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A rapid high-precision analytical method for triple oxygen isotope analysis of CO2 gas using tunable infrared laser direct absorption spectroscopy

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A rapid high-precision analytical method for triple oxygen isotope analysis of CO_2 gas using tunable infrared laser direct absorption spectroscopy

by

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B.S, GEOLOGY, UTAH VALLEY UNIVERSITY, 2020

THESIS

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A rapid high-precision analytical method for triple oxygen isotope analysis of CO_2 gas using tunable infrared laser direct absorption spectroscopy

by

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B.S, Geology, Utah Valley University, 2020
M.S, Earth and Planetary Sciences, University of New Mexico, 2022

ABSTRACT

Rationale

The simultaneous analysis of the three stable isotopes of oxygen – triple oxygen isotope analysis – has become an important analytical technique in natural sciences. Determination of the abundance of the rare ^{17}O isotope in CO_2 gas using magnetic sector isotope ratio mass spectrometry is complicated by the isobaric interference of ^{17}O by ^{13}C ($^{13}C^{16}O^{16}O$ and $^{12}C^{16}O^{17}O$ both have mass 45 amu). A number of analytical techniques have been used to measure the $^{17}O/^{16}O$ ratio of CO_2 gas. They are either time consuming and technically challenging or have limited precision. A rapid and precise alternative to the available analytical methods is desirable.

Methods

We present the results of triple oxygen isotope analyses using an Aerodyne Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS) CO_2 analyzer configured for ^{16}O, ^{17}O, and ^{18}O, combined with a custom gas inlet system. We evaluate the sensitivity of our results to a number of parameters. CO_2 samples with a wide range of $\delta^{18}O$ values (from -9.28 ‰ to 39.56 ‰) were measured and compared to results using the well-established fluorination-gas source mass spectrometry method.

Results

The TILDAS system has a precision (standard error, 2σ) of better than ±0.03 ‰ for $\delta^{18}O$ and ±10 per meg for $\Delta'^{17}O$ values, equivalent to the precision of previous analytical methods. Samples as small as 3 micromoles CO_2 (equivalent to 300 micrograms $CaCO_3$) can be analyzed with a total analysis time of ~30 minutes.

Conclusions

We have successfully developed an analytical technique for the simultaneous determination of the $\delta^{17}O$ and $\delta^{18}O$ values of CO_2 gas. The precision is equal to or better than existing techniques with no additional chemical treatments required. Analysis time is rapid and the system is easily automated so that large numbers of samples can be analyzed with minimal effort.

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PREFACE

This thesis has been published in the journal *Rapid Communications in Mass Spectrometry* (DOI: 10.1002/rcm.9391) with coauthors Zachary Sharp, Dave Nelson Jr., Rick Wher, and Christoph Dyroff. The authors confirm contribution to the paper as follows: study conception and design: Nathan Perdue, Zachary Sharp, Dave Nelson Jr., Rick Wher, Christoph Dyroff; data collection: Nathan Perdue, Zachary Sharp; analysis and interpretation of results: Nathan Perdue, Zachary Sharp; draft manuscript preparation: Nathan Perdue, Zachary Sharp, Dave Nelson Jr., Rick Wehr. All authors reviewed the results and approved the final version of the manuscript.

In accordance with the Department of Earth and Planetary Sciences at the University of New Mexico requirements, Nathan Perdue is the primary author and performed more than or equal to 51% of the work in preparing this thesis. This research was supported by NSF grant #EAR 2025107 to Zachary Sharp.

1. INTRODUCTION

Following the discovery of the temperature-dependent fractionation between calcite and water over 70 years ago [1], numerous studies have used this relationship as a paleoclimate indicator to reconstruct ocean water temperatures. Despite the prevalence of measuring carbonates to reconstruct temperatures, researchers are still trying to develop new techniques to minimize the assumptions associated with carbonate palaeothermometry. These assumptions include the following: the original oxygen isotope composition of the ocean, that the carbonate formed in oxygen isotope equilibrium with ocean water, and that the carbonate is free of diagenetic alteration [2].

New carbonate isotope techniques have been developed, including clumped isotopes [3] and triple oxygen isotopes [4]. The relatively new field of triple oxygen isotopes for carbonates uses the rare stable isotope of oxygen, ^{17}O, in addition to the traditional measurements of ^{18}O and ^{16}O, to evaluate the equilibrium conditions under which the carbonates precipitated. For terrestrial processes, oxygen isotopes undergo mass-dependent fractionations such that δ^{17}O $\approx 0.5(\delta^{18}$O$)$, where δ^{x}O $= (R_{\text{sample}}/R_{\text{standard}} - 1)\times 1000$ in per mil (‰) notation, where R is ^{17}O/^{16}O or ^{18}O/^{16}O. Because the δ^{17}O and δ^{18}O values of terrestrial materials generally plot with a slope of ½, it was assumed that the δ^{17}O value provided no additional information to the δ^{18}O value alone. It is now known that the δ^{17}O and δ^{18}O values of terrestrial materials deviate slightly from this near-linear relationship, and that these deviations have geological or biological significance. Triple oxygen isotope data are presented in terms of Δ'^{17}O (also called ^{17}O excess), defined as:

$$\Delta'^{17}\mathrm{O} = (\delta'^{17}\mathrm{O} - \lambda * \delta'^{18}\mathrm{O}) \tag{1}$$

in per mil (‰) notation and

$$\Delta'^{17}O = (\delta'^{17}O - \lambda * \delta'^{18}O) * 1000 \quad (2)$$

in per meg notation, where λ is a reference slope (0.528 in this work), and $\delta'^{17}O$ and $\delta'^{18}O$ are linearized versions of $\delta^{17}O$ and $\delta^{18}O$ ($\delta'^{x}O = 1000ln(\delta^{x}O/1000+1)$) [5]. The small but measurable $\Delta'^{17}O$ values provide meaningful information about carbonates and other minerals [4,6-8].

The benefit of measuring both $\delta^{17}O$ and $\delta^{18}O$ of carbonates becomes apparent when plotted in triple oxygen isotope space with the carbonate-water isotope equilibrium curve [8]. The triple oxygen isotope composition of marine carbonates can be used to assess the degree of post-depositional diagenesis, and to estimate the temperature of deposition[8]. Therefore, the triple oxygen isotope composition of carbonates provides us with an independent estimate of temperature and the ability to assess the preservation of a sample.

The development and wide usage of high-precision triple oxygen isotope measurements of carbonates ($\Delta'^{17}O$ ±10 per meg) is hindered by the difficulty of current available analytical techniques. Traditional measurements of carbonates for $\delta^{13}C$ and $\delta^{18}O$ are made from CO_2 produced by phosphoric acid digestion [9]. However, due to the isobaric interference at mass 45 between $^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$, the ^{17}O contribution to CO_2 at mass 45 cannot be resolved with conventional magnetic sector mass spectrometry. A number of techniques have been developed to overcome this problem, including the following: 1) high-temperature fluorination of CO_2 to O_2, which is then analyzed in a conventional gas source mass spectrometer [10]; 2) conversion of CO_2 to H_2O using a Fischer–Tropsch process followed by fluorination of the resultant H_2O to O_2 [6,11]; 3) high-temperature Pt catalyzed exchange between CO_2 and subordinate O_2 gas, in which the O_2 gas essentially ‘acquires’ the isotopic composition of the CO_2 gas [12,13]; 4) analysis of the O^+ fragment of CO_2 gas in an electron impact source ultrahigh-resolution mass spectrometer [14]. None of these methods is ideal for measuring relatively large numbers of samples, due to cost, time of analysis, or limited precision; see [15] for a full review.

New developments using laser-based spectrometry show significant progress towards high-precision triple oxygen isotope measurements directly from CO_2. Previous studies using tunable infrared laser direct absorption spectroscopy (TILDAS) have successfully measured $^{17}O/^{16}O$ and $^{18}O/^{16}O$ of CO_2 simultaneously but have not yet achieved the precision required for application to natural materials (~10 per meg for $\Delta'^{17}O$) [16,17].

Here we report the simultaneous analyses of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ of CO_2 through the development of a new TILDAS instrument for high precision and rapid analysis of triple oxygen isotope composition. In order to obtain high-precision results, it is necessary to rapidly (on the order of 1-2 minutes) switch between sample and reference gas (to calibrate drift), and it is critical to balance the mixing ratios and pressures of the sample and reference gases. A sample preparation system was constructed to reach these objectives. This new instrument and sampling system significantly reduce the analysis time and sample size while achieving the necessary precision of ±10 per meg for $\Delta'^{17}O$. The cost of the triple oxygen CO_2 analyzer and sampling system is less than that of a traditional mass spectrometer required to acquire such precision. The rapidity and ease of analysis, combined with the potential for full automation, allows for large numbers of samples to be analyzed with a reasonable effort, opening up the technique to numerous applications in the physical sciences.

2. EXPERIMENTAL

2.1 Tunable Infrared Laser Direct Absorption Spectroscopy

Spectroscopic analyses were performed using a tunable infrared laser direct absorption spectroscopy (TILDAS CO_2 Isotope Monitor for $\Delta^{17}O - CO_2$) designed and manufactured by Aerodyne Research, Inc, configured for triple oxygen isotope analyses of CO_2. The TILDAS instrument uses a mid-infrared distributed-feedback interband-cascade laser (nanoplus Nanosystems and Technologies GmbH) tuned to sweep a 0.4 cm^{-1} wide spectral region near 2349 cm^{-1} to measure the absorption of CO_2 isotopologues 628 ($C^{12}O^{18}O^{16}$), 627 ($C^{12}O^{17}O^{16}$), 626 ($C^{12}O^{16}O^{16}$) (Figure 1). The notation 628, 627, and 626 used here follows the notation of the atmospheric database for **hi**gh-resolution **tran**smission molecular absorption HITRAN: [18].

Analyses of the three stable isotopes of oxygen directly from CO_2 is possible using laser spectroscopy due to the well-resolved spectral lines for each isotopologue, which result from their highly characteristic rotational-vibrational bands [19]. Laser light is absorbed only when the frequency of the laser closely matches the absorption frequency of a CO_2 isotopologue, and the amount of absorption is proportional to the concentration of that isotopologue, as per the Beer–Lambert law [20]:

$$A = L * N * \alpha \tag{3}$$

where A is the absorbance, L is the path length of the laser within the absorption cell: 36 m, [21], N is the concentration of the isotopologue, and α is the absorption coefficient, which differs for each isotopologue and the spectral region. The narrow spectral region of the laser was selected by Aerodyne Research Inc. (ARI) to include one well-resolved spectral line for each isotopologue, all with similar absorbances at ambient concentrations (Figure 1).

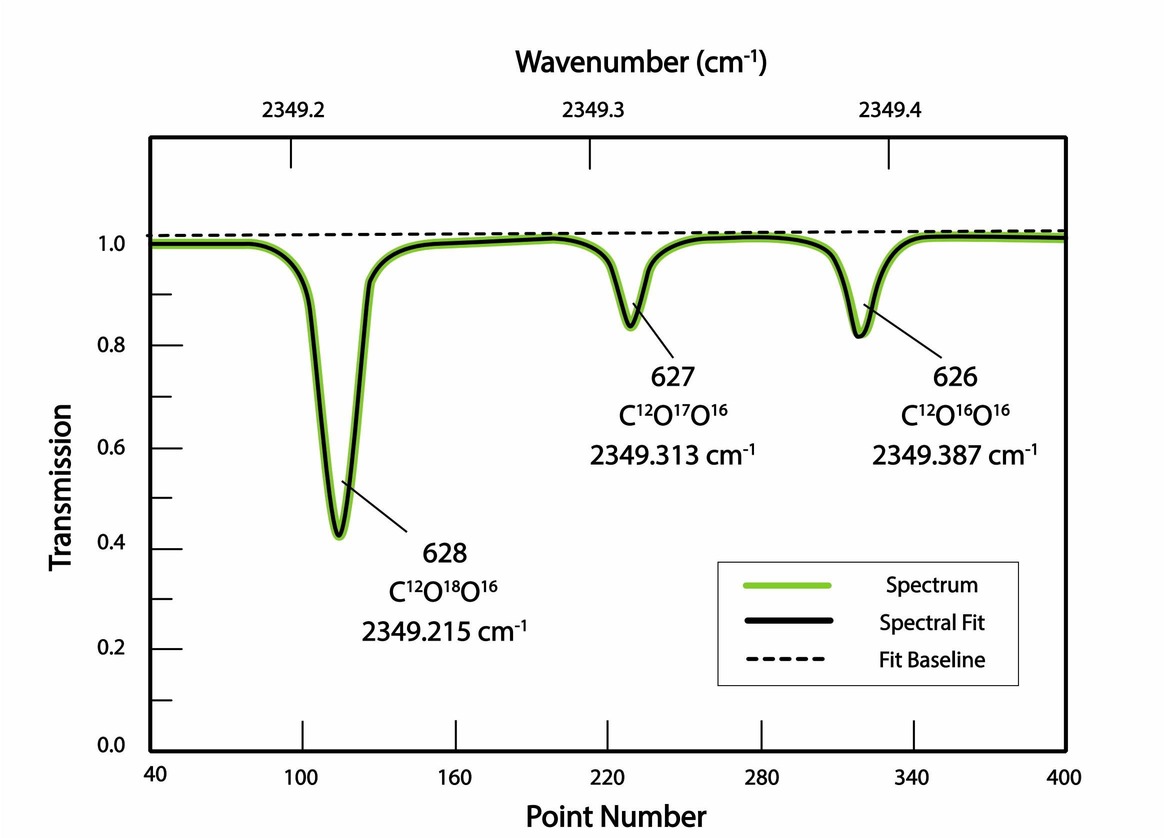


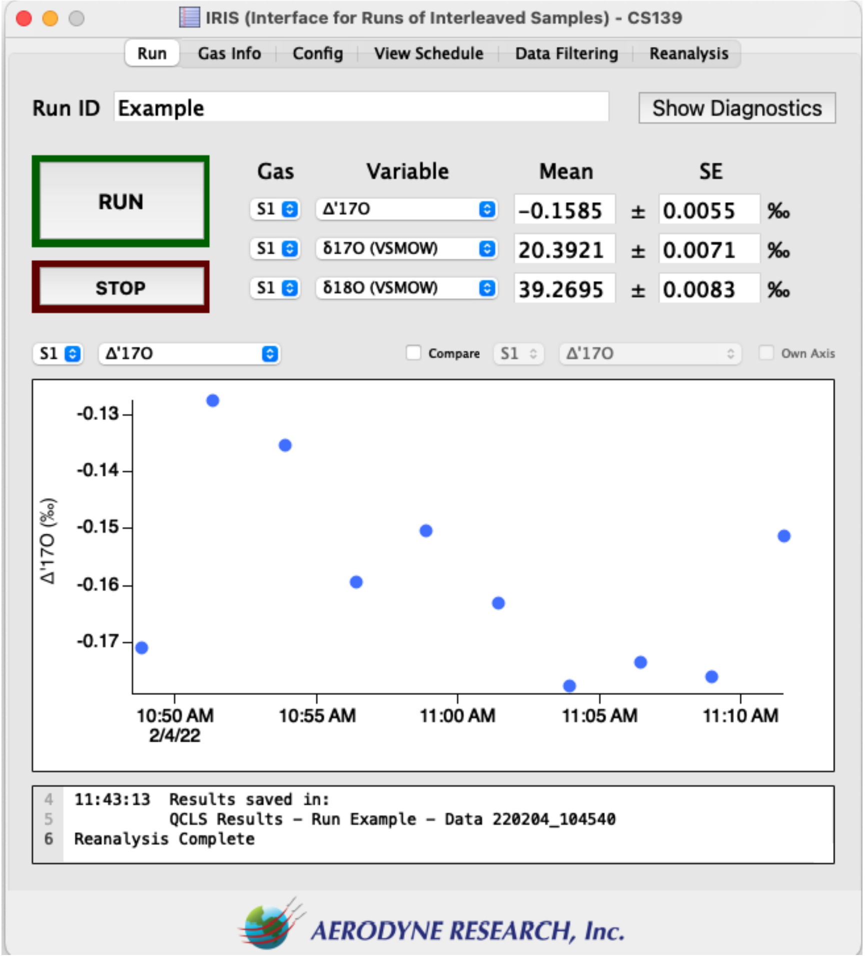
Figure 1: CO_2 triple oxygen isotope spectrum. Measured (green) and fitted-model (black) transmission spectrum from the TILDAS triple oxygen isotope analyzer for CO_2.

The TILDAS instrument uses a scan rate of 2.4 kHz and averages the 2400 spectra acquired each second. The laser frequency is swept across the spectral region by ramping the electrical current supplied to the laser, and the temperature of the laser is maintained to within 0.005 K by thermoelectric coolers and a recirculating liquid chiller (Oasis T-Three Thermoelectric Chiller). The light signal is detected using a thermoelectrically cooled photovoltaic (HgCdTe) detector whose zero level is calibrated by briefly turning the laser off at the end of each sweep.

Absorption of the laser beam by CO_2 occurs in an absorption cell wherein the laser beam bounces 182 times between two astigmatic mirrors in order to lengthen the absorption path and thereby increase sensitivity. Most Aerodyne TILDAS instruments have a flow-through absorption cell that provides continuous monitoring of air. In the present configuration, the absorption cell is designed for discrete sampling: the cell is evacuated, then filled with sample or reference gas, and then sealed for 30 seconds while the spectrum is measured. In this configuration, gas enters and exits the absorption cell through a single port to minimize the required sample volume. The optics outside the absorption cell (mirrors etc.) are thermally stabilized and purged with nitrogen at a constant flow rate of 1 L/min to prevent any absorption of the laser light by CO_2 outside of the absorption cell.

Spectrometer control and data acquisition are performed by TDLWintel, dedicated software produced by ARI to run their TILDAS instruments. A separate graphical user interface called IRIS, created by ARI for discrete sampling applications, coordinates with TDL Wintel to automate the inlet system and perform real-time $\Delta'^{17}O$ analysis (Figure 2). IRIS runs within the Igor Pro computing environment (Wavemetrics, Inc.).

More details about the spectrometer design can be found in McManus et al. [22], and Wang et al. [23], which describe nearly identical instruments used for other isotopologues.



Run ID Example

Gas	Variable	Mean		SE	
S1	Δ'17O	-0.1585	±	0.0055	‰
S1	δ17O (VSMOW)	20.3921	±	0.0071	‰
S1	δ18O (VSMOW)	39.2695	±	0.0083	‰

```
11:43:13  Results saved in:
          QCLS Results – Run Example – Data 220204_104540
Reanalysis Complete
```

Figure 2: TILDAS User Interface. Sample image of the TILDAS user interface run in IgorPro. The user interface communicates with TDLWintel, providing sampling system automation and real-time data analysis.

2.2 Preparation of CO_2 from carbonate samples

Carbonates are converted to CO_2 using the well-established phosphoric acid digestion method [9]. Minimum sample requirements for the TILDAS are ~3 µmoles CO_2, corresponding to 300 µg calcite. For the purposes of testing the precision of the TILDAS instrument, large samples (3 mg calcite) were reacted to minimize errors associated with the CO_2 extraction step. The gas was then cut by a factor of 10 for analysis. Smaller samples are easily introduced into the TILDAS system by quantitatively freezing the CO_2 gas into a cold finger in the mixing volume. Calcite is loaded into a glass reaction vessel with a central glass divider. 1 ml of 100% phosphoric acid is loaded in the glass reaction vessel on the opposite side of the divider from the calcite. The vessel is evacuated and placed in a water bath held at a constant temperature of 25ºC and then the phosphoric acid is introduced into the calcite section of the reaction vessel by pouring the acid across the divider. The reaction vessel remained in the water bath at a constant temperature of 25ºC for 16 hours. The resulting gas is purified using a cryogenic trap to remove water and any noncondensable gases before the CO_2 is cryogenically frozen into a separate gas sampling tube for transfer to the TILDAS analyzer.

2.3 Fluorination

In order to determine the actual $\delta^{17}O$ value of our reference gases relative to VSMOW, CO_2 was fluorinated to produce O_2 to be measured for triple oxygen isotopes using the conventional nickel bomb fluorination method by Sharma and Clayton [24], modified by Wostbrock et al. [10]. 1 ml of CO_2 (~45 µmol CO_2) was injected into the fluorination line through a septum and cryogenically transferred to a high purity nickel reaction vessel. 30 times stoichiometric excess of bromine pentafluoride (BrF_5) was cryogenically transferred into the nickel reaction vessel with the CO_2. The nickel reaction vessel was sealed with a valve and heated to 700ºC for five days to ensure quantitative conversion of CO_2 to O_2 by the reaction $CO_2 + 4/5BrF_5 = O_2 + CF_4 + 2/5Br_2$.

Following the fluorination reaction, the reaction vessels were cooled with liquid nitrogen. The reaction byproducts CF_4, Br_2, and unreacted BrF_5 remained frozen in the vessel and the O_2 released from fluorination was purified by passing through two liquid nitrogen traps, followed by a 100ºC NaCl trap to remove any F_2 by converting it to NaF and Cl_2 gas, which were then trapped in a third liquid nitrogen cooled trap. The O_2 gas produced through fluorination was absorbed on a 5 Å molecular zeolite sieve cooled with liquid nitrogen. The molecular sieve containing the O_2 was then isolated from the fluorination line, and the O_2 was released into a stream of ultra-high purity helium carrier gas and passed through a 5 Å molecular sieve gas chromatograph at a flow rate of 5 mL/min to remove any trace contamination of NF_3 and N_2. The O_2 in the helium carrier gas was then collected on a second liquid nitrogen cooled molecular sieve attached to the inlet port of a Thermo Fisher MAT 253$^+$ isotope ratio mass spectrometer configured for triple oxygen isotope analyses. The helium was pumped away through the inlet pump on the mass spectrometer, and the molecular sieve was heated to release the absorbed O_2 into the sample bellows. The resultant O_2 was analyzed in dual-inlet mode relative to a reference gas calibrated to VSMOW, can provide a precision of better than 0.005‰ (5 per meg) for $\Delta'^{17}O$ e.g., [10].

Five CO_2 samples were analyzed in this study. They included three IAEA calcite standards (NBS-18, NBS-19 and IAEA-603 – see https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/Stable-Isotopes.aspx and https://www-s.nist.gov/srmors/view_detail.cfm?srm=8544 for details) and two internal CO_2 standards (CSI-8628 and CSI-040711). CSI-8628 is a commercial CO_2 tank ($\delta^{18}O$ = 29.97 ‰), and CSI-040711 is a very light sample produced by equilibrating CO_2 gas with water from an Antarctic ice core ($\delta^{18}O$ = -9.28 ‰). The $\delta^{13}C$ and $\delta^{18}O$ values of CSI-8628 and CSI-040711 were measured on CO_2 gas (prior to fluorination) using a Thermo-Fisher 253$^+$ dual-inlet isotope ratio mass spectrometer with a reference gas calibrated to IAEA standards NBS-18, NBS-19 and IAEA-603. All data are presented in Table 1.

2.4 TILDAS Sample Inlet System

A schematic of the sample system design is illustrated in Figure 3. The inlet system is represented by two primary components, the mixing volume (outlines in blue), and the TILDAS (outlined in red) and the accompanying valves that are controlled through TDLWintel (outlined in orange). The entire system in pumped by an oil-free scroll pump (Agilent IDP-15 Dry Scroll Pump) to prevent any back flow of oil vapors into the vacuum line. The purpose of the mixing volume is to produce a CO_2 sample gas diluted in CO_2-free dry air to get a reproduceable mixing ratio that matches that of the reference gas. The reference gas used in this study was made by filling an evacuated high pressure gas tank with CO_2 and then dry CO_2-free air to achieve a mixing ratio of 456 ppm CO_2.

For analysis in the TILDAS system, CO_2 produced by phosphoric acid digestion from calcite standards NBS18, NBS19, and IAEA-603 and collected in glass sample tubes was connected to the sample inlet port using a glass vacuum seal. For CSI standards CSI-8628 and CSI-040711, 0.07 ml of CO_2 was introduced into the line using a syringe and injected through a septum on the inlet port. The CO_2 was transferred into the mixing volume by freezing on a cold finger chilled with liquid nitrogen. The liquid nitrogen was removed and the CO_2 was heated to room temperature and expanded into the mixing volume. The motor-controlled bellows 1 (salvaged from an old VG Prism II mass spectrometer) adjusted the bellows volume until a pre-set pressure for CO_2 was attained on pressure sensor 1 (Kurt J. Lesker 300 Series Convection Vacuum Gauge). Zero air was then added to the mixing volume until the pressure on gauge 2 (Baratron 122AA-01000AD) reached the set pressure (approximately 1 bar) that produces a mixture of 456 ppm CO_2. (The Convection vacuum gauge has a higher precision in the millitorr to torr range while the Baratron has a higher precision at 500-1000 torr range). The CO_2 and zero air were mixed for twenty minutes by alternately opening and closing bellows 1 and 2. Incomplete mixing was observed when mixing times were less than 10 minutes as evidenced by a drift in the mixing ratio of the sample gas measured in the TILDAS between sample injections.

The TILDAS portion of the sampling system (Figure 3) includes the instrument and automated valve process controlled through TDLWintel and the IRIS interface developed by ARI. The operation procedure is outlined here. The optical cell and sample aliquot volume were evacuated and flushed with nitrogen. The absorption cell was filled to 30 Torr with dry nitrogen and a 15 second background measurement was recorded to be subtracted from subsequent measured spectra. The absorption cell was then evacuated, and the working reference was introduced through a 0.004-inch critical orifice (O'Keefe IC-PC4-4-SS Precision Metal Orifice) by an electronic valve automated to attain a target pressure of 38 Torr. Once the reference gas (or sample gas) was introduced into the absorption cell, the system was allowed to stabilize for 18 seconds, followed by data collection for 12 seconds. While the reference gas was being measured, an aliquot of the sample gas was prepared. The mixing volume pressure was adjusted by closing bellows 2 to hit a target pressure on pressure gauge 2 that would correspond to the same working pressure as the reference gas when expanded into the optical cell (38 Torr). Once the reference gas measurement was completed, the absorption cell was evacuated and then flushed with nitrogen and evacuated a second time. The sample aliquot was then expanded into the optical cell. Following the sample measurement, the absorption cell was evacuated and flushed with nitrogen and the process was repeated for 12 cycles. After each introduction of sample gas, the pressure of the sample gas in the manifold was adjusted to the correct pressure by compressing the bellows.

The isotope values of each sample measurement were determined relative to the reference gas by interpolating the prior and subsequent reference gas measurements in time. The total time required for 12 reference-sample cycles is 30 minutes.

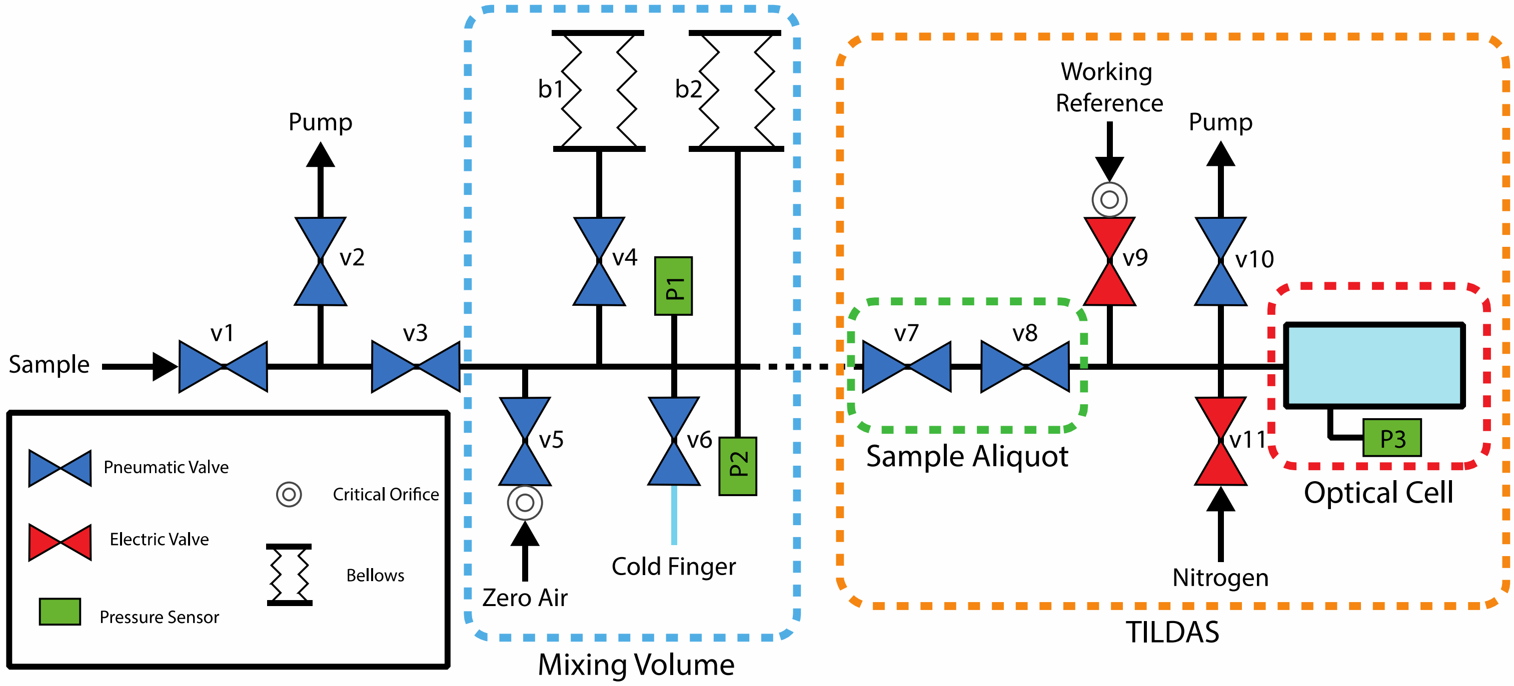


Figure 3: Schematic diagram of the sample gas inlet system for the TILDAS spectrometer. The system consists of a mixing volume for sample preparation (blue box), a small volume between two pneumatic valves (Swagelok bellows valves) to acquire aliquots of sample gas from the mixing volume (green box), the automated valves actuated on a schedule by IRIS (orange box), and the absorption cell in the TILDAS instrument (red box).

3. RESULTS AND DISCUSSION

3.1 Fluorination

The $\Delta'^{17}O$ values of CSI-8628 and CSI-040711 determined by fluorination are presented in Table 1. Both CSI-8628 and CSI-040711 were fluorinated three times with an average $\Delta'^{17}O$ of -121 and -111 per meg with standard deviations of ±7 and ±6 per meg, respectively. The $\delta^{17}O$ and $\delta^{18}O$ values from fluorination are generally slightly less than the correct value (due to incomplete fluorination of the CO_2 gas), but it has been shown that $\delta^{17}O$ and $\delta^{18}O$ covary with a λ of 0.528, such that the $\Delta'^{17}O$ value is constant and independent of the measured $\delta^{18}O$ value see [10 for further details]. Using the $\Delta'^{17}O$ obtained using fluorination and the $\delta^{18}O$ measured from the CO_2 gas, we can back-calculate to determine the $\delta^{17}O$ value of our CO_2 standard gasses. The fluorinated triple oxygen isotope values for IAEA-603, NBS-18, and NBS-19 of CO_2 produced by phosphoric acid digestion at 25ºC referenced in this study are from Wostbrock et al. [10] (Table 1) which was measured on the same extraction line.

Table 1: Triple oxygen isotope data for CO_2 standards. Results are given for TILDAS and fluorination for CO_2 sample gas, and CO_2 extracted from carbonate standards using phosphoric acid digestion at 25ºC. δ values are reported in ‰ relative to VSMOW, and Δ'^{17}O is reported in per meg relative to VSMOW. TILDAS data are presented without any further correction using equation 3.

Sample	**Analysis**	**Mole Fraction CO_2 (ppm)**	**δ^{17}O**	**δ^{18}O**	**δ'^{17}O**	**δ'^{18}O**	**Δ'^{17}O**	**$\delta^{17}O_{corr}$***	**$\delta^{18}O_{corr}$***	**$\delta'^{17}O_{corr}$***	**$\delta'^{18}O_{corr}$***
CSI-8628 1	Fluorination	--	15.119	29.077	15.006	28.662	-128	15.584	29.970	15.464	29.530
CSI-8628 2	Fluorination	--	15.367	29.528	15.250	29.100	-115	15.597	29.970	15.477	29.530
CSI-8628 3	Fluorination	--	15.366	29.537	15.249	29.109	-121	15.591	29.970	15.471	29.530
	Average	**--**	**15.284**	**29.381**	**15.168**	**28.957**	**-121**	**15.591**	**--**	**15.470**	**--**
	±1σ	**--**	**0.143**	**0.263**	**0.141**	**0.256**	**7**	**0.005**	**--**	**0.005**	**--**
CSI-8628 1	TILDAS	451.620	15.618	30.017	15.497	29.575	-119	15.593	29.970	15.473	29.530
CSI-8628 2	TILDAS	455.650	15.621	29.996	15.500	29.555	-105	15.607	29.970	15.487	29.530
CSI-8628 3	TILDAS	456.900	15.556	29.876	15.436	29.438	-107	15.605	29.970	15.485	29.530
CSI-8628 4	TILDAS	458.760	15.594	29.963	15.474	29.523	-114	15.598	29.970	15.477	29.530
	Average	**455.733**	**15.597**	**29.963**	**15.477**	**29.523**	**-111**	**15.601**	**--**	**15.480**	**--**
	±1σ	**3.025**	**0.030**	**0.062**	**0.029**	**0.060**	**6**	**0.006**	**--**	**0.006**	**--**
CSI-040711 1	Fluorination	--	-4.189	-7.582	-4.198	-7.611	-179	-5.089	-9.280	-5.102	-9.323
CSI-040711 2	Fluorination	--	-4.244	-7.689	-4.253	-7.719	-178	-5.088	-9.280	-5.101	-9.323
CSI-040711 3	Fluorination	--	-4.877	-8.901	-4.889	-8.941	-168	-5.078	-9.280	-5.091	-9.323
	Average	**--**	**-4.437**	**-8.057**	**-4.447**	**-8.090**	**-175**	**-5.085**	**--**	**-5.098**	**--**
	±1σ	**--**	**0.382**	**0.733**	**0.384**	**0.739**	**6**	**0.005**	**--**	**0.005**	**--**
CSI-040711 1	TILDAS	462.420	-4.763	-8.783	-4.774	-8.822	-116	-5.026	-9.280	-5.039	-9.323
CSI-040711 2	TILDAS	460.600	-4.786	-8.844	-4.798	-8.884	-107	-5.017	-9.280	-5.030	-9.323
CSI-040711 3	TILDAS	457.650	-4.872	-9.013	-4.884	-9.054	-103	-5.013	-9.280	-5.026	-9.323
CSI-040711 4	TILDAS	458.490	-4.940	-9.091	-4.952	-9.132	-130	-5.040	-9.280	-5.053	-9.323
CSI-040711 5	TILDAS	452.470	-4.817	-8.907	-4.829	-8.947	-105	-5.015	-9.280	-5.028	-9.323
	Average	**458.326**	**-4.836**	**-8.928**	**-4.847**	**-8.968**	**-112**	**-5.022**	**--**	**-5.035**	**--**
	±1σ	**3.765**	**0.071**	**0.125**	**0.071**	**0.126**	**11**	**0.010**	**--**	**0.010**	**--**
IAEA-603‡	Fluorination		20.262	39.012			-147	20.262	39.012		
IAEA-603 1	TILDAS	461.79	20.3869	39.2682	20.1819	38.5168	-155	20.254	39.012	20.052	38.270
IAEA-603 2	TILDAS	456.22	20.4034	39.2684	20.1980	38.5170	-139	20.270	39.012	20.068	38.270
IAEA-603 3	TILDAS	458.58	20.3903	39.2794	20.1852	38.5276	-157	20.252	39.012	20.049	38.270
IAEA-603 4	TILDAS	454.66	20.3571	39.192	20.1527	38.4435	-145	20.264	39.012	20.061	38.270
	Average	**457.813**	**20.384**	**39.252**	**20.179**	**38.501**	**-149**	**20.260**	**--**	**20.057**	**--**
	±1σ	**3.103**	**0.020**	**0.040**	**0.019**	**0.039**	**9**	**0.008**	**--**	**0.007**	**--**
NBS-18‡	Fluorination		9.114	17.524			-100	9.072	17.524		

NBS-18 1	TILDAS	467.130	9.276	17.806	9.233	17.649	-86	9.128	17.524	9.087	17.372
NBS-18 2	TILDAS	461.160	9.262	17.776	9.220	17.619	-83	9.131	17.524	9.089	17.372
NBS-18 3	TILDAS	464.940	9.250	17.735	9.208	17.580	-74	9.140	17.524	9.098	17.372
NBS-18 4	TILDAS	460.580	9.312	17.863	9.269	17.705	-79	9.135	17.524	9.093	17.372
	Average	**463.453**	**9.275**	**17.795**	**9.232**	**17.638**	**-81**	**9.133**	**--**	**9.092**	**--**
	±1σ	**3.122**	**0.027**	**0.054**	**0.026**	**0.053**	**5**	**0.004**	**--**	**0.004**	**--**
NBS-19-1‡	Fluorination		20.348	39.194			-155	20.348	39.194		
NBS-19 1	TILDAS	435.890	20.573	39.623	20.364	38.858	-153	20.350	39.194	20.146	38.445
NBS-19 2	TILDAS	440.310	20.524	39.561	20.316	38.799	-170	20.333	39.194	20.129	38.445
NBS-19 3	TILDAS	451.920	20.532	39.529	20.324	38.768	-145	20.358	39.194	20.154	38.445
NBS-19 4	TILDAS	451.220	20.520	39.542	20.312	38.780	-164	20.339	39.194	20.135	38.445
NBS-19 5	TILDAS	453.390	20.537	39.569	20.329	38.806	-161	20.342	39.194	20.138	38.445
	Average	**446.546**	**20.537**	**39.565**	**20.329**	**38.802**	**-159**	**20.345**	**--**	**20.141**	**--**
	±1σ	**7.906**	**0.021**	**0.036**	**0.021**	**0.035**	**10**	**0.009**	**--**	**0.009**	**--**

‡ Data from Wostbrock et al. [10].

corr*– Corrected using the calibrated δ^{18}O value of the sample gas by phosphoric acid digestion and analysis of CO$_2$ by conventional mass spectrometry , and the Δ’^{17}O value from fluorination (see section 3.1).

3.2 TILDAS Results

3.2.1 Precision

The five standard gases calibrated to the VSMOW-SLAP scale (CSI-8628, CSI-040711, IAEA-603, NBS-18, NBS-19) were analyzed using the TILDAS and inlet system described above. Each sample was analyzed 4 or 5 times, with an analysis consisting of 12 sample-reference cycles and a data filter threshold of 2σ. Comparison of the $\delta^{18}O$-$\Delta'^{17}O$ values obtained with TILDAS and conventional methods (phosphoric acid digestion for $\delta^{18}O$ and fluorination for $\Delta'^{17}O$) are shown in Figure 4. The averaged $\delta^{18}O$ values reported using the TILDAS agree with values calibrated by measuring CO_2 gas on the IRMS (Table 1) to within ±0.03 ‰ for all standards, except for CSI-040711, where the averaged $\delta^{18}O$ for all runs differs from the IRMS measurement by 0.35 ‰. The standard deviations of the $\delta^{17}O$ and $\delta^{18}O$ values for CSI-040711 were ±0.07 and ±0.12‰ (S.E. 2σ), respectively. All other references analyzed using TILDAS had a standard deviation of ≤0.03 ‰ for $\delta^{17}O$ and ≤0.06 ‰ for $\delta^{18}O$. Despite the variation in the $\delta^{17}O$ and $\delta^{18}O$ values for CSI-040711, $\delta^{17}O$ and $\delta^{18}O$ covary (Figure 5), and the standard deviation for $\Delta'^{17}O$ is 11 per meg over five analyses. The overall standard deviation of all analyses performed is 8 per meg for $\Delta'^{17}O$.

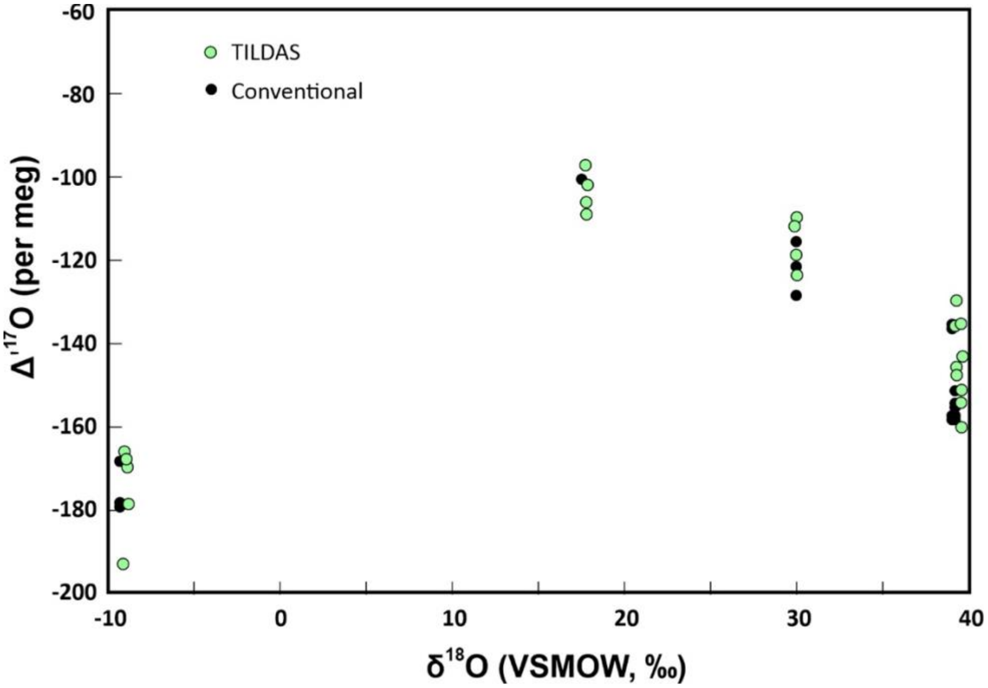


Figure 4: Results of TILDAS δ^{18}O and Δ'^{17}O measurements of CO_2 compared to those obtained using dual inlet mass spectrometry. For dual inlet, the Δ'^{17}O value was measured using conventional fluorination on O_2 and the δ^{18}O value was measured using conventional phosphoric acid digestion and analysis of CO_2 gas. The Δ'^{17}O values of the TILDAS data corrected following equation 3.

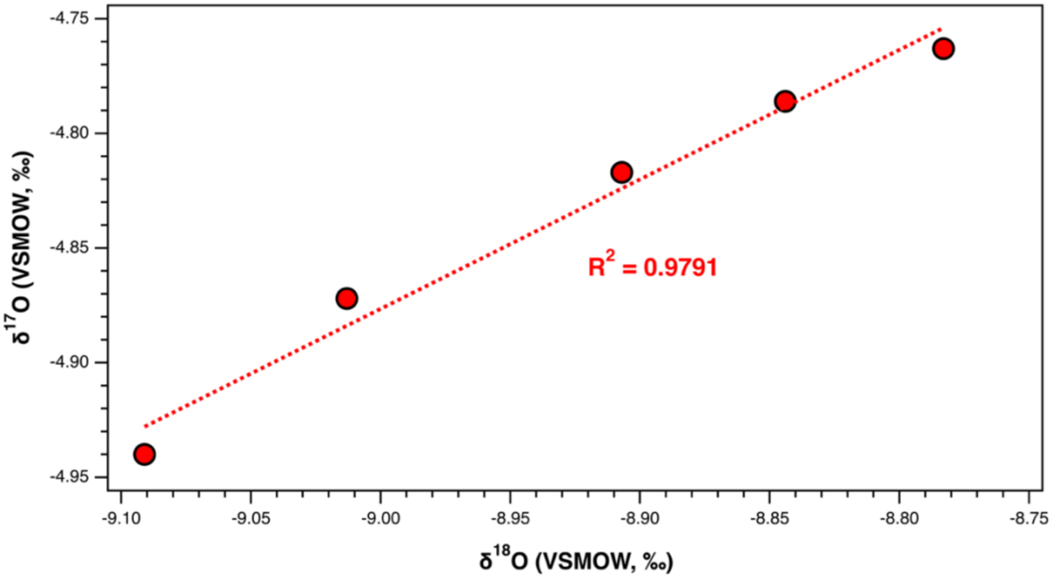


Figure 5: Covariance in δ^{17}O and δ^{18}O of CSI-040711. There is significant variation in the δ^{17}O and δ^{18}O values for subsequent analyses of CSI-040711, with a standard deviation of 0.07 and 0.12‰, respectively. δ^{17}O and δ^{18}O covary, and the standard deviation for Δ'^{17}O is 11 per meg for five analyses, giving us confidence in the Δ'^{17}O values. Fluorination values are $\delta^{18}O = -9.28‰$, $\delta^{17}O = -5.035‰$.

3.2.2 Testing analytical conditions for precision and accuracy

There are a number of variables which could affect the precision of the TILDAS system. These include the following: 1) fractionation during introduction of sample gas; 2) differences in the working pressure of the reference and sample gases; 3) differences in the CO_2 mole fraction of the reference and sample gases; 4) extreme differences in the $\delta^{18}O$ values of reference and sample. We tested the sensitivity of the system to these parameters, by purposely measuring samples where the sample and reference values were different.

3.2.3 Potential fractionation during introduction of sample gas

Potential fractionation associated with the inlet system and gas introduction process was assessed by filling the mixing volume with the working reference gas to act as the 'sample gas' and running it against itself (a so-called 'zero enrichment' measurement). The average $\delta^{17}O$ and $\delta^{18}O$ values of four zero enrichment analyses differ from the calibrated working reference value by 0.005 ‰ for $\delta^{17}O$ and 0.007 ‰ for $\delta^{18}O$ with standard deviations similar to those reported for the sample gasses analyzed in this study (≤0.024 ‰ for $\delta^{17}O$, and ≤0.036 ‰ for $\delta^{18}O$), excluding CSI-040711 (Table 2). The $\Delta'^{17}O$ values have a precision of 9 per meg (standard error; 2σ). With the results of the zero enrichment and the four other standards analyzed having reproducible results, it does not appear that there is fractionation associated with the sampling system and analysis procedure.

Table 2: Sampling system zero enrichments. Results for zero enrichment analysis, where working reference gas was loaded in the mixing volume of the inlet system and analyzed as ‘sample’ to test potentially fractionation associated with sample introduction.

Sample	**δ^{17}O**	**δ^{18}O**	**δ'^{17}O**	**δ'^{18}O**	**Δ'^{17}O**
Zero 1	17.407	32.724	17.257	32.200	256
Zero 2	17.450	32.782	17.299	32.256	268
Zero 3	17.476	32.818	17.325	32.291	276
Zero 4	17.418	32.722	17.268	32.198	267
Zero 5	17.435	32.771	17.284	32.245	259
Zero 6	17.429	32.772	17.279	32.246	253
Average	**17.436**	**32.765**	**17.285**	**32.239**	**263**
±1σ	**0.025**	**0.037**	**0.024**	**0.035**	**9**
Assumed Working Reference value	**17.445**	**32.779**	**17.295**	**32.253**	**265**

3.2.4 Total Working Pressure

The infrared-absorption lines follow well established shapes whose mathematical fit is determined using a Voigt line shape profile. A limited range of working pressures for a given spectral region provides well-defined peaks with sufficient absorption for all isotopologues within the spectral region. Too low of a working pressure results in insufficient signal and poorly defined absorption lines, whereas too high working pressure results in broadening the absorption peaks and interference between isotopologue spectral lines.

To validate a range of acceptable working pressures, we conducted zero enrichment analyses at working pressures of 30, 34, and 38 Torr for both the sample and reference gas. Working reference gas was analyzed against itself for the three different working pressures. The results for the zero enrichments at 30, 34, and 38 Torr are displayed in Figure 6. The results for each working pressure are within error of the Δ'^{17}O value of the working reference and a standard deviation of < 2 per meg for the three analyses.

The consistency of results over a range of working pressures allows us to be flexible with sample size. All analyses were made at 38 Torr, where an excess of the sample was reacted to allow for multiple analyses of the same gas. Reducing the working pressure from 38 Torr to 30 Torr reduces the sample size required by roughly 1/3.

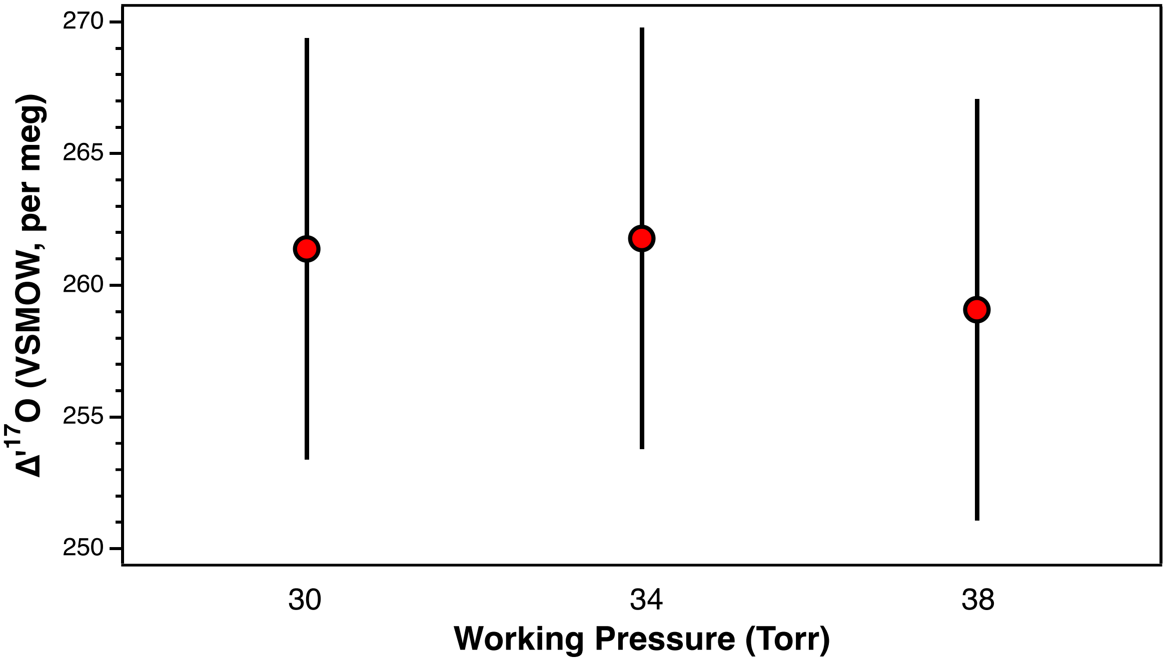


Figure 6: Effect of varying the working pressures in the sample cell. Averaged results of three zero enrichments analysis at each working pressures of 30, 34, and 38 Torr. All analyses are within error of the accepted value of the working reference gas, $\Delta'^{17}O$ = 265 per meg. Error bars are ±1σ (8 per meg).

3.2.5 Working Pressure mismatch

In order to determine the acceptable discrepancy between the sample and reference pressure, a series of zero enrichments was performed at mismatched pressures. The working pressure for the 'sample gas' was adjusted for each subsequent aliquot over 12 measurement cycles while the working reference pressure was held constant at 38 Torr. There is a strong linear relationship ($R^2 = 0.935$) between the difference in the measured $\Delta'^{17}O$ from the accepted working reference value and the difference between the working pressure of the 'sample' and the working reference (Figure 7).

The working pressure for the sample and reference gas during a measurement cycle must be within ±23 mTorr to achieve a precision of ±10 per meg (Figure 7). Using the bellows system in our sampling system, we can introduce the sample gas at a working pressure with high reproducibility (±10 mTorr). Generally, the range in working pressure for both sample and reference over 12 measurement cycles is less than 40 mTorr.

There are instances in which there are anomalous spikes or drops in the working reference pressure. These deviations in pressure result from fluctuations in the backing pressure of the working reference gas feeding through the critical orifice altering the flow rate, resulting in the valve being closed too early or late to hit the target pressure. Instances of spikes or drops in the working reference pressure are uncommon and, at most, occur for one reference measurement over a 12-cycle sample measurement. The difference in the reference pressure from the target pressure introduces an isotopic shift such that the data points calculated using the anomalous reference measurement are excluded from data analysis.

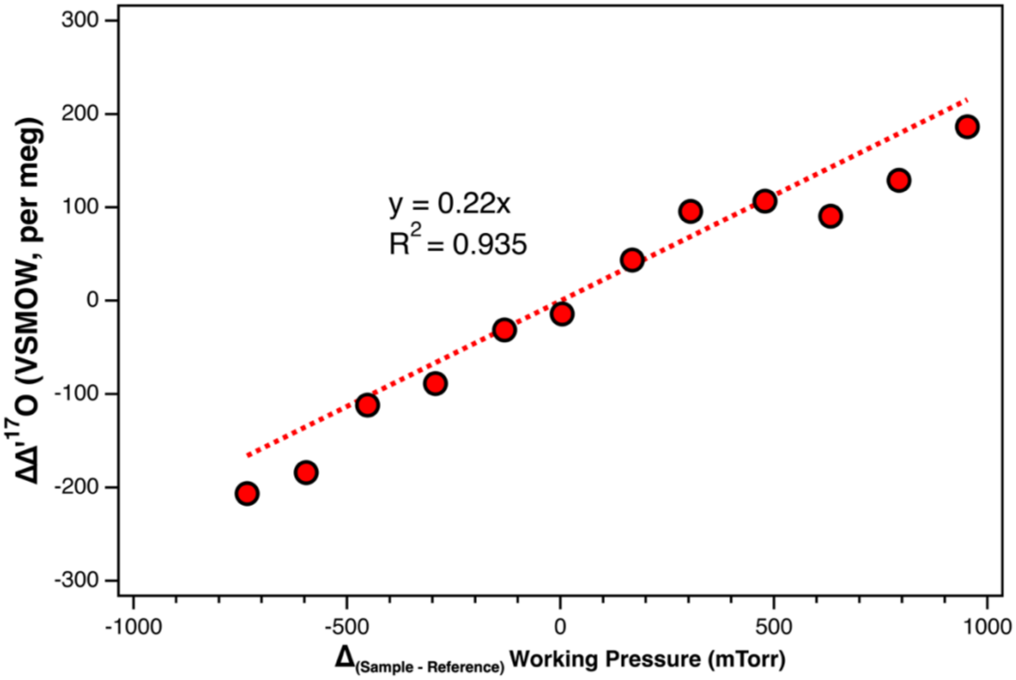


Figure 7: Sample vs working reference pressure effect. Graphical results for zero enrichment analysis illustrating the importance of matching the working pressure of the sample and reference gasses. Each dot represents one sample-reference measurement (12 cycles total). The working pressure of the sample was increased for each subsequent cycle while the reference pressure remained constant. The y-axis is the difference in the measured $\Delta'^{17}O$ value from the accepted $\Delta'^{17}O$ value of the working reference. To achieve a precision of 10 per meg for $\Delta'^{17}O$, the working pressure of the sample and working pressure must match and be constant within ±20 mTorr, which is easily achieved with our instrument.

3.2.6 Mole Fraction

The TILDAS instrument must be operated with a near-ambient dilution of CO_2 in zero air (or dry N_2). The precise dilution is not important so long as it is constant: the reference and sample gases must use the same dilution to avoid an artifactual dependence of the measured isotope ratios on the sample gas CO_2 mole fraction. Such dependence arises not from the spectrometer *per se* but rather from the use of only a single reference gas for calibration. In general, TILDAS measurement error is partly multiplicative (i.e. gain error) and partly additive (i.e. zero-offset error), and a single reference gas can only be used to correct for one kind of error or the other. The super-ratio used here to express a sample gas isotope ratio relative to the reference gas effectively assumes that all measurement error is multiplicative. The goal is therefore to minimize the impact of additive error by subtracting spectral background measurements (as mentioned above) and by keeping the sample and reference mole fractions as close as possible. When the sample and reference gas mole fractions are the same, the additive errors cancel out. Conversely, as the sample and reference gas mole fractions diverge, the additive errors cause increasing bias.

A major challenge in designing the sample system was the ability to mix a sample gas of CO_2 and dry air efficiently and with a reproducibly to within several ppm CO_2 of the reference gas. The target mole fraction is ~ 450 ppm CO_2 in zero air (456 ppm in our system). To examine the effects of differences in the mole fraction of the sample and working reference gas, the mixing ratio of the sample gas was varied slightly above and below the target mole fraction. A mismatch of 20 ppm between the mixing ratio of reference and sample gas was found to have no apparent effect (Figure 8).

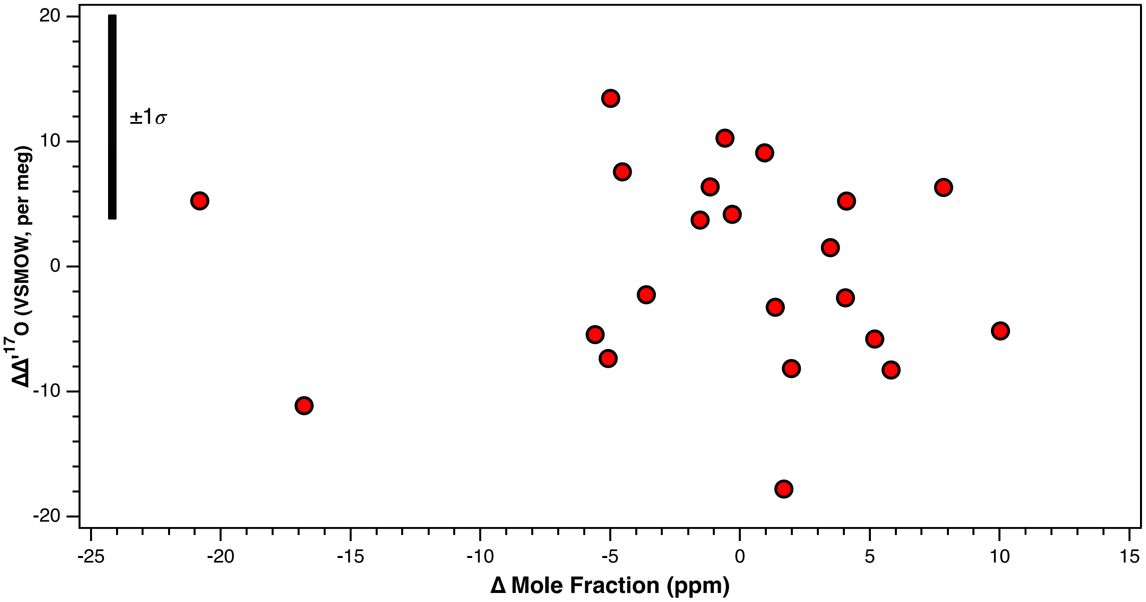


Figure 8: Sample vs working reference mole fraction. Dependance of Δ’17O based on the CO_2 mole fraction of the sample and working reference matching. The y-axis is the difference in the measured Δ’17O value of the analysis from the averaged Δ’17O for the standard from Table 1. The x-axis is the difference in the mole fraction of CO_2 in the sample gas (Table 1) and the mole fraction of CO_2 of the reference gas (456 ppm). Our sampling system reproducibly produces a sample gas within ± 2% of the target CO_2 mole fraction, and differences in the CO_2 mole fraction of ± 2% do not measurably affect the Δ’17O value.

3.2.7 Effect of different isotope values for sample and reference

In order to test the ‘linearity’ of the system related to extreme differences in the $\delta^{18}O$ values of the sample and reference on the measured $\Delta'^{17}O$ value, samples were specifically prepared to cover a wide $\delta^{18}O$ range of 48‰. Figure 9 shows the offset in the $\Delta'^{17}O$ values measured in the TILDAS unit vs those obtained by fluorination as a function of the $\delta^{18}O$ value. There is a systematic difference between the $\Delta'^{17}O$ values measured by both systems that varies linearly as a function of the difference in the $\delta^{18}O$ value of sample and reference. The larger the difference between the two $\delta^{18}O$ values, the greater the $\Delta'^{17}O$ value shifts from the true value. Over a range in $\delta^{18}O$ values from -9 to +38‰, $\Delta'^{17}O$ shifts by ~65 per meg. The linear relationship between the measured δ^{18}O and the offset in the Δ'^{17}O from the true value allows for using the equation (applicable to our instrument):

$$\Delta'^{17}O_{\text{corrected}} = \Delta'^{17}O_{\text{measured}} + 1.4513 \times (\delta^{18}O_{\text{measured}} - \delta^{18}O_{\text{reference gas}}) \quad (4)$$

The δ^{17}O value of the sample gas can then be back calculated using the measured δ^{18}O and the corrected Δ'^{17}O values. Over a period of 6 months, we have not seen any significant changes to this correction formula.

The shift in Δ'^{17}O over a large range of δ^{18}O values is potentially a result of cross correlation in the spectral fit between the isotopologues in the spectrum. Theoretically, the dependance in the spectral fit between the isotopologues could be reduced or removed with improvements in the spectral fit, and if the spectral lines for the isotopologues in the spectrum were completely independent from one another. But, due to subtle baseline curvature effects in the spectrum and spectral overlap between the isotopologues in the spectrum (Figure 1), the dependance in the spectral fit between the isotopologues cannot be resolved and calibration and correction of the Δ'^{17}O values is necessary.

Additional considerations for the future involve the possibility of trace organic compounds in the CO_2 sample gas due to phosphoric acid digestion of organic-rich carbonates[25]. The effect of this possible contaminant has not yet been evaluated.

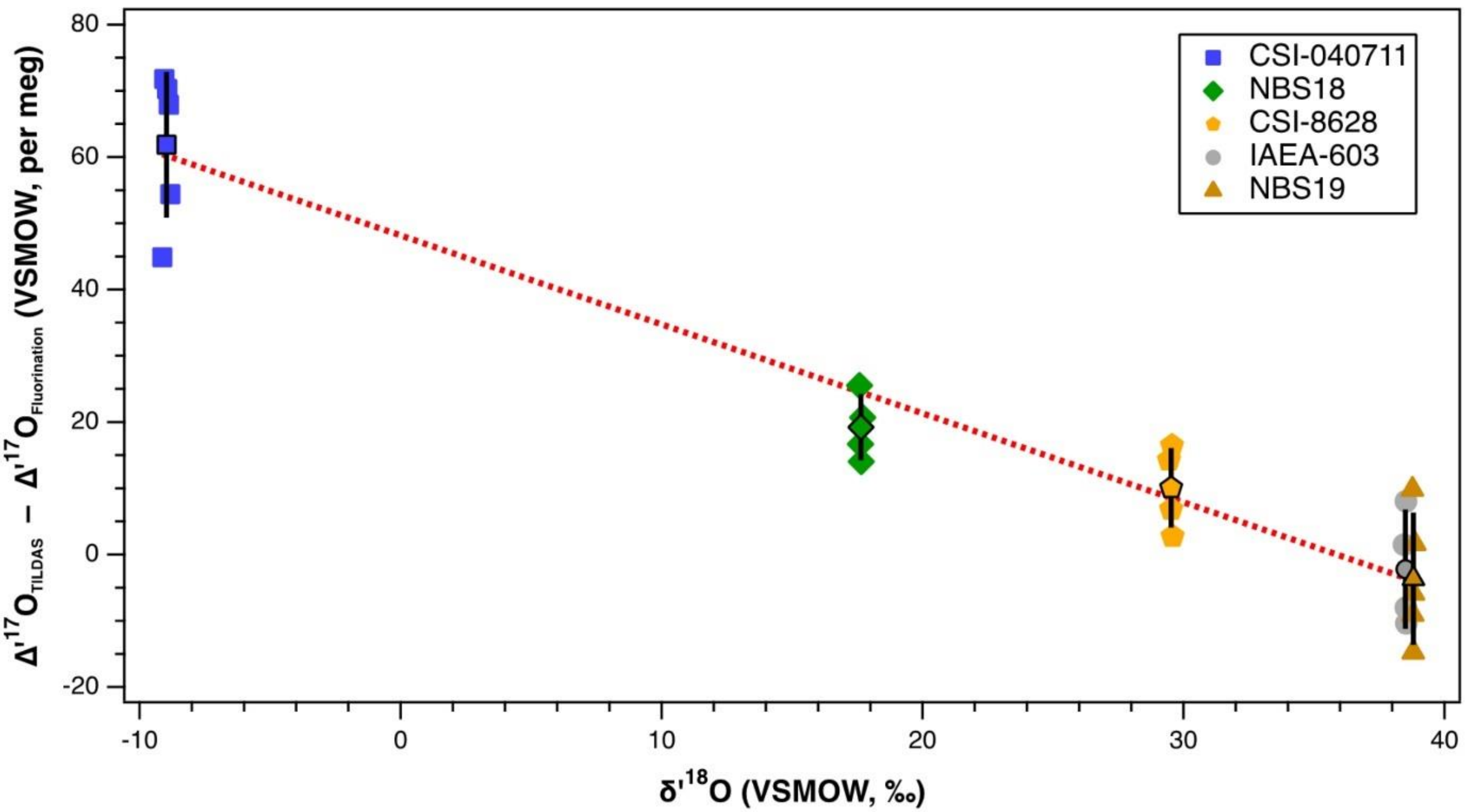


Figure 9: Effect of $\Delta'^{17}O$ on the $\delta^{18}O$ value of the sample relative to working gas. Offset in the $\Delta'^{17}O$ value reported from the TILDAS and the accepted value from fluorination. The y-axis is the difference in the $\Delta'^{17}O$ value from the TILDAS reference gas for each analysis and the accepted $\Delta'^{17}O$ value from fluorination (Table 1). The lighter the $\delta^{18}O$ value of a sample (the more different from the reference gas value of 32.77 ‰), the greater the $\Delta'^{17}O$ shifts from the actual value. The linear relationship between the measured $\delta^{18}O$ value and the shift in $\Delta'^{17}O$ can be corrected using Equation 3 based on the linear best fit (red dashed curve).

4. CONCLUSION

We have demonstrated that the Tunable Infrared Laser Direct Absorption Spectroscopy analyzer (TILDAS; Aerodyne Research Inc.) can measure the triple oxygen isotope composition of CO_2 with a precision of ±10 per meg for $\Delta'^{17}O$ and ±0.03‰ for $\delta^{18}O$ values. The system is accurate as long as the sample and reference gases have similar mixing ratios and $\delta^{18}O$ values. The effects of different $\delta^{18}O$ values between reference and sample is linear and small (~1 per meg $\Delta'^{17}O$ per 1 per mil $\delta^{18}O$), and easily corrected for.

With our sampling system configuration for the TILDAS instrument, sample size is reduced to a tenth of that needed to perform traditional fluorination reactions for triple oxygen isotope analyses. A70 µl injection of CO_2 needed for a 12-measurement cycle analysis is equivalent to 300 µg of pure carbonate reacted with phosphoric acid. The system can easily be modified to reduce the requirement to 200 µg carbonate equivalent.

The TILDAS instrument's ability to measure triple oxygen isotopes directly from CO_2 using laser spectroscopy removes the need to convert CO_2 to O_2 using methods such as fluorination to remove the isobaric interference at mass 45. Sample size (300 µg), analysis time (~30 min), and cost are significantly less using the TILDAS, while precision for $\Delta'^{17}O$ is ≤ 10 per meg, comparable to fluorination.

Operating parameters such as cell pressure and CO_2-N_2 mixing ratio must be controlled to a high tolerance. We have developed an inlet system that allows for sample and reference gas cell pressure to be the same within 0.02 Torr and CO_2 mixing ratios within 2% of each other. Differences of ± 2% between the sample and working reference CO_2 mixing ratios do not appreciably affect $\Delta'^{17}O$, but further work should be done to test this effects when mixing ratios are larger than this. The system can be fully automated so a large number of analyses can be made with minimal effort.

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