

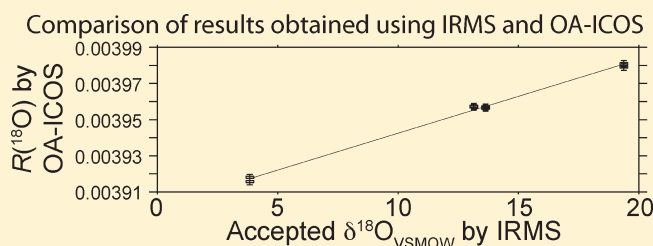
Use of Laser Spectroscopy To Measure the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ Compositions of Carbonate Minerals

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ABSTRACT: The stable carbon and oxygen isotope compositions of carbonate minerals are utilized throughout the earth and environmental sciences for various purposes. Here, we demonstrate the first application of a prototype instrument, based on off-axis integrated cavity output laser spectroscopy, to measure the carbon and oxygen isotope composition of CO_2 gas evolved from the acidification of carbonate minerals. The carbon and oxygen isotope ratios were recorded from absorption spectra of $^{12}\text{C}^{16}\text{O}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, and $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ in the near-infrared wavelength region. The instrument was calibrated using CaCO_3 minerals with known $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values, which had been previously calibrated by isotope ratio mass spectrometry relative to the international isotopic standards NBS 18 and NBS 19. Individual analyses are demonstrated to have internal precision (1 SE) of better than 0.15‰ for $\delta^{13}\text{C}$ and 0.6‰ for $\delta^{18}\text{O}$. Analysis of four carbonate standards of known isotopic composition over 2 months, determined using the original instrumental calibration, indicates that analyses are accurate to better than 0.5‰ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ without application of standard–sample–standard corrections.



In recent years, instruments based on off-axis integrated cavity output spectroscopy (OA-ICOS), a cavity-enhanced laser absorption technique, have become increasingly popular to measure trace gas concentrations and the isotopic composition of environmental water and gas samples in the laboratory and in the field.^{1–7} The development of OA-ICOS now offers an alternative to conventional stable isotope ratio mass spectrometry, with the ability to measure stable isotope ratios in several gas species (including water vapor, liquid water, carbon dioxide, methane, and nitrous oxide). The documented advantages of OA-ICOS include relatively low initial capital cost, low power consumption, benchtop size, lack of a high-vacuum system, no requirement for high-purity gases, and relatively simple operation.⁵ All of these factors contribute to field portability and significantly reduced operating costs.

The stable isotope composition of carbonate minerals has been of interest for more than 50 years, with initial research focusing on measurements of carbonates in the ocean for paleoceanography applications.^{8,9} Stable isotope studies of carbonates have also been used extensively to explore the role of fluid–rock reaction¹⁰ and geosphere–hydrosphere–atmosphere interactions^{11,12} in the earth and environmental sciences. In this paper, we present the results of $\varphi(\text{CO}_2)$, and the isotope number ratios $N(^{13}\text{C})/N(^{12}\text{C}) = R(^{13}\text{C})$ and $N(^{18}\text{O})/N(^{16}\text{O}) = R(^{18}\text{O})$, of CO_2 gas derived from the acidification of carbonate minerals. By analyzing a series of calcium carbonate minerals with known $\delta^{13}\text{C}$ (relative to VPDB) and $\delta^{18}\text{O}$ (relative to VSMOW) compositions, we are able to demonstrate that OA-ICOS can produce accurate and reproducible measurements of the carbon

($\delta^{13}\text{C}_{\text{VPDB}}$) and oxygen ($\delta^{18}\text{O}_{\text{VSMOW}}$) isotope compositions of carbonate minerals. We suggest that this instrument has applications in any area of research that requires rapid, high-throughput, and low-cost analyses of carbon and/or oxygen isotope compositions of carbonate minerals (or high-concentration CO_2 gases) and for measurements in locations with minimal logistical or technical support and infrastructure.

METHODS

Approximately 35 mg of pure CaCO_3 (calcite) was placed into 12 mL Labco Exetainer brand borosilicate glass vials that were sealed with butyl rubber septa. The vials were not evacuated or flushed due to the relatively small amount of CO_2 naturally present in the atmosphere compared to that generated from the CaCO_3 . Into each vial approximately 0.2 mL of 85% H_3PO_4 or 99% H_3PO_4 was injected through the rubber septum, and the sample was left to react at 72 °C for at least 1 h in a heated aluminum block.

During reaction of carbonate minerals with phosphoric acid, exchange of oxygen isotopes occurs between phosphoric acid and liberated CO_2 and water.^{9,13} Various concentrations of H_3PO_4 (from 85% to 103%) have been suggested as providing accurate results for oxygen isotope results.¹³ In our testing, we found no systematic difference between the results from 85% and 99%

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H₃PO₄ (Table 2). Thus, 85% H₃PO₄ was used for subsequent analysis of all samples. Any oxygen isotope fractionation induced by the use of acids of different strengths is likely masked by the noise inherent within the laser system.

Following reaction, the inlet to the instrument (Los Gatos Research (LGR), model 908-0021) was connected to the sample vials via a series of Swagelok stainless steel compression fittings, stainless steel tubing, and a glass cold trap. The sample vials were first “pricked”, meaning that the point of a Luerlock hypodermic needle, attached via a Swagelok Ultratorr fitting, was inserted into the rubber septum, without piercing through the septum. Following septum pricking, the analyzer began a systematic pump down and flushing cycle using laboratory atmosphere passed through a Drierite drying column as a zero gas to remove high-concentration CO₂ from the OA-ICOS measurement cell. The entire instrument and sampling line were then pumped down to a pressure of less than 0.5 kPa. Once this pressure was reached, the needle was manually pushed through the septum and the CO₂ in the sample vials moved through the sampling line, which has a glass coil contained within a bath of dry ice and ethanol (maintaining

a temperature of ~ -78 °C). During preliminary testing, it became apparent that water vapor acted as a significant interfering species and thus needed to be removed from gas samples prior to analysis. The glass coil serves as a water trap, freezing water vapor produced during the reaction of CaCO₃ and H₃PO₄ and yielding a relatively dry CO₂ gas sample. The sample is then drawn into a transfer cell inside the LGR analyzer due to the applied pressure gradient created by the vacuum pump. After a period of 60 s, 100 mL of dry laboratory air is mixed with the sample of CO₂ to produce a sample of approximately 115 mL of gas with $\phi(\text{CO}_2) = 5\text{--}8\%$.

Prior to each measurement, the instrument automatically purges the measurement cell twice with sample gas before filling the cell to a pressure of about 5.2 kPa. After a 30 s waiting period to allow for equilibration, the instrument determines $\phi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$, $\phi(^{13}\text{C}^{16}\text{O}^{16}\text{O})$, and $\phi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$ in the sample gas from the measured high-resolution laser absorption spectra, displays the measured high-resolution multiline carbon dioxide absorption spectra to the user on the embedded LCD monitor, and reports the measurements and spectra in text files stored on the instrument hard drive.

The LGR analyzer is based on off-axis integrated cavity output spectroscopy to measure $\phi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$, $\phi(^{13}\text{C}^{16}\text{O}^{16}\text{O})$, and $\phi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$ simultaneously. The theory of OA-ICOS has been described in detail previously.¹⁴ The present system consists of a distributed feedback diode laser (operating near 1.6 μm) and a measurement cell with a pair of highly reflective cavity mirrors ($\sim 99.995\%$ reflectivity). As a result, the effective optical path length inside the measurement cell is greater than 10 km, allowing for sensitive absorption measurements to be obtained by tuning the narrow-line-width (telecommunications-grade) diode laser over selected near-infrared rovibrational absorption transitions of $^{12}\text{C}^{16}\text{O}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, and $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. The transmitted light through the measurement cell is focused onto

Table 1. Isotopic Composition of Standards Used in This Study

standard	$\delta^{13}\text{C}_{\text{VPDB}} (\text{‰})$	$\delta^{18}\text{O}_{\text{VSMOW}} (\text{‰})$
Merck 99.95% CaCO ₃	−35.25	13.15
H6M	−0.69	3.84
BN13	1.84	13.64
BN83-2	4.35	19.38
LM4	1.93	26.22
LM1	−0.94	18.82
LM9	−0.58	26.42

Table 2. Analysis Number, Sample, Cell Pressure (kPa), Temperature (°C), $10^6\phi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$, $10^6\phi(^{13}\text{C}^{16}\text{O}^{16}\text{O})$, $10^6\phi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$, $R(^{13}\text{C}) \pm 1$ Standard Error, and $R(^{18}\text{O}) \pm 1$ Standard Error for CO₂ Gas Generated from BN13 and LM4^a

no.	sample	pressure	T	$\phi(^{12}\text{C}^{16}\text{O}_2)$	$\phi(^{13}\text{C}^{16}\text{O}_2)$	$\phi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$	$R(^{13}\text{C}) \times 10^{-2}$	$\pm 1 \text{ SE} \times 10^{-6}$	$R(^{18}\text{O}) \times 10^{-3}$	$\pm 1 \text{ SE} \times 10^{-6}$
1	LM4	5.21	29.10	26651	297	107	1.1130	2.98	3.9663	4.64
2	BN13	5.21	29.09	32385	360	128	1.1123	2.18	3.9216	3.85
3	LM4	5.21	29.10	71514	797	286	1.1143	1.40	3.9514	1.76
4	BN13	5.20	29.10	68131	759	269	1.1141	1.45	3.9069	2.05
5	LM4	5.21	29.08	69475	774	277	1.1142	1.28	3.9471	1.82
6	BN13	5.21	29.00	69925	779	276	1.1141	1.46	3.9029	1.82
7	LM4	5.21	29.00	74004	824	296	1.1140	1.46	3.9497	1.88
8	BN13	5.21	29.00	68994	769	273	1.1139	1.53	3.9067	1.90
9	LM4	5.21	29.00	69791	777	279	1.1138	1.44	3.9512	1.71
10	BN13	5.21	29.00	70435	784	278	1.1137	1.40	3.9054	1.83
11	LM4	5.20	29.00	45590	508	182	1.1133	1.95	3.9586	2.69
12	BN13	5.21	29.08	60517	674	239	1.1139	1.51	3.9060	2.16
13	LM4	5.21	29.07	66040	736	264	1.1138	1.35	3.9511	1.84
14	BN13	5.21	29.00	57238	637	226	1.1135	1.60	3.9102	2.21
15	LM4	5.21	29.00	61869	689	247	1.1139	1.46	3.9556	1.91
16	BN13	5.21	29.00	61706	687	244	1.1138	1.46	3.9088	1.97
17	LM4	5.21	29.00	57609	642	230	1.1140	1.74	3.9565	2.08
18	BN13	5.21	29.00	57894	645	229	1.1138	1.54	3.9137	2.06
19	LM4	5.21	29.00	40753	453	163	1.1127	2.11	3.9606	3.27
20	BN13	5.21	29.00	64188	715	254	1.1137	1.61	3.9116	1.84

^a Listed in the order of the columns from left to right. Analysis numbers 1–10 were carried out using 85% H₃PO₄, and analyses 11–20 were carried out using 99% H₃PO₄.

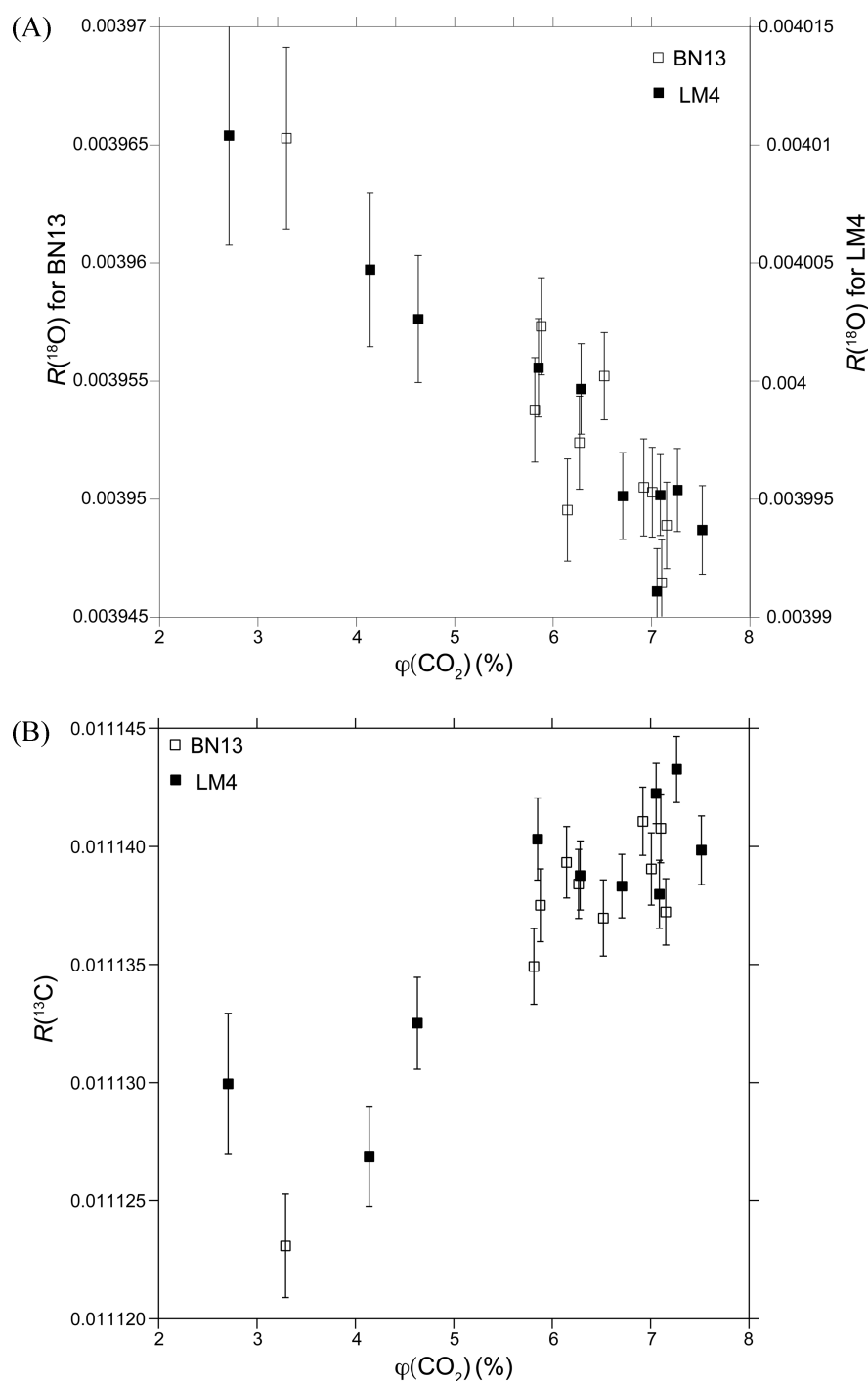


Figure 1. $\varphi(\text{CO}_2)$ (%) plotted against $R(^{13}\text{C})$ (± 1 SE) and $R(^{18}\text{O})$ (± 1 SE) for standard BN13 and sample LM4.

a photodetector and converted to an analog voltage, which is then digitized for analysis with the on-board internal computer in real time. Combined with known line intensities and accurately measured pressure, temperature, and cavity ringdown time, the mixing ratios of all three species can be calculated from the measured absorption spectra (which are displayed on the instrument LCD display).

The OA-ICOS instrument measures the volume fraction of several isotopologues of CO₂ ($\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$, $\varphi(^{13}\text{C}^{16}\text{O}^{16}\text{O})$, and $\varphi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$). To convert these to isotope ratio numbers,

we assume a negligible contribution from other isotopologues of CO₂ (such as $^{13}\text{C}^{18}\text{O}^{16}\text{O}$). Thus, we assume that

$$R(^{13}\text{C}) = \frac{\varphi(^{13}\text{C}^{16}\text{O}^{16}\text{O})}{\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})}$$

and

$$R(^{18}\text{O}) = \frac{\varphi(^{12}\text{C}^{18}\text{O}^{16}\text{O})}{\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})}$$

To convert $R(^{13}\text{C})$ and $R(^{18}\text{O})$ to conventional δ notation (i.e., $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$), it was necessary to measure stable isotope working standards. The standards of known isotopic compositions can be used to convert the measured isotopic ratios to the international isotopic scales relative to VPDB and VSMOW.¹⁵ The analyzer is calibrated using the identical treatment principle,¹⁶ whereby standards with known isotopic compositions are treated in the same manner as samples with unknown isotopic compositions. Here, we present the results of analyses of five samples of calcium carbonate, four of which are “in-house” UBC calcite standards, which have been measured and calibrated relative to the international standards NBS 18 ($\delta^{13}\text{C}_{\text{VPDB}} = -5.01\text{‰}$, $\delta^{18}\text{O}_{\text{VSMOW}} = +7.2\text{‰}$) and NBS 19 ($\delta^{13}\text{C}_{\text{VPDB}} = +1.95\text{‰}$, $\delta^{18}\text{O}_{\text{VSMOW}} = +28.65\text{‰}$)^{17,18} by continuous flow isotope ratio mass spectrometry. The fifth sample is a sample of limestone composed of calcite, collected from near Lone Mountain, NV (see Table 1), which was used to examine the reproducibility of data during initial testing, as this sample

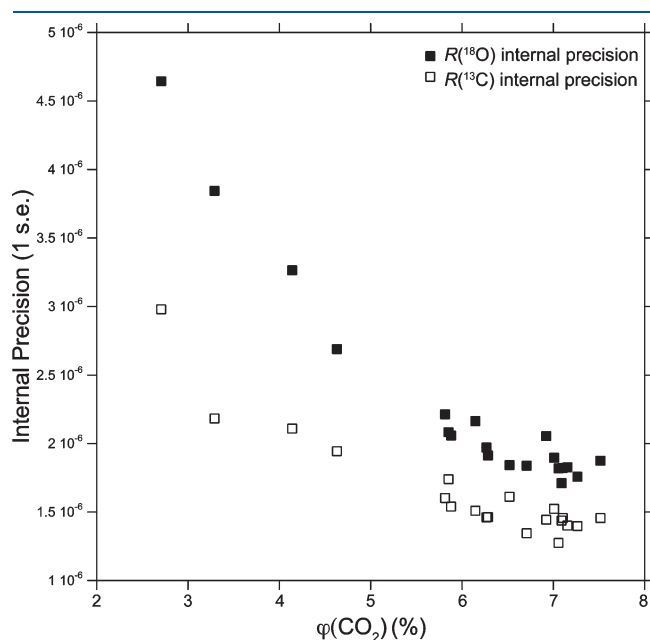


Figure 2. $\phi(\text{CO}_2)$ plotted against the internal precision (1 SE) of measurements of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$.

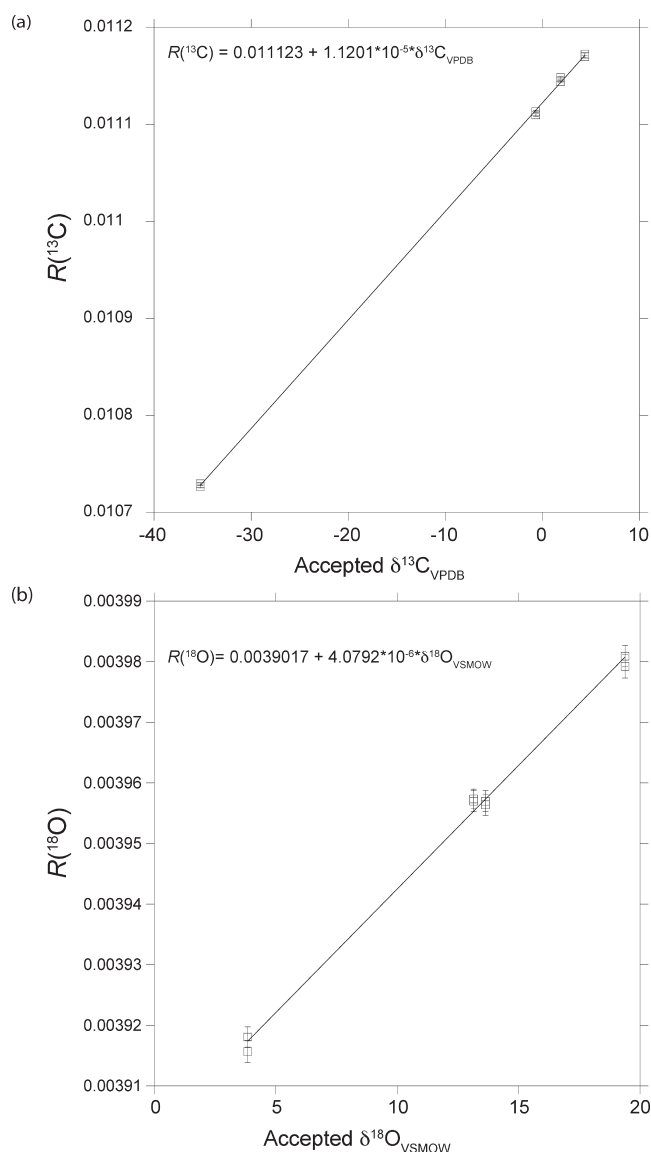


Figure 3. Results for standards Merck 99.95% CaCO_3 , H6M, BN13, and BN83-2: (a) accepted $\delta^{13}\text{C}_{\text{VPDB}}$ values plotted against $R(^{13}\text{C})$ (± 1 SE), (b) accepted $\delta^{18}\text{O}_{\text{VSMOW}}$ compositions versus the isotope number ratio for $R(^{18}\text{O})$ (± 1 SE).

Table 3. Sample, Cell Pressure (kPa), Temperature ($^{\circ}\text{C}$), $10^6\phi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$, $10^6\phi(^{13}\text{C}^{16}\text{O}^{16}\text{O})$, $10^6\phi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$, $R(^{13}\text{C}) \pm 1$ Standard Error, and $R(^{18}\text{O}) \pm 1$ Standard Error for CO_2 Gas Generated from Standards BN13, BN83-2, H6M, and Merck^a

sample	pressure	T	ϕ ($^{12}\text{C}^{16}\text{O}_2$)	ϕ ($^{13}\text{C}^{16}\text{O}_2$)	ϕ ($^{12}\text{C}^{16}\text{O}^{18}\text{O}$)	$R(^{13}\text{C}) \times 10^{-2}$	$\pm 1 \text{ SE} \times 10^{-6}$	$R(^{18}\text{O}) \times 10^{-3}$	$\pm 1 \text{ SE} \times 10^{-6}$	corr $R(^{18}\text{O}) \times 10^{-3}$	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{VSMOW}}$
BN13	5.22	29.09	65428	729	259	1.1148	1.28	3.9512	1.73	3.9570	2.3	13.5
BN13	5.21	29.14	66637	743	263	1.1144	1.18	3.9495	1.77	3.9564	1.9	13.4
BN83	5.21	29.07	66457	742	264	1.1172	1.19	3.9742	1.75	3.9810	4.5	19.4
BN83	5.22	29.16	61742	690	246	1.1170	1.18	3.9768	1.95	3.9792	4.2	19.0
H6M	5.22	29.11	68147	757	266	1.1113	1.17	3.9098	1.68	3.9181	-0.8	4.0
H6M	5.22	29.15	61151	679	239	1.1110	1.20	3.9138	1.84	3.9157	-1.1	3.4
Merck	5.22	29.10	71171	764	281	1.0729	1.13	3.9464	1.62	3.9574	-35.1	13.7
Merck	5.23	29.15	65632	704	259	1.0726	1.21	3.9510	1.74	3.9570	-35.4	13.6

^a Listed in the order of the columns from left to right. The values calculated for $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ are given on the basis of the calibration lines shown in Figure 3. H_3PO_4 (85%) was used for all samples.

Table 4. Isotopic Ratios (Average $\pm 1\sigma$) Determined by OA-ICOS (and Accepted Isotopic Values Determined by IRMS) for Four Different Standard Materials over a 3 Month Period Using the Calibration Given in Figure 3

standard	$\delta^{13}\text{C}_{\text{VPDB}}$ (OA-ICOS)	$\pm 1\sigma$	accepted $\delta^{13}\text{C}_{\text{VPDB}}$ (IRMS)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (OA-ICOS)	$\pm 1\sigma$	accepted $\delta^{18}\text{O}_{\text{VSMOW}}$ (IRMS)
BN13 ($n = 16$)	1.8	0.67	1.8	14.3	0.67	13.6
LM4 ($n = 28$)	2.0	0.55	1.9	26.0	0.87	26.2
LM1 ($n = 6$)	−1.1	0.3	−0.9	19.2	0.5	18.8
LM9 ($n = 6$)	0.3	0.5	−0.6	26.1	0.4	26.4

Table 5. Data Collected in a 4 h Analytical Period^a

sample	$\delta^{13}\text{C}_{\text{VPDB}}$ (OA-ICOS)	± 1 SE	$\delta^{13}\text{C}_{\text{VPDB}}$ (IRMS)	$\delta^{13}\text{C}$ discrepancy (calcd − actual)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (OA-ICOS)	$\delta^{18}\text{O}_{\text{VSMOW}}$ discrepancy (accepted − actual)
BN13	1.9	0.13	1.84	0.07	13.64	0.00
LM4	2.2	0.15	1.93	0.24	25.69	−0.53
H6M	−0.9	0.14	−0.69	−0.25	3.31	−0.53
LM1	−0.6	0.10	−0.94	0.35	19.61	0.79
BN13	1.8	0.12	1.84	−0.07	13.57	−0.07
BN13	2.0	0.13	1.84	0.16	13.64	0.00
LM4	2.2	0.15	1.93	0.25	25.36	−0.86
BN13	1.7	0.11	1.84	−0.11	13.32	−0.32
LM4	2.4	0.11	1.93	0.42	26.82	0.60
H6M	−0.9	0.13	−0.69	−0.21	3.94	0.10
BN13	1.7	0.12	1.84	−0.15	13.64	0.00
LM4	2.0	0.12	1.93	0.09	25.68	−0.54
LM1	−0.9	0.12	−0.94	0.00	19.25	0.43
BN13	1.6	0.12	1.84	−0.24	13.63	−0.01
LM4	2.1	0.11	1.93	0.16	25.50	−0.72
BN13	1.8	0.14	1.84	−0.03	13.87	0.23
LM1	−0.8	0.11	−0.94	0.10	19.05	0.23
LM4	1.8	0.13	1.93	−0.09	25.15	−1.07
BN13	1.7	0.12	1.84	−0.10	14.09	0.45
BN13	1.8	0.13	1.84	−0.05	13.64	0.00

^a OA-ICOS $\delta^{13}\text{C}$ values were corrected to VPDB values using the correction factor given in Figure 3. OA-ICOS $\delta^{18}\text{O}$ values were corrected using the correction factor given in Figure 3 to convert samples to VSMOW values. $\delta^{18}\text{O}$ values were then corrected for drift by bracketing with four BN13 standards (gray samples), and a simple linear interpolation was used among these four standards. The discrepancies between calculated and actual values are shown in the $\delta^{13}\text{C}$ discrepancy and $\delta^{18}\text{O}$ discrepancy columns.

was available in sufficiently large volume that we could use it for testing for a prolonged period of time. The overall objectives of this study are to examine whether this novel laser-based instrument can accurately measure the carbon and oxygen isotope compositions of carbonate minerals, examine factors which influence isotopic measurements, and evaluate the accuracy and precision of the measurements.

RESULTS

Measurements of three CO_2 isotopologues, $\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$, $\varphi(^{13}\text{C}^{16}\text{O}^{16}\text{O})$, and $\varphi(^{12}\text{C}^{16}\text{O}^{18}\text{O})$, and isotope number ratios, $R(^{13}\text{C})$ and $R(^{18}\text{O})$, of CO_2 gas generated from BN13 and LM4 in the same analytical session are presented in Table 2 and Figure 1. Carbon isotopic ratios show no systematic relationship to $\varphi(\text{CO}_2)$, with carbon isotopes showing slightly lower $R(^{13}\text{C})$ ratios in samples which had $\varphi(\text{CO}_2) \leq 5\%$ (Figure 1a). Oxygen isotope ratios show a linear dependence on $\varphi(\text{CO}_2)$ for measurements made for $\varphi(\text{CO}_2) = 3\text{--}8\%$. Thus, oxygen isotope ratios can be corrected for samples to a single volume fraction baseline at which all analyses can be compared relative to one another. The internal precision of the analyses is strongly

dependent on $\varphi(\text{CO}_2)$ (Figure 2), which is intrinsically due to the relative strengths of the $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}^{16}\text{O}$, and $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ absorption features. All measurements were recorded after the instrument was allowed to warm and reach a steady-state temperature, which requires approximately 1–2 h. In our laboratory, the instrument is running continuously to avoid a daily warm-up period.

The comparison of the measured $\varphi(^{13}\text{C}^{16}\text{O}^{16}\text{O})/\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$ ratios determined by OA-ICOS and the accepted $\delta^{13}\text{C}_{\text{VPDB}}$ for four calcium carbonate standards are given in Figure 3a (Table 3). The comparison of the measured $\varphi(^{12}\text{C}^{18}\text{O}^{16}\text{O})/\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$ ratios determined by OA-ICOS and the accepted $\delta^{18}\text{O}_{\text{VSMOW}}$ for four calcium carbonate standards are given in Figure 3b (Table 3). For these measurements, all were analyzed at a constant temperature over several hours ($<0.1^\circ\text{C}$ variation, Table 3). Oxygen isotope number ratios were corrected for variable $\varphi(\text{CO}_2)$ using the relationship shown in Figure 1, with all oxygen isotope number ratios corrected to $\varphi(\text{CO}_2) = 6\%$. A linear relationship can be demonstrated between the known $\delta^{13}\text{C}_{\text{VPDB}}$ value of standards and the isotope number $R(^{13}\text{C})$ ratios measured by OA-ICOS (Figure 3a, Table 3). Thus, a linear calibration may be established, where

carbon isotope ratio numbers measured by OA-ICOS can be converted to $\delta^{13}\text{C}_{\text{VPDB}}$:

$$\delta^{13}\text{C}_{\text{VPDB}} = \frac{(\varphi(^{13}\text{C}^{16}\text{O}^{16}\text{O})/\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})) - 0.01123}{0.00001201}$$

Figure 3b also shows the relationship between the accepted oxygen isotope values on four calcium carbonate standards and the isotope number ratios determined by OA-ICOS. A strong linear relationship exists between accepted $\delta^{18}\text{O}$ values (on the VSMOW scale) and measured $R(^{18}\text{O})$, and a linear calibration may be established where $R(^{18}\text{O})$ measured by OA-ICOS can be converted to $\delta^{18}\text{O}_{\text{VSMOW}}$:

$$\delta^{18}\text{O}_{\text{VSMOW}} = \frac{(\varphi(^{12}\text{C}^{18}\text{O}^{16}\text{O})/\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})) - 0.0039017}{0.00000407919}$$

After the correction with a suitable reference standard, a measurement uncertainty of less than 0.3‰ (1 SE) for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is achieved.

Accuracy can also be estimated from repeated analysis of standards with known composition that are not used as part of a calibration. During analysis of unknown samples over a 2 month period, we analyzed the following standards multiple times: LM4 ($n = 28$), BN13 ($n = 16$), LM1 ($n = 6$), and LM9 ($n = 6$; see Table 1 for standard values). To assess the robustness of the OA-ICOS measurement technique, we applied correction factors and calibration identical to those described above, without allowing for day-to-day variations in instrument behavior or standard-sample-standard corrections. Values obtained for $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ using OA-ICOS for these standards over this period (Table 4) are within the uncertainty of those determined by isotope ratio mass spectrometry (IRMS), except for the average $\delta^{13}\text{C}_{\text{VPDB}}$ value of sample LM9 determined by OA-ICOS, which is slightly higher ($\delta^{13}\text{C}_{\text{VPDB}} = 0.3\text{‰}$) than the accepted value ($\delta^{13}\text{C}_{\text{VPDB}} = -0.6\text{‰}$).

The use of standard-sample-standard bracketing was employed over a 4 h interval in which four standards (BN13, LM1, LM4, and H6M) were measured. BN13 was used to assess drift during the analytical interval. BN13 was used for calibration and indicated that the correction factor required to convert $\varphi(^{13}\text{C}^{16}\text{O}^{16}\text{O})/\varphi(^{12}\text{C}^{16}\text{O}^{16}\text{O})$ to $\delta^{13}\text{C}_{\text{VPDB}}$ was almost identical to that determined at the start of the study (see Figure 3 and Table 3) and did not vary significantly during the analytical session. Using this correction, standards were between -0.2‰ and $+0.4\text{‰}$ (1 SE) of the accepted values for $\delta^{13}\text{C}_{\text{VPDB}}$, with an average variance (accepted – calculated) of 0.03‰ and a standard deviation of 0.18‰ (1 σ). This suggests that analyses of $\delta^{13}\text{C}$ are accurate to within 0.3‰ (1 SE, i.e., similar to the internal precision of analyses) when standard-sample-standard bracketing is employed. Measurements of $\delta^{18}\text{O}_{\text{VSMOW}}$ showed more variation during the analytical session, and four samples of BN13 (of eight total measurements of BN13) were used to correct other samples using simple linear interpolation (Table 5). Following this correction, the average value for BN13 (four unknown samples) was 13.73‰ (accepted value 13.72‰), the average $\delta^{18}\text{O}_{\text{VSMOW}}$ for H6M (two samples) was 3.63‰ (accepted value 3.84‰), the average $\delta^{18}\text{O}_{\text{VSMOW}}$ for LM1 was 19.31‰ (accepted value 18.82‰), and the average $\delta^{18}\text{O}_{\text{VSMOW}}$ for LM4 was 25.70‰ (accepted $\delta^{18}\text{O}_{\text{VSMOW}}$ 26.22‰; see Table 5). This suggests that measurements of $\delta^{18}\text{O}$ are accurate to within 0.5‰ (1 SE) when standard-sample-standard bracketing is employed.

Considering both the internal precision of the analyses (Figure 2) and reproducibility from multiple analyses of the same samples (Tables 4 and 5), we suggest that, even with infrequent calibration, the present prototype OA-ICOS instrument has an intrinsic accuracy of better than 0.6‰ (1 SE) for measurements of $\delta^{18}\text{O}_{\text{VSMOW}}$ and 0.5‰ (1 SE) for measurements of $\delta^{13}\text{C}_{\text{VPDB}}$ and a precision of better than 0.5‰ (1 SE) for measurements of $\delta^{18}\text{O}_{\text{VSMOW}}$ and 0.3‰ (1 SE) for measurements of $\delta^{13}\text{C}_{\text{VPDB}}$. Such accuracy and precision would most likely not be adequate for many paleoclimate applications, which require very high precision data. However, the prototype OA-ICOS instrument that we present here has considerable application in many other fields of interest that utilize carbon and oxygen isotope data. Furthermore, extension of the technique to longer laser wavelengths that access stronger mid-infrared rovibrational transitions offers the potential for even higher sensitivity, precision, and accuracy.

CONCLUSIONS

The carbon and oxygen isotope compositions of CO_2 gas evolved from carbonate minerals with known isotopic compositions have been measured using a novel prototype portable instrument based on off-axis ICOS, a cavity-enhanced laser absorption technique. The results demonstrate that a linear relationship can be defined between the known $\delta^{13}\text{C}_{\text{VPDB}}$ of isotopic standards and the $R(^{13}\text{C})$ ratios measured in CO_2 gas by OA-ICOS and the known $\delta^{18}\text{O}_{\text{VSMOW}}$ of isotopic standards and the $^{12}\text{C}^{18}\text{O}^{16}\text{O}/^{12}\text{C}^{16}\text{O}^{16}\text{O}$ measured in the CO_2 gas (when data are corrected for the variable volume fraction of CO_2). We determined that the measurements are accurate with a total uncertainty of less than 0.6‰ (1 SE) for $\delta^{18}\text{O}_{\text{VSMOW}}$ and 0.5‰ (1 SE) for $\delta^{13}\text{C}_{\text{VPDB}}$, even though the system was not frequently calibrated. The accuracy and precision can be significantly improved by simply using standard-sample-standard bracketing, as is done using conventional laboratory IRMS methods. Furthermore, due to its portability, high throughput, ease of use, low consumable requirements, and low power consumption (150 W), the instrument offers the potential for rapid, real-time isotopic measurements of carbonates in the field.

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