



**Continuous-flow
IRMS technique for
triple-isotope
measurements of
CO₂**

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**Continuous-flow IRMS technique for
determining the ¹⁷O excess of CO₂ using
complete oxygen isotope exchange with
cerium oxide**

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Abstract

This paper presents an analytical system for analysis of all single substituted isotopologues ($^{12}\text{C}^{16}\text{O}^{17}\text{O}$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $^{13}\text{C}^{16}\text{O}^{16}\text{O}$) in nanomolar quantities of CO_2 extracted from atmospheric air samples. CO_2 is separated from bulk air by gas chromatography and CO_2 isotope ratio measurements (ion masses 45/44 and 46/44) are performed using isotope ratio mass spectrometry (IRMS). The ^{17}O excess ($\Delta(^{17}\text{O})$) is derived from isotope measurements on two different CO_2 aliquots: unmodified CO_2 and CO_2 after complete oxygen isotope exchange with cerium oxide (CeO_2) at 700°C . Thus, a single measurement of the ^{17}O excess requires two injections of 1 mL of air with a CO_2 mole fraction of $390\ \mu\text{mol mol}^{-1}$ at 293 K and 1 bar pressure (corresponding to 16 nmol CO_2 each). The required sample air size (including flushing) is 2.7 mL of air. A single analysis (one pair of injections) takes 15 min. The analytical system is fully automated for unattended measurements over several days. The standard deviation of the ^{17}O excess analysis is 1.7‰. Repeated analyses of an air sample reduce the measurement uncertainty, as expected for the statistical standard error. Thus, the uncertainty for a group of ten measurements is 0.58‰ for $\Delta(^{17}\text{O})$ in 2.5 h analysis. 270 repeat analyses of one air sample decrease the standard error to 0.20‰. The instrument performance was demonstrated by measuring CO_2 on stratospheric air samples obtained during the EU project RECONCILE with the high-altitude aircraft Geophysica. The precision for RECONCILE data is 0.03‰ (1σ) for $\delta^{13}\text{C}$, 0.07‰ (1σ) for $\delta^{18}\text{O}$ and 0.55‰ (1σ) for $\delta^{17}\text{O}$ for sample of 10 measurements. The samples measured with our analytical technique agree with available data for stratospheric CO_2 .

1 Introduction

Isotopic studies of carbon dioxide (CO_2) play an important role in understanding the global carbon cycle (Ciais et al., 1997; Farquhar et al., 1993; Troler et al., 1996). CO_2 is the end product of carbon oxidation processes in the atmosphere and is chemically

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inert in the troposphere and stratosphere. Nevertheless, it can exchange oxygen isotopes with liquid water (e.g. the oceans) and in plants via the enzyme carbonic anhydrase (Farquhar et al., 1993; Trolier et al., 1996). These exchange processes largely determine the oxygen isotope composition of CO₂ in the troposphere. Measurements of stratospheric and mesospheric samples, however, reveal strong enrichments of the heavy oxygen isotopes in CO₂ (Alexander et al., 2001; Boering, 2004; Kawagucci et al., 2008; Lämmerzahl et al., 2002; Thiemens et al., 1995a, b; Wiegel et al., 2013). These oxygen isotope enrichments derive from isotope exchange of CO₂ with O(¹D) via a short-lived CO₃^{*} intermediate (Liang et al., 2007; Perri et al., 2003; Yung et al., 1991).

The isotope delta (δ) represents the relative isotope ratio difference of a sample to a reference material, e.g. $\delta(^n\text{O}/^{16}\text{O}, \text{sample/reference}) = R(^n\text{O}/^{16}\text{O}, \text{sample})/R(^n\text{O}/^{16}\text{O}, \text{reference}) - 1$. ^nO stands for ^{17}O or ^{18}O . R is the isotopic abundance ratio, e.g. $x(^{17}\text{O})/x(^{16}\text{O})$ or $x(^{18}\text{O})/x(^{16}\text{O})$. Usually, δ values are reported in ‰. Here, we also use the abbreviated notations $\delta^n\text{O}_{\text{sample/reference}}$ or $^n\delta_{\text{sample/reference}}$ and omit the subscript index where not required. For oxygen isotopes, the international reference materials are Vienna Standard Mean Ocean Water (VSMOW), Vienna Pee Dee Belemnite (VPDB) and atmospheric O₂.

Most isotope fractionation processes are mass dependent because they arise from differences in chemical and physical properties that depend on mass such as vibrational zero point energies. For mass dependent fractionation processes, variations in ^{17}O and ^{18}O are closely linked via the relationship $1 + \delta^{17}\text{O} = (1 + \delta^{18}\text{O})^\lambda$, with λ between 0.501 and 0.531 (Kaiser, 2008). Where $\delta(^{17}\text{O})$ deviates from this relation between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, the deviation can be expressed as ^{17}O excess, here defined as $\Delta^{17}\text{O} = [1 + \delta(^{17}\text{O})]/[1 + \delta(^{18}\text{O})]^\lambda - 1$. Other definitions are also in use (Kaiser et al., 2004).

The isotopic composition of CO₂ can be determined by isotope ratio mass spectrometry (IRMS), measuring the ion currents for the isotopologues with mass 44, 45 and 46. A significant complication is that three isotope ratios ($^{17}\text{O}/^{16}\text{O}$, $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$)

o. d. stainless steel (SS). The mass flow controllers together with V1, V2 and V3 are assembled on a SS plate. A metal cover protects the whole construction and capillaries from temperature variations.

The five subunits of the system will be described in the following sub-sections: an automated air sample injection system (Sect. 2.1.1), the CO₂ separation unit (2.1.2), the oxygen isotope exchange unit (2.1.3), the post-CO₂ peak focusing unit (2.1.4) and the mass spectrometer (2.1.5). All parts of the analytical system (except for the sample injection system) are continuously flushed with helium (He) carrier gas (99.99 % purity; Air Products). Three mass flow controllers (MFCs; MKS Instruments) control the gas flow in the system: MFC-injection controls sample air flow in the sample injection unit, MFC-GC provides a stable He flow in the CO₂ separation unit, and MFC-oven controls He flow in the isotope exchange unit.

2.1.1 Automated sample injection

Following the “identical treatment principle” (Werner and Brand, 2001) the automated sample injection system allows isotope analysis of atmospheric samples against air from a reference air cylinder in one measurement cycle (Fig. 2). MPort, a multiport eight-position Valco valve, forms the core of the sample injection unit. Ports 1 and 5 are connected to the reference air cylinder and sample bottles (SA1, SA2) are connected to ports 3 and 7. Ports 2, 4, 6 and 8 are capped to avoid gas mixing in the lines; they are used as STOP positions in between measurements. Note that this could also be realized in principle with a 4-port-8-position valve or be extended to an 8-port-16-position valve where the stop positions are already manufactured into the valve. The pressure sensor (Sensor Techniques) monitors the gas pressure in the injection line (1–5 bars), and the MFC-injection controls sample gas flow to a flow rate of 1.0 mL min⁻¹ during sample loop loading and zero flow during intermediate times in order to limit sample consumption. The selected air sample fills the sample loop and enters the gas chromatography column by switching V1. For ambient air, we use a sample loop of 1 mL, and the loop is filled to ambient pressure. Each complete isotope analysis

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requires two separate air injections. The first aliquot is subsequently isotopically equilibrated with oxygen from CeO₂ (“PostCO₂”), and the second aliquot is measured directly (“PreCO₂”). In order to improve analytical precision, multiple measurements (usually ten) are performed on one air sample.

It is important to avoid gas mixing in the injection lines between two air samples introduced to the system through MPort. Therefore, an automated vent is used to clean the injection lines between different air samples. To avoid gas mixing in the injection lines we use a two-step procedure. First, after the last measurement of a certain air sample or reference air, the MPort valve switches to a STOP position and the SS injection lines are depressurized by shortly opening the automated vent valve. Second, the MPort valve switches to the new air flask and the inlet system together with a sample loop in Valco-1 (in position LOAD) is flushed at higher flow rate with the new sample. After this flushing step the protocol described in Sect. 2.2.2 applies.

2.1.2 CO₂ separation from air

CO₂ is separated from the air and residual gases (N₂, O₂, Ar, N₂O and hydrocarbons) on a gas chromatography (GC) capillary column (PoraPLOT Q 25 m × 0.53 mm, Varian) maintained at 40 °C, with helium as carrier gas. At a flow rate of 4 mL min⁻¹, the air peak (mainly N₂ and O₂) elutes at 120 s after the sample injection, CO₂ at 160 s and N₂O at 190 s. The non-CO₂ gases leave the analytical system either through the open split capillary or through the vent in V3 (depending on whether V3 is in position LOAD or INJECT). The separated CO₂ aliquot is directed either to the oxygen isotope exchange unit or to the IRMS.

2.1.3 Oxygen isotope exchange unit

Following Assonov and Brenninkmeijer (2001), we use solid cerium(IV) oxide (CeO₂) to exchange oxygen atoms with CO₂. For our experiments, we use high purity CeO₂ powder (Merck, #102263). The powder is crushed in a mortar, and the size fraction

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of 0.25–0.5 mm is selected to fill a quartz glass reaction tube (1.4 mm i. d., 3.0 mm o. d., 300 mm length). Scanning Microscopy elemental composition scans performed at the Institute of Non-Ferrous Metals in Gliwice, Poland showed no presence of sulfur on the CeO₂ grains. Therefore, unlike Assonov and Brenninkmeijer (2001), we did not attempt to eliminate sulfate impurities from CeO₂ by high temperature treatment. The quartz tube is filled up manually with 1.000 ± 0.050 g (6 mmol) of the CeO₂ powder and capped from both sides with quartz wool, preventing CeO₂ grains from entering other parts of the system. The reaction tube is placed in a tube furnace regulated by a temperature controller. We refer to this assembly as the “CeO₂ oven”. The isotope exchange reaction proceeds at high temperature (700 °C) and is fast and highly efficient. However, the CeO₂ oven presents an additional flow resistance, so therefore MFC-oven provides He with higher head pressure so that a flow rate of 20 mL min⁻¹ is reached. Before the first use, the CeO₂ exchange reagent is preconditioned with oxygen gas, see Sect. 2.2.1. For this, we supply O₂ manually via opening an oxygen gas line with a needle valve placed before the MFC-oven. Mixed He/O₂ gas flushes the oven and leaves the analytical system via the vent in V3.

2.1.4 Collection of CO₂ after isotope exchange

The isotopically equilibrated CO₂ peak is strongly broadened after passing through the CeO₂ oven and needs to be refocused before entering the isotope detection unit in our analytical system. Therefore, after the isotope exchange reaction, the equilibrated CO₂ is collected on a U-shaped tube (1/8 inch SS, $L = 500$ mm) immersed in a liquid nitrogen (LN₂) bath. After complete collection, the trap is lifted up above the LN₂ level; CO₂ is released and is flushed further to V3 with He. The cryogenically focused peak is very sharp, and an empty 1 mL SS volume is placed before V3 in order to broaden the peak so that the PreCO₂ and PostCO₂ peaks appear on chromatogram with similar intensity. We have found that keeping the level of liquid nitrogen in the LN₂ dewar constant improves system reproducibility. In our system a constant level is provided by

a microdosing liquid nitrogen pump (NORHOF Holland) connected to a big 50 L dewar, which is sufficient to keep measurements running for three days.

2.1.5 Isotope detection unit and isotope ratio mass spectrometry

Pre- and post-equilibrated CO₂ aliquots are transferred via V3 through a Nafion™ dryer to a custom-made open split system (Röckmann et al., 2003) and finally detected with an IRMS (Thermo Fisher Scientific Delta V Advantage). The three molecular ion masses *m/z* 44, 45 and 46 are measured simultaneously. ⁴⁵δ and ⁴⁶δ are measured relative to a rectangular CO₂ working reference gas peak. As the instrument software assumes mass dependent oxygen isotope fractionation, the data reduction is performed separately to derive ¹³δ, ¹⁷δ and ¹⁸δ (see calculation Sect. 2.3).

2.1.6 The laboratory standards

For our measurements we use two working reference gases: reference CO₂ (RefCO₂) and reference oxygen (RefO₂) and helium as a carrier gas. The isotope values for the laboratory standards are: δ¹³C(RefCO₂) = -32.39‰ vs. VPDB, δ¹⁸O(RefCO₂) = 5.34‰, δ¹⁷O(RefO₂) = 9.33‰ and δ¹⁸O(RefO₂) = 19.00‰ vs. VS-MOW.

2.2 Measurement procedure

The measurement routine is fully automated and most items are controlled via the ISO-DAT 3.0 software (Thermo Fisher). ISODAT controls the positions of the three Valco valves, the pneumatic lifter of the LN₂ trap and the movement of the open split capillaries. The MPort valve is controlled with a commercial electronic switching unit that can communicate with ISODAT. The gas flow rate for MFC-injection is controlled via an ISO-DAT signal that switches between two set points of the MKS module, type PR4000B. We use a sample flow rate of 1 mL min⁻¹ during sample loop loading and zero flow for

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intermediate times in order to save sample. Instead of the MKS modules, we use custom made electronic controllers for MFC-GC and MFC-oven. For MFC-GC, we use only one of two possible set points and He of 4 mL min⁻¹ flow rate continuously flushes the GC column. For MFC-oven, the two set points for the He flow are 20 mL min⁻¹ to push the post-equilibrated CO₂ through the oven and 6 mL min⁻¹ for intermediate times.

A single measurement of an unmodified aliquot and a CO₂ aliquot after isotope exchange takes 15 min. The short analysis time and a low sample usage allow multiple measurements on each air sample. In 2.5 h of analysis, we can repeat measurements ten times and improve the analytical precision statistically, see Sect. 3.4.

An example of an IRMS chromatogram is shown in Fig. 3. PreCO₂ is detected between 450 and 500 s (peak number 6 on chromatogram) and PostCO₂ is detected between 850 and 900 s (peak number 10 on chromatogram). The other peaks are the working laboratory reference CO₂ (RefCO₂) injected to the IRMS via the open split interface.

2.2.1 Preconditioning of CeO₂ reagent

Before the first use the CeO₂ oven is preconditioned with oxygen gas of constant isotopic composition. Additionally oxygen cleans the isotope exchange reactant from contaminations that may occur during tube preparation. To equilibrate CeO₂ powder with oxygen, we open the needle valve placed before MFC-oven, allowing O₂ to mix into the He flow. We flush the oven with the He/O₂ mixture for 3 h at 600 °C. Next, we close the needle valve and increase the oven temperature to 700 °C. The CeO₂ oven remains under He flow for 1 h, and then the analytical system is ready to measure atmospheric air samples. As mentioned by Perrichon et al. (1995) and Assonov and Brenninkmeijer (2001), under long annealing the catalytic behavior of CeO₂ grains may degrade due to changes in CeO₂ surface area. Usually, we oxygenate the oven every 6 weeks (depending on use) and replace the whole quartz reaction tube with new CeO₂ grains every 5 months.

2.2.2 Single measurement routine

Each Valco valve has two possible positions: LOAD or INJECT. At time zero, V1 is in position LOAD (sample loop is flushed with sample air), V2 is in position INJECT (main flow bypasses the oxygen exchange unit), and V3 is in position LOAD (main flow bypasses the LN₂ trap). During the first 80 s, sample air fills the sample loop via V1. Next, V1 switches to position INJECT for 40 s, and the sample air is transferred to the GC column in a He carrier gas (4 mL min⁻¹). CO₂ is separated on the GC column from the air and other minor gases such as N₂O (see below). The air peak starts at 200 s while CO₂ starts at 240 s. To direct CO₂ through the oxygen isotope exchange unit, V2 switches to position LOAD from 240 s to 290 s. At that time, the purified CO₂ has been injected to the CeO₂ oven where it is isotopically equilibrated with the oxygen from CeO₂. The cryogenic trap is immersed in the LN₂ bath at 260 s. When V2 switches back to position INJECT, the He supply is provided by MFC-oven, and the flow rate is increased to 20 mL min⁻¹ in order to speed up transfer through the CeO₂ oven. The equilibrated CO₂ is then directed via V2 and V3 to the cryogenic trap where it is collected. At 835 s, collection of isotopically exchanged CO₂ is complete, the LN₂ trap is lifted up, V3 switches to position INJECT, and PostCO₂ is transferred via the open split interface to the IRMS. The *m/z* 44, 45 and 46 ion currents of PostCO₂ are detected between 850 and 900 s with peak intensity around 2500 mV.

While CO₂ from the first air injection is transferred through the CeO₂ oven and to the cryogenic trap, the second aliquot of the same sample air is introduced into the analytical system. This air injection is used for direct isotope measurement of CO₂ (PreCO₂). Similar to the first injection, the sample loop is flushed with sample air for 80 s (V1 in position LOAD between 215 and 295 s). At 295 s V1 switches from LOAD to INJECT for 40 s, and the sample air is transferred to the GC column. After PreCO₂ is separated from the air and other minor gases, it is directed via V2 (INJECT) and V3 (LOAD) to the IRMS. PreCO₂ appears on the chromatogram between 450 to 500 s and

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with peak intensity around 2500 mV. Since PreCO₂ takes a much shorter path through the analytical system and does not require focusing, it is detected before PostCO₂.

Eight peaks of the working laboratory reference CO₂ (RefCO₂) are injected via the open split interface during the run. The molecular delta values ⁴⁵δ(CO₂) and ⁴⁶δ(CO₂) of PreCO₂ and PostCO₂ are calculated by ISODAT relative to the working gas reference peaks. We choose the CO₂ peaks number five and nine in the chromatogram to be our working gas reference peaks.

2.2.3 Measurement cycle

Full automation of our analytical technique allows measurement of air samples against the reference air in one measurement cycle. This allows monitoring and correcting for daily changes in the analytical system performance or long-term trends in the system. Our reference air cylinder is filled with tropospheric air collected at the Cabauw tall tower (51.971° N, 4.927° E). The reference air cylinder is always connected to MPort positions 1 and 5 while the air samples are connected to positions 3 and 7. We define a *measurement cycle* as a sequence of measurements in the following order: Reference air – Sample air 1 – Reference air – Sample air 2 – Reference air. There are no significant differences between different ports. Since we repeat measurements on each port ten times, the measurement cycle is composed of 50 measurements.

2.3 Calculations

We calculate the ¹⁷O-excess in CO₂ from the signals on *m/z* 44, 45 and 46 of CO₂ directly measured on IRMS (PreCO₂) and CO₂ measured on IRMS after equilibration with oxygen from CeO₂ (PostCO₂). The parameters used for our calculations are from Kaiser and Röckmann (2008): $C = {}^{17}R_{\text{ref}}/{}^{13}R_{\text{ref}} = 0.03516$, $D = {}^{13}R_{\text{ref}} \cdot {}^{17}R_{\text{ref}}/2{}^{18}R_{\text{ref}} = 0.001042$ and $\lambda = 0.528$. λ describes the mass-dependent relationship between the three oxygen isotopes. The theoretical range of λ is 0.50 to 0.53, and it varies for different fractionation processes. Hofmann et al. (2012) have shown that for CO₂-water

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equilibration $\lambda = 0.522$ while Kaiser (2008) have argued for the use of 0.528, for mass dependently fractionated CO_2 samples, as have Assonov and Brenninkmeijer (2003) for the ^{17}O -correction algorithm. For results shown in this paper $\Delta^{17}\text{O}$ varies by about 0.06 ‰ when taking $\lambda = 0.522$ instead of $\lambda = 0.528$.

Note the calculations of the ^{17}O -excess in CO_2 do not depend on the actual isotope ratios as demonstrated by Kaiser (2008). Rather, only the quantities

$$C = \frac{{}^{13}R_{\text{ref}}}{{}^{17}R_{\text{ref}}} = \frac{{}^{13}R_{\text{VPD}\text{BCO}_2} [1 + \delta^{13}\text{C}_{\text{ref}/\text{VPD}\text{BCO}_2}]}{{}^{17}R_{\text{VPD}\text{BCO}_2} [1 + \delta^{17}\text{O}_{\text{ref}/\text{VPD}\text{BCO}_2}]} \quad (1)$$

and

$$D = \frac{{}^{13}R_{\text{ref}} {}^{17}R_{\text{ref}}}{2^{18}R_{\text{ref}}} = \frac{{}^{13}R_{\text{VPD}\text{BCO}_2} [1 + \delta^{13}\text{C}_{\text{ref}/\text{VPD}\text{BCO}_2}] {}^{17}R_{\text{VPD}\text{BCO}_2} [1 + \delta^{17}\text{O}_{\text{ref}/\text{VPD}\text{BCO}_2}]}{2^{18}R_{\text{VPD}\text{BCO}_2} [1 + \delta^{18}\text{O}_{\text{ref}/\text{VPD}\text{BCO}_2}]} \quad (2)$$

are required, where ref = Ref CO_2 . The conversion equations from $^{45}\delta$ and $^{46}\delta$ of Post CO_2 (with respect to working reference CO_2) to $^{13}\delta$, $^{17}\delta$ and $^{18}\delta$ can be written in terms of C and D as follows:

$$^{18}\delta = ^{46}\delta + D[(2 + C)^{46}\delta - (2 + 4C)^{45}\delta(1 + ^{17}\delta) - (2 - 2C)^{17}\delta + 3C^{17}\delta^2] \quad (3)$$

$$^{17}\delta = (1 + ^{18}\delta)^\lambda - 1 \quad (4)$$

These equations are solved iteratively and typically converge to better than 0.001 ‰ after 3 iterations.

$$^{13}\delta = (1 + 2C)^{45}\delta - 2C^{17}\delta \quad (5)$$

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Using $^{13}\delta(\text{PostCO}_2) = ^{13}\delta(\text{PreCO}_2)$, $^{17}\delta(\text{PreCO}_2)$ is calculated as

$$^{17}\delta(\text{PreCO}_2) = \left(1 + \frac{1}{2C}\right) \left[^{45}\delta(\text{PreCO}_2) - ^{45}\delta(\text{PostCO}_2) \right] + ^{17}\delta(\text{PostCO}_2) \quad (6)$$

Then, $^{18}\delta(\text{PreCO}_2)$ is calculated using Eq. (3).

To correct for daily variability of the system, we calculate $\delta^{13}\text{C}$, $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of the sample (SA) relative to the average of the reference air measured before and after the sample (RefAir) following Eq. (7). Note Std stands for international standards.

$$\delta_{\text{SA/RefAir}} = [(\delta_{\text{SA/Std}} + 1)/(\delta_{\text{RefAir/Std}} + 1)] - 1 \quad (7)$$

The CO₂ in the reference air was calibrated vs. international standards at UC Berkeley (group of K. Boering) and has been assigned isotope values of $\delta^{13}\text{C}(\text{RefAir/VPDB}) = (-8.25 \pm 0.10)\%$; $\delta^{17}\text{O}(\text{RefAir/VSMOW}) = (16.95 \pm 0.40)\%$; $\delta^{18}\text{O}(\text{RefAir/VSMOW}) = (32.74 \pm 0.08)\%$ and $\Delta^{17}\text{O} = (-0.20 \pm 0.40)\%$. We calculate the final δ values of the sample according to:

$$\delta_{\text{SA/Std}} = \delta_{\text{SA/RefAir}} \cdot \delta_{\text{RefAir/Std}} + \delta_{\text{SA/RefAir}} + \delta_{\text{RefAir/Std}} \quad (8)$$

Finally, the $\Delta^{17}\text{O}$ is calculated as follows:

$$\Delta^{17}\text{O} = [1 + \delta(^{17}\text{O})]/[1 + \delta(^{18}\text{O})]^\lambda - 1 \quad (9)$$

3 Performance of the analytical system

3.1 Blank measurements

Blank measurements were carried out not only to verify that the analytical system is leak tight but also to detect possible contamination from the GC column or from the oxygen isotope exchange unit. During the blank measurement, pure He carrier gas was

injected into the analytical system and the usual measurement routine was applied (described in Sect. 2.2.1). No peak was detected on the chromatogram between 450 to 500 s suggesting no contamination from the GC and the absence of leaks. A peak with an area of 0.3 Vs was detected in the PostCO₂ detection window (between 850 to 900 s). This peak originates from the CeO₂ oven. As this is only 1.4 % of a typical sample peak and it would affect sample and reference air in the same way, no corresponding correction is applied.

3.2 N₂O contamination

Because it has the same molecular mass, the isotopologues of N₂O interfere with CO₂ isotopologues in IRMS measurements at m/z 44, 45 and 46 (Mook and van der Hoek, 1983). The N₂O mixing ratio of atmospheric air is about 1200 times smaller than for CO₂. In our system, we expect N₂O peak areas to be as small as 0.02 Vs for 20 Vs CO₂ peak areas. This is at the peak detection limit, and it is difficult to detect N₂O on the IRMS chromatogram. However, the distribution of molecular ion masses 44, 45 and 46 in N₂O is very different from the distribution in CO₂, and therefore N₂O interfering with CO₂ can decrease $\Delta^{17}\text{O}$ by 3‰ (Wiegel et al., 2013). For precise isotope measurements, CO₂ has to be separated from N₂O or a correction for the N₂O interference needs to be applied. In our online technique, N₂O is separated from CO₂ on the gas chromatography capillary column. To verify that CO₂ and N₂O are well separated, we prepared a mixture of 400 ppm N₂O in synthetic air. We injected this N₂O-rich gas to our system from MPort position 3. The N₂O was detected on the chromatogram between 250–275 s. While the SS injection line between MPort and MFC-injection still contained the N₂O-rich gas, venting was not applied. MPort was moved to position 5 allowing the reference air to mix with the N₂O-rich gas in subsequent runs. The reference air became contaminated with N₂O in quantities that are similar to the CO₂ mixing ratio. On the following IRMS chromatogram, both CO₂ and N₂O appeared, and even for these high amounts of N₂O, the peaks were almost baseline-separated (see Fig. 4). This shows that for normal air, N₂O and CO₂ are separated on the GC capillary

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column, and a corresponding N₂O correction does not need to be applied, similar to what was shown by Ferretti et al. (2000).

3.3 Equilibration efficiency

In order to quantify CeO₂ equilibration efficiency, four atmospheric air samples with different $\delta^{18}\text{O}(\text{CO}_2)$ values were measured against RefAir in two measurement cycles. In the first measurement cycle, SA1 and SA2 were connected to MPort position 3 and 7 while reference air was connected to positions 1 and 5. In the second cycle, SA3 and SA4 were connected to position 3 and 7 instead of SA1 and SA2. Ten measurement repetitions were performed on each gas, so therefore the whole measurement sequence was 90 runs long.

The $\delta^{46}\text{CO}_2$ isotope values of PreCO₂ were the following: RefAir = 24.50‰; SA1 = 35.40‰; SA2 = 36.77‰; SA3 = 32.65‰ and SA4 = 36.84‰ all relative to RefCO₂ ($1\sigma = 0.10\text{‰}$). Figure 5 shows $^{46}\delta$ of these four samples and the reference air after isotopic equilibration. In all cases, $\delta^{46}\text{CO}_2$ is equilibrated to 21.82‰ with precision of 0.08‰, after the isotopic exchange reaction. In other experiments, when the initial $\delta^{18}\text{O}$ between RefAir and the air samples were 30‰ different, the $\delta^{18}\text{O}$ was indistinguishable within 0.09‰. This proves that oxygen equilibration reaction in CeO₂ oven is highly efficient and that the exchange rate is > 99.7% (1–0.09/30).

3.4 System reproducibility and long stability test

RefAir (directly from the cylinder) and two SS 2L cans (filled separately from the RefAir cylinder) were connected into the analytical system via the four different injection ports (MPort position 1, 3, 5 and 7) and measured continuously for several days. The MPort position was changing for each 10 measurements, and a total of 270 measurements were performed. Figure 6 shows the results for each single measurement (blue points) and for each group of 10 measurements (diamonds). There is no significant difference between measurements from the main cylinder and from the aliquots in the smaller

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flasks (p value of ANOVA significance test is 0.8). The $\Delta^{17}\text{O}$ values are randomly distributed within the measurement error, and the long-term analytical system stability does not vary.

The mean value of $\Delta^{17}\text{O}$ for our RefAir is -0.30‰ (rel. to VSMOW), which reflects the calibration of the UC Berkeley measurements to our reference air ($\Delta^{17}\text{O} = -0.20 \pm 0.40\text{‰}$). The standard deviation for all 270 individual measurements is 1.68‰ , but this improves to a standard deviation of 0.58‰ when they are split into 27 groups of ten measurements each.

The reproducibility (1σ) of 27 groups of the raw data, i.e. the isotopologue ratios (45/44 and 46/44) is 0.02‰ and 0.13‰ for non-equilibrated CO_2 and 0.04‰ and 0.08‰ for equilibrated CO_2 , respectively. The main contribution to the measurement error of $\Delta^{17}\text{O}$ is the uncertainty in the isotope ratio 45/44 after the isotopic exchange reaction. $^{12}\text{C}^{16}\text{C}^{17}\text{C}$ contributes only about 1/15 to the signal at m/z 45 (Kawagucci et al., 2008; Röckmann and Brenninkmeijer, 1998); therefore, the approximate precision of $\Delta^{17}\text{O}$ in a sample of ten measurements is $15 \times 0.04\text{‰} = 0.60\text{‰}$. This value is in good agreement with our experimental uncertainty of 0.58‰ .

In order to show how multiple measurements on one sample can improve our system precision further, we divide 270 measurements from the long stability test into groups of different size: 2 groups of 135 runs; 3 groups of 90 runs; 5 groups of 54 runs; etc. For each case, we calculate the standard error (SE) of the individual samples. As $\text{SE} = \sigma/n^{0.5}$, a linear correlation between $\ln(\text{SE})$ and $\ln(n)$ is expected with slope -0.5 with the results shown in Fig. 7. The standard error shows a generally monotonic decrease with increasing number of measurements per package. The expected slope for this graph is -0.5 and the experimental slope is -0.468 . The results indicate that for large air samples (with a volume 750 mL and larger), we are able to determine $\Delta^{17}\text{O}$ with a precision of 0.2‰ .

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3.5 Linearity test

Possible non-linearity effects of the analytical system were examined by diluting the reference air with 5% and 10% of synthetic air (CO₂-free). This means a reduction of the initial mixing ratio of 400 ppm to 380 and 360 ppm. Dilutions were prepared barometrically in 2 L and 150 mL SS flasks. Figure 8 shows the difference in $\Delta^{17}\text{O}$ between the dilution and the undiluted RefAir sample as a function of CO₂ peak area: 5% dilution peak > 17.5 Vs and 10% dilution peak < 17.5 Vs. The $\Delta^{17}\text{O}$ results are not statistically different from the reference air, and not from each other (p value of an ANOVA significance test is 0.7). We conclude that the $\Delta^{17}\text{O}$ signal is not affected by decreases in the mixing ratio up to 10% as they may occur in the stratosphere. As such, our system is suitable for measurement of atmospheric air samples with CO₂ mole fractions between 400 ppm and 360 ppm.

4 Stratospheric air samples

The scientific potential of our analytical system was established by measuring stratospheric air samples obtained within the EU project RECONCILE. Samples were collected in the polar region (aircraft base in Kiruna/Sweden) with the high-altitude aircraft M55-Geophysica during December 2011. The air samples were measured for numerous tracers, such as N₂O, CFC-11, CFC-12, CH₄ (Kaiser et al., 2006; Laube et al., 2010; Röckmann et al., 2011) and the remaining air was used for measurement of the isotopic composition of CO₂ with the analytical technique described here. In Fig. 9, we show the oxygen isotopic composition of three stratospheric air samples together with already published data. The samples measured with our analytical technique agree with available data for stratospheric CO₂ (Kawagucci et al., 2008; Lämmerzahl et al., 2002; Wiegel et al., 2013). The precision for the RECONCILE data is 0.03‰ (1 σ) for $\delta^{13}\text{C}$, 0.07‰ (1 σ) for $\delta^{18}\text{O}$ and 0.55‰ (1 σ) for $\delta^{17}\text{O}$ for a group of 10 measurements. An in-depth analysis of the new dataset will be published in a separate paper.

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We have established an online measurement system for measurement of $\Delta^{17}\text{O}$ in CO_2 based on complete oxygen isotope exchange with CeO_2 at 650°C (Assonov et al., 2001) and similar to the online system using a copper oxide exchange reagent by Kawagucci et al. (2005). Our method is the first fully automated analytical system that uses CeO_2 as the isotope exchange medium. The 3 h labor characterized for a single measurement in the offline techniques (Assonov et al., 2001; Hofmann and Pack, 2010; Mahata et al., 2012) was decreased to minimum: connecting air samples to the injection lines, filling LN_2 dewar and running the measurement sequence by pressing start bottom. That was possible by constructing the automated sample injection, by applying ISODAT 3.0 software and electronic devices to control movement of valves, LN_2 trap and gas flow in the MFC's, and finally by using microdosing LN_2 pump to keep the liquid nitrogen level in CO_2 trap constant.

Although the standard deviation of a single run is higher than for already established methods that use CeO_2 (Assonov and Brenninkmeijer, 2001; Hofmann and Pack, 2010; Mahata et al., 2012) it can be decreased statistically with multiple measurements on one sample. The reproducibility of measured $\Delta^{17}\text{O}$ is 0.6‰ for ten measurements (usage of the air sample 30 mL) and can be decreased statistically to 0.2‰ (usage of the air sample 750 mL). Our system is designed for measuring atmospheric air samples with CO_2 mole fractions between 360 and 400 ppm. The most promising application of our system is analysis of stratospheric CO_2 from air samples of volume 100 mL and less. So far, we have successfully measured three oxygen isotope composition of CO_2 from air samples collected above Kiruna/Sweden and polar region in December 2011. In the present setup a limitation is the requirement of overpressure of the sample gas in the injection unit of at least 1.4 bar. The current focus is on further development of the injection unit to allow measurement of air samples at ambient pressure.

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Community's Seventh Framework Program (FP7/2007–2013), Grant 237890. The stratospheric samples were collected on flights of the high-altitude aircraft Geophysica, financed by the European Commission (FP7 project RECONCILE-226365-FP7-ENV-2008-1). We thank the Institute of Non-Ferrous Metals in Gliwice, Poland and Marzena Lech-Grega for the Scanning Microscope analysis on CeO₂ powder. We thank Kristie Boering and her research group for help in calibrating our reference air relative to VSMOW.

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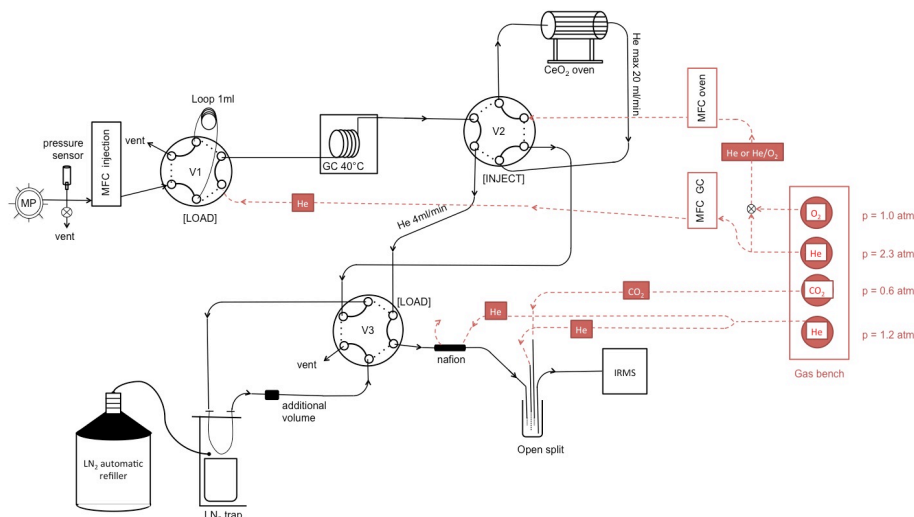


Figure 1. Schematic set-up of the analytical system (black) with the gas supply system (red). The sample injection unit (shown in detail in Fig. 2) contains a Multiport Valve (MPort), Mass Flow Controller (MFC), Valco valve 1 (V1) and is used to inject 1 mL of sample air into the analytical system. The gas chromatography column (GC) separates CO_2 from the rest of sample air. V2 injects the first CO_2 aliquot to the CeO_2 oven and the second straight to IRMS; V3 provides the possibility to collect isotopically equilibrated CO_2 in a liquid nitrogen trap. The 1 mL volume after the trap is used to broaden the peak without providing a flow restriction. The CO_2 peaks are injected into the IRMS through an open split interface. Crossed circles are valves.

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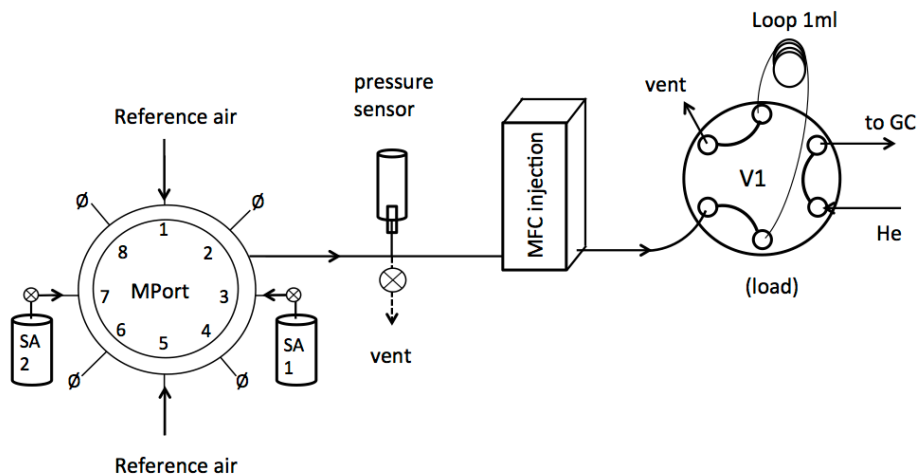


Figure 2. Schematic setup of the sample injection unit. From left: multiport valve (MPort), sample air canisters (SA1 and SA2), reference air ports, pressure sensor, an automated vent valve, mass flow controller (MFC-injection) and Valco V1 with 1 mL sample loop. All injection lines are 1/8 inch stainless steel tubes. Sample injection is fully automated. Crossed circles above the air sample flask are valves.

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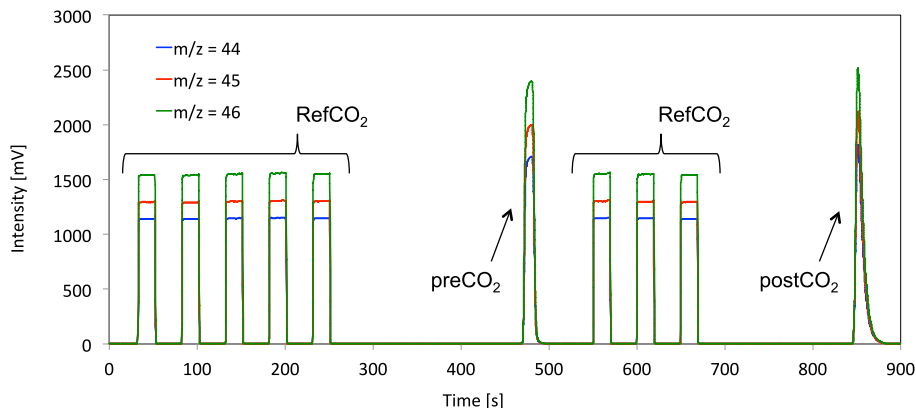


Figure 3. Example of a typical IRMS chromatogram. Eight square peaks of the working laboratory reference CO₂ (RefCO₂) are injected, and two CO₂ peaks of the measured air sample. Peak number 6 is non-equilibrated CO₂ (PreCO₂). Peak number 10 is isotopically equilibrated CO₂ (PostCO₂).

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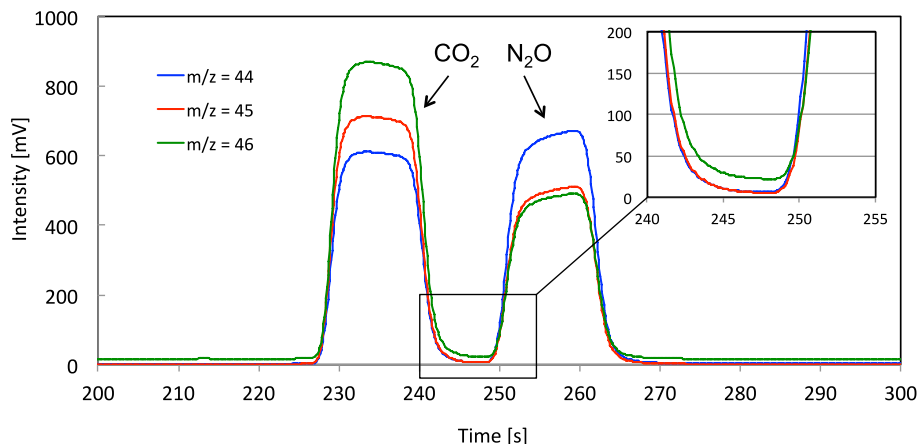


Figure 4. Chromatogram showing the separation of CO₂ from N₂O in the artificially prepared mixture. The sample was injected to the analytical system at 60 s. CO₂ appeared on chromatogram at 220–243 s and N₂O appeared at 248–275 s. Peaks are well separated, the interval between the CO₂ and N₂O peaks is 5 s. The air peak (normally visible at 180–210 s) is not included on this chromatogram.

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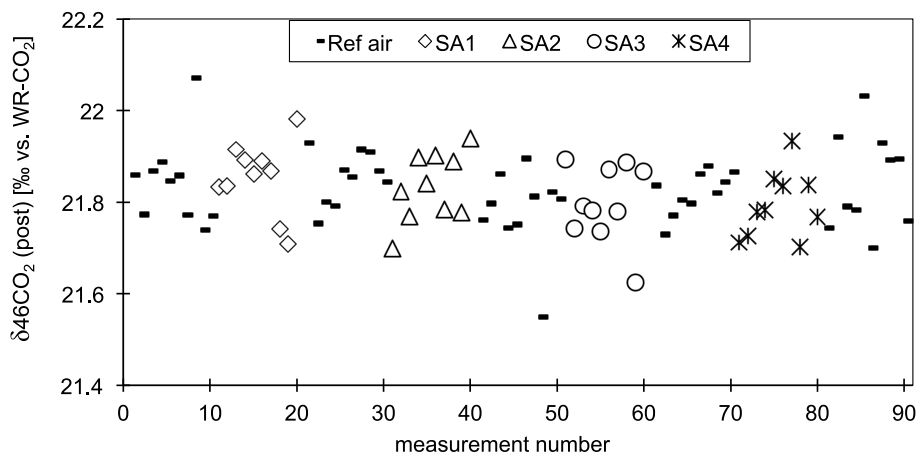


Figure 5. Full and highly efficient oxygen equilibration reaction in the CeO_2 oven represented by isotopically exchanged CO_2 of four diverse atmospheric air samples (SA1 – rhombs, SA2 – triangles, SA3 – circles and SA4 – stars) measured against the reference air (stripes). The initial differences in $\delta^{18}\text{O}$ between the reference air and the air samples were up to 12‰.

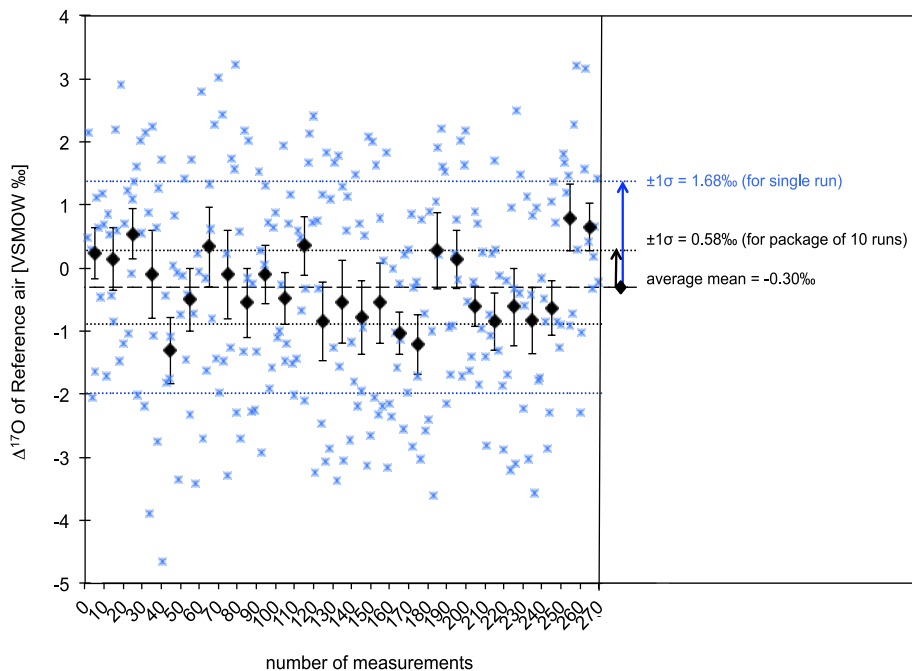


Figure 6. Stability and reproducibility test for the analytical system: $\Delta^{17}\text{O}$ values of reference air were measured constantly for several days. Striped black line indicates the average value of 270 runs and for 27 groups of ten measurements respectively. The dotted lines indicate standard deviation over 270 individual runs (blue) and over 27 groups of 10 measurements (black) and show how multiple measurements on the same sample decrease the measurement error.

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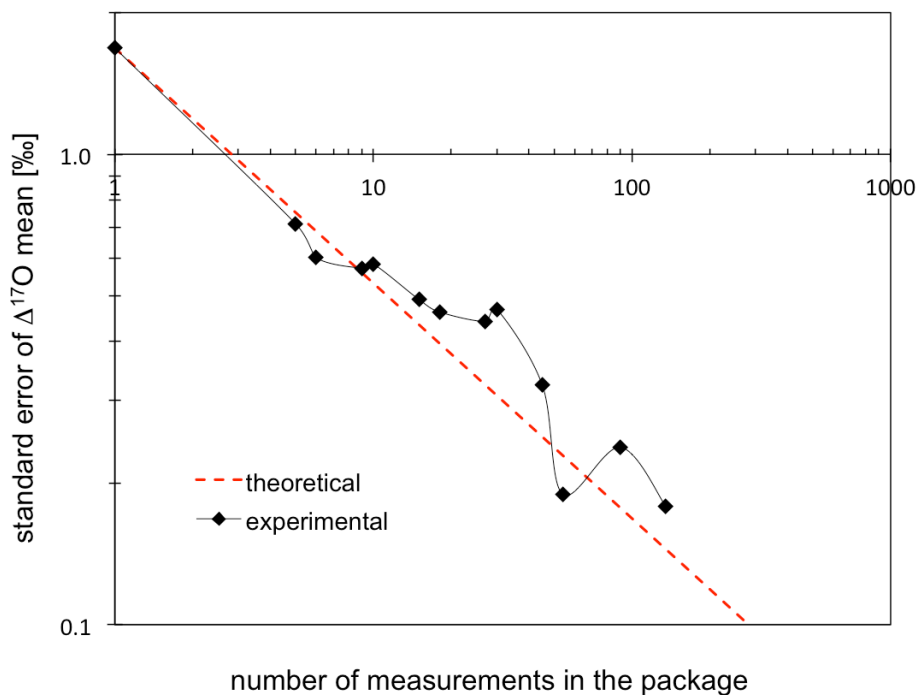


Figure 7. Improvement of the measurement precision by performing multiple measurements on the same air sample. The \ln of the standard error (SE) is plotted vs. \ln of the number of measurements (n) that were included in the calculation of the SE. A SE of about 0.2‰ can be reached after about 100 measurements. The experimentally derived slope for the error reduction is -0.468 , which is close to theoretical value -0.500 .

**Continuous-flow
IRMS technique for
triple-isotope
measurements of
CO₂**

D. J. Mrozek et al.

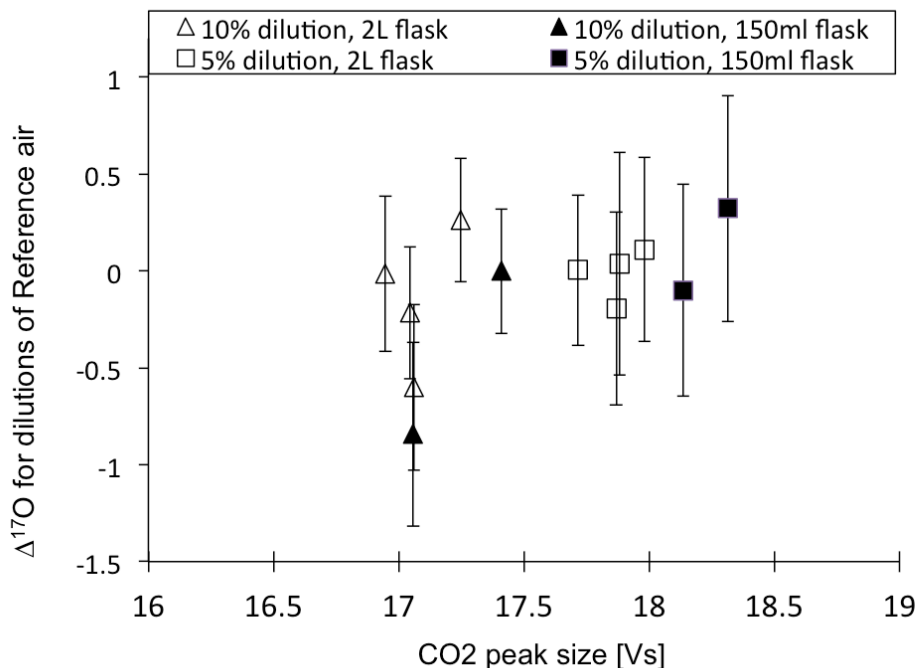


Figure 8. $\Delta^{17}\text{O}$ of CO_2 in aliquots of the laboratory reference gas that was filled into flasks of 2 L and 150 mL volume, respectively. These are the flasks in which the stratospheric samples were measured. The reference air was additionally diluted by 5 % (squares) or 10 % (triangles) with zero air. There is no significant difference between different types of flask, and for the different dilutions, thus no non-linearity can be detected.

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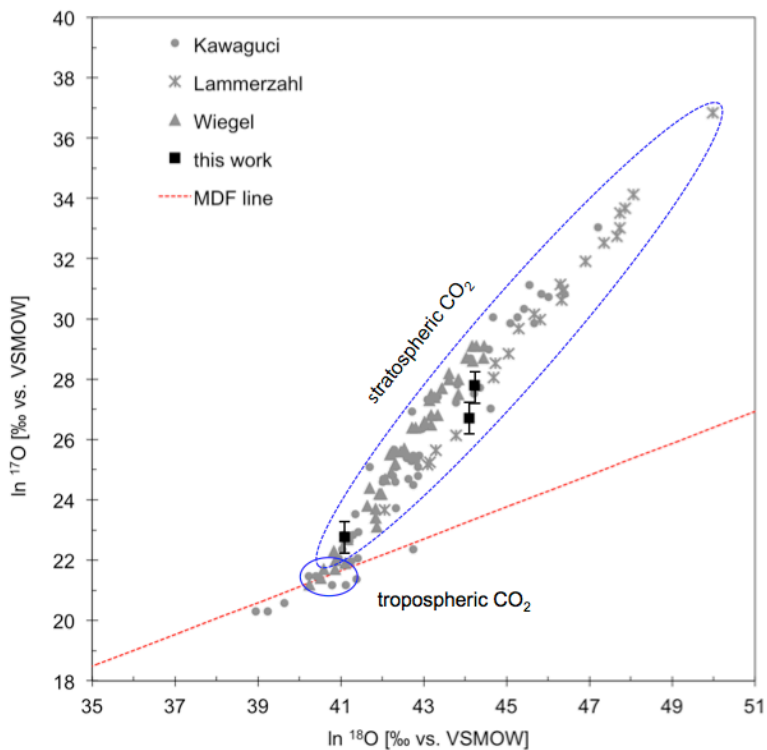


Figure 9. Three-isotope plot for oxygen isotopes in CO₂ from atmospheric air samples. Previous observations are from Kawagucci et al. (2008) circles, Lämmerzahl et al. (2002) diamonds and Wiegel et al. (2013) triangles. Three samples from the RECONCILE project (squares) fall in the range of previously published values. Two blue circles distinguish tropospheric air samples (continuous blue circle) from stratospheric ones (dashed blue circle). The red line is the mass dependent fractionation line with slope 0.528. Note logarithmic scale $\ln^{17}\text{O} = \ln(\delta^{17}\text{O} + 1)$ and $\ln^{18}\text{O} = \ln(\delta^{18}\text{O} + 1)$.

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