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High-Precision Simultaneous $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{17}\text{O}/^{16}\text{O}$ Analyses for Microgram Quantities of CaCO_3 by Tunable Infrared Laser Absorption Spectroscopy

Saburo Sakai^{*,†,‡,§}, Shinichi Matsuda^{||}, Toshihide Hikida[⊥], Akio Shimono[⊥], J. Barry McManus[#], Mark Zahniser[#], David Nelson[#], David L. Dettman[§], Danzhou Yang[‡], and Naohiko Ohkouchi[†]

[†]Institute of Biogeochemistry, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Kaganaga 237-0061, Japan

[‡]Department of Medical Chemistry and Molecular Pharmacology, College of Pharmacy, Purdue University, West Lafayette, Indiana 47907, United States

[§]Department of Geosciences, University of Arizona, Tucson, Arizona 85721, United States

^{||}Izumo Web, Ltd., Izumo, Shimane 693-0002, Japan

[⊥]Shoreline Science Research Inc., Hachioji, Tokyo 192-0045, Japan

[#]Center of Atmospheric and Environmental Chemistry, Aerodyne Research, Inc., Billerica, Massachusetts 01821, United States

Abstract

Stable isotope ratios ($^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{17}\text{O}/^{16}\text{O}$) in carbonates have contributed greatly to the understanding of Earth and planetary systems, climates, and history. The current method for measuring isotopologues of CO_2 derived from CaCO_3 is primarily gas-source isotope ratio mass spectroscopy (IRMS). However, IRMS has drawbacks, such as mass overlap by multiple CO_2 isotopologues and contaminants, the requirement of careful sample purification, and the use of major instrumentation needing permanent installation and a high power electrical supply. Here, we report simultaneous $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{17}\text{O}/^{16}\text{O}$ analyses for microgram quantities of CaCO_3 using a tunable mid-infrared laser absorption spectroscopy (TILDAS) system, which has no mass overlap problem and yields high sensitivity/precision measurements on small samples, as small as 0.02 μmol of CO_2 (equivalent to 2 μg of CaCO_3) with standard errors of less than 0.08 ‰ for $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ (± 0.136 ‰ and ± 0.387 ‰ repeatability; $n = 10$). In larger samples of CO_2 , 0.68 μmol (or 68 μg of CaCO_3), standard error is less than 0.04 ‰ for $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ($< \pm 0.1$ ‰ repeatability; $n = 10$) and 0.03 ‰ for $^{17}\text{O}/^{16}\text{O}$ (± 0.069 ‰ repeatability; $n = 10$). We also show, for the first time, the relationship between $^{17}\text{O}/^{16}\text{O}$ ratios measured using the TILDAS system and published $\delta^{17}\text{O}$ values of international standard materials (NBS-18 and -19) measured by IRMS. The benchtop TILDAS system, with cryogen-free sample preparation vacuum lines for microgram

*Corresponding Author: Phone: +81 46 867 9960. Fax: +81 46 867 9775. saburos@jamstec.go.jp.

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quantities of carbonates, is therefore a significant advance in carbonate stable isotope ratio geochemistry and is a new alternative to conventional IRMS.

Graphical Abstract

Light-element stable isotope ratios have made major contributions to the understanding of Earth systems, climates, and geologic history. In particular, the stable isotope ratios of oxygen and carbon ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in biogenic and sedimentary carbonates have been used to reconstruct highly detailed histories of climate on the Earth and played an outsized role in the discussion of the Earth's temperature, ocean salinity, sea level, ice-sheet volume changes, and carbon cycles.¹ Recent studies have suggested that the ^{17}O excess (^{17}O) in carbonates has great potential as a new paleo-environmental proxy.² Gas-source isotope ratio mass spectroscopy (IRMS) has been the dominant method for measurement of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{17}\text{O}$ in carbonates for many decades. However, IRMS systems are expensive and have some operational drawbacks, such as relatively elaborate sample preparation and purification, dedicated laboratory space, and the requirement of dedicated high power lines.

In recent years, laser spectroscopy has increasingly become an alternative to conventional IRMS for the measurement of isotopic ratios in atmospheric CO_2 .^{3–11} Laser systems use the mid-IR spectral region, which allows particularly high-sensitivity isotopic measurements, because CO_2 exhibits highly characteristic rotational–vibrational bands of strong fundamental vibrations in this region. Sensitivity can be further enhanced by acquiring spectra using a very fast scan rate. For example, in these instrument spectra, scanning takes place at 1.4 kHz, allowing the averaging of 1400 spectra per second for ratio calculation. In addition, laser spectroscopy eliminates the IRMS problem of common mass isotopologues that require assumed abundances to calculate final isotope ratios because the majority of trace gas molecules have unique absorption responses. Laser isotope analysis systems also offer lower cost, lower power consumption, and a benchtop size footprint and do not require high-purity gases or high-vacuum systems. These advantages have led to a number of studies that use laser spectroscopy for field monitoring of stable isotopes of CO_2 .^{3–11} Laser systems, however, remain much less common than IRMS for batch analyses in laboratory settings, with the exception of devices for medical diagnosis, such as *H. pylori* infection detection via human breath CO_2 .¹² Barker et al. reported the first application of batch analyses using an off-axis integrated cavity output laser spectroscopy instrument to measure $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of carbonate minerals.¹³ However, they used very large quantities of CaCO_3 (ca. 35 mg) for the analyses, which is impractical for most earth science studies, and the precision of the measurement was not comparable to conventional IRMS.

Here, we report simultaneous $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{17}\text{O}/^{16}\text{O}$ analyses for microgram quantities of CaCO_3 by tunable infrared laser direct absorption spectroscopy (TILDAS), coupled to a cryogen-free preparation vacuum line (Sakai and Matsuda),¹⁵ in a system that provides sensitivity and precision comparable to well established conventional IRMS. Three major innovations are described in this paper: (1) modification of a flow-through TILDAS absorption cell for measurement of low pressure, pure CO_2 gas yielding rapid high precision isotope ratio measurements, (2) the development of a cryogen-free carbonate preparation line for CO_2 sample introduction under precisely controlled conditions, and (3) direct measurement of $^{17}\text{O}/^{16}\text{O}$ ratios in small CO_2 samples.

EXPERIMENTAL SECTION

Tunable Infrared Laser Direct Absorption Spectroscopy.

Spectroscopic measurements were performed with a tunable infrared laser direct absorption spectroscopy (TILDAS; Aerodyne Research Inc.) system, represented by the multipass absorption cell in Figure 1. The instrument used a quantum cascade laser (QCL) tuned to 2310 cm^{-1} to measure the absorption spectrum of four CO_2 isotopologues: $^{12}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{17}\text{O}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}^{16}\text{O}$, and $^{13}\text{C}^{16}\text{O}_2$ (Figure 2). The design of the instrument and characteristics of the absorption lines are described in detail in McManus et al.¹¹ In most other applications, the TILDAS system is used to measure gases and/or isotope ratios in a flow-through gas handling system yielding continuous measurement of gas mixtures (primarily atmosphere samples). In our modified instrument, the absorption cell is miniaturized and vacuum tight, allowing CO_2 gas to be introduced into the pre-evacuated cell and isolated at a low pressure for measurement under highly stable and repeatable conditions. This is similar to the system shown for methane isotope measurements by Ono et al.¹⁴ In our system, the cell is approximately 200 mL in volume and designed with a 36 m optical path length within the cell. The detector is a thermoelectrically cooled photovoltaic detector. Laser control, data acquisition and real-time signal processing are performed by dedicated software (TDLWintel). The output for each isotopologue is calculated by nonlinear least-squares fitting of its absorption spectrum, yielding a peak area that can be used to find a ratio with other peaks. These peak-area ratios are then calibrated against CO_2 derived from standard carbonates with known stable isotope ratios.

The optical bench is thermally insulated and the temperature of the bench and absorption cell is regulated using air–liquid heat exchangers and cooling liquid supplied by a recirculating chiller. The inside of an optical bench housing is purged with N_2 at a constant flow rate of 4.5 standard liters per minute (slpm) to prevent any laser light absorption by ambient CO_2 outside of the multipass cell. The careful stabilization of cell temperature and sample pressure allows samples to be measured at high precision and with high repeatability.

Automated Cryogen-Free CO_2 Preparation System.

This system prepares CO_2 gas from carbonate samples and delivers it to the absorption chamber (Figure 1). The preparation system is divided into two main units: a calcium–carbonate reaction unit and a CO_2 gas purification/pressure-adjustment unit.

The carbonate reaction unit consists of a thermoblock (NDM01; Nisshinrika, Ltd.), a phosphoric metering pump (PiP1CTC-LF; Fluid Metering, Inc.), and a needle assembly for carbonate reaction (JASCO International Co., Ltd.). Carbonate samples are loaded into 1.5-mL reaction vials sealed with septum caps (0.8 mm thick PTFE/butyl/PTFE). These vials are then heated to 90°C in the temperature-controlled thermoblock. A double-hole needle is inserted into the reaction vial, and air is pumped out of the vial using the upper needle hole. After pumping the vial to <0.05 Torr (7 Pa), three drops of phosphoric acid (~50 μ L) are introduced from the lower hole using the fluid metering pump, which initiates the reaction ($\text{CaCO}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{CaHPO}_4 + \text{H}_2\text{O} + \text{CO}_2$). Once the acid has been delivered, the fluid pump reverses flow to draw back the acid that remains inside the needle volume. The needle remains in the sample vial until the sample reaction is complete (~10 min).

The CO₂ gas purification/pressure-adjustment unit consists of a stainless-steel vacuum-tight purification line with pneumatic diaphragm valves (DP series; Swagelok), a capacitance manometer (722B; MKS Instruments, Inc.), metering valves for N₂ purging (SS-2MA; Seagelok), a portable free-piston stirling cooler (FPSC; Product number: SC-UF01; Twinbird Corp.),¹⁵ an actuator-driven bellows (14 to 98 mL), and two cells of a fixed volume, all of which are connected to a dry pump (DeoDry 15E; Kashiya Industries Ltd.). All components are controlled by custom-built software.

The gases generated by the calcium–carbonate reaction (CO₂, water, and other trace gases) are transferred from the reaction cell through the upper hole of a double-hole needle and frozen in a cold-trap at –196°C, cooled by the cryogen-free stirling cooling method.¹⁵ After pumping any noncondensable gases from the cold trap, the CO₂ is released into the line by warming the stirling cooling unit to –115°C.¹⁶ At this temperature, water and many other contaminants will remain frozen. Previous studies have reported that water vapor acts as an interfering species for laser spectroscopy, not because of H₂O spectral absorption features but because of collisional broadening effects.^{3,7,13} The amount of CO₂ generated is then measured with the manometer and expanded into the bellows. The adjustable volume allows the CO₂ gas pressure to be controlled within $\pm 3 \times 10^{-4}$ Torr (0.04 Pa) precision, and the targeted amount of CO₂ gas can then be expanded into the absorption cell of TILDAS for stable isotopic analysis. For the reference gas measurement, small amounts of a pure standard CO₂ gas (Oztech isotopic ratio reference CO₂ gas) can be introduced to the absorption cell using the same adjustable volume as the sample measurement.

Steps in a Spectroscopic Gas Measurement.

Each measurement is processed as follows. First, the absorption cell is flushed with dry N₂ supplied from metering valve-1 or –2 (Figure 1), followed by pumping the cell and lines to 0.0 Torr/Pa using a dry pump. After flushing, a 1 min baseline measurement is taken. Then metered quantities of CO₂ by manometer and N₂ (valve-2) are introduced to the absorption cell. After a 3 min delay for complete mixing, the CO₂ sample sealed in the absorption cell is measured at 1.4 kHz, integrated for 5 min resolution. After measurement, the absorption cell is again flushed with N₂ from metering valve-1 or –2 and evacuated.

RESULTS AND DISCUSSION

Because cell pressure and temperature have a significant impact on the stability of ratio measurements, we will first examine the impact each has on the resulting ratio precision. After this, we will describe the instrument stability observed when operated under optimal conditions.

Pressure Effects on Absorption Spectra.

The leak rate of the absorption cell is quite low (0.018 Torr/h; 2.4 Pa/h), which is suitable for batch analyses. Pressure dependence of the absorption spectra was evaluated by adding N₂ to a fixed amount of CO₂ gas (Oztech CO₂ gas; 0.4 Torr) in the multipass cell (Figure 3a,b). Stability of the absorption peaks seems to be enhanced by the addition of N₂ to the CO₂ in the absorption cell, perhaps due to pressure broadening. We can see that the ratios of absorption peaks, R¹⁸O (¹²C¹⁸O/¹²C¹⁶O₂), R¹³C (¹³C¹⁶O/¹²C¹⁶O₂), and R¹⁷O (¹²C¹⁷O/¹²C¹⁶O₂), show linear relationships with total cell pressure change, which suggests that ratio measurement is most accurate at a single pressure condition (Figure 3a). This also suggests that the isotopic ratio can be calibrated to different pressures by using the observed linear relationships. The impact of leak rate of the absorption cell (0.018 Torr/h; 2.4 Pa/h) on sample precision for R¹⁸O, R¹³C, and R¹⁷O is negligible, being only 0.002 ‰, 0.011 ‰, and 0.035 ‰ per hour, respectively. Figure 3b shows that across a range of cell pressures the standard error for a 5 min measurement of R¹⁸O and R¹³C is better than 0.06 ‰. This is true from 0.1 to 50 Torr (13 to 6666 Pa). Note that the standard error of R¹³C is better than 0.03 ‰ at all pressures over 10.0 Torr (1333 Pa; Figure 3b). The standard error of R¹⁷O shows a minimum at cell pressures of 10 to 15 Torr (1333 to 2000 Pa). As a result, we conclude that a total pressure range of 10 to 15 Torr (1333 to 2000 Pa) is an optimal choice for high-precision data for all three ratios.

Temperature Effects on Absorption Spectra.

The optical bench of the TILDAS instrument is thermally insulated, and temperature is regulated using air–liquid heat exchangers and cooling water supplied by a recirculating chiller. This system maintains the temperature stability of the multipass cell within ±0.02 K.¹⁴ The temperature dependence of the absorption response and the isotopic ratios were evaluated by changing the target temperature setting of the recirculating chiller while repeatedly measuring one CO₂ gas sample (Oztech CO₂ gas). The temperature dependence of the results was isolated by subtracting the effect of pressure differences during the test using the pressure dependence of the isotopic ratios (Figure 3a). The results show a broadly similar linear relationship with cell temperature (Figure 4a). The resulting isotopic ratios calculated from the concentrations of each isotopologue are approximately uniform, although there are slight slope differences from a simple linear relationship in each isotopologues' peak area and resulting isotope ratios (Figure 4a,b). The TILDAS instrument can generally keep the cell temperature stable to better than 0.006 ± 0.042 K (5 min measurement; n = 20), which would reflect a precision of R¹⁸O, R¹³C, and R¹⁷O better than 0.04 ‰, 0.02 ‰, and 0.11 ‰, respectively, before any temperature correction is applied.

CO₂ Concentration Effects on Absorption Spectra.

The isotopic ratios observed by spectroscopy are dependent on CO₂ concentration since instrumental linearity may cause changes in the peak-area ratios with concentration.^{6,8,13} Our study also confirmed that R¹⁸O, R¹³C, and R¹⁷O show a dependence on the amount of CO₂ (Oztech CO₂ gas) in the cell when the CO₂ pressure in the cell is below approximately 0.45 Torr (Figure 5a). This suggests that, in this system, the optimum amount for calcium carbonate measurement is between 28 and 100 μg of CaCO₃. Above the 100 μg level, the primary CO₂ absorption peak is saturated. The standard errors of R¹⁸O and R¹³C are better than ±0.08 ‰ (Figure 5b) across a range of CO₂ concentrations that corresponds to 3–94 μg of CaCO₃. This shows that our system can achieve high-precision R¹⁸O and R¹³C analyses with microgram quantities of CaCO₃. In contrast, the standard error of R¹⁷O is much larger than those of R¹⁸O and R¹³C at lower CO₂ amounts. This is because the amplitude of the ¹²C¹⁷O¹⁶O absorption peak is much smaller than those of the ¹²C¹⁶O₂, ¹²C¹⁸O¹⁶O, and ¹³C¹⁶O₂ absorption spectra¹¹ (Figure 2). This leads to a narrower concentration window for accurate measurement of R¹⁷O, where the standard error of R¹⁷O in larger samples, greater than approximately 50 μg of CaCO₃, shows comparable precision with R¹⁸O and R¹³C (Figure 5b).

Instrument Stability under Optimal Conditions.

Instrument stability over the short term was evaluated using the Allan variance technique.¹⁷ The ratios of individual CO₂ isotopologues were measured with one second resolution over 1 h using 0.6 μmol of CO₂ (Oztech CO₂ gas; equivalent to 60 μg of CaCO₃) combined with 10.0 Torr (1333 Pa) of pure N₂ (Figure 6). The optimum averaging time is between 160 and 330 s, which corresponds to a relative precision of 0.039 ‰ (300 s), 0.085 ‰ (240 s), and 0.173 ‰ (300 s) for R¹⁸O, R¹³C, and R¹⁷O, respectively. However, system drift begins to confound the calculated ratio average beyond 330 s; this suggests that 5 min (300 s) or less is the best interval for each measurement sequence.

Conversion of R¹³C and R¹⁸O to Conventional δ¹³C and δ¹⁸O Values.

The peak areas of individual isotopologues are correlated with the concentration of each isotopologue in the cell, and ratios of the absorption peaks (R¹³C, R¹⁸O, and R¹⁷O) will vary in systematic ways in response to isotope ratio differences in the CO₂ gas. We therefore use a simple correlation between accepted isotope ratios and the ratios measured by the TILDAS system. To convert R¹³C and R¹⁸O to conventional δ¹³C_{PDB} and δ¹⁸O_{PDB} values, a two-point calibration derived from two standards, JNOC-86 and LSVEC, with very different isotope ratios was measured by TILDAS, while treating the two additional standards (JNOC-127 and Baker calcite) as external standards (Table 1; Figure 7). These measurements all used CO₂ gas derived from 60 μg of CaCO₃ under 10.0 Torr (1333 Pa) total cell pressure measurement conditions. This test produced a highly linear relationship between the accepted δ¹³C_{PDB} and δ¹⁸O_{PDB} values of standards and R¹³C and R¹⁸O measured by TILDAS (Figure 7a,b). The linear calibrations are as follows:

$$\delta^{18}\text{O}_{\text{PDB}} = 1070.7 \times \text{R}^{18}\text{O} - 1055.8 \left(R^2 = 0.99 \right)$$

$$\delta^{18}\text{C}_{\text{PDB}} = 1014.5 \times R^{13}\text{C} - 1018.2 \left(R^2 = 0.99 \right)$$

The $R^{13}\text{C}$ and $R^{18}\text{O}$ measured by TILDAS of the two external standards, JNOC-127 and Baker calcite, coincided well with the accepted $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values, implying a good linearity of response. The differences between IRMS and TILDAS data are better than 0.28 ‰ for $\delta^{13}\text{C}_{\text{PDB}}$ and 0.27 ‰ for $\delta^{18}\text{O}_{\text{PDB}}$ (Table 1).

To assess measurement repeatability, a subdivided standard CO_2 gas (Oztech gas; Figure 1) was measured 10 times with a 5 min measurement time at 10.0 Torr (1333 Pa) total cell pressure. The repeatability results of five different CO_2 concentrations are shown in Table 2. The standard errors of $R^{18}\text{O}$ and $R^{13}\text{C}$ above 0.16 Torr CO_2 were better than 0.1 ‰, which is comparable to conventional IRMS under small-sample batch-analysis conditions.¹⁸

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ Microanalysis of CaCO_3 .

For high-spatial and temporal resolution studies of carbonates, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses with microgram quantities of carbonates are required. Some examples of research requiring extremely small samples include growth band analysis of small fish otoliths, shell, corals, and microfossil studies of foraminifers and ostracods. Ishimura et al. reported $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of samples as small as 0.2 μg of CaCO_3 with standard deviations of 0.1 ‰ for $\delta^{13}\text{C}$ and 0.18 ‰ for $\delta^{18}\text{O}$ in a study of individual foraminifers using a customized continuous-flow IRMS.¹⁶ Routine measurement of 6 μg of CaCO_3 by conventional IRMS has been reported,¹⁸ with standard deviations of 0.05 ‰ for $\delta^{13}\text{C}$ and 0.1 ‰ for $\delta^{18}\text{O}$. As shown in Figure 5, our instrument is capable of measuring isotope ratios for CO_2 amounts equivalent to 2 μg of CaCO_3 with standard errors of 0.08 ‰ for $\delta^{13}\text{C}$ and 0.07 ‰ for $\delta^{18}\text{O}$. The repeatability test for samples of this size produced standard errors of 0.387 ‰ for $\delta^{13}\text{C}$ and 0.135 ‰ for $\delta^{18}\text{O}$ (Table 2). To achieve the highest accuracy in a ratio measurement, samples are compared with a reference CO_2 gas, for which the effect of concentration dependency is removed by carefully adjusting the reference CO_2 to match the sample gas cell concentration using the high-precision bellows system (Figure 1). The TILDAS system, with cryogen-free sample preparation vacuum-lines for microgram quantities of carbonates, is therefore a significant advance in carbonate stable isotope ratio geochemistry and is useful as an alternative to conventional IRMS.

$^{17}\text{O}/^{16}\text{O}$ of CaCO_3 .

The study of ^{17}O in carbonates is not widespread, mainly due to the difficulty of the measurement. The $^{17}\text{O}/^{16}\text{O}$ ratio in meteorites has been studied with large anomalies in ^{17}O content relative to terrestrial materials.¹⁹ In recent years, $\delta^{17}\text{O}$ and ^{17}O -excess measurements in carbonates have been recognized as useful data in paleo-environmental studies, especially terrestrial studies where the effect of evaporation is important.² High-precision measurement of $^{17}\text{O}/^{16}\text{O}$ using IRMS is difficult, because the $^{12}\text{C}^{17}\text{O}^{16}\text{O}$ isotopologue (~760 ppm) is masked by the much more abundant $^{13}\text{C}^{16}\text{O}_2$ isotopologue (~11 000 ppm) of the same nominal mass. Measurement, therefore, required a complicated preparation processes, involving quantitative (for oxygen) conversion of CO_2 to O_2 or

conversion of CO₂ to H₂O, which has no native interfering isobars, by an acid digestion/reduction/fluorination approach.^{2,20} Kawaguchi et al. measured $\delta^{17}\text{O}$ by continuous-flow IRMS using two different CO₂ streams. One aliquot flows into the IRMS directly, while the other aliquot flows through a CuO unit (900°C) prior to injection into IRMS, to exchange oxygen atoms in the sample CO₂ molecules with those of CuO whose ^{17}O anomaly is assumed to be zero.²¹ Our TILDAS system is the first example of direct measurement of $^{17}\text{O}/^{16}\text{O}$ ratios in CO₂ gas. This CO₂ is generated from carbonate through a conventional acid digestion method using our automated CO₂ purification system. Analytical precision of $^{17}\text{O}/^{16}\text{O}$ of CO₂ derived from 68 μg of CaCO₃ at 10.0 Torr (1333 Pa) total cell pressure is better than 0.03 ‰ (± 0.069 ‰ repeatability; $n = 10$, Figure 5). Figure 8 and Table 3 show the relationship between $^{17}\text{O}/^{16}\text{O}$ by the TILDAS method and the $\delta^{17}\text{O}$ of international standard materials (NBS-19 and NBS-18) by IRMS.²² Our laser spectroscopic system with cryogen-free sample preparation vacuum lines thus can become a powerful tool for $^{17}\text{O}/^{16}\text{O}$ analyses of carbonates.

CONCLUSIONS

We demonstrated the simultaneous $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{17}\text{O}/^{16}\text{O}$ measurement of microgram quantities of CaCO₃ by tunable infrared laser direct absorption spectroscopy (TILDAS), coupled to a cryogen-free preparation vacuum line, in a system that provides sensitivity and precision comparable to well established conventional IRMS. We also showed the first example of high-precision direct measurement of $^{17}\text{O}/^{16}\text{O}$ ratios in CO₂ gas and a small amount of carbonates (below 70 μg of CaCO₃) with a conventional acid digestion method. Additional work on the sample preparation system design could reduce the inlet-line dead volume even further, which would reduce the amount of CO₂ or CaCO₃ required for a measurement. The TILDAS system, coupled to a cryogen-free preparation vacuum line for microgram quantities of carbonates, is therefore a significant advance in carbonate stable isotope ratio geochemistry, and may be additionally expanded into high-precision rare isotopologue measurements, such as carbonateclumped isotopes.

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Figure 1.

Schematic diagram of the measurement system. The system consists of a CaCO₃ reaction unit, CO₂ purification unit, and tunable infrared laser absorption spectroscopy (TILDAS) system. A cryogen-free CO₂ preparation system developed by Sakai and Matsuda was employed. TILDAS is shown as the multipass cell and two valves, enclosed in the orange box.

Figure 2.

Example of absorption spectrum for CO₂ obtained by the TILDAS system with a 36 m absorption path at 10 Torr (1333 Pa) total cell pressure. The measured spectrum is the green trace, and the fit is the black trace. The fit background is the black dotted line. The quantum cascade laser (QCL) scans the laser frequency range using 800 channels (point number) at a rate of 1.4 kHz as shown in the horizontal axis.

Figure 3.

Pressure dependence of absorption spectrum of CO₂ isotopologues. (a) Each isotopic ratio is strongly correlated with cell pressure change. R^2 of the equations shows coefficient of determination. (b) Standard errors of $R^{18}O$ and $R^{13}C$ for a 5 min measurement are better than 0.06 ‰ (1 S.E.) at 10–50 Torr (1333– 6666 Pa) total cell pressure. Standard error of $R^{17}O$ shows a minimum at 10 to 15 Torr (1333–1999 Pa) cell pressure. Overall 10 to 15 Torr is an optimum cell pressure for measurement.

Figure 4.

Temperature dependence of the absorption spectrum of CO₂ isotopologues. (a) All isotopologues show broadly similar linear relationships with cell temperature. (b) Peak area ratios change slightly with temperature change due to the subtle slope differences in the mostly linear response of each isotopologue. R² of the equations shows coefficient of determination.

Figure 5.

Plots of isotopic ratios and standard error with CO_2 concentrations. All plots are produced using a 5 min measurement at 10.0 Torr total cell pressure. (a) Isotopic ratios show CO_2 concentration dependency below 0.45 Torr CO_2 . (b) Standard errors of $R^{18}\text{O}$ and $R^{13}\text{C}$ are all better than 0.08 ‰ (1 S.E.) across the entire range tested, CaCO_3 equivalents from 2 μg to 94 μg . The standard errors of $R^{17}\text{O}$ measurement when CO_2 pressure is above 0.8 Torr (50 μg of CaCO_3) are comparable with $R^{18}\text{O}$ and $R^{13}\text{C}$. Top and bottom x axes are equivalent.

Figure 6. Allan variance plots for $R^{18}O$, $R^{13}C$, and $R^{17}O$ of 1.0 Torr CO_2 (equivalent to $60 \mu g$ of $CaCO_3$) measured by TILDAS. Measurement was performed under the absorption cell total pressure of 10.0 Torr for 1 h. Shaded area shows the optimal averaging time (horizontal level) for one measurement sequence.

Figure 7. Accepted $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ by IRMS values plotted against $R^{18}\text{O}$ and $R^{13}\text{C}$ by TILDAS.

Figure 8. $\delta^{17}\text{O}$ by IRMS values plotted against $R^{17}\text{O}$ by TILDAS. International standard materials (NBS-18 and -19) are used for tie points in this relationship. Values for the other carbonates are extrapolated from our $R^{17}\text{O}$ measurements with the TILDAS system.

Table 1.

 $R^{18}O(^{12}C^{16}O/^{12}C^{16}O_2)$, $R^{13}C(^{13}C^{16}O_2/^{12}C^{16}O_2)$, and $R^{17}O(^{12}C^{17}O/^{12}C^{16}O_2)$ from the TILDAS System^a

standard	n	$R^{18}O$	S.E.	$R^{13}C$	S.E.	$R^{17}O$	S.E.	cell pressure (Torr)	cell temperature (K)	calculated $\delta^{18}O_{VPDB}$	calculated $\delta^{13}C_{VPDB}$
JNOC-86	6	0.9866	0.00006	1.0062	0.00013	1.0131	0.00107	10.04	297.62	0.521	2.617
JNOC-127	5	0.9816	0.00013	0.9976	0.00029	1.0076	0.00034	10.07	297.64	-4.767	-5.924
Baker calcite	4	0.9712	0.00012	0.9625	0.00021	1.0021	0.00010	10.06	297.63	-15.92	-41.70
LSVEC	6	0.9611	0.00012	0.9577	0.00012	0.9990	0.00041	10.06	297.63	-26.7	-41.70

^a Cell pressure (Torr), cell temperature (K), and calculated isotopic values obtained from the TILDAS system are also shown. Accepted δ values are reported by IRMS, $R^{18}O$, $R^{13}C$, and $R^{17}O$ are normalized at 10.0 Torr (1333 Pa) in total pressure and 297.65 K (24.5°C) conditions based on the equations of Figures 3a and 4b.

Table 2.

Repeatability Test for $R^{18}O$ ($^{12}C^{18}O^{16}O/^{12}C^{16}O_2$), $R^{13}C$ ($^{13}C^{16}O_2/^{12}C^{16}O_2$), and $R^{17}O$ ($^{12}C^{17}O^{16}O/^{12}C^{16}O_2$) with Different CO_2 Concentrations that Correspond to between 2 μg of $CaCO_3$ and 100 μg of $CaCO_3$ ^a

standard	n	calculated CaCO ₃		R18 ± 1 S.E.		R13 ± 1 S.E.		R17 ± 1 S.E.		cell pressure (Torr)	cell temperature (K)
		volume (μg)		R18 (%)	R13 (%)	(%)	R17 (%)	(%)			
Oztech-1.46 Torr	10	90		0.9877	0.058	0.9984	0.099	1.0109	0.129	10.07	297.58
Oztech-1.09 Torr	10	67		0.9861	0.067	0.9984	0.129	1.0101	0.069	10.06	297.57
Oztech-0.65 Torr	10	40		0.9865	0.067	1.0033	0.105	1.0010	0.248	10.06	297.60
Oztech-0.16 Torr	10	10		0.9910	0.094	1.0385	0.108	0.9239	0.477	10.06	297.59
Oztech-0.03 Torr	10	2		0.9975	0.136	1.0725	0.387	0.8102	2.006	10.07	297.60

^a CO_2 concentrations are represented by major isotopologue ($^{12}C^{16}O_2$) concentration. Cell pressure (Torr) and cell temperature (K) are also shown. $R^{18}O$, $R^{13}C$, and $R^{17}O$ are normalized at 10.0 Torr (1333 Pa) in total pressure and 297.65 K (24.5°C) conditions based on the equations of Figures 3a and 4b.

Table 3. $R^{17}\text{O}$ ($^{12}\text{C}^{17}\text{O}^{16}\text{O}/^{12}\text{C}^{16}\text{O}_2$) by TILDAS^a

standard	n	$R^{17}\text{O} \pm 1$		calculated	$\delta^{17}\text{O}_{\text{VSMOW}}$
		$R^{17}\text{O}$	S.E.	$\delta^{17}\text{O}_{\text{VSMOW}}$	Barkan et al.
NBS-18	3	0.9984	0.00020		9.253
NBS-19	3	1.0083	0.00005		20.257
JNOC-86	6	1.0131	0.00107	25.787	
JNOC-127	5	1.0076	0.00034	19.612	
Baker calcite	4	1.0021	0.00010	13.475	
LSVEC	6	0.9990	0.00041	9.970	

^a Accepted δ values of NBS-18 and NBS-19 are reported by IRMS. $\delta^{17}\text{O}$ values of the other four samples were calculated with the two point calibration equation of NBS-18 and NBS-19. $R^{17}\text{O}$ is normalized at 10.0 Torr (1333 Pa) in total pressure and at 297.65 K (24.5°C) conditions based on the equations of Figures 3a and 4b.