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High-Precision Triple Oxygen Isotope Analysis of Carbon Dioxide by Tunable Infrared Laser Absorption Spectroscopy

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Abstract

Precision measurements of the stable isotope ratios of oxygen ($^{18}O/^{16}O$, $^{17}O/^{16}O$) in CO_2 are critical to atmospheric monitoring and terrestrial climate research. High-precision ^{17}O measurements by isotope ratio mass spectrometry (IRMS) are challenging because they require complicated sample preparation procedures, long measurement times, and relatively large samples sizes. Recently, tunable infrared laser direct absorption spectroscopy (TILDAS) has shown significant potential as an alternative technique for triple oxygen isotope analysis of CO_2, although the ultimate level of reproducibility is unknown, partly because it is unclear how to relate TILDAS measurements to an internationally-accepted isotope abundance scale (e.g. VSMOW2-SLAP2). Here, we present a method for high-precision triple oxygen isotope analysis of CO_2 by TILDAS, requiring ~8-9 μmol of CO_2 (or 0.9 mg carbonate) in 50 minutes, plus ~1.5 hours for sample preparation and dilution of CO_2 in N_2 to a nominal 400 μmol mol^{-1}. Overall reproducibility of $\Delta'^{17}O$ (CO_2) was 0.004 ‰ (4 per meg) for IAEA603 (SE, $n = 6$), and 10 per meg for NBS18 (SE, $n = 4$). Values corrected to the VSMOW2-SLAP2 scale are in good agreement with established techniques of high-precision IRMS, with the exception of $\Delta'^{17}O$ measured by platinum-catalyzed exchange of CO_2 with O_2. Compared to high-precision IRMS, TILDAS offers the advantage of $\sim$ 10 times less sample, and greater throughput, without loss of reproducibility. The flexibility of the technique should allow for many important applications to global biogeochemical monitoring, and investigation of ^{17}O anomalies in a range of geological materials.

The most commonly measured isotopologues of CO_2 are $^{12}C^{16}O^{16}O$, $^{13}C^{16}O^{16}O$, and $^{12}C^{16}O^{18}O$. Paleoenvironmental proxies based on these isotopologues (i.e. $\delta^{13}C$ and $\delta^{18}O$) are widely used to reconstruct past climates, as well as to quantify the sources and sinks of CO_2, which are essential to understanding the global carbon budget. However, on their own these proxies are often insufficient, and additional constraints are needed to resolve carbon fluxes, past and present. Photochemical reactions during the formation of ozone are associated with mass-independent isotope effects which lead to anomalous enrichment in ^{17}O in stratospheric CO_2.[1–4] The ^{17}O enrichment is passed to the troposphere, and reset close to zero by mass-dependent isotopic exchange between CO_2 and the terrestrial biosphere (mostly leaves) and oceans.[5] In terrestrial materials that contain oxygen, as well as the troposphere, the ^{17}O anomaly (expressed as $\Delta'^{17}O$)[6] is a promising tracer for carbon exchange between reservoirs,[2,5,7] as well as an exciting new proxy for paleoenvironmental change.[8–11] For the investigation of these effects, high-precision measurement ($\sim$0.01 ‰, or 10 per meg) of $\Delta'^{17}O$ is required, which is a challenging task for IRMS methods. These methods require the transformation of CO_2 to O_2 analyte, thereby avoiding isobaric interference between the $^{13}C^{16}O^{16}O$ and $^{12}C^{17}O^{16}O$ isotopologues, both of nominal mass 45. For this, various complicated techniques have been developed, including: conversion of CO_2 to O_2;[9,12] isotopic exchange of subequal quantities of CO_2 and O_2 over a hot platinum catalyst;[13–15] or by careful equilibration of CO_2 with H_2O, and subsequent water fluorination to produce O_2.[16]

Recent advances in optical detection of rare isotopologues have led to a rapidly expanding array of applications to biogeochemistry, e.g. detection of radiocarbon dioxide at sensitivities approaching that of accelerator mass spectrometry;[17] high-precision measurement of multiply-substituted isotopologues of both CH_4,[18] and CO_2.[19] The latter techniques all utilise tunable infrared laser direct absorption spectroscopy (TILDAS) for the direct measurement of isotopologue abundance ratios. Promisingly, Sakai *et al.*[20,21] report TILDAS measurements of $^{18}O/^{16}O$, $^{17}O/^{16}O$ from small quantities of CO_2 (2-68 μmol), with a precision of up to 30 per meg (SE, $n = 10$). The advantage of these methods over IRMS is that they require simpler laboratory procedures, and offer the potential of smaller samples sizes, and greater throughput. However, their overall reproducibility remains uncertain, and it is unclear how to relate TILDAS $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios to commonly-used abundance scales, such as VSMOW2-SLAP2 or VPDB.

Here, we present a relatively simple method for triple oxygen isotope analysis by TILDAS, which uses CO_2 evolved by acid digestion of interlaboratory carbonate reference standards, as well as a working reference gas, to produce high-precision $\Delta'^{17}O$ analyses, alongside $\delta^{13}C$. We have integrated TILDAS with an automated sample preparation system, which can also accept CO_2 from break-seal vials, acid digestion of ~ 0.9 mg of carbonate samples, or dry air from atmospheric flasks. The system ensures that CO_2 is well-mixed in N_2 prior to measurement, eliminating the possibility of isotope fractionation due to diffusion. We also present a framework for correcting spectroscopic $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios to the VSMOW2-SLAP2 scale, and show that overall reproducibilities from TILDAS can match those of IRMS methods. The three main areas of progress of our study, as compared to previous studies, are the following: (1) careful and proper mixing of gas is critical when analysing CO_2 in N_2 at trace concentrations; (2) correlation to an international scale for $\Delta'^{17}O$ study is possible; and (3) minimizing large instantaneous TILDAS electronics temperature changes is key to achieving high-precision measurements.

Experimental Section

Tunable Infrared Laser Direct Absorption Spectroscopy

Our instrument is a commercial Aerodyne Research Inc. (ARI) tunable infrared laser direct absorption spectrometer (TILDAS).[19,20,22] The instrument is based on the ARI dual-laser monitor platform, but is customized to the requirements of measuring CO_2 from carbonates, diluted to ~400 μmol mol^{-1} in N_2. In the configuration presented here, the instrument enables the measurement of multiple isotopologues of CO_2 simultaneously. The instrument was equipped with two co-aligned distributed-feedback interband-cascade lasers (DFB-ICL, nanoplus Nanosystems and Technology GmbH). The $^{12}C^{16}O^{16}O$, $^{12}C^{18}O^{16}O$, and $^{13}C^{16}O^{16}O$ isotopologues were targeted in the region of 2310 cm^{-1}, and the $^{12}C^{17}O^{16}O$ isotopologue was targeted in the region of 2349 cm^{-1}. The wavelengths of the two lasers (Table 1) were chosen to achieve both strong and relatively similar absorption signals of the individual isotopologues of interest at the expected sample-isotopologue ratios. Strong absorption lines provide excellent signal-to-noise ratios, whilst similar line strengths avoid potential errors due to non-linearity effects.

Table 1: Main transitions of each CO_2 isotopologue, targeted by lasers 1 and 2. All transition frequencies, line strengths, and broadening coefficients used in this study are from the HITRAN database.[23]

Isotopologue	wavenumber (cm^{-1})	line strength (cm molecules^{-1})	ground state (cm^{-1})
Laser 1			
$^{12}C^{17}O^{16}O$	2309.98236^a	4.226×10^{-22}	476.8538
$^{12}C^{16}O^{16}O$	2310.00242	4.856×10^{-21}	1454.9686
$^{12}C^{18}O^{16}O$	2310.20548	4.597×10^{-21}	278.2797
$^{13}C^{16}O^{16}O$	2310.34718	6.700×10^{-21}	639.6307
Laser 2			
$^{12}C^{18}O^{16}O$	2349.21536	5.369×10^{-21}	239.2698
$^{12}C^{17}O^{16}O$	2349.31321	1.196×10^{-21}	59.0607
$^{12}C^{16}O^{16}O$	2349.38705	1.357×10^{-21}	1885.5422

[a] Note that this weaker line is also included in the fitting of laser 1 spectra, for best accuracy of $\delta^{18}O_{meas}$ and $\delta^{13}C_{meas}$. However, the calculation of $\delta^{17}O_{meas}$ is based only on the stronger line, targeted at 2349.31320 cm^{-1} by laser 2.

The lasers and data acquisition were controlled by the ARI software TDLWintel, which also controlled the valve switching system (valves P9-P15 in Fig. 1), which is identical to the system reported elsewhere.[19] Both lasers were scanned sequentially at a frequency of 1.5 kHz. Before analysis, 1500 spectra were averaged to achieve a 1-second average spectrum. This improved the signal-to-noise ratio by approximately $\sqrt{1500} = 38\times$. The averaged spectra were then individually fit to one spectroscopic model per laser. These models include: the relevant absorption lines of all isotopologues present in each spectral window; a baseline of a polynomial form; as well as the zero-light signal. The zero-light signal is equivalent to complete absorption, and the baseline is equivalent to no absorption (complete transmission).

Absorption signal enhancement was achieved by increasing the optical absorption path-length to 36 m using a multipass absorption cell. In this cell, the laser beams were reflected between two mirrors such that they accumulated 194 passes. Upon exiting the cell, the co-aligned beams were focused on a thermoelectrically cooled HgCdTe detector (J19, Teledyne Judson). The sample pressure was around 28 Torr (10:1 reduction when expanding from volume 1, V1, in the valve switching system, previously filled via critical orifice through solenoid valves E1 (for sample gas) or E2 (for reference gas) see Fig. 1). The reduced pressure was used to sharpen the absorption lines and provide excellent isotopologue selectivity. This combined with the 36 m path length provided sufficient signal for very-high precision measurements.

Automated CO_2 Preparation System

The automated CO_2 sample preparation system is designed to cryogenically purify, dilute, and mix sample CO_2 with N_2. Samples are able to be introduced to the system by any of 3 methods: loaded in break-seal tubes, from acid digestion of carbonates (via a Thermo GasBench II), or directly from a removable atmospheric sampling flask. Each sample introduction pathway is handled with a unique preparation sequence based in a custom LabVIEW program. The system consists of a break-seal manifold, liquid N_2 cryogenic trap, 3 mixing volumes (MV1, MV2, MV3 - combined volume 687 mL), and a circulation loop with in-line diaphragm pump (CTS Series, Parker Hannifin Corp., USA) (Fig. 1). Valves 1-7, 16-21, and those on the circulation loop are Swagelok SS4-BK-VA-1C bellows-sealed valves. V8 is a three-way solenoid valve (P/N 009-0294-900, Parker Hannifin Corp., USA). Non-alphanumerically identified valves are manually toggled. Pressure gauges and corresponding data are handled by a data acquisition unit (cDAQ-9171, National Instruments Corp., USA). The sampling flask, which doubles as MV1, is custom made (GlassChem CC, South Africa, 576 mL) and designed to maximize turbulent mixing, see Supporting Information for photographs.

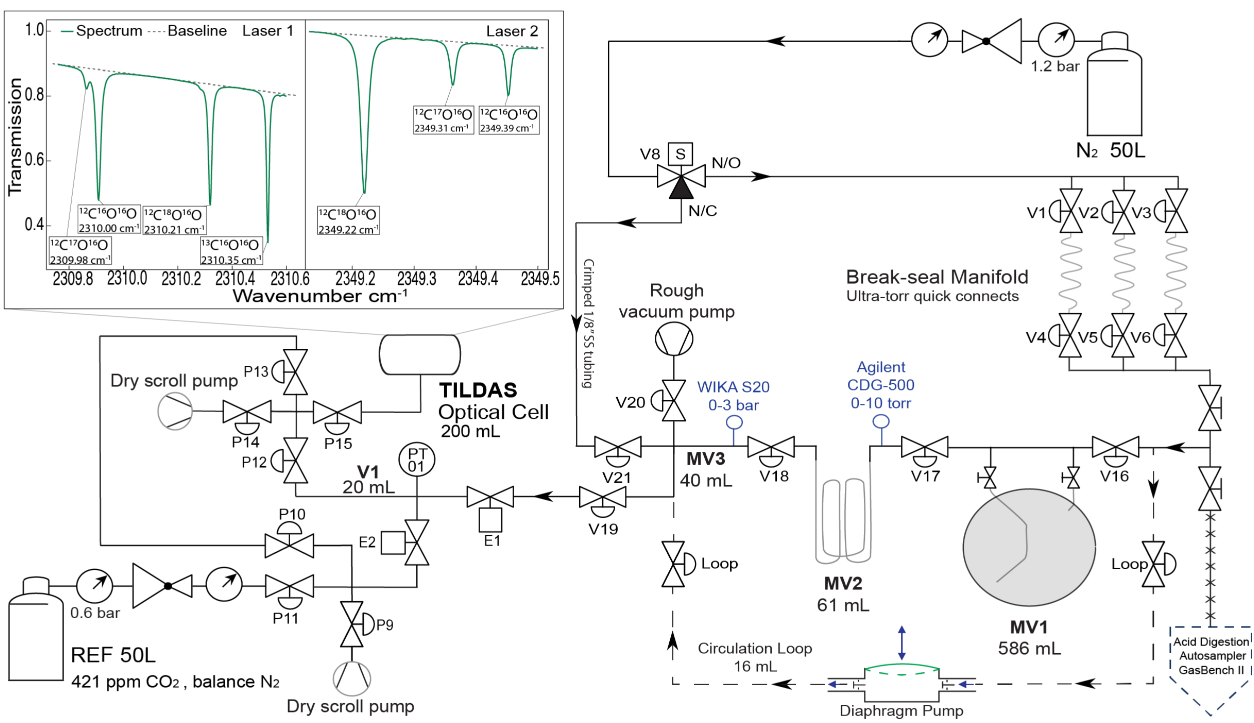

Figure 1: Schematic diagram of the system for automated preparation of CO_2 for high-precision TILDAS measurements of triple oxygen isotopes. MV1, MV2, and MV3 refer to mixing volumes 1 (586 mL), 2 (61 mL), and 3 (40mL). CO_2 from either acid digestion of carbonates (GasBench II) or alternatively, crackers, is frozen into MV2, and then diluted to ∼400 μmol mol^{-1} in N_2 in a specially-designed flask (MV1). The entire mixing volume (MV1,2,3) is then circulated for 2.5 minutes to ensure complete mixing prior to measurement. TILDAS sampling valves (pneumatic valves P9-P15, electronic valves E1 and E2) are the same as a previous system.[19] Sampling valves allow for repeated comparisons between a 50L reference tank (421 μmol mol^{-1} CO_2), and well-mixed sample in volume MV1,2,3.

Samples are introduced from their respective source and first cryogenically trapped in MV2. After a short pump-over to promote purification and complete sample collection, CO_2 is thawed for 6 minutes and the yield measured (Agilent Varian CDG-500, 0-10 Torr). Sample yield is then used to calculate dilution and mixing requirements on a sample specific basis (target dilution is 400 μmol mol^{-1}) before being expanded into MV1. Ultra high-purity N_2 as the diluent is regulated into the system at 1.2 bar and directed through a critical orifice, three-way solenoid valve, and crimped 1/8" diameter stainless steel tubing into MV3 via valve V21. Dilution and initial mixing occur simultaneously as MV3 and MV2 are repeatedly pressurized with N_2 to 1450 mbar (WIKA S-20, 0-3 bar) and turbulently expanded into MV1. The exact number of repeated expansions is unique to each sample as calculated from the sample yield. See Supporting Information for detailed sequence summaries and mixing steps.

After dilution and initial mixing, samples are further mixed by opening the circulation loop and activating the diaphragm pump. Pump circulation is 750 mL min^{-1}, meaning that three complete circulations occur through MV1,2,3 in 2.5 minutes. After 2.5 minutes the circulation loop closes and sample preparation is complete. Sample gas is then introduced to the TILDAS valve switching system via valve V19, a critical orifice, and valve E1. Sample pressures in the combined mixing volume typically begin around ~750 mbar and decrease to ~450 mbar over the course of an analysis. Overall repeatability of the sample concentration (evaluated from the $^{12}C^{16}O^{16}O$ isotopologue) was 403.6 ± 8.2 μmol mol^{-1} (1σ, $n = 17$). Within sample (aliquot) concentration repeatability ranged from 0.4 to 0.9 μmol mol^{-1} (1σ). Of importance to the success of our system are the high-precision Agilent Varian CDG-500 pressure gauge, sampling flask design, and circulation loop.

Reference Gas

The working reference gas used is a custom-made 50L high pressure cylinder of 421 μmol mol^{-1} CO_2 in ultra high-purity N_2 (99.999%), made by Air Liquide South Africa (Pty) Ltd in July of 2021. The reference gas tank was allowed to sit for several months before initial measurements were made. Reference gas is regulated into the TILDAS at 0.6 bar using a sub-ambient high-purity absolute pressure regulator (3396 series, Matheson Tri-gas Inc., USA). Aliquots of reference gas are introduced via valve P11 (Fig. 1), a critical orifice, and valve E2 to an intermediate volume (V1, 20mL) all of which are part of the TILDAS sampling valve system, described in detail elsewhere.[19] Sub-ambient regulation of the reference gas is of critical importance as slowing the fill rate of V1 allows for greater accuracy in achieving the target fill pressure of 300 Torr, and therefore greater repeatability in optical cell pressure throughout an analysis. 0.6 bar is also comparable to sample filling pressures, promoting similar V1 filling accuracy between gases. Overall aliquot repeatability of the working reference gas concentration for the $^{12}C^{16}O^{16}O$ isotopologue was 421.4 ± 0.4 μmol mol^{-1}, evaluated over 12 hours of repeated measurement (1σ, $n = 148$).

Definition of Spectroscopic δ-values, and Measurement Procedure

Optical isotope spectrometers, such as our TILDAS instrument, determine raw δ-values by measuring mole fractions of isotopologues.[24] We can write, e.g. for the $^{12}C^{17}O^{16}O$ isotopologue:

$$\delta(627) = \Big(\frac{\chi_{627}/\chi_{626}}{X_{627}/X_{626}} - 1\Big) \times 1000 \ , \tag{1}$$

where the mole fraction, χ_{627}=$C_{627}V/n$, is related to the measured concentration (C) of the $^{12}C^{17}O^{16}O$ isotopologue in the optical cell (of volume, V). $\delta(627)$ is shorthand spectroscopic notation that is used by the Air Force Geophysics Laboratory (AFGL), where isotopologues are identified by the second digits of the atoms' atomic mass. Similar expressions can be derived for mole fractions of other isotopologues (i.e. $\delta(628)$ for $^{12}C^{18}O^{16}O$, and $\delta(636)$ for $^{13}C^{16}O^{16}O$). For Aerodyne Research Inc. TILDAS instruments, X is the isotopologue abundance ratio (mol mol^{-1}) as specified in the high-resolution transmission molecular absorption database (HITRAN), a standard database of *ab initio* atmospheric simulations.[23,25] In eq. (1), χ is analogous to the isotope ratio of the sample, e.g. $(^{17}O/^{16}O)_{\text{sample}}$, in the usual definition of an IRMS δ-value, and X is analogous to the isotope ratio of the standard, $(^{17}O/^{16}O)_{std}$. Briefly, we also note that a spectroscopic δ-value is technically a molecular abundance ratio, and not an atomic abundance ratio, as is measured by IRMS. However, it is assumed (for now) that the difference between the two is negligible.[26]

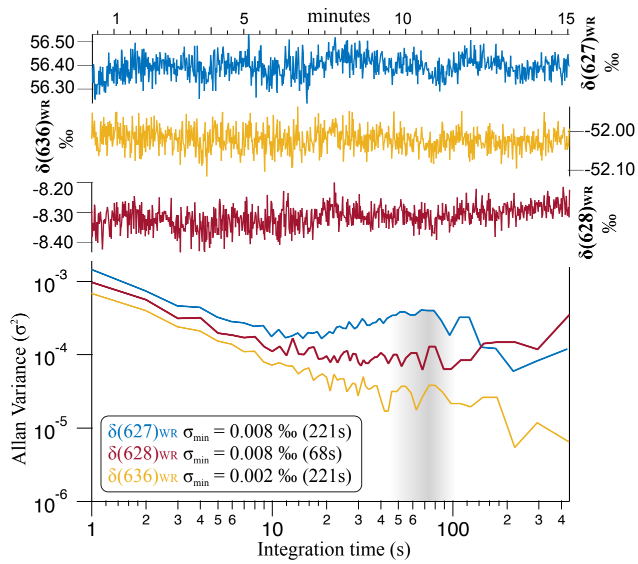

Figure 2: Allan variance plot for 15 minutes of reference gas measurement at 28.32 Torr by TILDAS, under optimal conditions. Working reference gas is 421.5 μmol mol^{-1} CO_2 in N_2. Cell volume was 200 mL, and cell temperature was 296.845 K. Electronics temperature variability was 0.04 ^{o}K min^{-1}. Shaded area shows the optimal averaging time for measurement of a single aliquot. Blue data, $\delta(627)_{WR}$; yellow data, $\delta(636)_{WR}$; and red data, $\delta(628)_{WR}$, are the raw isotopologue mixing ratios of our reference gas, relative to HITRAN abundance ratios (see definitions in main text).

Raw δ-values measured by our instrument (eq. 1) are not relative to a scale such as VPDB or VSMOW2-SLAP2, but rather, relative to HITRAN simulations of isotopologue abundance ratios. In our measurement procedure, we convert raw $\delta(627)$ values to spectroscopic $\delta^{17}O$ values relative to our working reference gas. Adopting IUPAC notation,[27,28] we define this relationship as:

$$\delta^{17}O_{meas} = \Big(\frac{\delta(627)_{samp}/1000 + 1}{\delta(627)_{WR}/1000 + 1} - 1\Big) \times 1000 \ , \tag{2}$$

where the subscripts "samp" and "WR" refer to sequential sample and working reference aliquots, respectively. Similar expressions are used for $\delta^{18}O_{meas}$ and $\delta^{13}C_{meas}$. This definition has two advantages. First, the dependence of δ-values on HITRAN is eliminated.

Second, repeated comparisons to the stable working reference gas compensates for drift in e.g. $\delta(627)_{\text{samp}}$ values over time. Analyses are performed by repeatedly alternating aliquots of sample and reference gas into the TILDAS, analogous to dual-inlet IRMS methods. This is done by filling V1 to 300 Torr of either sample or reference gas, followed by expansion into the pre-evacuated optical cell (200 mL).

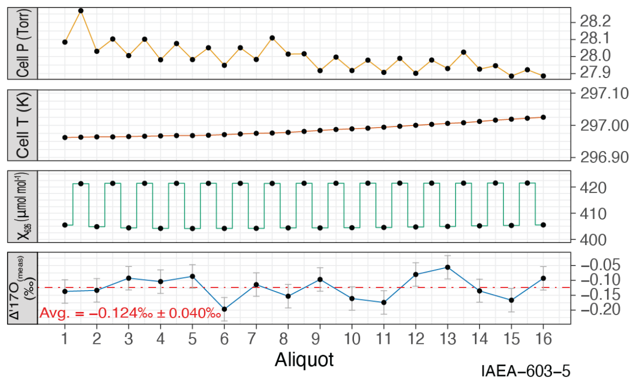

Figure 3: Example of measurement procedure for high-precision Δ'^{17}O. Repeated comparisons between a 50L reference tank (421 μmol mol^{-1} CO_2), and well-mixed sample of 8.645 μmol CO_2, evolved from 0.914 mg of IAEA603 carbonate, by phosphoric acid digestion (70^{o}C for 2 hours) and mixed to 404.8 μmol mol^{-1} in N_2 (703.53 mbar total sample). The measurement sequence takes around 50 minutes. Optical cell temperatures and pressures during this time were stable to within <0.1 K and <300 mTorr, respectively. Laboratory temperature variations were less than 0.20°K min^{-1}. 16 aliquots were averaged in total. χ_{626} is concentration of the $^{12}C^{16}O^{16}O$ isotopologue. Error bars for $\Delta'^{17}O_{\text{meas}}$ are 1σ.

For our system, each aliquot is measured in the optical cell for $\sim$ 60 seconds (occasionally up to $\sim$ 80s, depending on fill rate), during which the next aliquot is filled into V1, before the cell is evacuated and the next aliquot introduced. A measurement cycle, defined as the measurement of subsequent aliquots of sample and reference gas in order to calculate a $\delta^{17}O_{\text{meas}}$ value, takes ~3 minutes. The measurement time for a single aliquot is chosen by analysis of an Allan variance plot (Fig. 2), which shows that, under optimal conditions and a closed cell, substantial drift begins to occur in $\delta(628)$ after an integration time of 68 seconds (Allan minimum of $\sigma_{\min}$ = 0.008 ‰). The Allan minima for $\delta(627)$ and $\delta(636)$ were both obtained at 221s ($\sigma_{\min}$ = 0.008 ‰, and 0.002 ‰, respectively). Beyond 68 seconds, there is a sustained upwards trend in the Allan variance for $\delta(628)$, meaning that drift begins to dominate this measurement thereafter.

All aspects of the TILDAS measurement system, (e.g. timings, laser control, data acquisition, signal processing, etc.) are controlled by the TDLWintel software. Optical cell pressure is typically ~28 Torr, and generally stable to <300 mTorr. Cell temperature is typically ~297 K and stable to within 0.1 K (Fig. 3). A complete analysis, typically comprising of 18-20 measurement cycles, takes around 50 minutes. For all analyses, the first 3 measurement cycles are ignored due to stabilization of temperature within the optical cell.

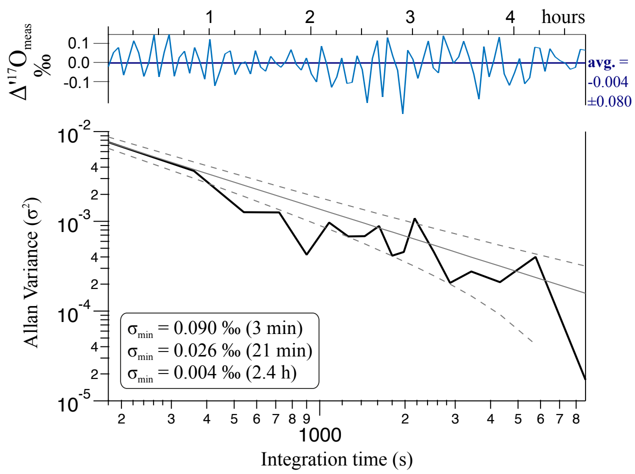

Figure 4: Upper: $\Delta'^{17}O_{meas}$ of reference gas against reference gas over 4.5 hours using 3 minute measurement cycles (blue line: grand average, and standard deviation). Lower: Allan variance plot. Dashed grey lines show theoretical simulation of white noise.

The stability of our reference gas isotopic composition, and of our measurement procedure, was further evaluated by series of repeated working reference gas comparisons (i.e. compared against itself). The Allan variance plot (Fig. 4) for $\Delta'^{17}O_{meas}$ (calculated from $\delta^{17}O_{meas}$ and $\delta^{18}O_{meas}$) shows a declining trend with increasing integration time, obeying ideal noise-limited behaviour over 4.5 hours of measurement. After 2.4 hours integration time, the Allan variance was 0.004 ‰. Overall, the average $\Delta'^{17}O_{meas}$ (for working reference gas relative to itself) was statistically indistinguishable from zero (-0.004 ± 0.008 ‰ , SE $n = 93$), which also suggests that there is no significant drift in working reference gas isotopic composition, over several hours.

From 31 March to 5 April lab air conditioning control malfunctioning was noted. During this period it was identified that poor Δ'^{17}O precision was correlated to the rate of change of TILDAS electronics temperature (dT/dt, °K min^{-1}). Samples analyzed between these dates were excluded as the amplitude of the resulting dT/dt curve, A(dT/dt), as evaluated by a centered 100-second moving average, was greater than 0.20 °K min^{-1}. All other samples as reported in this study showed A(dT/dt) $\leq$ 0.20 °K min^{-1}. To further investigate this effect, a series of experiments focusing on changes in electronics temperature were conducted, presented in the Results and Discussion below.

Concentration Dependence due to Scale-Offset Errors

Because δ-values measured by our TILDAS procedure are relative to isotopologue abundances of our working reference gas (eq. 2), an extra step is needed to convert them to the VSMOW2-SLAP2 scale. A conversion procedure has previously been outlined to correct spectroscopic $\delta^{13}C_{\text{meas}}$ for the offset from the VPDB scale.[24] We extend this procedure to the triple oxygen isotope system (and VSMOW2-SLAP2) as follows. Adopting the notation $\chi'_{627} = (\chi_{627})_{\text{samp}}/(\chi_{627})_{\text{WR}}$, and $\chi'_{626} = (\chi_{626})_{\text{samp}}/(\chi_{626})_{\text{WR}}$, we can modify eq. (2) thus:

$$\delta^{17}\text{O}_{\text{meas}} = \Big(\frac{a_{627}\chi'_{627} + b_{627}}{a_{626}\chi'_{626} + b_{626}} - 1\Big) \times 1000 \ , \tag{3}$$

where a_{627}, b_{627}, a_{626}, and b_{626} are empirical scale factors which relate the measured isotopologue mole fractions (i.e. relative to our working reference gas) to the equivalent isotopologue mole fractions on VSMOW2-SLAP2. We briefly note that there are also instrument-specific responses that might result in apparent scale offsets. In this case, the empirical factors in eq. (3) are expected to be unique to each instrumental setup. Assuming $A_{627} = a_{627}/a_{626}$, and dropping the factor of 1000 for convenience, with further modification it can be shown[24] that:

$$\delta^{17}\text{O}_{\text{std}} = \frac{\chi'_{626}}{A_{627}(\chi'_{626} - b_{626})}\left[\delta^{17}\text{O}_{\text{meas}} + \frac{(A_{627}b_{626} - b_{627})}{\chi'_{626}} - A_{627} + 1\right] \ . \tag{4}$$

This provides a general equation to correct TILDAS δ-values to the VSMOW2-SLAP2 scale. For interlaboratory carbonate standards, the value of $\delta^{17}O_{std}$ is assumed (or is measured by IRMS), and $\delta^{17}O_{meas}$ and χ_{626} are both then measured by TILDAS on multiple samples of CO_2 evolved from e.g. NBS18 and IAEA603 (mixed with dry N_2). The constants A_{627}, b_{627}, and b_{626} are then determined by non-linear least squares fitting to eq. (4). The same procedure is then performed to correct $\delta^{18}O_{meas}$ to $\delta^{18}O_{std}$ (with constants A_{628}, b_{628}, and b_{626}). Note that if $A_{627} = 1$ and b_{627}, $b_{626} = 0$, then eq. (4) reduces to $\delta^{17}O_{std} = \delta^{17}O_{meas}$, and the two scales are equal, as expected.

Significantly, eq. (4) shows that uncorrected TILDAS δ-values will depend on the measured concentration of the most abundant $^{12}C^{16}O^{16}O$ isotopologue (χ'_{626}). We call this effect a *"concentration dependence due to scale-offset errors"*, because it arises as an arithmetic consequence of the definition of the δ-value (eq. 1), and because there are offsets between our working reference gas and VSMOW2-SLAP2 isotopologue abundance scales, and also instrument-specific responses.

Results and Discussion

Isotope Effects due to Diffusion of CO_2 During Sample Preparation

Our TILDAS protocol requires highly-repeatable dilutions of CO_2 in N_2 to trace concentration. However, if dilution is incomplete, and the sample is not very well mixed, isotope fractionation due to diffusion will be reflected in $\delta^{17}O_{meas}$ and $\delta^{18}O_{meas}$ values, in addition to concentration dependence (described above). Diffusion effects were found to be negligible in TILDAS measurements of the clumped isotopologue $^{13}C^{16}O^{18}O$ (CO_2 in N_2 at 0.35%), due to cancellation of factors in the equation for the clumped equilibrium constant, K.[19] However, diffusion is likely to be more important in the triple oxygen isotope system, where very small differences in $\delta^{17}O$ and $\delta^{18}O$ propagate into large errors in ($\Delta'^{17}O$).[6]

For triple oxygen isotopes, the relationship between fractionation factors during diffusion is defined[6] as $\alpha^{17/16} = (\alpha^{18/16})^{\theta}$, which, rearranging, gives:

$$\theta_{\text{diff}} = \frac{\ln\left(\alpha^{17/16}\right)}{\ln\left(\alpha^{18/16}\right)} \ . \tag{5}$$

Where the subscript "diff" indicates a diffusion process. For diffusion of CO_2 in N_2, the binary diffusion coefficient can be calculated from Chapman-Enskog theory using:

$$D_{ab} = \frac{AT^{3/2}}{p\sigma_{ab}^2\Omega}\sqrt{\frac{m_a + m_b}{m_a m_b}} \ . \tag{6}$$

The subscripts a and b refer to the two gases, m is the molecular mass of each gas, and σ and Ω are the average collision diameter (4.15 Å) and temperature dependent collision integral ($\sim$ 1), respectively. At 21 ^{o}C and 700 mbar, D is 0.1879 cm^2 s^{-1}. eq. (6) can be modified to describe the ratios of isotopologue concentrations, and thereby related to fractionation factors. With further algebra, common terms such as T, p, etc. will cancel, and it can be shown that the ratio of fractionation factors is just the ratio of diffusivities for each isotopologue:

$$\begin{aligned}\theta_{\text{diff}} &= \frac{\ln\left(\frac{D_{45,28}}{D_{44,28}}\right)}{\ln\left(\frac{D_{46,28}}{D_{44,28}}\right)} \\ &= \frac{\ln(\frac{44}{45})+\ln(\frac{45+28}{44+28})}{\ln(\frac{44}{46})+\ln(\frac{46+28}{44+28})} \\ &= 0.509\end{aligned}$$

According to the conventional δ-notation definition of the triple oxygen isotope system,

$$\Delta'^{17}\text{O} \equiv \delta'^{17}\text{O} - \theta\delta'^{18}\text{O} \ , \tag{7}$$

where $\theta = 0.528$ (global reference line) and $\delta'^{17}\text{O} = 1000\ln(\delta^{17}\text{O}/1000 + 1)$, and a similar expression exists for δ'^{18}O. Hence, the mass-dependent fractionation exponent, θ, is lower for diffusion than for the global reference line. When CO_2 diffuses in N_2, $\delta'^{18}O$ and $\delta'^{17}O$ values will be shifted lower relative to their original values (i.e. relative to the pure CO_2). This gas will also tend to be under-diluted with respect to the target concentration (400 μmol mol^{-1}). And by mass balance, $\delta'^{18}O$ and $\delta'^{17}O$ values of the remaining (un-mixed) CO_2 will be shifted higher.

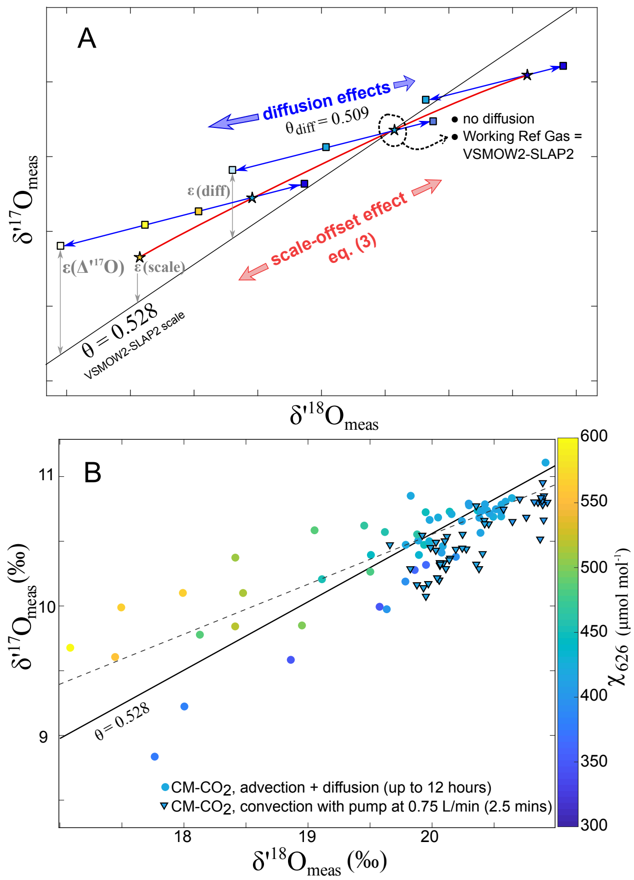

Figure 5: (A) Graphical framework for errors in TILDAS measurements of triple oxygen isotope composition of CO_2 (see further discussion in text). Stars are samples of different target concentration. Squares are aliquots drawn from each sample (under- or over-diluted). (B) shows the effects of incomplete mixing of CO_2 in N_2 on $\delta'^{17}O_{meas}$ and $\delta'^{18}O_{meas}$. Filled triangles show multiple aliquots from 4 samples of CO_2 evolved from an internal standard, Cavendish Marble (CM), circulated by diaphragm pump (Parker CTS) for 2.5 minutes to allow proper mixing before measurement. Other datapoints are aliquots from five samples of CM, mixed only by advection and diffusion (for up to 12 hours).

A framework for errors due to diffusion, as well as scale-offset, is shown in Fig. 5A for a hypothetical gas with a true value of $\Delta'^{17}O_{meas} = 0$. If the sample gas is well-mixed, with no diffusion, and no offset error, then all aliquots would be measured along a line of slope $\theta = 0.528$ in $\delta'^{17}O_{meas}$-$\delta'^{18}O_{meas}$ space. Samples with scale-offset error would lie along a curve (shown in red) depending on the measured concentration of $^{12}C^{16}O^{16}O$ (χ'_{626}, eq. 4), as well as the values of A_{627}, A_{628}, etc. In addition, if there are diffusion effects, then individual aliquots will lie along a slope of $\theta = 0.509$ (shown in blue). In reality, the two effects occur together, so that the total error, $\varepsilon(\Delta'^{17}O)$, is the sum of errors due to scale offset, ε(scale), and diffusion, ε(diff). Aliquots of higher concentration will be found above the true slope, and lower concentrations below it, resulting in a "cone" of scatter, with an average gradient lower than $\theta = 0.528$ (and erroneously high $\Delta'^{17}O_{meas}$ values).

To test this framework, we conducted an experiment on samples with and without our circulating pump, using CO_2 from ∼0.8 mg samples of an internal laboratory standard, Cavendish Marble (CM-CO_2). 5 samples were mixed into MV1,2,3 by turbulent advection and diffusion only, without the circulating pump. The time taken for diffusive mixing was varied on a sample-by-sample basis from ∼10 minutes to 12 hours. In addition, the average χ'_{626} of each sample varied from 400 to 466 μmol mol^{-1}. 4 samples of the same material were mixed for ∼2.5 minutes with the pump, immediately after turbulent advection. χ'_{626} of these samples varied from 368 to 405 μmol mol^{-1}.

For the samples unmixed by pump, Fig. 5B shows good agreement with the framework in Fig. 5A. Aliquots from all samples form a cone of scatter, with an average slope (dashed line) lower than $\theta = 0.528$. Better-mixed aliquots, close to the target concentration range, cluster more closely to $\theta = 0.528$. When the circulating pump is added (filled triangles), all aliquots have an average slope very near $\theta = 0.528$. Without the pump, 1σ sample repeatability for $\Delta'^{17}O_{meas}$ was 30 ± 130 per meg, and aliquot repeatability for χ'_{626} was between 4 and 80 μmol mol^{-1}. With the pump, sample repeatability for $\Delta'^{17}O_{meas}$ improved substantially to -230 ± 10 per meg, in significantly less time (∼2.5 minutes vs hours). With the pump, aliquot repeatability for χ'_{626} was also excellent (between 0.4 and 0.9 μmol mol^{-1}). This result supports the conclusion that, without proper mixing, diffusion effects can be very significant in sample preparation, necessitating very long times for well-mixed sample gases, prior to TILDAS measurements of Δ'^{17}O. Promisingly, forced convection via circulating loop solves these issues. Preparation of the entire sample gas prior to measurement (as opposed to aliquot-by-aliquot basis) also provides a useful check on the extent of mixing, which may be evaluated by aliquot repeatability of χ'_{626}.

Correction of Spectroscopic δ^{17}O and δ^{18}O values to the VSMOW2-SLAP2 Scale

In what follows, we compare triple oxygen isotope measurements both without correction ($\delta'^{17}O_{meas}$, $\delta'^{18}O_{meas}$), and corrected to VSMOW2-SLAP2 ($\delta'^{17}O_{corr}$, $\delta'^{18}O_{corr}$). These data are shown in Table 2. All samples were well-mixed by circulating pump for 2.5 minutes prior to TILDAS measurement (described in detail above). For conciseness, corresponding δ^{13}C data for these samples are reported in the Supporting Information. For the correction, we used interlaboratory carbonate standards IAEA603 ($n = 6$), and NBS18 ($n = 4$). Assuming VSMOW2-SLAP2 values for CO_2 from IAEA603 and NBS18 given by Wostbrock *et al.*,[12] we fitted eq. (4) to all aliquots of $\delta^{17}O_{meas}$, and χ'_{626}, in MATLAB. The same procedure was then performed for $\delta^{18}O_{meas}$. For δ^{17}O, the fitted parameters were: $A_{627} = 0.674$, $b_{627} = -1974$, $b_{626} = -168$, $R^2 = 0.999$; and for δ^{18}O, they were $A_{628} = 0.632$, $b_{628} = -3782$, $b_{626} = -207$, $R^2 = 0.999$.

We have corrected our δ-values to the VSMOW2-SLAP2 scale using previously-published values for carbonate standards from an IRMS method[12] because this particular method is regarded as a relatively assumption-free for triple oxygen isotope analysis.[29] A more nuanced approach, for future investigation, would be to perform equilibrations between CO_2 gas and VSMOW2, SLAP2 water directly on our cart within MV1, thereafter trapping and analyzing the equilibrated CO_2. The extension of our system to this procedure would be fairly straightforward, and it might further reduce the intrinsic dependence of spectroscopic Δ'^{17}O measurements on IRMS methods. Using eq. (4), our $\delta^{17}O_{meas}$ values could be effectively

Table 2: Triple oxygen isotope data for CO_2 evolved by phosphoric acid digestion of interlaboratory carbonate standards at 70°C, measured by TILDAS. Between 13 and 18 aliquots were measured per sample ($\sim$ 0.9 mg total carbonate). δ^{17}O and δ^{18}O values from individual aliquots are corrected to the VSMOW2-SLAP2 scale using the IAEA603 (CO_2) and NBS18 (CO_2) values of Wostbrock et al. (2020). The corrected values, $\delta'^{17}O_{corr}$ and $\delta'^{18}O_{corr}$, were then used to calculate $\Delta'^{17}O_{corr}$. χ_{626} is the concentration of the $^{12}C^{16}O^{16}O$ isotopologue in each sample, μmol.mol^{-1}, with 1σ repeatability of aliquots in parentheses. All isotope data are ‰, with the exception of $\Delta'^{17}O_{corr}$, which are per meg, $\theta = 0.528$.

Sample	χ_{626}	$\delta'^{17}O$ [a]	$\delta'^{18}O$ [a]	$\delta'^{17}O_{corr}$ [b]	$\delta'^{18}O_{corr}$ [b]	$\Delta'^{17}O_{corr}$
IAEA603-4	393.3(0.5)	14.311	27.560	20.036	38.250	-158
IAEA603-5	404.8(0.6)	14.290	27.435	20.045	38.220	-140
IAEA603-6	412.8(0.8)	14.288	27.471	20.097	38.374	-161
IAEA603-7	393.8(0.8)	14.287	27.493	20.012	38.181	-147
IAEA603-9	405.3(0.7)	14.277	27.435	20.034	38.224	-149
IAEA603-10	415.6(0.7)	14.216	27.300	20.000	38.172	-158
	Average	**14.291**	**27.479**	**20.037**	**38.237**	**-151**
	± 1σ	**0.013**	**0.052**	**0.015**	**0.043**	**10**
	St. err [c]	**0.006**	**0.023**	**0.007**	**0.019**	**4**
NBS18-8	397.7(0.4)	3.605	6.925	8.941	17.148	-113
NBS18-12	409.6(0.5)	3.791	7.374	9.075	17.389	-106
NBS18-13	405.1(0.5)	3.840	7.409	9.150	17.463	- 71
NBS18-14	401.8(0.9)	3.763	7.313	9.112	17.461	-107
	Average	**3.750**	**7.255**	**9.070**	**17.365**	**- 99**
	± 1σ	**0.102**	**0.224**	**0.091**	**0.149**	**19**
	St. err [c]	**0.051**	**0.112**	**0.046**	**0.074**	**10**
NBS19-5	401.4(0.6)	14.164	27.295	19.895	38.052	-196
NBS19-6	409.0(0.6)	14.269	27.435	20.0533	38.266	-151
NBS19-7	397.6(0.5)	14.244	27.500	19.9783	38.222	-203
NBS19-11	397.3(0.7)	14.406	27.796	20.146	38.524	-195
NBS19-12	388.5(0.7)	14.492	27.868	20.208	38.515	-127
NBS19-13	411.3(0.5)	14.443	27.678	20.224	38.530	-120
NBS19-14	416.6(0.7)	14.418	27.798	20.184	38.582	-177
	Average	**14.348**	**27.624**	**20.098**	**38.385**	**-150**
	± 1σ	**0.122**	**0.217**	**0.126**	**0.203**	**60**
	St. err [c]	**0.046**	**0.081**	**0.048**	**0.077**	**22**

[a] Molecular abundance ratios by spectroscopy, e.g. $\delta(627)$ are assumed equal to atomic abundance ratios, e.g. δ^{17}O, and the atomic notation is retained; [b] Corrected using eq. (4); [c] Standard error $= 1\sigma/\sqrt{n}$

calibrated directly to VSMOW2-SLAP2 (and likewise for $\delta^{18}O_{meas}$). Analysing equilibrated CO_2 would thereby also calibrate our working reference gas.[24] We anticipate that this calibration procedure would need to be performed periodically, in order to monitor potential long-term drift that might occur as our 50L working reference tank empties (for instance, due to potential effusion effects).

Although we also report NBS19 ($n = 7$) in Table 2, it was excluded from the fitting because these samples had substantially worse reproducibility for $\Delta'^{17}O_{corr}$ ($1\sigma = 60$ per meg, $n = 7$). Although the experimental conditions for all standard samples were identical, we used an almost-empty vial of NBS19, whereas a fresh vial of IAEA603 was opened for this experiment. We suggest that the significantly greater degree of scatter in NBS19 might be related to slight but significant exchange of this standard with moisture in this old vial, over ~30 years of regular use, a phenomenon discussed by other authors.[30] Alternatively, this might be due to heterogeneity in the stable isotopic composition of NBS19 itself.[31]

Reproducibility of $\Delta'^{17}O$ was significantly improved by correction to VSMOW2-SLAP2 using eq. (4), for IAEA603 and NBS19. After correction, reproducibility of IAEA603 improved significantly from 7 per meg (1 SE) to 4 per meg; NBS19 also improved from 25 to 21 per meg. Reproducibilility of NBS18 was similar before and after correction, at ~10 per meg. The reproducibility of our $\delta'^{17}O_{corr}$ and $\delta'^{18}O_{corr}$ values for IAEA603 (7 and 19 per meg, respectively), are significantly improved over previously-published TILDAS measurements of isotopologue ratios of CO_2 (reproducibilities of 30 and 40 per meg for $^{17}O/^{16}O$ and $^{18}O/^{16}O$, respectively).[20,21] Reproducibilities for NBS18 and NBS19 are a similar order of magnitude to these measurements. These results further emphasise the importance of correcting for scale-offset effects, at least for some samples, and provides a relatively simple strategy for correcting spectroscopic δ-values to VSMOW2-SLAP2.

Utility of High-precision $\Delta'^{17}O$ (CO_2) TILDAS Measurements in Comparison to IRMS

Mean $\Delta'^{17}O_{corr}$ values of IAEA603, NBS18, and NBS19 by TILDAS are internally consistent with Wostbrock *et al.*,[12] and are in excellent agreement with other high-precision IRMS methods which rely on conversion of CO_2 to O_2[9,32] to within 1 SE reproducibility (Fig. 6). Encouragingly, our methodology requires substantially less sample (~0.9 mg of carbonate) compared to all current IRMS methods (typically 5-10 mg).[9,12,30,32] In addition, TILDAS requires somewhat less complicated sample preparation and shorter measurement times than IRMS. Furthermore, the internal consistency between our results and IRMS supports the assumption that differences between atomic and molecular abundance ratios are negligible, at this level of reproducibility.

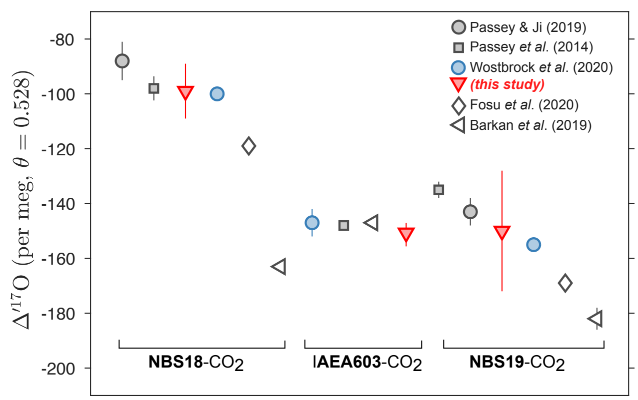

Figure 6: Comparison between TILDAS (red triangles, this study) and IRMS measurements of $\Delta'^{17}O$, for CO_2 evolved from Interlaboratory Standards. Errorbars denote 1 SE. Filled grey symbols denote conversion methods (CO_2 to O_2, or direct BrF_5 fluorination of carbonate). Open symbols indicate methods reliant on platinum-catalyzed exchange of CO_2 with O_2.

One challenge of our method is the requirement that samples are very well-mixed. However, mixing the sample prior to measurement (as opposed to on a per aliquot basis), means that the degree of mixing is easily evaluated from successive measurements of aliquot concentration(s). We also note that there is significant disagreement between some IRMS methods of triple oxygen analysis (see Fig. 6).[29] Typically, methods that rely on platinum-catalyzed exchange of CO_2 with O_2[14,15,30] have systematically lower $\Delta'^{17}O$ values than conversion methods. Our Δ'^{17}O values are corrected to values from a conversion method, and are therefore in disagreement with exchange methods, with the exception of NBS19, which, to within its large uncertainty, agrees with most methods. Because this problem seems to be unique to our NBS19, we argue that these errors are likely related to sample heterogeneity and contamination issues (discussed above). The result underscores the importance of using carefully-chosen standards in triple oxygen isotope research, for which future interlaboratory comparison is warranted.

Effect of Electronics Temperature Variability on Δ'^{17}O Precision

To assess the impact of changes in TILDAS electronics temperature on analytical precision, a series of experiments was conducted in which the working reference gas was measured against itself in discrete aliquots, whilst lab air conditioning was modified (thereby changing electronics temperature stability). From each experiment, temperature variability (dT/dt) was calculated using a centered 100-second moving average on 1 Hz temperature data. The amplitude of electronics temperature variability, A(dT/dt), closely tracks lab air conditioning cycling. A selection of these experiments are shown in Fig. 7A. Subpanel *i* shows an experiment in which the fan intake on the electronics box was temporarily blocked, causing rapid heating and subsequent cooling after the cover was removed. Correspondingly, increased measurement error in Δ'^{17}O ($1\sigma = 0.12$ ‰, $n = 13$) is observed as a direct result of the large instantaneous changes in electronics temperature (0.95 °K min^{-1}). In contrast, the experiment in subpanel *iv* shows that more gradual changes in electronics temperature (0.09 °K min^{-1}) minimizes the measurement error ($1\sigma = 0.04$ ‰, $n = 12$). The absolute temperature of the electronics exerts no discernible influence.

Spanning all experiments, a trend is observed correlating A(dT/dt) to measured Δ'^{17}O precision (Fig. 7B), in which half the variability in measurement precision is explained by dT/dt of the electronics ($R^2 = 0.5$). These experiments also investigated the effects of variability in TILDAS internal N_2 purge rate, and optical cell temperature, which were both

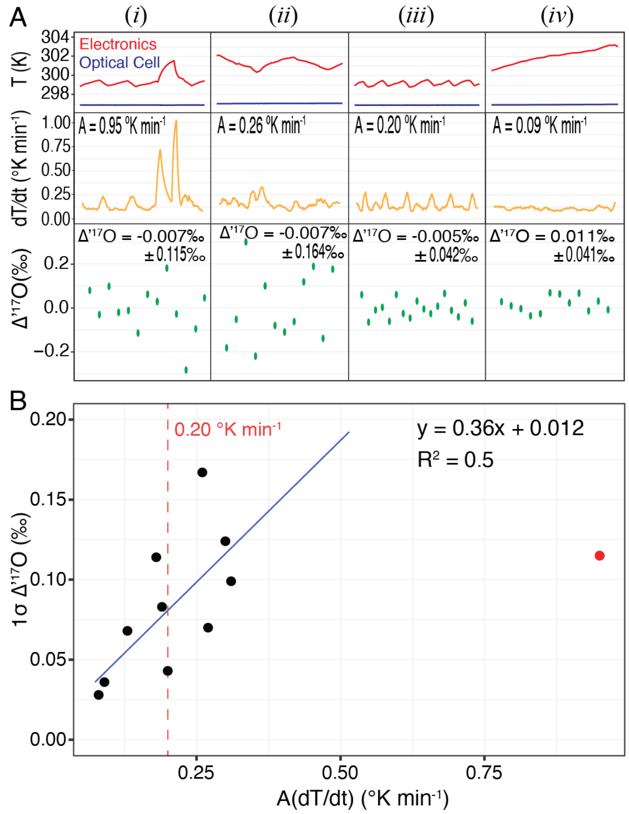

Figure 7: (A) shows optical cell temperatures (blue curves) and electronics temperatures (red curves) for experiments with higher instantaneous electronics temperature variability (subpanels *i* and *ii*) and lower instantaneous variability (subpanels *iii* and *iv*). Yellow curves show corresponding electronics dT/dt, and measured $\Delta'^{17}O$ values of discrete aliquots are shown as green data. (B) shows correlation between amplitude of instantaneous temperature variability and $\Delta'^{17}O$ precision for all experiments (see all subfigures in SI). Red data point indicates repeatability of green data points in panel *i* - an experiment in which fan intake was intentionally blocked.

found to have no impact on measurement error (within their respective ranges). Further information regarding experimental conditions and results of all experiments are presented in the Supporting Information.

TILDAS electronics temperature is measured by a thermistor located inside the electronics box near the air intake fan. It is suspected that room air temperature impacts measurement precision by means of its effect on electronic components with a temperature coefficient (e.g. resistors). In this manner, it is possible that changes in room air temperature affect laser parameters, such as current offset and span, via said components. The extremely high sensitivity of the lasers implies that even tiny changes in applied current could increase measurement errors apparent on the per meg scale.

Conclusions

We have presented a method for triple oxygen isotope analysis by TILDAS, with a sample reproducibility for $\Delta'^{17}O$ of CO_2 from interlaboratory carbonate standards that equals that of current high-precision IRMS methods (provided the sample is well-mixed in N_2). Our method brings several additional advantages, such as smaller sample size (e.g. ~0.9 mg of carbonate), increased throughput, and direct measurement of $\Delta'^{17}O$ in CO_2. In addition, our system is readily modifiable. It is able to handle several different sources of CO_2, e.g. via GasBench acid digestion, break-seal vials, or dry atmospheric samples collected in our removable flask (~586 mL). We have set out a simple procedure for the correction of TILDAS δ-values to the VSMOW2-SLAP2 scale. Future work will allow for more direct calibration via equilibration of CO_2 with VSMOW2 and SLAP2 waters, and combine TILDAS measurements of $\Delta'^{17}O$ with multiply-substituted CO_2 isotopologues,[19] so that $\delta^{17}O$, $\delta^{18}O$, $\delta^{13}C$, and δ_{47} of the same sample are measured simultaneously. We expect this, or similar techniques, to have significant impact on future atmospheric monitoring and terrestrial (paleo)climate research.

Supporting Information

Supporting Information: Additional experimental details, including photographs of experimental setup, and LabVIEW and ECL code (PDF).

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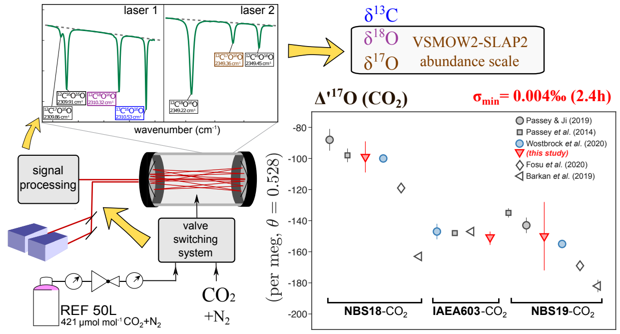

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