg et al., 2013) which are attributed to scale contraction issues at INSTAAR. The secondary standards used to routinely calibrate the NOAA system have isotopic assignments made by direct measurement by INSTAAR and are all relatively close to ambient (see figures 5 and 6) where the INSTAAR scale contraction is very small. By using these standards and calibrating our measurements in mole fraction space we are not sensitive to the scale contraction issues in the INSTAAR measurement of depleted tanks. The  $\delta^{18}\text{O}$  data do show a pronounced “hook” above  $\sim 490\text{ }\mu\text{mol mol}^{-1}$ . This is thought to be due to issues when sampling air from cylinders into flasks and not to the measurements either at INSTAAR or NOAA. A tertiary standard with  $497\text{ }\mu\text{mol mol}^{-1}$   $\text{CO}_2$  showed excellent agreement when measured directly by both NOAA ( $\delta^{18}\text{O} = -8.92 \pm 0.04\text{‰}$ ) and ~~SL-INSTAAR~~ ( $\delta^{18}\text{O} = -8.94 \pm 0.1\text{‰}$ ). A comparison can also be made using the secondary standards which were calibrated directly by INSTAAR and by NOAA verses the primary standards. The assigned values of the secondary standards (as measured directly by INSTAAR) and the NOAA minus INSTAAR differences are shown in Figs. 5 and 6 for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  respectively. Agreement is very good but there is a loss of precision on the NOAA calibration system near the wings of the  $\text{CO}_2$  scale. NOAA measurements show some decrease in performance as total  $\text{CO}_2$  moves away from the reference cylinder, which is always an ambient  $\text{CO}_2$  cylinder. However, even on the wings of the range the performance is more than adequate for the purpose of correcting total  $\text{CO}_2$  for isotopic differences. The reproducibility of  $\delta^{13}\text{C}$  ( $\pm 0.2\text{‰}$ , 68% CI) and  $\delta^{18}\text{O}$  ( $\pm 0.2\text{‰}$ , 68% CI) measurements are again estimated from target tanks measurements. The uncertainty of the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements is dependent on the uncertainty of the total  $\text{CO}_2$  values of the standards in addition to the reproducibility of the measurement system (Flores et al., 2017). This will be treated in an upcoming publication describing the  $\text{CO}_2$  scale revision (Hall et al., in preparation). The uncertainties of our measurement results for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are more than adequate for correcting atmospheric  $\text{CO}_2$  measurements for standard vs sample isotopic differences. However, we caution against using them as standards for high precision  $\text{CO}_2$  isotopic measurements. The uncertainty for the isotope measurements is too large for these results to be used as true  $\text{CO}_2$  isotope standards but is more than adequate for correcting atmospheric  $\text{CO}_2$  measurement for standard vs sample isotope differences.

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The new calibration system was run in parallel with the NDIR system from April 2016 through October 2016. Agreement between the two systems near ambient  $\text{CO}_2$  is good but there are significant offsets between  $300$  to  $360\text{ }\mu\text{mol mol}^{-1}$  and  $430$  to  $500\text{ }\mu\text{mol mol}^{-1}$  (Fig. 7). These offsets can be traced primarily to the effects of calibrating the NDIR system with subsets of the primary standards when transferring the scale to secondary standards. Using subsets in this way makes the results from the NDIR system sensitive to uncertainty in the assigned values of the individual primary standards. Additional manometric determinations have been made since the assignments were made in 2007. Also the use of the new calibration system for correcting the average manometer values for residuals

of a fit to the entire set will help to improve the consistency of the individual assignments and thus reduce the CO<sub>2</sub> dependency of the NDIR measurements. These improvements, as well as two additional subtle bias corrections in the manometer calculations, will be incorporated in an upcoming scale revision (scheduled for mid-2017) ~~(Brad Hall, personal communication)~~. The revised scale should remove most of the CO<sub>2</sub> dependent bias between the two analysis systems. Although there may be a component due to gas handling issues on the NDIR system that cannot be resolved. This is still under investigation and will be addressed in a forthcoming paper discussing the scale revision ~~(Hall et al., in preparation)~~. After the scale revision all past calibrations of tertiary standards will be revised to the new scale. Calibrating the new system by fitting all primary standards makes the new system very insensitive to the assignment of individual cylinders. Thus results from the new system are more accurate than from the NDIR, however, caution should be used when evaluating cylinders for drift when comparing historical results from the NDIR system and new measurements from the new calibration system as these systematic system differences could be incorrectly interpreted as drift.

Figure 7 also has results from highly depleted tanks ( $\delta^{13}\text{C} < -20\text{‰}$ ) that shows a greater NDIR minus laser system difference. This is consistent with the NDIR having reduced sensitivity to the minor isotopologues. Quantifying the sensitivity of the current NDIR (LI-COR 6252) is difficult due to the CO<sub>2</sub> dependent biases and would not be possible for historical NDIR analyzers used on the NDIR CO<sub>2</sub> calibration system. Measurements of isotopically depleted cylinders by NOAA via NDIR need to be considered more uncertain due to this unknown isotope sensitivity of NDIR's used for CO<sub>2</sub> calibrations.

## 9 Conclusions

We describe here the expected distribution of isotopologues of CO<sub>2</sub> based on measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  and its application in calibrating cylinders for total CO<sub>2</sub>,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$ . The distribution accounts for all isotopologues, including rare doubly substituted isotopologues. The methods are applicable to CO<sub>2</sub> or any other molecule where isotopologue (or isomer) specific values are required to reach desired precision goals.

The new calibration system provides total CO<sub>2</sub> values that are insensitive to isotopic differences between standards and provides to users of the standards a characterization of the isotopic composition of the standards. The isotopic values are not intended for propagating the isotopic standard scales. ~~They~~ they are only to be used to make corrections to atmospheric CO<sub>2</sub> measurements made by instruments that have selective sensitivities to the isotopologues. For CO<sub>2</sub> isotopic measurements we encourage users to continue to have standards calibrated by dedicated isotope measurement facilities where the isotopic scales can be propagated with lower uncertainty. Isotopic standards should be calibrated by IRMS measurements.

The performance of the new calibration system improves our ability to propagate the CO<sub>2</sub> scale and is expected to lead to improvements in the compatibility of measurement networks provided laboratories maintain tight connection with the CCL. Although the system has not run long enough to fully evaluate the reproducibility of the scale

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transfer, it is expected to be approximately  $\pm 0.01 \mu\text{mol mol}^{-1}$  (68% CI). Comparison of the new calibration system with the historical NDIR based system shows significant CO<sub>2</sub> dependence in the NDIR measurements. This results from a combination of errors in the assigned values of the primary standards and the use of small subsets of the primary standards when the scale is transferred to secondary standards. This is under further investigation and we expect to resolve the issue with an upcoming revision to the CO<sub>2</sub> in air scale.

#### **Code availability**

Available upon request.

#### **Data availability**

Cylinder calibration results presented in this work include those used by laboratories outside of NOAA. We can provide results in anonymous form upon request.

## Appendix

We will derive expressions for  $\Delta$  in terms of conventional  $\delta$  values because we currently supply standards to users within the greenhouse gas measurement community with their  $\delta$  values as information in addition to the total  $X_{CO_2}$   $X_{CO_2}$  calibration.

$$^{13}\Delta = \frac{^{13}R_x}{^{13}R_{VPDB}} - 1 = \frac{^{13}R}{^{13}R_{VPDB}} \frac{1 + ^{13}R_{VPDB}}{1 + ^{13}R} - 1 = (1 + ^{13}\delta)(1 + ^{13}R_{VPDB})(1 - ^{13}R + ^{13}R^2) - 1$$

Where we have used the first 3 terms of the series expansion  $(1+r)^{-1} = 1 - r + r^2 - r^3 + \dots$  and the definitions of  $R$ ,  $\delta$ , and  $\Delta$ . Expanding,

$$^{13}\Delta = (1 - ^{13}R + ^{13}R^2) + ^{13}R_{VPDB}(1 - ^{13}R + ^{13}R^2) + ^{13}\delta(1 - ^{13}R + ^{13}R^2) + ^{13}\delta^{13}R_{VPDB}(1 - ^{13}R + ^{13}R^2) - 1$$

and rearranging, we get

$$^{13}\Delta = (-^{13}R + ^{13}R^2) + (^{13}R_{VPDB} + ^{13}\delta)(1 - ^{13}R + ^{13}R^2) + ^{13}\delta^{13}R_{VPDB}(1 - ^{13}R + ^{13}R^2)$$

Rearranging further,

$$^{13}\Delta = ^{13}\delta - (^{13}R - ^{13}R_{VPDB}) + ^{13}R(^{13}R - ^{13}R_{VPDB}) - ^{13}\delta(^{13}R - ^{13}R_{VPDB}) - ^{13}\delta^{13}R_{VPDB}^{13}R$$

Then, using Eq. (5),

$$^{13}\Delta = ^{13}\delta - ^{13}R_{VPDB}^{13}\delta + ^{13}R^{13}R_{VPDB}^{13}\delta - ^{13}\delta^{13}R_{VPDB}^{13}\delta - ^{13}\delta^{13}R_{VPDB}^{13}R$$

The third and the last term cancel, and then keeping only the two leading terms, we obtain

$$^{13}\Delta = ^{13}\delta(1 - ^{13}R_{VPDB}) \quad \text{---(A1)}$$

Equation (A1) is an excellent approximation. Using the values for  $^{13}R_{VPDB}$  in Table 1 and assuming that  $^{13}\delta = -0.00800$  (−8.00 permil, an approximate value for CO<sub>2</sub>-in-air) we calculate both  $^{13}R - ^{13}R_{VPDB}$  for the air sample and  $^{13}R_{VPDB} - ^{13}R_{VPDB}$ , and using the definition (Eq. (6)) for  $^{13}\Delta$ , we obtain  $^{13}\Delta = -0.00791292$ . Equation (A1) gives us  $-0.00791064$ .

A very similar derivation holds for  $^{17}\Delta$  and  $^{18}\Delta$  but it is a bit more complicated because the terms for  $^{17}R - ^{17}R_{VPDB}$  and  $^{18}R - ^{18}R_{VPDB}$  get mixed.

$$^{17}\Delta = \frac{^{17}R}{^{17}R_{VPDB}} \frac{1 + ^{17}R + ^{18}R}{1 + ^{17}R_{VPDB} + ^{18}R_{VPDB}} - 1 = \frac{^{17}R}{^{17}R_{VPDB}} \frac{1 + ^{78}R}{1 + ^{78}R_{VPDB}} - 1$$

To keep the notation simpler and stressing the analogy with the derivation for  $^{13}\Delta$  we have written in the above  $^{78}R = ^{17}R + ^{18}R$  for the air sample and  $^{78}R_{VPDB} = ^{17}R_{VPDB} + ^{18}R_{VPDB}$  for the standard.

After keeping only the leading terms we have

$$^{17}\Delta = ^{17}\delta - (^{78}R - ^{78}R_{VPDB}) = ^{17}\delta - ^{17}R_{VPDB}^{17}\delta - ^{18}R_{VPDB}^{18}\delta \quad \text{(A2)}$$

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And similarly for  $^{18}\text{O}$ :

$$^{18}\Delta = ^{18}\delta - ^{17}r_{\text{VPDB}} ^{17}\delta - ^{18}r_{\text{VPDB}} ^{18}\delta \quad \text{---(A3)}$$

These are the equivalents of Eq. (A1) for  $^{13}\Delta$ . Because  $^{17}r$  and  $^{18}r$  are significantly smaller than  $^{13}r$ , we approximate further  $^{17}\Delta \cong ^{17}\delta$  and  $^{18}\Delta \cong ^{18}\delta$ . Since  $^{17}\delta$  is not usually measured and also is often very closely related as  $^{17}\delta = 0.53 ^{18}\delta$ , we can write for the oxygen correction terms in Eq. (16)  $\left( \frac{^{17}r_{\text{PDB}}}{^{17}r_{\text{VPDB}}} - \frac{^{17}r_{\text{PDB}}}{^{17}r_{\text{VPDB}}} \right) ^{17}\delta + \left( \frac{^{18}r_{\text{PDB}}}{^{18}r_{\text{VPDB}}} - \frac{^{18}r_{\text{PDB}}}{^{18}r_{\text{VPDB}}} \right) ^{18}\delta = (0.53$

$$0.53 \cdot 395 \cdot 10^{-6} \cdot ^{18}\delta + 2088 \cdot 10^{-6} \cdot ^{18}\delta = 2297 \cdot 10^{-6} \cdot ^{18}\delta \cong 0.0023 \cdot ^{18}\delta$$

Now we return to Eq. (4718) in the main text, applicable when the isotopic composition of measured air is different from the standard that is used. We restate it as

$$\Delta y_{\text{totCO}_2} = y_{\text{totCO}_2} [0.0110644 (^{13}\delta_{\text{air}} - ^{13}\delta_{\text{st}}) + 2 \cdot 0.0023 ( ^{18}\delta_{\text{air}} - ^{18}\delta_{\text{st}}) ] \quad \text{(A4)}$$

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### Supplemental links

None

### Author contribution

5 P. Tans derived the equations used to apportion total CO<sub>2</sub> into component isotopologues and their application. A. Crotwell designed and built the calibration system. K. Thoning wrote software for operating the calibration system and managing the data.

### Competing interests

The authors declare that they have no conflict of interest.

### Disclaimer

10 None

### Acknowledgements

We thank Thomas Mefford for running the calibration system, Duane Kitzis for standards preparation, and Ed Dlugokencky [and three anonymous reviewers](#) for reviewing this manuscript. In addition, we thank Sylvia Michel, Natalie Cristo, and the other members of the INSTAAR Stable Isotope Laboratory for isotopic measurements.

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## References

- Andres, R. J., Marland, G., Boden, T., and Bischof, S.: Carbon ~~Dioxide-dioxide~~ emissions from fossil fuel consumption and cement manufacture, 1751-1991, and an estimate of their isotopic composition and latitudinal distribution, in: The Carbon Cycle, edited by: Wigley, T. M. L., and Schimel, D. S., Cambridge University Press, 53-62, 2000.
- Allison, C. E., Francey, R. J., and Meijer, A. J.: Recommendations for the reporting of stable isotope measurements of carbon and oxygen in CO<sub>2</sub> gas, ~~Reference-reference~~ and intercomparison materials for stable isotopes of light elements, IAEA-TECDOC-825, Vienna, 155-162, 1995.
- 10 Assonov, S. S., and Brenninkmeijer, C. A. M.: A redetermination of absolute values for <sup>17</sup>R<sub>VPDB-CO<sub>2</sub> and <sup>17</sup>R<sub>VSMOW</sub>, Rapid Commun. Mass Spectrom., 17, 1017-1029, 2003.</sub>
- Baer, D. S., Paul, J. B., Gupta, J. B., and O'Keefe, A.: Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy, Applied Physics B-Lasers and Optics, 75, 261-265, doi:10.1007/s00340-002-0971-z, 2002.
- 15 Baertschi, P.: Absolute <sup>18</sup>O-~~18 Content-content~~ of Standard Mean Ocean Water, Earth Planet. Sci. Lett., 31, 341-344, 1976.
- Brand, W. A., Assonov, S. S., and Coplen, T. B.: Correction for the <sup>17</sup>O interference in ~~delta~~(<sup>13</sup>C) measurements when analysing CO<sub>2</sub> with stable isotope mass spectroscopy (IUPAC Technical Report), Pure Appl. Chem., 82, 1719-1733, 2010.
- 20 Carbon Dioxide WMO Scale: [https://www.esrl.noaa.gov/gmd/cc1/co2\\_scale.html](https://www.esrl.noaa.gov/gmd/cc1/co2_scale.html), last access: 30 January 2017.
- Coplen, T. B., Krouse, H. R., and Bohlke, J. K.: Reporting of ~~Nitrogen-nitrogen-Isotope-isotope~~ ~~Abundancesabundances~~, Pure Appl. Chem., 64, 907-908, 1992.
- Coplen, T. B.: Guidelines and recommended terms for expression of stable isotope-ratio and gas-ratio measurement results. Rapid Commun. Mass Spectrom., 25, 2538-2560, 2011.
- 25 Craig, H.: Isotopic ~~Standards-standards~~ for ~~Carbon-carbon~~ and ~~Oxygen-oxygen~~ and ~~Correction-correction~~ ~~Factors~~ ~~factors~~ for ~~Mass-mass Spectrometric-spectrometric Analysis-analysis~~ of ~~Carbon-carbon Dioxide-dioxide~~, Geochim. Cosmochim. Acta, 12, 133-149, 1957.
- Crosson, E. R.: A cavity ring-down analyser for measuring atmospheric levels of methane, carbon dioxide, and water vapor, Appl. Phys. B: Lasers Opt., 92, 403-408, doi:10.1007/s00340-008-3135-y, 2008.

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- Flores, E., Viallon, J., Moussay, P., Griffith, D. W. T., and Wielgosz, R. I.: Calibration strategies for FT-IR and other isotope ratio infrared spectrometer instruments for accurate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements of  $\text{CO}_2$  in air, *Anal. Chem.*, 89, 3648-3655, 2017.
- Hall, B. D., Kitzis, D. R., Crotwell, A. M., Mefford, T. K., Miller, B. R., Tans, P. P.: Revision of the WMO/GAW  $\text{CO}_2$  calibration scale, *Manuscript in preparation*, 2017.
- Hagemann R., Nief, G., Roth, E.: Absolute isotopic scale for deuterium analysis of natural waters, absolute D/H ratio for SMOW, *Tellus*, 22, 712-715, 1970.
- IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org>, created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins, 2006.
- Junk, G., and Svec, H. J.: Absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources, *Geochim. Cosmochim. Acta*, 14, 234-243, 1958.
- Kitzis, D.: Preparation and ~~Stability-stability of Standard-standard Reference-reference Air-air Mixturesmixtures~~. <https://www.esrl.noaa.gov/gmd/cc/airstandard.html>, last access: 30 January 2017, 2009.
- Lee, J. Y., Yoo, H. S., Marti, K., Moon, D. M., Lee, J. B., and Kim, J. S.: Effect of carbon isotopic variations on measured  $\text{CO}_2$  abundances in reference gas mixtures, *J. Geophys. Res.: Atmos.*, 111, doi:10.1029/2005jd006551, 2006.
- Loh, Z. M., Steele, L. P., Krummel, P. B., Van der Schoot, M., Etheridge, D. M., Spencer, D. A., and Francey, R. J.: Linking isotopologue specific measurements of  $\text{CO}_2$  to the existing international mole fraction scale. In: *Report of 15<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurements Techniques*, Jena, Germany, 7-10 September 2009, 2011.
- McManus, J. B., Nelson, D. D., and Zahniser, M. S.: Design and performance of a dual-laser instrument for multiple isotopologues of carbon dioxide and water, *Opt. Express*, 23, 6569-6586, doi:10.1364/OE.23.006569, 2015.
- O'Keefe, A., and Deacon, D. A. G.: Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources, *Rev. Sci. Instrum.*, 59, 2544-2551, 1988.
- Paul, J. B., Lapson, L., and Anderson, J. G.: Ultrasensitive absorption spectroscopy with a high-finesse optical cavity and off-axis alignment, *Applied Optics*, 40, 4904-4910, 2001.
- Rothman, L.S., Gordon, I.E., Babikov, Y., Barbe, A., Benner, D. C., Bernath, P.F., Birk, M., Bizzocchi, L., Boudon, V., Brown, L.R., Campargue, A., Chance, K., Cohen, E.A., Coudert, L.H., Devi, V.M., Drouin, B.J., Fayt, A., Flaud, J.M., Gamache, R.R., Harrison, J.J., Hartmann, J.M., Hill, C., Hodges, J.T., Jacquemart, D., Jolly, A., Lamouroux,

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- J., Le Roy, R.J., Li, G., Long, D.A., Lyulin, O.M., Mackie, C.J., Massie, S.T., Mikhailenko, S., Müller, H.S.P., Naumenko, O.V., Nikitin, A.V., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E.R., Richard, C., Smith, M.A.H., Starikova, E., Sung, K., Tashkun, S., Tennyson, J., Toon, G.C., Tyuterev, V.I.G., Wagner, G.: The HITRAN2012 molecular spectroscopic database. *J. of Quant. Spectrosc. Ra.*, 130, 4-50, 2013.
- 5 Santrock, J., Studley, S. A., and Hayes, J. M.: Isotopic analyses based on the mass spectrum of carbon dioxide, *Anal. Chem.*, 57, 1444-1448, 1985.
- Schumacher, M., Werner, R. A., Meijer, H. A. J., Jansen, H. G., Brand, W. A., Geilmann, H., and Neubert, R. E. M.: Oxygen isotopic signature of CO<sub>2</sub> from combustion processes, *Atmos. Chem. Phys.*, 11, 1473-1490, 2011.
- 10 Swart, P. K., Burns, S. J., and Leder, J. J.: Fractionation of the ~~Stable-stable Isotopes-isotopes~~ of ~~Oxygen-oxygen~~ and ~~Carbon-carbon~~ in ~~Carbon-carbon-Dioxide-dioxide~~ during the ~~Reaction-reaction~~ of ~~Calcite-calcite~~ with ~~Phosphoric-Acid-acid~~ as a ~~Function-function~~ of ~~Temperature-temperature~~ and ~~Technique-technique~~, *Chem. Geol.*, 86, 89-96, 1991.
- Tohjima, Y., Katsumata, K., Morino, I., Mukai, H., Machida, T., Akama, I., Amari, T., and Tsunogai, U.: Theoretical and experimental evaluation of the isotope effect of NDIR analyser on atmospheric CO<sub>2</sub> measurement, *J. Geophys. Res.: Atmos.*, 114, doi:10.1029/2009jd011734, 2009.
- 15 Trolter, M., White, J. W. C., Tans, P. P., Masarie, K. A., and Gemery, P. A.: Monitoring the isotopic composition of atmospheric CO<sub>2</sub>: Measurements from the NOAA Global ~~Air-Air~~ Sampling Network, *J. of Geophys. Res.*, 101, 25897-25916, 1996.
- Tuzson, B., Zeeman, M. J., Zahniser, M. S., and Emmenegger, L.: Quantum cascade laser based spectrometer for in situ stable carbon dioxide isotope measurements, *Infrared Phys. Technol.*, 51, 198-206, 2008.
- 20 Weiss, R. F.: Determinations of ~~Carbon-carbon-Dioxide-dioxide~~ and ~~Methane-methane~~ by ~~Dual-dual Catalyst-catalyst~~ ~~Flame-flame Ionization-ionization Chromatography-chromatography~~ and ~~Nitrous-nitrous-Oxide-oxide~~ by ~~Electron-electron-Capture-capture Chromatography-chromatography~~, *J. Chromatogr. Sci.*, 19, 611-616, 1981.
- 25 Wendeberg, M., Richter, J. M., Rothe, M., and Brand, W. A.: Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO<sub>2</sub> in air. *Atmos. Meas. Tech.*, 6, 817-822, 2013.
- WMO: Report of the 18<sup>th</sup> WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17 September, 2015, World Meteorological Organization, Global Atmosphere Watch Report Series No. 229, available at [http://www.wmo.int/pages/prog/arep/gaw/gaw\\_reports.html](http://www.wmo.int/pages/prog/arep/gaw/gaw_reports.html), 2016.

Zhang, Q. L., Change, T. L., and Li, W. J.: A calibrated measurement of the atomic weight of carbon, Chin. Sci. Bull., 35, 290-296, 1990.

Zhao, C. L., Tans, P. P., and Thoning, K. W.: A high precision manometric system for absolute calibrations of CO<sub>2</sub> in dry air, J. Geophys. Res.: Atmos., 102, 5885-5894, 1997.

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- 5 Zhao, C. L., and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, J. Geophys. Res.: Atmos., 111, D08S09, doi:10.1029/2005JD006003, 2006.

## Tables

Table 1: Isotopic ratios of international standard reference materials.

Reference Material	Ratio	Reference
5 $(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}$	0.0020052	(Baertschi, 1976)
$(^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}}^{\text{a}}$	0.00038672	(Assonov and Brenninkmeijer, 2003)
$(^{18}\text{O}/^{16}\text{O})_{\text{VPDB-CO}_2}$	0.0020883549	(Allison et al., 1995)
$(^{17}\text{O}/^{16}\text{O})_{\text{VPDB-CO}_2}^{\text{b}}$	0.00039511	(Assonov and Brenninkmeijer, 2003)
$(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}^{\text{c}}$	0.0111802372	(Zhang, 1990; Craig, 1957)
10 $(^2\text{H}/^1\text{H})_{\text{VSMOW}}$	0.00015576	(Hagemann et al., 1970)
$(^{15}\text{N}/^{14}\text{N})_{\text{air-N}_2}$	0.0036765	(Junk and Svec, 1958; Coplen, et al., 1992)

<sup>a</sup> In other literature, it is possible to find different  $^{17}\text{O}/^{16}\text{O}$  ratio values for these standard reference materials than those given here. However, for the determination of  $^{17}\text{O}$  isotopic effects on atmospheric  $\text{CO}_2$  measurements, differences from the values given in this table are insignificant.

15 <sup>b</sup> This  $^{17}\text{O}/^{16}\text{O}$  ratio of VPDB- $\text{CO}_2$  is consistent with  $[(^{17}\text{O}/^{16}\text{O})_{\text{VPDB-CO}_2}/(^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}}] = \text{derived from } [(^{18}\text{O}/^{16}\text{O})_{\text{VPDB-CO}_2}/(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}]^{0.528} \times (^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}}$ .

<sup>c</sup> We used the revised value of  $(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}$  was revised to 0.011180 by Zhang et al. (1990). However the value given in this table is still widely used. For the determination of  $^{13}\text{C}$  isotopic effects on atmospheric  $\text{CO}_2$  measurements the difference between this value and the original value 0.0112372 (Craig, 1957) is insignificant.

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## Figure captions

Figure 1: Schematic for the NOAA laser spectroscopic CO<sub>2</sub> calibration system. The CRDS analyzer is used with one of the CO<sub>2</sub> isotope analyzers which are interchangeable.

Figure 2: Total CO<sub>2</sub> calibration results for four target tanks measured on the laser spectroscopic CO<sub>2</sub> calibration system over approximately 1 year. Error bars are the standard deviation of 8 measurements per calibration episode. The results span multiple gas handling system modifications. Values since April 2016 are on a consistent design. Average and standard deviations of the four target tanks results are: A) CC71624 356.628 ± 0.007 μmol mol<sup>-1</sup>, B) CB11127 392.985 ± 0.006 μmol mol<sup>-1</sup>, C) CA05008 406.652 ± 0.006 μmol mol<sup>-1</sup>, and D) CB10826 455.734 ± 0.008 μmol mol<sup>-1</sup>. The average standard deviation for the 4 tanks is ± 0.007 μmol mol<sup>-1</sup>.

Figure 3: Discrete samples from tertiary standards were collected in flasks and measured by INSTAAR. The average INSTAAR flask  $\delta^{13}\text{C}$  result is compared to the average  $\delta^{13}\text{C}$  tank calibration result on NOAA's laser spectroscopic CO<sub>2</sub> calibration system. Top panel is the difference (NOAA – INSTAAR) as a function of the INSTAAR  $\delta^{13}\text{C}$  value and the bottom panel is the difference vs total CO<sub>2</sub>. Error bars in both plots are the standard deviation of multiple calibration episodes by NOAA. ~~SIL-INSTAAR~~ uncertainties are typically ± 0.03 ‰ (68 % CI) (Troler et al., 1996) but do not account for problems with the collection of the discrete air sample. Highly depleted cylinders ( $\delta^{13}\text{C} < -20$  ‰) are shown with open circles in each panel.

Figure 4: The same as Figure 3 for  $\delta^{18}\text{O}$ . ~~SIL-INSTAAR~~ uncertainties are typically ± 0.05 ‰ (68 % CI) (Troler et al., 1996) but again do not account for problems with the collection of the discrete air samples. Differences greater than 1.5 ‰ are assumed to be caused by problems during discrete sample collection. These results are shown but are not included in the statistics. Highly depleted cylinders ( $\delta^{18}\text{O} < -20$  ‰) are shown with open circles in each panel.

Figure 5: Secondary standards used to calibrate the laser spectroscopic system have  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from direct measurement by INSTAAR and they have measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from calibration on the laser spectroscopic system against the primary CO<sub>2</sub> standards. The top panel shows the INSTAAR  $\delta^{13}\text{C}$  values as a function of CO<sub>2</sub>. Uncertainties on the INSTAAR values (less than 0.02 ‰) are not visible. The bottom panel shows the difference between the NOAA and INSTAAR measurements of the secondary standards (NOAA – INSTAAR) also as a function of CO<sub>2</sub>. Error bars are the standard deviation of ~~three-four~~ calibration episodes of the secondary standards vs the primary standards on the NOAA CO<sub>2</sub> calibration system.

Figure 6: The same as Figure 5 for  $\delta^{18}\text{O}$ . The ~~X<sub>CO2</sub>-CO<sub>2</sub>~~ dependent depletion of  $\delta^{18}\text{O}$  in cylinders above ambient CO<sub>2</sub> results from the depleted  $\delta^{18}\text{O}$  of the spike gas.

Figure 7: The laser spectroscopic CO<sub>2</sub> calibration system was run in parallel with the NDIR CO<sub>2</sub> calibration system for approximately 6 months. The differences (average NDIR – average laser spectroscopic system) are plotted as a function of CO<sub>2</sub>. Typical reproducibility of the NDIR measurements (± 0.03, 68 % CI) are shown with dashed lines. Highly depleted cylinders ( $\delta^{13}\text{C} < -20$  ‰) are shown by open circles. These clearly indicate enhanced offsets due to the NDIR being somewhat sensitive to the isotopic composition differences between the samples and the standards used to calibrate the instrument.

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