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Continuous-flow IRMS technique for determining the ^{17}O excess of CO_2 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 stratospheric 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 $\Delta^{17}\text{O}$ 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 size (including flushing) is 2.7 mL of air. A single analysis (one pair of injections) takes 15 minutes. The analytical system is fully automated for unattended measurements over several days. The standard deviation of the ^{17}O excess analysis is 1.7 ‰. Multiple measurements on an air sample reduce the measurement uncertainty, as expected for the statistical standard error. Thus, the uncertainty for a group of 10 measurements is 0.58 ‰ for $\Delta^{17}\text{O}$ in 2.5 h of analysis. 100 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

a sample of 10 measurements. This is sufficient to examine stratospheric enrichments, which at altitude 33 km go up to 12 ‰ for $\delta^{17}\text{O}$ and up to 8 ‰ for $\delta^{18}\text{O}$ with respect to tropospheric CO_2 : $\delta^{17}\text{O} \approx 21$ ‰ Vienna Standard Mean Ocean Water (VSMOW), $\delta^{18}\text{O} \approx 41$ ‰ VSMOW (Lämmerzahl et al., 2002). 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; Trolier et al., 1996). CO_2 is the end product of the carbon oxidation processes in the atmosphere and is chemically 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 CO_2 in the troposphere. Measurements of stratospheric and mesospheric samples, however, reveal strong enrichments of the heavy oxygen isotopes in CO_2 (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 CO_2 with $\text{O}(^1D)$ via a short-

lived CO_3^* 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 O_2 .

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 CO_2 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 $^{13}\text{C}/^{12}\text{C}$) contribute to these masses, but only two ion current ratios are measured (45/44 and 46/44). For example, ^{17}O - and ^{13}C -substituted CO_2 cannot be distinguished by isotope ratio mass spectrometry since mass 45 consists of both $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{17}\text{O}^{16}\text{O}$. Traditionally, the approach has been to assume a mass-dependent relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, effectively eliminating one unknown isotope ratio. However, this does not work for atmospheric trace gases that do not follow mass-dependent fractionation laws. In these cases, measurements of $\delta^{17}\text{O}$ actually provide additional information, but independent determination of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in CO_2 is not straightforward.

One possibility is to convert CO_2 to O_2 and to determine $\delta^{17}\text{O}$ by measuring the 33/32 ion current ratio. Several different conversion methods have been developed (Barkan and Luz, 2012; Brenninkmeijer and Röckmann, 1998; Thiemens et al., 1991).

One possibility to determine $\delta^{17}\text{O}$, is by measuring the 33/32 ion current ratio of O_2 originated from CO_2 . Following this approach several methods have been developed: Bhattacharya and Thiemens (1989) converted CO_2 to O_2 by reacting it with BrF_5 ; Brenninkmeijer and Röckmann (1998) used conversion of CO_2 into CH_4 and H_2O by reaction with H_2 ; in a second step they fluorinated the H_2O with F_2 to produce O_2 and HF ; Barkan and Luz (2012) equilibrated CO_2 with H_2O and used water fluorination to produce O_2 . These methods are labour-intensive and time-consuming, but can

be very precise because the ^{13}C interference is effectively removed.

Assonov and Brenninkmeijer (2001) developed a technique where a hot metal oxide acts as an oxygen isotope exchange medium for CO_2 . To investigate the complete oxygen isotopic composition of CO_2 , the isotopic composition of CO_2 is measured before and after isotopic exchange with oxygen from a solid oxide (CeO_2) of known isotopic composition (Assonov and Brenninkmeijer, 2003; Kaiser, 2008). This technique was developed as an offline analytical technique where the isotope ratios are measured with dual-inlet IRMS. The CO_2 sample sizes were 16 to 29 μmol , equivalent to 1.0 to 1.8 L of tropospheric air. The standard deviation for $\Delta^{17}\text{O}$ was 0.33 ‰. Mahata et al. (2012) modified the method by including an additional step of gas chromatographic separation of CO_2 from N_2O , which improved the standard deviation to 0.06 ‰.

Kawagucci et al. (2005) described the first online method for measuring the isotopic composition of CO_2 . In contrast to Assonov and Brenninkmeijer, Kawagucci used CuO as isotope exchange medium instead of CeO_2 . Applying continuous-flow IRMS allowed reducing the sample size from micromoles to 8.7 nmol of CO_2 for one set of measurements (9 repeat analyses of an air sample), the standard deviation for $\Delta^{17}\text{O}$ of one set was 0.35 ‰.

Instead of isotope exchange with a solid oxide, Mahata et al. (2013) recently described a technique where CO_2 is isotopically equilibrated with O_2 gas in the presence of hot platinum wire. The O_2 can then be analysed without ^{13}C interference. High measurement precision (0.045 ‰ for $\Delta^{17}\text{O}$) was obtained for 20–30 μmol CO_2 , corresponding to an air sample of 2 L volume.

In this paper we present a new system that combines the fast and highly effective oxygen isotope exchange with CeO_2 (Assonov and Brenninkmeijer, 2001) and the online design by Kawagucci et al. (2005). The approach involves measurement of two CO_2 aliquots (first directly, and then after complete isotope exchange with CeO_2) in 15 min for a single run. Since our analytical system is fully automated, the method is not labour-intensive. The injection loop volume determines the sample size. Usually, we inject two aliquots of 1 mL each of an unknown air sample. Using this system, we measured the triple oxygen isotope composition of three stratospheric CO_2 samples obtained during the EU project RECONCILE.

2 Method

2.1 Experimental set-up

The skeleton of the analytical system is a combination of three 6-port 2-position Valco valves (VICI, model C6UWM), which direct the sample through different parts of the system (Fig. 1). Valco valve number 1 (V1) is used to flush and fill the 1 mL-sample loop with sample air and inject the sample

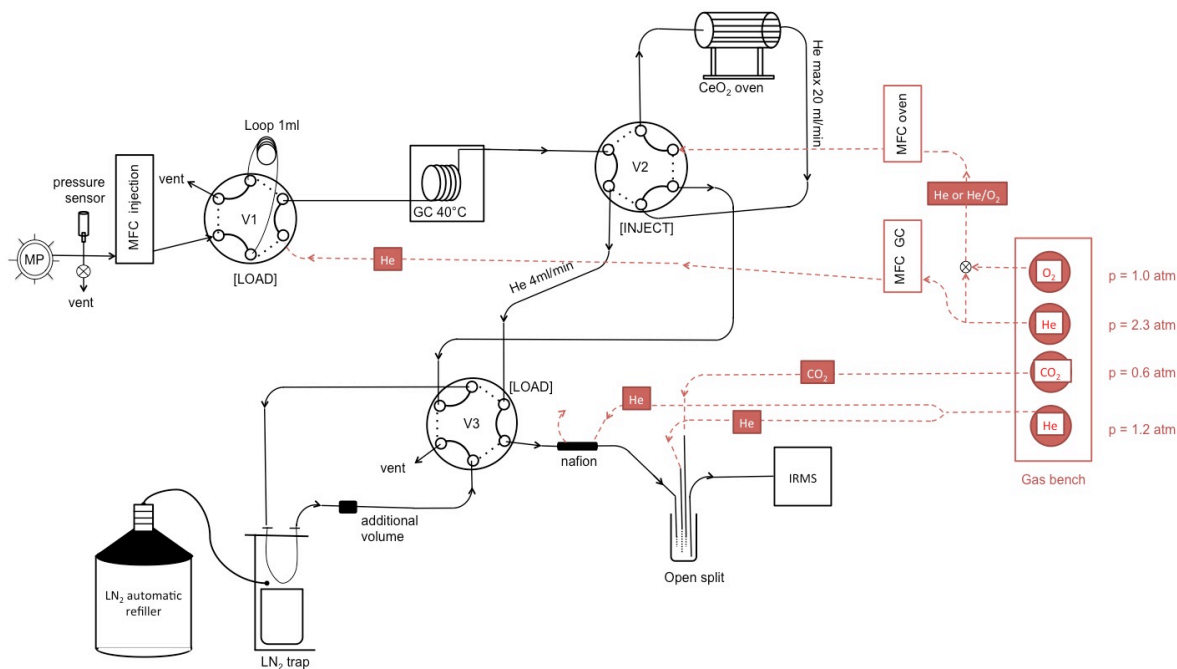


Figure 1. Schematic set-up of the analytical system (black) with the gas supply system (red). The sample injection unit (shown in detail in Fig. 2) contains a multiport valve (MPort), mass flow controller (MFC), Valco valve 1 (V1) and is used to inject 1 mL of sample air into the analytical system. The 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.

into the extraction and conversion part of the system. After gas chromatography (GC) separation of CO_2 from the bulk air, Valco valve number 2 (V2) directs CO_2 either through the oxygen isotope exchange unit or bypasses it. Valco valve number 3 (V3) comprises a loop with a cold trap to collect the isotopically equilibrated CO_2 before directing it into the IRMS. The connections between different sections of the system are made of fused silica capillary tubing (320 μm internal diameter (i.d.) / 430 μm outer diameter (o.d.), SGE Analytical Science) whereas lines in the sample injection part (see below) are made of 1/8 inch 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 CO_2 separation unit (Sect. 2.1.2), the oxygen isotope exchange unit (Sect. 2.1.3), the post- CO_2 peak focusing unit (Sect. 2.1.4) and the mass spectrometer (Sect. 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 CO_2 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.

In the setup described here, we need to provide air samples at an overpressure of 1.4 bar because of the mass flow controller (MFC injection). After the automated sample injection unit, the pressure in the analytical system corresponds to ambient pressure. 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

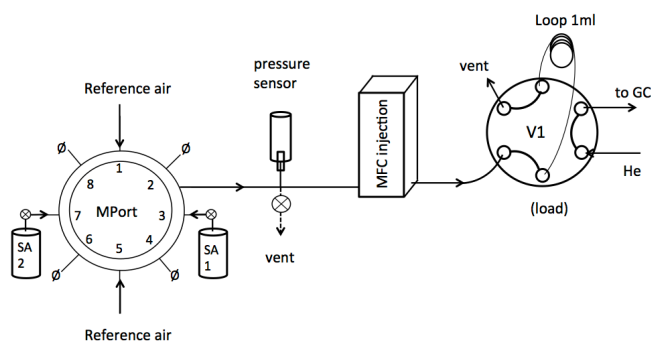


Figure 2. Schematic setup of the sample injection unit. From left: multiport valve (MPort), sample air canisters (SA1 and SA2), reference air ports, pressure sensor, an automated vent valve, mass flow controller (MFC-injection) and Valco V1 with 1 mL sample loop. All injection lines are 1/8 inch stainless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

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 pressure, we use a sample loop of 1 mL, and the loop is filled to ambient pressure. Each complete isotope analysis requires two separate air injections. The first aliquot is subsequently isotopically equilibrated with oxygen from CeO_2 (“Post CO_2 ”), and the second aliquot is measured directly (“Pre CO_2 ”).

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 V1 (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.

In order to improve analytical precision, multiple measurements (usually 10) are performed on one air sample. For a sample of 10 measurements only 30 mL of the sample air (corresponding to 480 nmol of CO_2) is used.

2.1.2 CO_2 separation from air

CO_2 is separated from the air and residual gases (N_2 , O_2 , Ar, N_2O and hydrocarbons) on a gas chromatography (GC) capillary column (PoraPLOT Q 25 m \times 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 N_2 and O_2) elutes at 120 s after the sample injection, CO_2 at 160 s and N_2O at

190 s. The non- CO_2 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 CO_2 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 (CeO_2) to exchange oxygen atoms with CO_2 . For our experiments, we use high purity CeO_2 powder (Merck, #102263). The powder is crushed in a mortar, and the size fraction 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 CeO_2 grains. Therefore, unlike Assonov and Brenninkmeijer (2001), we did not attempt to eliminate sulfate impurities from CeO_2 by high temperature treatment. The quartz tube is filled up manually with 1.000 ± 0.050 g (6 mmol) of the CeO_2 powder and capped from both sides with quartz wool, preventing CeO_2 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 “ CeO_2 oven”. The isotope exchange reaction proceeds at high temperature (700 °C) and is fast and highly efficient. However, the CeO_2 oven presents an additional flow resistance, so therefore the 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 CeO_2 exchange reagent is preconditioned with oxygen gas, see Sect 2.2.1. For this, we supply O_2 manually via opening an oxygen gas line with a needle valve placed before the MFC-oven. Mixed He / O_2 gas flushes the oven and leaves the analytical system via the vent in V3.

2.1.4 Collection of CO_2 after isotope exchange

The isotopically equilibrated CO_2 peak is strongly broadened after passing through the CeO_2 oven and needs to be refocused before entering the isotope detection unit in our analytical system. Therefore, after the isotope exchange reaction, the equilibrated CO_2 is collected on a U-shaped tube (1/8 inch SS, $L = 500$ mm) immersed in a liquid nitrogen (LN_2) bath. After complete collection, the trap is lifted up above the LN_2 level; CO_2 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 Pre CO_2 and Post CO_2 peaks appear on chromatogram with similar intensity. We have found that keeping the level of liquid nitrogen in the LN_2 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 CO_2 aliquots are transferred via V3 through a NafionTM 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. $^{45}\delta$ and $^{46}\delta$ are measured relative to a rectangular CO_2 working reference gas peak. As the instrument software assumes mass dependent oxygen isotope fractionation, the data reduction is performed separately to derive $^{13}\delta$, $^{17}\delta$ and $^{18}\delta$ (see calculation Sect. 2.3).

2.1.6 The laboratory standards

For our measurements we use helium as a carrier gas and two working reference gases: reference CO_2 (Ref CO_2) and reference oxygen (Ref O_2). The isotope values for the laboratory standards are $\delta^{13}\text{C}(\text{RefCO}_2) = -34.84\text{‰}$ vs. VPDB, $\delta^{18}\text{O}(\text{RefCO}_2) = 5.20\text{‰}$ vs. VSMOW, $\delta^{17}\text{O}(\text{RefO}_2) = 9.33\text{‰}$ vs. VSMOW and $\delta^{18}\text{O}(\text{RefO}_2) = 19.00\text{‰}$ vs. VSMOW. The isotope values of Ref CO_2 were measured at the Department of Earth Science of Utrecht University, the Netherlands, relative to the calcite reference material NBS-19 ($\delta^{18}\text{O} = 28.65\text{‰}$ vs. VSMOW; $\delta^{13}\text{C} = 1.95\text{‰}$ vs. VPDB). The carbonate was reacted at 70°C and the oxygen isotopic composition of the Ref CO_2 was calculated using an acid fractionation factor $\alpha(\text{CO}_2\text{-calcite}) = 1.00871$ (Kim et al., 2007). The isotope values of Ref O_2 were measured in Grenoble (Joël Savarino group, Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France). The calibration of the O_2 gas can be traced back to the original SMOW of H. Craig via the laboratories in Grenoble and UCSD (J. Savarino and M. Thiemens). Due to multiple transfers of the scale between gas-bottles there may be a small systematic offset to the VSMOW scale, however, this is not relevant for the data presented here (see Sect. 2.2.1).

2.2 Measurement procedure

The measurement routine is fully automated and most items are controlled via the ISODAT 3.0 software (Thermo Fisher). ISODAT controls the positions of the three Valco valves, the pneumatic lifter of the LN_2 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 ISODAT 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 intermediate times in order to save sample. Instead of the MKS modules, we use custom made elec-

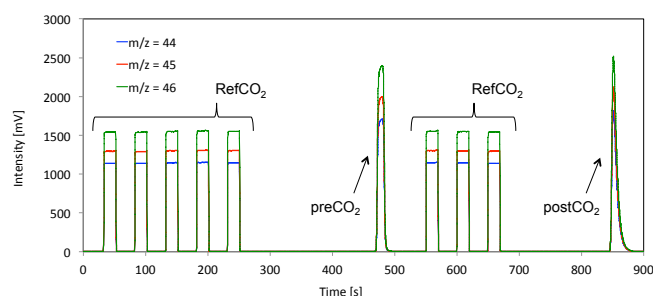


Figure 3. Example of a typical IRMS chromatogram. Eight square peaks of the working laboratory reference CO_2 (Ref CO_2) are injected, and two CO_2 peaks of the measured air sample. Peak number 6 is non-equilibrated CO_2 (Pre CO_2). Peak number 10 is isotopically equilibrated CO_2 (Post CO_2).

tronic 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 CO_2 through the oven and 6 mL min^{-1} for intermediate times.

A single measurement of an unmodified aliquot and a CO_2 aliquot after isotope exchange takes 15 min. The short analysis time and a low sample usage allow injecting multiple aliquots of the same sample into the analytical system, giving possibility of multiple measurements on each sample. In 2.5 h of analysis, we can repeat measurement on each air sample 10 times and improve the analytical precision statistically, see Sect. 3.4.

An example of an IRMS chromatogram is shown in Fig. 3. Pre CO_2 is detected between 450 and 500 s (peak number 6 on chromatogram) and Post CO_2 is detected between 850 and 900 s (peak number 10 on chromatogram). The other peaks are the working laboratory reference CO_2 (Ref CO_2) injected to the IRMS via the open split interface.

2.2.1 Preconditioning of CeO_2 reagent

Before the first use the CeO_2 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 the CeO_2 powder with oxygen, we open the needle valve placed before the MFC-oven, allowing O_2 to mix into the He flow. We flush the oven with the He / O_2 mixture for 3 h at 600°C . Next, we close the needle valve and increase the oven temperature to 700°C . The CeO_2 oven remains under He flow for 1 h, and then the analytical system is ready to measure atmospheric air samples. As mentioned by Perriçon et al. (1995) and Assonov and Brenninkmeijer (2001), under long annealing the catalytic behaviour of CeO_2 grains may degrade due to changes in CeO_2 surface area. Usually, we oxygenate the oven every 6 weeks (depending on use) and

replace the whole quartz reaction tube with new CeO_2 grains every 5 months.

The isotopic composition of O_2 used for oxygenation is given in Sect. 2.1.6. It is important to underline that CeO_2 is being oxygenated with O_2 of non-mass dependently fractionated O_2 and hence the “anomaly” of O_2 is further transferred to PostCO_2 of each gas measured. Because of that we cannot calculate delta values of the sample air directly on the VSMOW scale. Instead, we use measurements of reference air, measured before and after the sample, to calculate delta values of the sample air relative to the average of reference air. Since both (reference air and sample air) were equilibrated with virtually the same CeO_2 the “anomaly” cancels out (see Eqs. 7–9). Additionally, knowing isotopic composition of reference air on the VSMOW scale allows us to calculate δ values of the sample on the VSMOW scale (see Eq. 8).

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 LN_2 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}). CO_2 is separated on the GC column from the air and other minor gases such as N_2O (see below). The air peak starts at 200 s while CO_2 starts at 240 s. To direct CO_2 through the oxygen isotope exchange unit, V2 switches to position LOAD from 240 to 290 s. At that time, the purified CO_2 has been injected to the CeO_2 oven where it is isotopically equilibrated with the oxygen from CeO_2 . The cryogenic trap is immersed in the LN_2 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 CeO_2 oven. The equilibrated CO_2 is then directed via V2 and V3 to the cryogenic trap where it is collected. At 835 s, collection of isotopically exchanged CO_2 is complete, the LN_2 trap is lifted up, V3 switches to position INJECT, and PostCO_2 is transferred via the open split interface to the IRMS. The m/z 44, 45 and 46 ion currents of PostCO_2 are detected between 850 and 900 s with peak intensity around 2500 mV.

While CO_2 from the first air injection is transferred through the CeO_2 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 CO_2 (PreCO_2). 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 PreCO_2 is separated from the air and other minor gases, it is directed via V2 (IN-

JECT) and V3 (LOAD) to the IRMS. PreCO_2 appears on the chromatogram between 450 to 500 s and with peak intensity around 2500 mV. Since PreCO_2 takes a much shorter path through the analytical system and does not require focusing, it is detected before PostCO_2 .

Eight peaks of the working laboratory reference CO_2 (RefCO_2) are injected via the open split interface during the run. The molecular delta values $^{45}\delta(\text{CO}_2)$ and $^{46}\delta(\text{CO}_2)$ of PreCO_2 and PostCO_2 are calculated by ISODAT relative to the working gas reference peaks. We choose the CO_2 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 10 times, the measurement cycle is composed of 50 measurements.

2.3 Calculations

We calculate the ^{17}O -excess in CO_2 from the signals on m/z 44, 45 and 46 of CO_2 directly measured on IRMS (PreCO_2) and CO_2 measured on IRMS after equilibration with oxygen from CeO_2 (PostCO_2). The parameters used for our calculations are from Kaiser and Röckmann (2008): $C = {}^{17}R_{\text{ref}} / {}^{13}R_{\text{ref}} = 0.03516$, $D = {}^{13}R_{\text{ref}} \cdot {}^{17}R_{\text{ref}} / {}^{218}R_{\text{ref}} = 0.001042$ and $\lambda = 0.528$.

λ describes the mass-dependent relationship between the three oxygen isotopes. The theoretical range for many mass-dependent fractionation processes is $0.501 < \lambda < 0.531$ (but values outside this range may be attained even for mass-dependent fractionation where $^{18}\alpha$ fractionation factor straddles the value of 1). Kaiser (2008) has adopted $\lambda = 0.528$ for mass dependently fractionated CO_2 samples, as have Assonov and Brenninkmeijer (2003) for their ^{17}O -correction algorithm. However Hofmann et al. (2012) have shown that for CO_2 -water equilibration $\lambda = 0.522 \pm 0.002$. This value was supported by Barkan and Luz (2012) who found $\lambda = 0.5229 \pm 0.0001$ for the same process. However, as pointed out by Kaiser (2008), $\Delta^{17}\text{O}$ is not a measured quantity and may be reported relative to an arbitrarily chosen mass-dependent fractionation line. In the absence of an inter-

national recommendation with respect to the preferred definition, any definition should be treated on an equal footing to any other. Comparing data between laboratories always requires recalculation of $\Delta^{17}\text{O}$ from measured quantities, i.e. $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, and with different λ . For results shown in this paper we define $\lambda \equiv 0.528$ because it has often been used in the past for CO_2 triple isotope studies.

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

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

and

$$D = \frac{{}^{13}R_{\text{ref}}{}^{17}R_{\text{ref}}}{{}^{218}R_{\text{ref}}} = \frac{{}^{13}R_{\text{VPDBCO}_2} [1 + \delta^{13}\text{C}_{\text{ref/VPDBCO}_2}] {}^{17}R_{\text{VPDBCO}_2} [1 + \delta^{17}\text{O}_{\text{ref/VPDBCO}_2}]}{{}^{218}R_{\text{VPDBCO}_2} [1 + \delta^{18}\text{O}_{\text{ref/VPDBCO}_2}]} \quad (2)$$

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:

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

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

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

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

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 the daily variability of the system, we monitor isotopic composition of reference air before and after the sample. 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 (RefAir) following Eq. (7). Note Std stands for international standards.

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

The CO_2 in the reference air was calibrated versus international standards at UC Berkeley (group of K. Boering). Three samples of 20 μmol CO_2 each, were extracted cryogenically from the reference air at IMAU laboratory,

flame sealed in glass ampoules and shipped to UC Berkeley. The method of Assonov and Brenninkmeijer (2001) was applied for the isotope ratio measurements of CO_2 . Detailed description of the procedure can be found in the appendix of Wiegel et al. (2013). At UC Berkeley the samples from Utrecht were measured against the secondary laboratory standard, which, in turn, was calibrated against the three NIST CO_2 reference materials RM8562, RM8563 and RM8564. The $\delta^{17}\text{O}$ value of the UC Berkeley lab standard is not known, but calculated from its $\delta^{18}\text{O}$ with respect to VM-SOW assuming $\lambda = 0.528$ and $\Delta^{17}\text{O} = (0 \pm 0.5) \text{‰}$ (Wiegel et al., 2013). The measurements at UC Berkeley resulted in the following isotope deltas for CO_2 in Utrecht reference air: $\delta^{13}\text{C}(\text{RefAir/VPDB}) = (-8.25 \pm 0.10) \text{‰}$; $\delta^{17}\text{O}(\text{RefAir/VSMOW}) = (16.95 \pm 0.40) \text{‰}$; $\delta^{18}\text{O}(\text{RefAir/VSMOW}) = (32.74 \pm 0.08) \text{‰}$ and $\Delta^{17}\text{O} = (-0.2 \pm 0.5) \text{‰}$. The uncertainty in brackets corresponds to the average of three samples measured.

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:

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

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 Post CO_2 detection window (between 850 to 900 s). This peak originates from the CeO_2 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 N_2O contamination

Because it has the same molecular mass, the isotopologues of N_2O interfere with CO_2 isotopologues in IRMS measurements at m/z 44, 45 and 46 (Mook and van der Hoek, 1983). The N_2O mixing ratio of atmospheric air is about 1200 times smaller than for CO_2 . In our system, we expect N_2O peak areas to be as small as 0.02 Vs for 20 Vs CO_2 peak areas. This is at the peak detection limit, and it is difficult to detect

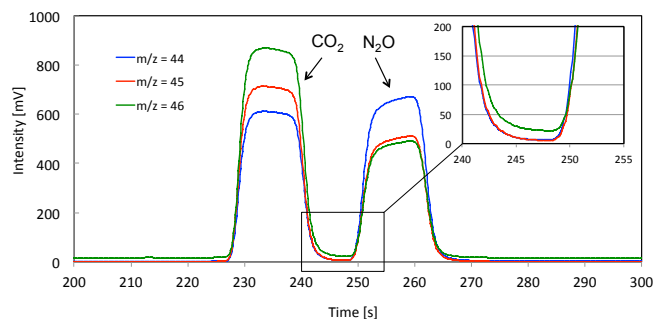


Figure 4. Chromatogram showing the separation of CO_2 from N_2O in the artificially prepared mixture. The sample was injected to the analytical system at 60 s. CO_2 appeared on chromatogram at 220–243 s and N_2O appeared at 248–275 s. Peaks are well separated, the interval between the CO_2 and N_2O peaks is 5 s. The air peak (normally visible at 180–210 s) is not included on this chromatogram.

N_2O on the IRMS chromatogram. However, the distribution of molecular ion masses 44, 45 and 46 in N_2O is very different from the distribution in CO_2 , and therefore N_2O interfering with CO_2 can decrease $\Delta^{17}\text{O}$ by 3‰ (Wiegel et al., 2013). For precise isotope measurements, CO_2 has to be separated from N_2O or a correction for the N_2O interference needs to be applied. In our online technique, N_2O is separated from CO_2 on the gas chromatography capillary column. To verify that CO_2 and N_2O are well separated, we prepared a mixture of 400 ppm N_2O in synthetic air. We injected this N_2O -rich gas to our system from MPort position 3. The N_2O was detected on the chromatogram between 250–275 s. While the SS injection line between MPort and MFC-injection still contained the N_2O -rich gas, venting was not applied. MPort was moved to position 5 allowing the reference air to mix with the N_2O -rich gas in subsequent runs. The reference air became contaminated with N_2O in quantities that are similar to the CO_2 mixing ratio. On the following IRMS chromatogram, both CO_2 and N_2O appeared, and even for these high amounts of N_2O , the peaks were almost baseline-separated (see Fig. 4). This shows that for normal air, N_2O and CO_2 are separated on the GC capillary column, and a corresponding N_2O 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 CeO_2 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.

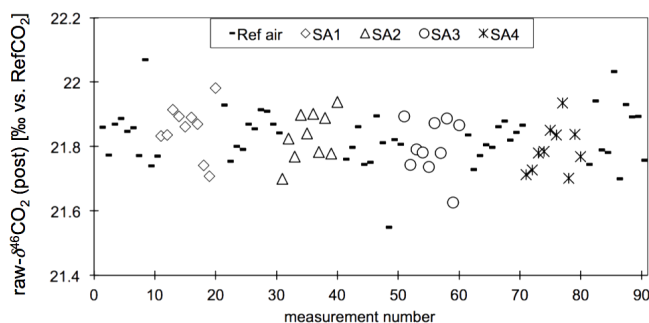


Figure 5. Full and highly efficient oxygen equilibration reaction in the CeO_2 oven represented by isotopically exchanged CO_2 of four diverse atmospheric air samples (SA1 – rhombs, SA2 – triangles, SA3 – circles and SA4 – stars) measured against the reference air (stripes). The initial differences in $\delta^{18}\text{O}$ between the reference air and the air samples were up to 12‰ (relative to RefCO_2).

The raw- $\delta^{46}\text{CO}_2$ isotope values of PreCO_2 were the following: RefAir = 24.50‰; SA1 = 35.40‰; SA2 = 36.77‰; SA3 = 32.65‰ and SA4 = 36.84‰ all relative to RefCO_2 ($1\sigma = 0.10\%$). Figure 5 shows $^{46}\delta$ of these four samples and the reference air after isotopic equilibration. In all cases, after the isotopic exchange reaction raw- $\delta^{46}\text{CO}_2$ is equilibrated to 21.82‰ (relative to working reference CO_2 , (RefCO_2)) with precision of 0.08‰. 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 CeO_2 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 2 L 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 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 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% (relative to VSMOW, $\lambda = 0.528$), which reflects the calibration of the UC Berkeley measurements to our reference air ($\Delta^{17}\text{O} = -0.20 \pm 0.40\%$). 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 10 measurements each.

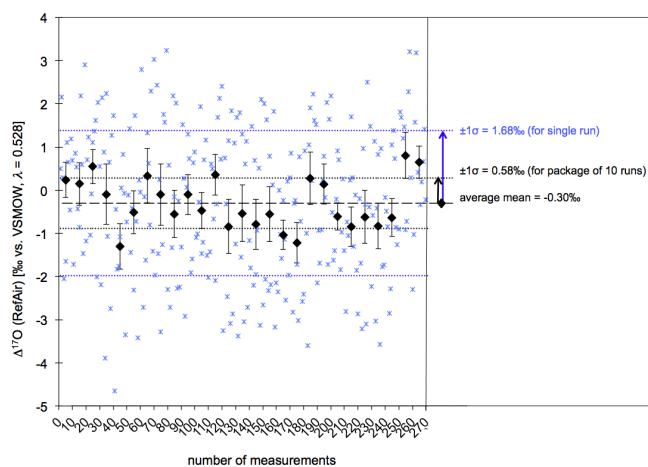


Figure 6. Stability and reproducibility test for the analytical system: $\Delta^{17}\text{O}$ values of reference air were measured constantly for several days. Striped black line indicates the average value of 270 runs and for 27 groups of 10 measurements respectively. The dotted lines indicate standard 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.

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; Brenninkmeijer and Röckmann, 1998); therefore, the approximate precision of $\Delta^{17}\text{O}$ in a sample of 10 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: two groups of 135 runs; three groups of 90 runs; five 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 ‰.

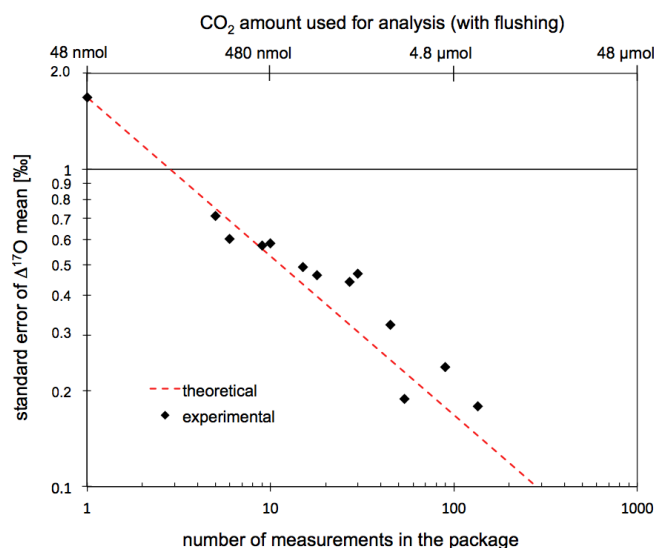


Figure 7. Improvement of the measurement precision by performing multiple measurements on the same air sample. The \ln of the standard error (SE) is plotted versus \ln of the number of measurements (n) that were included in the calculation of the SE. The upper axis represents the amount of CO_2 used for analysis including sample loop flushing. 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 .

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 (CO_2 -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 CO_2 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 CO_2 mole fractions between 400 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 N_2O , CFC-11, CFC-12, CH_4 (Kaiser et al., 2006;

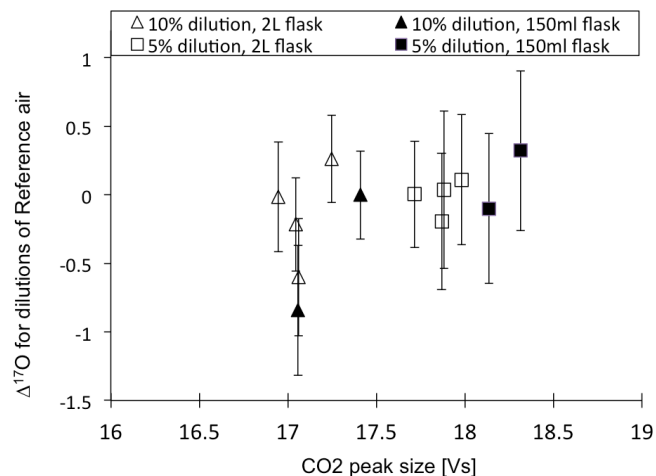


Figure 8. $\Delta^{17}\text{O}$ of CO_2 in aliquots of the laboratory reference gas that was filled into flasks of 2 L and 150 mL volume, respectively. These are the flasks in which the stratospheric samples were measured. The reference air was additionally diluted by 5% (squares) or 10% (triangles) 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.

Laube et al., 2010; Röckmann et al., 2011) and the remaining air was used for measurement of the isotopic composition of CO_2 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. At 18 km the observed ^{17}O excess values for stratospheric CO_2 go up to 7‰ for $\delta^{17}\text{O}$ and up to 3‰ for $\delta^{18}\text{O}$ with respect to tropospheric CO_2 ($\delta^{17}\text{O} \approx 21$ ‰ VSMOW, $\delta^{18}\text{O} \approx 41$ ‰ VSMOW). The samples measured with our analytical technique agree with available data for stratospheric CO_2 (Kawagucci et al., 2008; Lämmerzahl et al., 2002; Wiegel et al., 2013). The precision for the 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 a group of 10 measurements. An in-depth analysis on the new data set will be published in a separate paper.

5 Conclusions

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 and Brenninkmeijer, 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 labour characterized for a single measurement in the offline techniques (Assonov and Brenninkmeijer, 2001; Hofmann and Pack, 2010; Mahata et al., 2012) was decreased to a minimum: connecting air samples to the injection lines, filling the LN_2 dewar and running the measurement sequence by press-

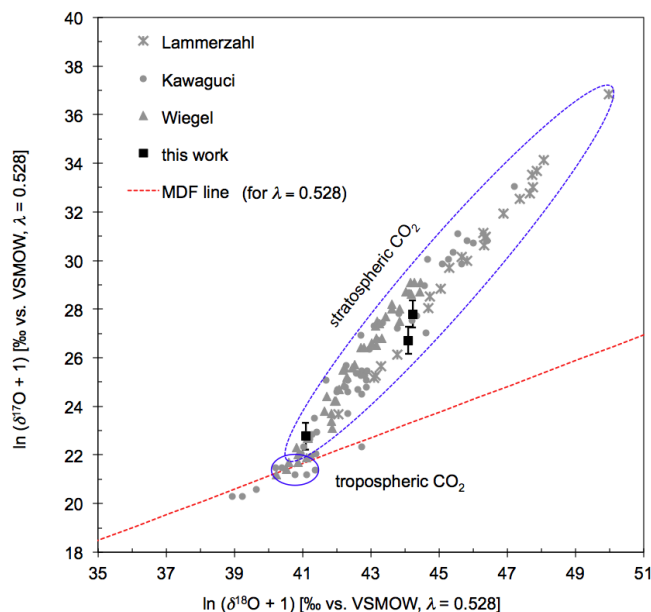


Figure 9. Three-isotope plot for oxygen isotopes in CO_2 from atmospheric air samples. Previous observations are from Kawagucci et al. (2008) (circles); Lämmerzahl et al. (2002) (diamonds) and Wiegel et al. (2013) (triangles). Three samples from the RECONCILE project (squares) fall in the range of previously 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 $\ln^{18}\text{O} = \ln(\delta^{18}\text{O} + 1)$.

ing the start button. 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 MFCs, and finally by using a microdosing LN_2 pump to keep the liquid nitrogen level in the 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 injecting multiple aliquots of the same sample.

The reproducibility of measured $\Delta^{17}\text{O}$ is 0.6‰ for 10 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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