



# Continuous-flow IRMS technique for determining the $^{17}\text{O}$ excess of $\text{CO}_2$ 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  $\text{CO}_2$  extracted from stratospheric air samples.  $\text{CO}_2$  is separated from bulk air by gas chromatography and  $\text{CO}_2$  isotope ratio measurements (ion masses 45 / 44 and 46 / 44) are performed using isotope ratio mass spectrometry (IRMS). The  $^{17}\text{O}$  excess ( $\Delta^{17}\text{O}$ ) is derived from isotope measurements on two different  $\text{CO}_2$  aliquots: unmodified  $\text{CO}_2$  and  $\text{CO}_2$  after complete oxygen isotope exchange with cerium oxide ( $\text{CeO}_2$ ) at 700 °C. Thus, a single measurement of  $\Delta^{17}\text{O}$  requires two injections of 1 mL of air with a  $\text{CO}_2$  mole fraction of 390  $\mu\text{mol mol}^{-1}$  at 293 K and 1 bar pressure (corresponding to 16 nmol  $\text{CO}_2$  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  $^{17}\text{O}$  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  $\text{CO}_2$  on stratospheric air samples obtained during the EU project RECONCILE with the high-altitude aircraft Geophysica. The precision for RECONCILE data is 0.03 ‰ (1 $\sigma$ ) for  $\delta^{13}\text{C}$ , 0.07 ‰ (1 $\sigma$ ) for  $\delta^{18}\text{O}$  and 0.55 ‰ (1 $\sigma$ ) 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  $\text{CO}_2$ :  $\delta^{17}\text{O} \approx 21$  ‰ Vienna Standard Mean Ocean Water (VSMOW),  $\delta^{18}\text{O} \approx 41$  ‰ VSMOW (Lämmenzahl et al., 2002). The samples measured with our analytical technique agree with available data for stratospheric  $\text{CO}_2$ .

## 1 Introduction

Isotopic studies of carbon dioxide ( $\text{CO}_2$ ) play an important role in understanding the global carbon cycle (Ciais et al., 1997; Farquhar et al., 1993; Trolier et al., 1996).  $\text{CO}_2$  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  $\text{CO}_2$  in the troposphere. Measurements of stratospheric and mesospheric samples, however, reveal strong enrichments of the heavy oxygen isotopes in  $\text{CO}_2$  (Alexander et al., 2001; Boering, 2004; Kawagucci et al., 2008; Lämmenzahl et al., 2002; Thiemens et al., 1995a, b; Wiegel et al., 2013). These oxygen isotope enrichments derive from isotope exchange of  $\text{CO}_2$  with  $\text{O}^{1\text{D}}$  via a short-

lived  $\text{CO}_3^*$  intermediate (Liang et al., 2007; Perri et al., 2003; Yung et al., 1991).

The isotope delta ( $\delta$ ) represents the relative isotope ratio difference of a sample to a reference material, e.g.  $\delta(^n\text{O} / ^{16}\text{O, sample/reference}) = R(^n\text{O} / ^{16}\text{O, sample}) / R(^n\text{O} / ^{16}\text{O, reference}) - 1$ .  $^n\text{O}$  stands for  $^{17}\text{O}$  or  $^{18}\text{O}$ .  $R$  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,  $\delta$  values are reported in ‰. Here, we also use the abbreviated notations  $\delta^n\text{O}_{\text{sample / reference}}$  or  $\delta_{\text{sample / reference}}$  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  $\text{O}_2$ .

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  $^{17}\text{O}$  and  $^{18}\text{O}$  are closely linked via the relationship  $1 + \delta^{17}\text{O} = (1 + \delta^{18}\text{O})^\lambda$ , with  $\lambda$  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  $^{17}\text{O}$  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  $\text{CO}_2$  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,  $^{17}\text{O}$ - and  $^{13}\text{C}$ -substituted  $\text{CO}_2$  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  $\text{CO}_2$  is not straightforward.

One possibility is to convert  $\text{CO}_2$  to  $\text{O}_2$  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  $\text{O}_2$  originated from  $\text{CO}_2$ . Following this approach several methods have been developed: Bhattacharya and Thiemens (1989) converted  $\text{CO}_2$  to  $\text{O}_2$  by reacting it with  $\text{BrF}_5$ ; Brenninkmeijer and Röckmann (1998) used conversion of  $\text{CO}_2$  into  $\text{CH}_4$  and  $\text{H}_2\text{O}$  by reaction with  $\text{H}_2$ ; in a second step they fluorinated the  $\text{H}_2\text{O}$  with  $\text{F}_2$  to produce  $\text{O}_2$  and  $\text{HF}$ ; Barkan and Luz (2012) equilibrated  $\text{CO}_2$  with  $\text{H}_2\text{O}$  and used water fluorination to produce  $\text{O}_2$ . These methods are labour-intensive and time-consuming, but can

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

Assonov and Brenninkmeijer (2001) developed a technique where a hot metal oxide acts as an oxygen isotope exchange medium for  $\text{CO}_2$ . To investigate the complete oxygen isotopic composition of  $\text{CO}_2$ , the isotopic composition of  $\text{CO}_2$  is measured before and after isotopic exchange with oxygen from a solid oxide ( $\text{CeO}_2$ ) 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  $\text{CO}_2$  sample sizes were 16 to 29  $\mu\text{mol}$ , 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  $\text{CO}_2$  from  $\text{N}_2\text{O}$ , which improved the standard deviation to 0.06 ‰.

Kawagucci et al. (2005) described the first online method for measuring the isotopic composition of  $\text{CO}_2$ . In contrast to Assonov and Brenninkmeijer, Kawagucci used  $\text{CuO}$  as isotope exchange medium instead of  $\text{CeO}_2$ . Applying continuous-flow IRMS allowed reducing the sample size from micromoles to 8.7 nmol of  $\text{CO}_2$  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 ‰.

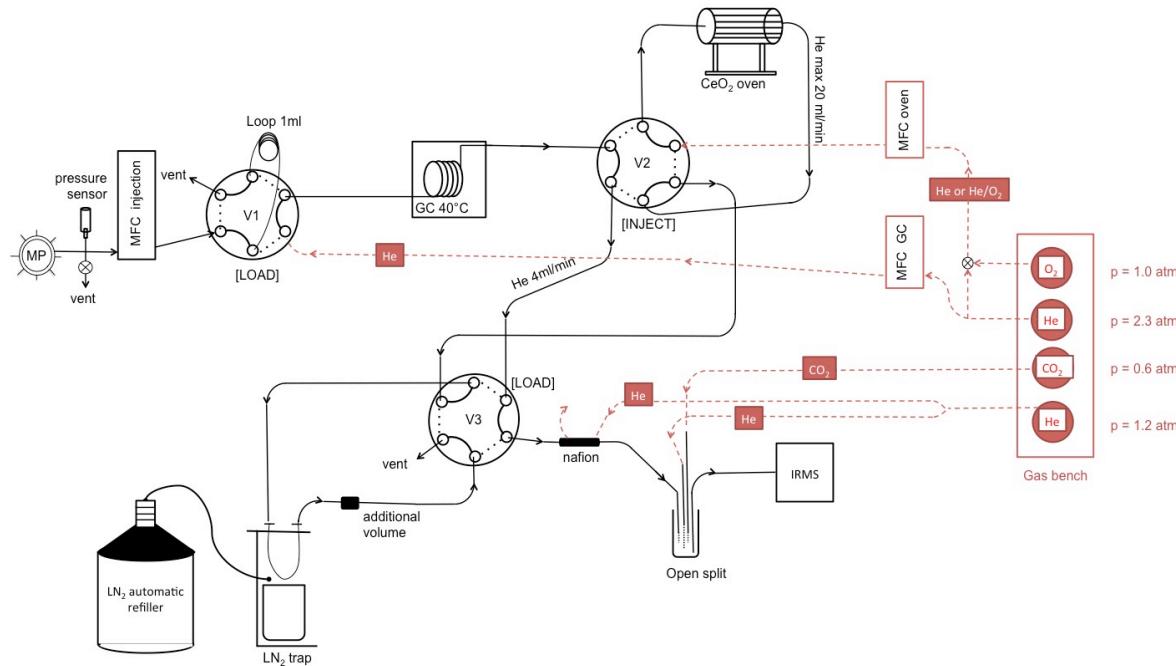
Instead of isotope exchange with a solid oxide, Mahata et al. (2013) recently described a technique where  $\text{CO}_2$  is isotopically equilibrated with  $\text{O}_2$  gas in the presence of hot platinum wire. The  $\text{O}_2$  can then be analysed without  $^{13}\text{C}$  interference. High measurement precision (0.045 ‰ for  $\Delta^{17}\text{O}$ ) was obtained for 20–30  $\mu\text{mol}$   $\text{CO}_2$ , 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  $\text{CeO}_2$  (Assonov and Brenninkmeijer, 2001) and the online design by Kawagucci et al. (2005). The approach involves measurement of two  $\text{CO}_2$  aliquots (first directly, and then after complete isotope exchange with  $\text{CeO}_2$ ) 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  $\text{CO}_2$  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  $\text{CO}_2$  from the rest of sample air. V2 injects the first  $\text{CO}_2$  aliquot to the  $\text{CeO}_2$  oven and the second straight to IRMS; V3 provides the possibility to collect isotopically equilibrated  $\text{CO}_2$  in a liquid nitrogen trap. The 1 mL volume after the trap is used to broaden the peak without providing a flow restriction. The  $\text{CO}_2$  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  $\text{CO}_2$  from the bulk air, Valco valve number 2 (V2) directs  $\text{CO}_2$  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  $\text{CO}_2$  before directing it into the IRMS. The connections between different sections of the system are made of fused silica capillary tubing (320  $\mu\text{m}$  internal diameter (i.d.) / 430  $\mu\text{m}$  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.

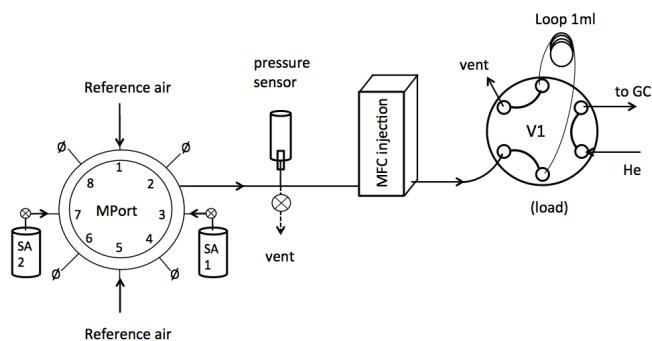
The five subunits of the system will be described in the following sub-sections: an automated air sample injection system (Sect. 2.1.1), the  $\text{CO}_2$  separation unit (Sect. 2.1.2), the oxygen isotope exchange unit (Sect. 2.1.3), the post- $\text{CO}_2$  peak focusing unit (Sect. 2.1.4) and the 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  $\text{CO}_2$  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  $1.0 \text{ mL min}^{-1}$  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  $\text{CeO}_2$  (“Post $\text{CO}_2$ ”), and the second aliquot is measured directly (“Pre $\text{CO}_2$ ”).

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  $\text{CO}_2$ ) is used.

## 2.1.2 $\text{CO}_2$ separation from air

$\text{CO}_2$  is separated from the air and residual gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ ,  $\text{N}_2\text{O}$  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  $\text{mL min}^{-1}$ , the air peak (mainly  $\text{N}_2$  and  $\text{O}_2$ ) elutes at 120 s after the sample injection,  $\text{CO}_2$  at 160 s and  $\text{N}_2\text{O}$  at

190 s. The non- $\text{CO}_2$  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  $\text{CO}_2$  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 ( $\text{CeO}_2$ ) to exchange oxygen atoms with  $\text{CO}_2$ . For our experiments, we use high purity  $\text{CeO}_2$  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  $\text{CeO}_2$  grains. Therefore, unlike Assonov and Brenninkmeijer (2001), we did not attempt to eliminate sulfate impurities from  $\text{CeO}_2$  by high temperature treatment. The quartz tube is filled up manually with  $1.000 \pm 0.050 \text{ g}$  (6 mmol) of the  $\text{CeO}_2$  powder and capped from both sides with quartz wool, preventing  $\text{CeO}_2$  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 “ $\text{CeO}_2$  oven”. The isotope exchange reaction proceeds at high temperature (700 °C) and is fast and highly efficient. However, the  $\text{CeO}_2$  oven presents an additional flow resistance, so therefore the MFC-oven provides He with higher head pressure so that a flow rate of  $20 \text{ mL min}^{-1}$  is reached. Before the first use, the  $\text{CeO}_2$  exchange reagent is preconditioned with oxygen gas, see Sect 2.2.1. For this, we supply  $\text{O}_2$  manually via opening an oxygen gas line with a needle valve placed before the MFC-oven. Mixed He /  $\text{O}_2$  gas flushes the oven and leaves the analytical system via the vent in V3.

## 2.1.4 Collection of $\text{CO}_2$ after isotope exchange

The isotopically equilibrated  $\text{CO}_2$  peak is strongly broadened after passing through the  $\text{CeO}_2$  oven and needs to be refocused before entering the isotope detection unit in our analytical system. Therefore, after the isotope exchange reaction, the equilibrated  $\text{CO}_2$  is collected on a U-shaped tube (1/8 inch SS,  $L = 500 \text{ mm}$ ) immersed in a liquid nitrogen ( $\text{LN}_2$ ) bath. After complete collection, the trap is lifted up above the  $\text{LN}_2$  level;  $\text{CO}_2$  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 $\text{CO}_2$  and Post $\text{CO}_2$  peaks appear on chromatogram with similar intensity. We have found that keeping the level of liquid nitrogen in the  $\text{LN}_2$  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

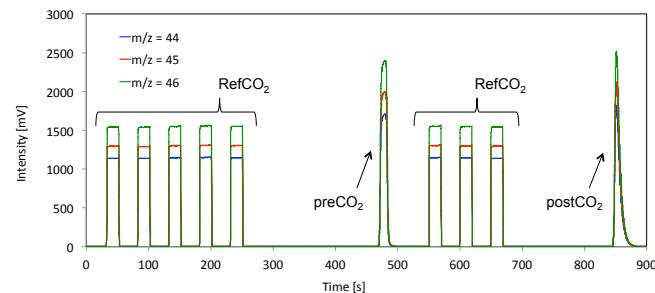
Pre- and post-equilibrated  $\text{CO}_2$  aliquots are transferred via V3 through a Nafion<sup>TM</sup> dryer to a custom-made open split system (Röckmann et al., 2003) and finally detected with an IRMS (Thermo Fisher Scientific Delta V Advantage). The three molecular ion masses  $m/z$  44, 45 and 46 are measured simultaneously.  $^{45}\delta$  and  $^{46}\delta$  are measured relative to a rectangular  $\text{CO}_2$  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  $\text{CO}_2$  (Ref $\text{CO}_2$ ) and reference oxygen (Ref $\text{O}_2$ ). The isotope values for the laboratory standards are  $\delta^{13}\text{C}(\text{RefCO}_2) = -34.84\text{\textperthousand}$  vs. VPDB,  $\delta^{18}\text{O}(\text{RefCO}_2) = 5.20\text{\textperthousand}$  vs. VSMOW,  $\delta^{17}\text{O}(\text{RefO}_2) = 9.33\text{\textperthousand}$  vs. VSMOW and  $\delta^{18}\text{O}(\text{RefO}_2) = 19.00\text{\textperthousand}$  vs. VS-MOW. The isotope values of Ref $\text{CO}_2$  were measured at the Department of Earth Science of Utrecht University, the Netherlands, relative to the calcite reference material NBS-19 ( $\delta^{18}\text{O} = 28.65\text{\textperthousand}$  vs. VSMOW;  $\delta^{13}\text{C} = 1.95\text{\textperthousand}$  vs. VPDB). The carbonate was reacted at 70 °C and the oxygen isotopic composition of the Ref $\text{CO}_2$  was calculated using an acid fractionation factor  $\alpha$  ( $\text{CO}_2$ -calcite) = 1.00871 (Kim et al., 2007). The isotope values of Ref $\text{O}_2$  were measured in Grenoble (Joël Savarino group, Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France). The calibration of the  $\text{O}_2$  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  $\text{LN}_2$  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  $1\text{ mL min}^{-1}$  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  $\text{CO}_2$  (Ref $\text{CO}_2$ ) are injected, and two  $\text{CO}_2$  peaks of the measured air sample. Peak number 6 is non-equilibrated  $\text{CO}_2$  (Pre $\text{CO}_2$ ). Peak number 10 is isotopically equilibrated  $\text{CO}_2$  (Post $\text{CO}_2$ ).

tronic controllers for MFC-GC and MFC-oven. For MFC-GC, we use only one of two possible set points and He of  $4\text{ mL min}^{-1}$  flow rate continuously flushes the GC column. For MFC-oven, the two set points for the He flow are  $20\text{ mL min}^{-1}$  to push the post-equilibrated  $\text{CO}_2$  through the oven and  $6\text{ mL min}^{-1}$  for intermediate times.

A single measurement of an unmodified aliquot and a  $\text{CO}_2$  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 $\text{CO}_2$  is detected between 450 and 500 s (peak number 6 on chromatogram) and Post $\text{CO}_2$  is detected between 850 and 900 s (peak number 10 on chromatogram). The other peaks are the working laboratory reference  $\text{CO}_2$  (Ref $\text{CO}_2$ ) injected to the IRMS via the open split interface.

### 2.2.1 Preconditioning of $\text{CeO}_2$ reagent

Before the first use the  $\text{CeO}_2$  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  $\text{CeO}_2$  powder with oxygen, we open the needle valve placed before the MFC-oven, allowing  $\text{O}_2$  to mix into the He flow. We flush the oven with the He /  $\text{O}_2$  mixture for 3 h at 600 °C. Next, we close the needle valve and increase the oven temperature to 700 °C. The  $\text{CeO}_2$  oven remains under He flow for 1 h, and then the analytical system is ready to measure atmospheric air samples. As mentioned by Perri-chon et al. (1995) and Assonov and Brenninkmeijer (2001), under long annealing the catalytic behaviour of  $\text{CeO}_2$  grains may degrade due to changes in  $\text{CeO}_2$  surface area. Usually, we oxyginate the oven every 6 weeks (depending on use) and

replace the whole quartz reaction tube with new  $\text{CeO}_2$  grains every 5 months.

The isotopic composition of  $\text{O}_2$  used for oxygenation is given in Sect. 2.1.6. It is important to underline that  $\text{CeO}_2$  is being oxygenated with  $\text{O}_2$  of non-mass dependently fractionated  $\text{O}_2$  and hence the “anomaly” of  $\text{O}_2$  is further transferred to Post $\text{CO}_2$  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  $\text{CeO}_2$  the “anomaly” cancels out (see Eqs. 7–9). Additionally, knowing isotopic composition of reference air on the VSMOW scale allows us to calculate  $\delta$  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  $\text{LN}_2$  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 ( $4 \text{ mL min}^{-1}$ ).  $\text{CO}_2$  is separated on the GC column from the air and other minor gases such as  $\text{N}_2\text{O}$  (see below). The air peak starts at 200 s while  $\text{CO}_2$  starts at 240 s. To direct  $\text{CO}_2$  through the oxygen isotope exchange unit, V2 switches to position LOAD from 240 to 290 s. At that time, the purified  $\text{CO}_2$  has been injected to the  $\text{CeO}_2$  oven where it is isotopically equilibrated with the oxygen from  $\text{CeO}_2$ . The cryogenic trap is immersed in the  $\text{LN}_2$  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  $20 \text{ mL min}^{-1}$  in order to speed up transfer through the  $\text{CeO}_2$  oven. The equilibrated  $\text{CO}_2$  is then directed via V2 and V3 to the cryogenic trap where it is collected. At 835 s, collection of isotopically exchanged  $\text{CO}_2$  is complete, the  $\text{LN}_2$  trap is lifted up, V3 switches to position INJECT, and Post $\text{CO}_2$  is transferred via the open split interface to the IRMS. The  $m/z$  44, 45 and 46 ion currents of Post $\text{CO}_2$  are detected between 850 and 900 s with peak intensity around 2500 mV.

While  $\text{CO}_2$  from the first air injection is transferred through the  $\text{CeO}_2$  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  $\text{CO}_2$  (Pre $\text{CO}_2$ ). 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 Pre $\text{CO}_2$  is separated from the air and other minor gases, it is directed via V2 (IN-

JECT) and V3 (LOAD) to the IRMS. Pre $\text{CO}_2$  appears on the chromatogram between 450 to 500 s and with peak intensity around 2500 mV. Since Pre $\text{CO}_2$  takes a much shorter path through the analytical system and does not require focusing, it is detected before Post $\text{CO}_2$ .

Eight peaks of the working laboratory reference  $\text{CO}_2$  (Ref $\text{CO}_2$ ) 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 Pre $\text{CO}_2$  and Post $\text{CO}_2$  are calculated by ISODAT relative to the working gas reference peaks. We choose the  $\text{CO}_2$  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 ( $51.971^\circ \text{N}$ ,  $4.927^\circ \text{E}$ ). 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  $^{17}\text{O}$ -excess in  $\text{CO}_2$  from the signals on  $m/z$  44, 45 and 46 of  $\text{CO}_2$  directly measured on IRMS (Pre $\text{CO}_2$ ) and  $\text{CO}_2$  measured on IRMS after equilibration with oxygen from  $\text{CeO}_2$  (Post $\text{CO}_2$ ). The parameters used for our calculations are from Kaiser and Röckmann (2008):  $C = {}^{17}\text{R}_{\text{ref}} / {}^{13}\text{R}_{\text{ref}} = 0.03516$ ,  $D = {}^{13}\text{R}_{\text{ref}} \cdot {}^{17}\text{R}_{\text{ref}} / 2{}^{18}\text{R}_{\text{ref}} = 0.001042$  and  $\lambda = 0.528$ .

$\lambda$  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  $\text{CO}_2$  samples, as have Assonov and Brenninkmeijer (2003) for their  $^{17}\text{O}$ -correction algorithm. However Hofmann et al. (2012) have shown that for  $\text{CO}_2$ -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  $\lambda$ . For results shown in this paper we define  $\lambda \equiv 0.528$  because it has often been used in the past for  $\text{CO}_2$  triple isotope studies.

Note the calculations of the  $^{17}\text{O}$ -excess in  $\text{CO}_2$  do not depend on the actual isotope ratios as demonstrated by Kaiser (2008). Rather, only the quantities

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

and

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

are required, where  $\text{ref} = \text{RefCO}_2$ . The conversion equations from  $^{45}\delta$  and  $^{46}\delta$  of Post $\text{CO}_2$  (with respect to working reference  $\text{CO}_2$ ) to  $^{13}\delta$ ,  $^{17}\delta$  and  $^{18}\delta$  can be written in terms of  $C$  and  $D$  as follows:

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

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

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

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

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.

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

The  $\text{CO}_2$  in the reference air was calibrated versus international standards at UC Berkeley (group of K. Boering). Three samples of 20 µmol  $\text{CO}_2$  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  $\text{CO}_2$ . 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  $\text{CO}_2$  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 VMSOW 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  $\text{CO}_2$  in Utrecht reference air:  $\delta^{13}\text{C}(\text{RefAir}/\text{VPDB}) = (-8.25 \pm 0.10)\text{‰}$ ;  $\delta^{17}\text{O}(\text{RefAir}/\text{VSMOW}) = (16.95 \pm 0.40)\text{‰}$ ;  $\delta^{18}\text{O}(\text{RefAir}/\text{VSMOW}) = (32.74 \pm 0.08)\text{‰}$  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  $\delta$  values of the sample according to

$$\begin{aligned} \delta_{\text{SA}/\text{Std}} &= \delta_{\text{SA}/\text{RefAir}} \cdot \delta_{\text{RefAir}/\text{Std}} \\ &\quad + \delta_{\text{SA}/\text{RefAir}} + \delta_{\text{RefAir}/\text{Std}}. \end{aligned} \quad (8)$$

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

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

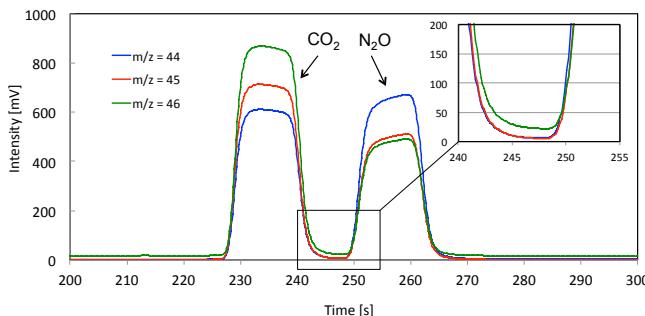
### 3 Performance of the analytical system

#### 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 $\text{CO}_2$  detection window (between 850 to 900 s). This peak originates from the  $\text{CeO}_2$  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 $\text{N}_2\text{O}$ contamination

Because it has the same molecular mass, the isotopologues of  $\text{N}_2\text{O}$  interfere with  $\text{CO}_2$  isotopologues in IRMS measurements at  $m/z$  44, 45 and 46 (Mook and van der Hoek, 1983). The  $\text{N}_2\text{O}$  mixing ratio of atmospheric air is about 1200 times smaller than for  $\text{CO}_2$ . In our system, we expect  $\text{N}_2\text{O}$  peak areas to be as small as 0.02 Vs for 20 Vs  $\text{CO}_2$  peak areas. This is at the peak detection limit, and it is difficult to detect

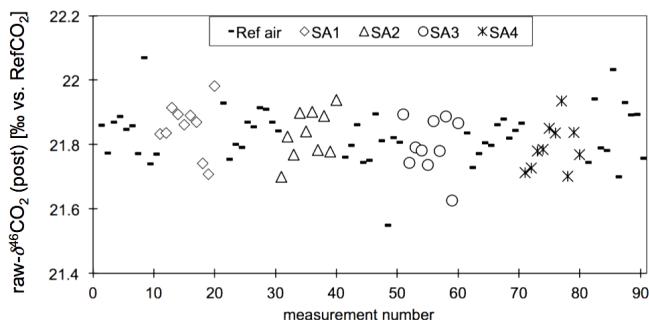


**Figure 4.** Chromatogram showing the separation of  $\text{CO}_2$  from  $\text{N}_2\text{O}$  in the artificially prepared mixture. The sample was injected to the analytical system at 60 s.  $\text{CO}_2$  appeared on chromatogram at 220–243 s and  $\text{N}_2\text{O}$  appeared at 248–275 s. Peaks are well separated, the interval between the  $\text{CO}_2$  and  $\text{N}_2\text{O}$  peaks is 5 s. The air peak (normally visible at 180–210 s) is not included on this chromatogram.

$\text{N}_2\text{O}$  on the IRMS chromatogram. However, the distribution of molecular ion masses 44, 45 and 46 in  $\text{N}_2\text{O}$  is very different from the distribution in  $\text{CO}_2$ , and therefore  $\text{N}_2\text{O}$  interfering with  $\text{CO}_2$  can decrease  $\Delta^{17}\text{O}$  by 3‰ (Wiegel et al., 2013). For precise isotope measurements,  $\text{CO}_2$  has to be separated from  $\text{N}_2\text{O}$  or a correction for the  $\text{N}_2\text{O}$  interference needs to be applied. In our online technique,  $\text{N}_2\text{O}$  is separated from  $\text{CO}_2$  on the gas chromatography capillary column. To verify that  $\text{CO}_2$  and  $\text{N}_2\text{O}$  are well separated, we prepared a mixture of 400 ppm  $\text{N}_2\text{O}$  in synthetic air. We injected this  $\text{N}_2\text{O}$ -rich gas to our system from MPort position 3. The  $\text{N}_2\text{O}$  was detected on the chromatogram between 250–275 s. While the SS injection line between MPort and MFC-injection still contained the  $\text{N}_2\text{O}$ -rich gas, venting was not applied. MPort was moved to position 5 allowing the reference air to mix with the  $\text{N}_2\text{O}$ -rich gas in subsequent runs. The reference air became contaminated with  $\text{N}_2\text{O}$  in quantities that are similar to the  $\text{CO}_2$  mixing ratio. On the following IRMS chromatogram, both  $\text{CO}_2$  and  $\text{N}_2\text{O}$  appeared, and even for these high amounts of  $\text{N}_2\text{O}$ , the peaks were almost baseline-separated (see Fig. 4). This shows that for normal air,  $\text{N}_2\text{O}$  and  $\text{CO}_2$  are separated on the GC capillary column, and a corresponding  $\text{N}_2\text{O}$  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  $\text{CeO}_2$  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.



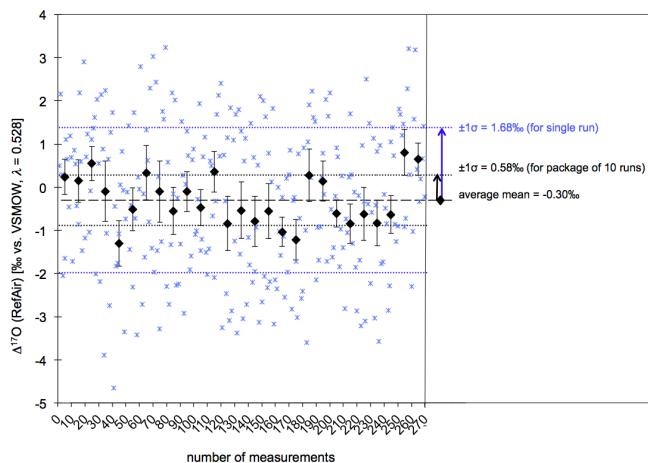
**Figure 5.** Full and highly efficient oxygen equilibration reaction in the  $\text{CeO}_2$  oven represented by isotopically exchanged  $\text{CO}_2$  of four diverse atmospheric air samples (SA1 – rhombs, SA2 – triangles, SA3 – circles and SA4 – stars) measured against the reference air (stripes). The initial differences in  $\delta^{18}\text{O}$  between the reference air and the air samples were up to 12‰ (relative to Ref $\text{CO}_2$ ).

The raw- $\delta^{46}\text{CO}_2$  isotope values of Pre $\text{CO}_2$  were the following: RefAir = 24.50‰; SA1 = 35.40‰; SA2 = 36.77‰; SA3 = 32.65‰ and SA4 = 36.84‰ all relative to Ref $\text{CO}_2$  ( $1\sigma = 0.10\text{‰}$ ). Figure 5 shows  ${}^4\delta$  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  $\text{CO}_2$ , (Ref $\text{CO}_2$ )) 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  $\text{CeO}_2$  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.

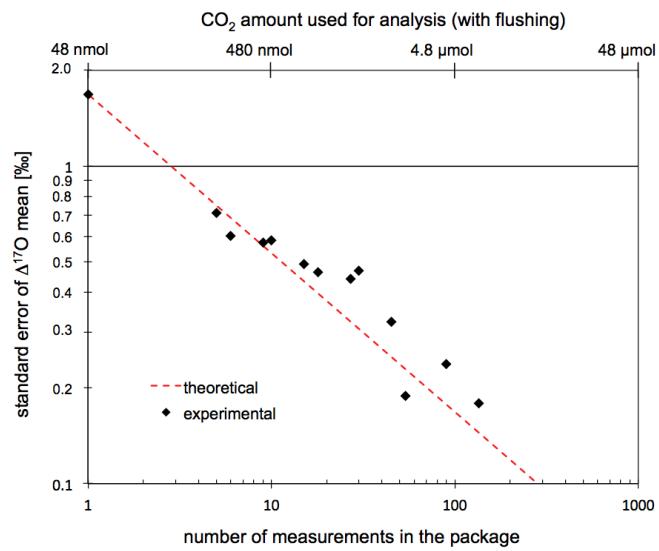
The mean value of  $\Delta^{17}\text{O}$  for our RefAir is  $-0.30\text{‰}$  (relative to VSMOW,  $\lambda = 0.528$ ), which reflects the calibration of the UC Berkeley measurements to our reference air ( $\Delta^{17}\text{O} = -0.20 \pm 0.40\text{‰}$ ). The standard deviation for all 270 individual measurements is 1.68‰, but this improves to a standard deviation of 0.58‰ when they are split into 27 groups of 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 ( $1\sigma$ ) 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  $\text{CO}_2$  and 0.04 and 0.08 ‰ for equilibrated  $\text{CO}_2$ , 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 ‰.



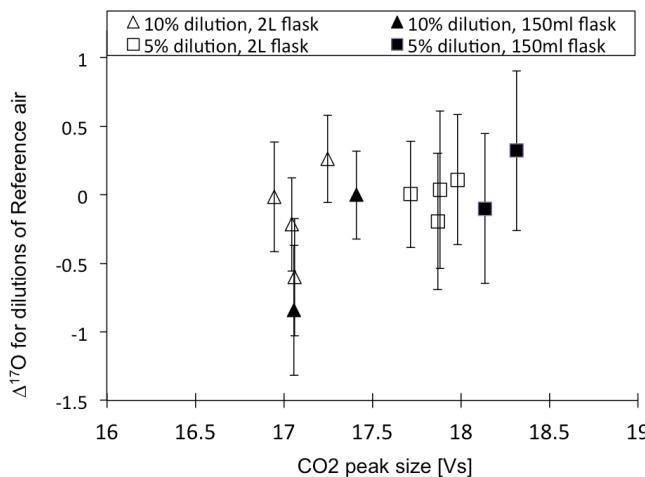
**Figure 7.** Improvement of the measurement precision by performing multiple measurements on the same air sample. The  $\ln$  of the standard error (SE) is plotted versus  $\ln$  of the number of measurements ( $n$ ) that were included in the calculation of the SE. The upper axis represents the amount of  $\text{CO}_2$  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 ( $\text{CO}_2$ -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  $\text{CO}_2$  peak area: 5 % dilution peak  $> 17.5\text{ Vs}$  and 10 % dilution peak  $< 17.5\text{ Vs}$ . 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  $\text{CO}_2$  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  $\text{N}_2\text{O}$ , CFC-11, CFC-12,  $\text{CH}_4$  (Kaiser et al., 2006;

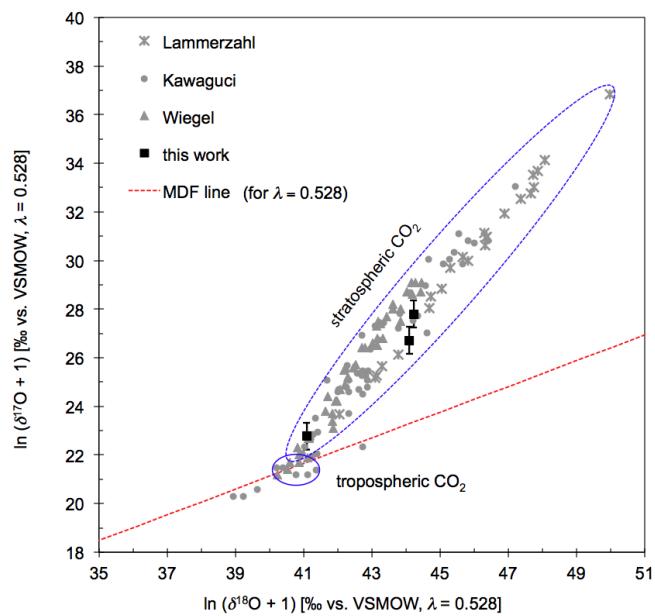


**Figure 8.**  $\Delta^{17}\text{O}$  of  $\text{CO}_2$  in aliquots of the laboratory reference gas that was filled into flasks of 2 L and 150 mL volume, respectively. These are the flasks in which the stratospheric samples were measured. The reference air was additionally diluted by 5 % (squares) or 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  $\text{CO}_2$  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  $^{17}\text{O}$  excess values for stratospheric  $\text{CO}_2$  go up to 7 ‰ for  $\delta^{17}\text{O}$  and up to 3 ‰ for  $\delta^{18}\text{O}$  with respect to tropospheric  $\text{CO}_2$  ( $\delta^{17}\text{O} \approx 21\text{ ‰ VSMOW}$ ,  $\delta^{18}\text{O} \approx 41\text{ ‰ VSMOW}$ ). The samples measured with our analytical technique agree with available data for stratospheric  $\text{CO}_2$  (Kawagucci et al., 2008; Lämmenzahl et al., 2002; Wiegel et al., 2013). The precision for the RECONCILE data is 0.03 ‰ (1 $\sigma$ ) for  $\delta^{13}\text{C}$ , 0.07 ‰ (1 $\sigma$ ) for  $\delta^{18}\text{O}$  and 0.55 ‰ (1 $\sigma$ ) 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  $\text{CO}_2$  based on complete oxygen isotope exchange with  $\text{CeO}_2$  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  $\text{CeO}_2$  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  $\text{LN}_2$  dewar and running the measurement sequence by press-



**Figure 9.** Three-isotope plot for oxygen isotopes in  $\text{CO}_2$  from atmospheric air samples. Previous observations are from Kawagucci et al. (2008) (circles); Lämmenzahl 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,  $\text{LN}_2$  trap and gas flow in the MFCs, and finally by using a microdosing  $\text{LN}_2$  pump to keep the liquid nitrogen level in the  $\text{CO}_2$  trap constant.

Although the standard deviation of a single run is higher than for already established methods that use  $\text{CeO}_2$  (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  $\text{CO}_2$  mole fractions between 360 and 400 ppm. The most promising application of our system is analysis of stratospheric  $\text{CO}_2$  from air samples of volume 100 mL and less. So far, we have successfully measured three oxygen isotope composition of  $\text{CO}_2$  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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## References

- Alexander, B., Vollmer, M. K., Jackson, T., Weiss, R. F., and Thiemens, M. H.: Stratospheric  $\text{CO}_2$  isotopic anomalies and  $\text{SF}_6$  and CFC tracer concentrations in the Arctic polar vortex, *Geophys. Res. Lett.*, 28, 4103–4106, 2001.
- Assonov, S. S. and Brenninkmeijer, C. A. M.: A new method to determine the  $^{17}\text{O}$  isotopic abundance in  $\text{CO}_2$  using oxygen isotope exchange with a solid oxide, *Rapid Commun. Mass Spectrom.*, 15, 2426–2437, 2001.
- Assonov, S. S. and Brenninkmeijer, C. A. M.: On the  $^{17}\text{O}$  correction for  $\text{CO}_2$  mass spectrometric isotopic analysis, *Rapid Commun. Mass Spectrom.*, 17, 1007–1016, 2003.
- Barkan, E. and Luz, B.: High-precision measurements of  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios in  $\text{CO}_2$ , *Rapid Commun. Mass Spectrom.*, 26, 2733–2738, 2012.
- Bhattacharya, S. K. and Thiemens, M. H.: Effect of Isotopic Exchange Upon Symmetry Dependent Fractionation in the  $\text{O}+\text{CO}$   $\text{CO}_2$  Reaction, *Zeitschrift für Naturforschung*, , J. Phys. Sci., 44, 811–813, 1989.
- Boering, K. A.: Observations of the anomalous oxygen isotopic composition of carbon dioxide in the lower stratosphere and the flux of the anomaly to the troposphere, *Geophys. Res. Lett.*, 31, L03109, doi:10.1029/2003GL018451, 2004.
- Brenninkmeijer, C. A. M. and Röckmann, T.: A rapid method for the preparation of  $\text{O}_2$  from  $\text{CO}_2$  for mass spectrometric measurement of  $^{17}\text{O}/^{16}\text{O}$  ratios, *Rapid Commun. Mass Spectrom.*, 12, 479–483, 1998.
- Ciais, P., Denning, A. S., Tans, P. P., Berry, J. A., Randall, D. A., Collatz, G. J., Sellers, P. J., White, J. W. C., Trolier, M., Meijer, H. A. J., Francey, R. J., Monfray, P., and Heimann, M.: A three-dimensional synthesis study of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . 1. Surface fluxes, *J. Geophys. Res.*, 102, 5857–5872, 1997.
- Farquhar, G. D., Lloyd, J., Taylor, J. A., Flanagan, L. B., Syvertsen, J. P., Hubick, K. T., Wong, S. C., and Ehleringer, J. R.: Vegetation effects on the isotope composition of oxygen in atmospheric  $\text{CO}_2$ , *Nature*, 363, 439–443, 1993.
- Ferretti, D. F., Lowe, D. C., Martin, R. J., and Brailsford, G. W.: A new gas chromatograph-isotope ratio mass spectrometry technique for high-precision,  $\text{N}_2\text{O}$ -free analysis of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$  from small air samples, *J. Geophys. Res.-Atmos.*, 105, 6709–6718, 2000.
- Hofmann, M. E. G. and Pack, A.: Technique for high-precision analysis of triple oxygen isotope ratios in carbon dioxide., *Anal. Chem.*, 82, 4357–4361, 2010.
- Hofmann, M. E. G., Horváth, B., and Pack, A.: Triple oxygen isotope equilibrium fractionation between carbon dioxide and water, *Earth Planet. Sci. Lett.*, 319–320, 159–164, 2012.
- Kaiser, J.: Reformulated  $^{17}\text{O}$  correction of mass spectrometric stable isotope measurements in carbon dioxide and a critical appraisal of historic “absolute” carbon and oxygen isotope ratios, *Geochim. Cosmochim. Acta*, 72, 1312–1334, 2008.
- Kaiser, J. and Röckmann, T.: Correction of mass spectrometric isotope ratio measurements for isobaric isotopologues of  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{SO}_2$ , *Rapid Commun. Mass Spectrom.*, 22, 3997–4008, 2008.
- Kaiser, J., Röckmann, T., and Brenninkmeijer, C. A. M.: Contribution of mass-dependent fractionation to the oxygen isotope anomaly of atmospheric nitrous oxide, *J. Geophys. Res.*, 109, D03305, doi:10.1029/2003JD004088, 2004.
- Kaiser, J., Engel, A., Borchers, R., and Röckmann, T.: Probing stratospheric transport and chemistry with new balloon and aircraft observations of the meridional and vertical  $\text{N}_2\text{O}$  isotope distribution, *Atmos. Chem. Phys.*, 6, 3535–3556, doi:10.5194/acp-6-3535-2006, 2006.
- Kawagucci, S., Tsunogai, U., Kudo, S., Nakagawa, F., Honda, H., Aoki, S., Nakazawa, T., and Gamo, T.: An analytical system for determining  $\delta^{17}\text{O}$  in  $\text{CO}_2$  using continuous flow-isotope ratio MS, *Anal. Chem.*, 77, 4509–4514, 2005.
- Kawagucci, S., Tsunogai, U., Kudo, S., Nakagawa, F., Honda, H., Aoki, S., Nakazawa, T., Tsutsumi, M., and Gamo, T.: Long-term observation of mass-independent oxygen isotope anomaly in stratospheric  $\text{CO}_2$ , *Atmos. Chem. Phys.*, 8, 6189–6197, doi:10.5194/acp-8-6189-2008, 2008.
- Kim, S., Mucci, A., and Taylor, B.: Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited, *Chem. Geol.*, 246, 135–146, 2007.
- Lämmertzahl, P., Rockmann, T., Brenninkmeijer, C. A. M., Krankowsky, D., and Mauersberger, K.: Oxygen isotope composition of stratospheric carbon dioxide, *Geophys. Res. Lett.*, 29, 1582, doi:10.1029/2001GL014343, 2002.
- Laube, J. C., Engel, A., Bönisch, H., Möbius, T., Sturges, W. T., Braß, M., and Röckmann, T.: Fractional release factors of long-lived halogenated organic compounds in the tropical stratosphere, *Atmos. Chem. Phys.*, 10, 1093–1103, doi:10.5194/acp-10-1093-2010, 2010.
- Liang, M.-C., Blake, G. A., Lewis, B. R., and Yung, Y. L.: Oxygen isotopic composition of carbon dioxide in the middle atmosphere, *Proc. Natl. Acad. Sci.*, 104, 21–25, 2007.
- Mahata, S., Bhattacharya, S. K., Wang, C. H., and Liang, M. C.: An improved  $\text{CeO}_2$  method for high-precision measurements of  $^{17}\text{O}/^{16}\text{O}$  ratios for atmospheric carbon dioxide., *Rapid Commun. Mass Spectrom.*, 26, 1909–1922, 2012.
- Mahata, S., Bhattacharya, S. K., Wang, C.-H., and Liang, M.-C.: Oxygen isotope exchange between  $\text{O}_2$  and  $\text{CO}_2$  over hot platinum: an innovative technique for measuring  $\Delta^{17}\text{O}$  in  $\text{CO}_2$ , *Anal. Chem.*, 85, 6894–6901, 2013.

- Mook, W. G. and Van der Hoek, S.: The  $\text{N}_2\text{O}$  correction in the carbon and oxygen isotopic analysis of atmospheric  $\text{CO}_2$ , *Chem. Geol.*, 41, 237–242, 1983.
- Perri, M. J., Van Wyngarden, A. L., Boering, K. A., Lin, J. J., and Lee, Y. T.: Dynamics of the  $\text{O}({}^1\text{D}) + \text{CO}_2$  oxygen isotope exchange reaction, *J. Chem. Phys.*, 119, 8213–8216, 2003.
- Perrichon, V., Laachir, A., Abouarnadasse, S., Touret, O., and Blanchard, G.: Thermal stability of a high surface area ceria under reducing atmosphere, *Appl. Catal. A Gen.*, 129, 69–82, 1995.
- Röckmann, T., Kaiser, J., Brenninkmeijer, C. A. M., and Brand, W. A: Gas chromatography/isotope-ratio mass spectrometry method for high-precision position-dependent  $^{15}\text{N}$  and  $^{18}\text{O}$  measurements of atmospheric nitrous oxide, *Rapid Commun. Mass Spectrom.*, 17, 1897–1908, 2003.
- Röckmann, T., Brass, M., Borchers, R., and Engel, A.: The isotopic composition of methane in the stratosphere: high-altitude balloon sample measurements, *Atmos. Chem. Phys.*, 11, 13287–13304, doi:10.5194/acp-11-13287-2011, 2011.
- Thiemens, M. H., Jackson, T. L., and Brenninkmeijer, C. A. M.: Observation of a mass independent oxygen isotopic composition in terrestrial stratospheric CO, the link to ozone chemistry, and the possible occurrence in the Martian atmosphere product, *Geophys. Res. Lett.*, 22, 255–257, 1995a.
- Thiemens, M. H., Jackson, T., Zipf, E. C., Erdman, P. W., and Egmond, C. van: Carbon Dioxide and Oxygen Isotope Anomalies in the Mesosphere and Stratosphere, *Science*, 270, 969–972, 1995b.
- Thiemens, M. H., Jackson, T., Mauersberger, K., Schueler, B., and Morton, J.: Oxygen isotope fractionation in stratospheric  $\text{CO}_2$ , *Geophys. Res. Lett.*, 18, 669–672, 1991.
- Trolier, M., White, J. W. C., Tans, P. P., Masarie, K. A., and Gemery, P. A: Monitoring the isotopic composition of atmospheric  $\text{CO}_2$ : Measurements from the NOAA Global Air Sampling Network, *J. Geophys. Res.*, 101, 25897–25916, 1996.
- Werner, R. A. and Brand, W. A.: Referencing strategies and techniques in stable isotope ratio analysis., *Rapid Commun. Mass Spectrom.*, 15, 501–519, 2001.
- Wiegel, A. A., Cole, A. S., Hoag, K. J., Atlas, E. L., Schauffler, S. M., and Boering, K. A.: Unexpected variations in the triple oxygen isotope composition of stratospheric carbon dioxide, *Proc. Natl. Aca. Sci.*, 110, 17680–17685, 2013.
- Yung, Y. L., DeMore, W. B., and Pinto, J. P.: Isotopic exchange between carbon dioxide and ozone via  $\text{O}({}^1\text{D})$  in the stratosphere, *Geophys. Res. Lett.*, 18, 13–16, 1991.