

Use of laser spectroscopy to measure the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of carbonate minerals

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RUNNING TITLE: Stable isotopes in carbonate minerals by laser spectroscopy

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ABSTRACT: The stable carbon and oxygen isotope composition 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 (OA-ICOS), to measure the carbon and oxygen isotope composition of CO_2 gas evolved from the acidification of carbonate minerals. The isotopic specific measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ 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 a known $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions, 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 of better than 0.15 ‰ for $\delta^{13}\text{C}$ and 0.6 ‰ for $\delta^{18}\text{O}$. Analysis of 4 carbonate standards of known isotopic composition over 2 months, determined using the original instrumental calibration, indicates that analyses are accurate. In comparison to CF-IRMS, OA-ICOS offers an extremely cost-effective, low power, and robust mechanism for measuring the stable isotopic composition of carbonate

minerals, as it uses very few consumables, can be used by non-expert users, and the instrument can be easily deployed into field-based research environments.

KEYWORDS: carbonate, mineral, isotope, OA-ICOS, CRDS, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, laser spectroscopy

Introduction

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^{1,2,3,4,5,6,7}. The development of OA-ICOS now offers an alternative to conventional stable isotope ratio mass spectrometry, with the ability to measure isotopic ratios in several gas species (including H_2O , CO_2 , CH_4 , N_2O). The documented advantages of OA-ICOS include relatively low initial capital cost, low power consumption, bench-top size, lack of a high-vacuum system, no requirement for high-purity gases, and relatively simple operation⁵. 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. Stable isotope studies of carbonates have also been used extensively to explore the role of fluid-rock reaction, and geosphere-hydrosphere-atmosphere interactions in the earth and environmental sciences⁸. In this paper, we present the results of measurements of the concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 gas, which was generated from the acidification of calcium carbonate minerals. By analyzing a series of calcium carbonate minerals with known $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions, we are able to demonstrate that OA-ICOS can produce accurate and reproducible measurements of the carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotope composition of carbonate minerals. We suggest that this instrument has applications in any area of research where rapid, high-throughput and low-cost analyses of carbon and/or oxygen isotope compositions of carbonate minerals (or high concentration CO_2 gases) are required, for deployment of instruments in locations which lack appropriate logistical support, and for field-based analysis of carbonate minerals which may become unstable once removed from ambient field conditions.

Methods

Approximately 35 mg of pure CaCO_3 was placed into 12 mL Labco exetainer® brand borosilicate glass vials, sealed with butyl rubber septum. 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 0.1 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 hour in a heated aluminum block.

Following reaction, the inlet to the instrument (Los Gatos Research, 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 firstly “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 in order to remove high concentration CO_2 from the OA-ICOS measurement cell. The entire instrument and sampling line was then pumped down to a pressure of less than 3.5 Torr. Once this pressure was reached, the needle was pushed through the septum, and the CO_2 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 CaCO_3 and H_3PO_4 , and yielding a dry CO_2 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 seconds, 100 mL of dry laboratory air is mixed with the sample of CO_2 to produce a sample of approximately 115 mL of gas with a concentration of $\sim 50,000$ to $\sim 70,000$ ppmv CO_2 .

Prior to each measurement, the instrument automatically purges the measurement cell twice with sample gas before filling the cell to a pressure of about 40 torr. After waiting 30 seconds to allow for equilibration, the instrument determines the values of CO_2 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the sample gas from the measured high-resolution laser absorption spectra, displays the measured multi-line 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 quantify the abundance of different isotopomers of CO₂ (¹²C¹⁶O¹⁶O, ¹³C¹⁶O¹⁶O and ¹²C¹⁶O¹⁸O) simultaneously. The theory of OA-ICOS has been described in detail previously⁹. 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 (~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-linewidth (telecommunications-grade) diode laser over selected near-infrared ro-vibrational absorption transitions of ¹²C¹⁶O¹⁶O, ¹³C¹⁶O¹⁶O and ¹²C¹⁶O¹⁸O, as illustrated in Figure 1. The transmitted light through the measurement cell is focused onto a photodetector, 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 of three species can be calculated from the measured absorption spectra (which is displayed on the instrument monitor), from which the isotopic ratios of carbon (¹³C/¹²C) and oxygen (¹⁸O/¹⁶O) are then extracted continuously.

Isotopic ratios from the LGR instrument are reported using standard delta notation, where:



and



To calibrate the measured ¹³C/¹²C and ¹⁸O/¹⁶O values of the unknown samples reported by the instrument, it was necessary to periodically 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 VSMOW¹⁰. The analyzer is calibrated using the identical treatment principal¹¹, whereby standards with known isotopic compositions are treated in the same manner as samples with unknown isotopic composition. Here, we present the results of analyses of five samples of calcium carbonate, four of which are “in-house” UBC calcium carbonate standards, which have been measured and calibrated relative to the international standards NBS-18 ($\delta^{13}\text{C} = -5.08 \text{ ‰}_{\text{VPDB}}$, $\delta^{18}\text{O} = +7.2 \text{ ‰}_{\text{VSMOW}}$) and NBS-19 ($\delta^{13}\text{C} = +1.92 \text{ ‰}_{\text{VPDB}}$, $\delta^{18}\text{O} = +28.64 \text{ ‰}_{\text{VSMOW}}$) by continuous flow isotope ratio mass spectrometry. The fifth sample is a sample of limestone collected from near Lone Mountain,

Nevada (see Table 1), which was used to examine the reproducibility of data, as this sample 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 instrument, based on OA-ICOS, can accurately measure the carbon and oxygen isotope composition of carbonate minerals, examine factors which influence isotopic measurements, and evaluate the precision of measurements.

Results

The concentration, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$, of CO_2 gas generated from BN13 and LM-4 in the same analytical session are presented in Table 2 and Figure 2. Carbon isotopic ratios show no relationship to CO_2 concentration. Oxygen isotope ratios show a strong, linear dependence on CO_2 concentration, for measurements made between $\sim 30,000$ and $80,000$ ppmv CO_2 (Figure 2, Table 2). Thus, oxygen isotope values can be corrected for samples to a single concentration baseline at which all analyses can be compared relative to the standard values. The internal precision of analyses is strongly dependent on CO_2 concentration (Figure 3), which influences the magnitude of the $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ peak. In our laboratory, the instrument is left running continuously in order that the cell maintains a constant temperature of $\sim 29^\circ\text{C}$. All measurements were recorded after the instrument was allowed to warm up and reach a steady-state temperature, which required approximately 1 to 2 hours.

The comparison of carbon isotope measurements made on 4 calcium carbonate standards using OA-ICOS and the accepted values for standards is shown in Figure 4 (Table 4). Here, samples were analyzed at a constant temperature over several hours ($< 0.1^\circ\text{C}$ variation, Table 4). Oxygen isotope values were corrected for variable CO_2 concentration using the corrections determined in Figure 1, with all concentrations corrected to a baseline of $60,000$ ppmv. An excellent fit is found for the known value of standards and the values determined by OA-ICOS for $\delta^{13}\text{C}$. Thus, a linear correction may be applied, and isotopic ratios calibrated relative to the VPDB scale may be determined, where $\delta^{13}\text{C}_{\text{VPDB}} = \delta^{13}\text{C}_{\text{OA-ICOS}} + 10.0$. Figure 5 shows the comparison of the accepted oxygen isotope values on 4 calcium carbonate standards versus the values determined by OA-ICOS. A strong linear relationship exists between accepted $\delta^{18}\text{O}$ values (on the VSMOW scale) and measured $\delta^{18}\text{O}$ values, and a linear correction may be applied, where $\delta^{18}\text{O}_{\text{VSMOW}} = \delta^{18}\text{O}_{\text{OA-ICOS}} + 27.0$, thus forming a multi-point normalization¹².

Accuracy and precision can be estimated from repeated analysis of standards with known composition which are themselves 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). In order to assess the robustness of the OA-ICOS measurement technique, we applied the identical correction factors and calibration described above, without allowing for day-to-day variations in instrument behaviour. The isotopic ratios for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ obtained using OA-ICOS for these standards over this period (Table 5) are within error of those determined by IRMS, excepting for the average $\delta^{13}\text{C}$ composition of sample LM1 determined by OA-ICOS, which is slightly higher ($\delta^{13}\text{C} = 0.3 \text{ ‰}$) than the accepted value ($\delta^{13}\text{C} = -0.6 \text{ ‰}$). Analytical results could be substantially improved during each analytical session by analyzing several standards of different isotopic composition, which will allow a daily calibration to be applied, as well as allowing temporal drift to be assessed and corrected. In addition, standard – sample – standard bracketing, which is commonly used in IRMS, could be employed. Use of these calibration strategies would improve the accuracy and precision of analyses. Considering both the internal precision of analyses (Figure 2) and reproducibility from multiple analyses of the same samples (Table 5), we suggest that the OA-ICOS has a precision of better than 1 ‰ for measurements of $\delta^{18}\text{O}$ and 0.5 ‰ for measurements of $\delta^{13}\text{C}$. Such precision would be adequate to distinguish isotopic variations for many applications of stable oxygen and carbon isotopes.

Conclusions

The isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) 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 standards with known isotopic values, and the ratios of $^{12}\text{C}^{16}\text{O}^{16}\text{O} : ^{13}\text{C}^{16}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}^{16}\text{O} : ^{12}\text{C}^{16}\text{O}^{18}\text{O}$ measured in the CO_2 gas evolved from those carbonate standards, when data are collected at fixed temperature and corrected for variable CO_2 concentration. With the use of reference standards, we have determined that measurements are accurate, with a precision of better than 1 ‰ for $\delta^{18}\text{O}$ and 0.5 ‰ for $\delta^{13}\text{C}$. While the measurement precision does not currently match that which may be obtained with conventional laboratory IRMS methods, due to its portability, speed and ease of use, low consumable requirements and low power consumption (150 watts), the prototype instrument offers the potential for rapid, real-time measurements in the field without the need for expert technical support.

ACKNOWLEDGMENTS

MDRU authors thank J. Vaughan and K. Li for assisting with analytical work.

FIGURE CAPTIONS

Figure 1: **Feng to add**

Figure 2: Graph of CO₂ concentration (parts per million by volume) plotted against the $\delta^{13}\text{C}$ (a) and $\delta^{18}\text{O}$ compositions (b) of standard BN13 and sample LM-4.

Figure 3: Graph of CO₂ concentration plotted against the internal precision of measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (1 standard error).

Figure 4: Graph of known versus measured $\delta^{13}\text{C}$ (a) and $\delta^{18}\text{O}$ compositions (b) of standards Merck 99.95% CaCO₃, H6M, BN13 and BN83-2.

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Tables

Table 1: Isotopic composition of standards used in this study.

| Standard | $\delta^{13}\text{C}$ (‰, VPDB) | $\delta^{18}\text{O}$ (‰, VSMOW) |
|------------------------------|---------------------------------|----------------------------------|
| Merck 99.95% CaCO_3 | -35.25 | 13.15 |
| H6M | -0.692 | 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: Concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 gas generated from BN13 and LM-4. Analysis numbers (#) 1-10 were carried out using 85% H_3PO_4 , analyses 11-20 were carried out using 99% H_3PO_4 .

| # | Sample | Press | T_°C | [$^{12}\text{CO}_2$] | [$^{13}\text{CO}_2$] | [$^{12}\text{C}^{16}\text{O}^{18}\text{O}$] | [CO_2] | $\delta^{13}\text{C}$ | s.e. | $\delta^{18}\text{O}$ | s.e. | Corr $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ |
|----|--------|-------|-------|------------------------|------------------------|---|-------------------|-----------------------|------|-----------------------|------|----------------------------|-----------------------|-----------------------|
| 1 | LM4 | 39.11 | 29.10 | 26651 | 297 | 107 | 27072 | -7.3 | 0.3 | 1.8 | 1.2 | -2.3 | 2.7 | 24.3 |
| 2 | BN13 | 39.07 | 29.09 | 32385 | 360 | 128 | 32898 | -8.6 | 0.2 | -9.8 | 1.0 | -13.1 | 1.4 | 13.9 |
| 3 | LM4 | 39.10 | 29.10 | 71514 | 797 | 286 | 72651 | -8.3 | 0.1 | -3.3 | 0.4 | -1.7 | 1.7 | 25.3 |
| 4 | BN13 | 39.00 | 29.10 | 68131 | 759 | 269 | 69215 | -8.5 | 0.1 | - | 0.5 | -13.2 | 1.5 | 13.8 |
| 5 | LM4 | 39.10 | 29.08 | 69475 | 774 | 277 | 70575 | -8.3 | 0.1 | -4.3 | 0.5 | -3.0 | 1.7 | 24 |
| 6 | BN13 | 39.10 | 29.00 | 69925 | 779 | 276 | 71032 | -8.5 | 0.1 | - | 0.5 | -14.1 | 1.5 | 12.9 |
| 7 | LM4 | 39.10 | 29.00 | 74004 | 824 | 296 | 75176 | -8.6 | 0.1 | -3.5 | 0.5 | -1.6 | 1.4 | 25.4 |
| 8 | BN13 | 39.10 | 29.00 | 68994 | 769 | 273 | 70089 | -8.5 | 0.1 | - | 0.5 | -13.0 | 1.5 | 14 |
| 9 | LM4 | 39.10 | 29.00 | 69791 | 777 | 279 | 70898 | -8.7 | 0.1 | -3.2 | 0.4 | -1.8 | 1.3 | 25.2 |
| 10 | BN13 | 39.10 | 29.00 | 70435 | 784 | 278 | 71546 | -8.8 | 0.1 | - | 0.5 | -13.4 | 1.2 | 13.6 |
| 11 | LM4 | 39.00 | 29.00 | 45590 | 508 | 182 | 46313 | -8.6 | 0.2 | -0.7 | 0.7 | -2.4 | 1.4 | 24.6 |
| 12 | BN13 | 39.10 | 29.08 | 60517 | 674 | 239 | 61474 | -8.6 | 0.1 | - | 0.5 | -14.2 | 1.4 | 12.8 |
| 13 | LM4 | 39.09 | 29.07 | 66040 | 736 | 264 | 67089 | -8.7 | 0.1 | -3.2 | 0.5 | -2.3 | 1.3 | 24.7 |
| 14 | BN13 | 39.10 | 29.00 | 57238 | 637 | 226 | 58147 | -8.9 | 0.1 | - | 0.6 | -13.7 | 1.1 | 13.3 |
| 15 | LM4 | 39.10 | 29.00 | 61869 | 689 | 247 | 62851 | -8.7 | 0.1 | -2.1 | 0.5 | -1.7 | 1.3 | 25.3 |
| 16 | BN13 | 39.05 | 29.00 | 61706 | 687 | 244 | 62684 | -8.7 | 0.1 | - | 0.5 | -13.5 | 1.3 | 13.5 |
| 17 | LM4 | 39.10 | 29.00 | 57609 | 642 | 230 | 58522 | -8.4 | 0.2 | -1.7 | 0.5 | -1.8 | 1.6 | 25.2 |
| 18 | BN13 | 39.08 | 29.00 | 57894 | 645 | 229 | 58815 | -8.7 | 0.1 | - | 0.5 | -12.8 | 1.3 | 14.2 |
| 19 | LM4 | 39.10 | 29.00 | 40753 | 453 | 163 | 41402 | -9.0 | 0.2 | -0.3 | 0.8 | -2.6 | 1.0 | 24.4 |
| 20 | BN13 | 39.04 | 29.00 | 64188 | 715 | 254 | 65208 | -8.8 | 0.1 | - | 0.5 | -12.5 | 1.2 | 13.5 |

Table 3: Concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 gas generated from BN13 and LM-4 with variable ICOS cell temperature. Samples were acidified with 85% H_3PO_4 .

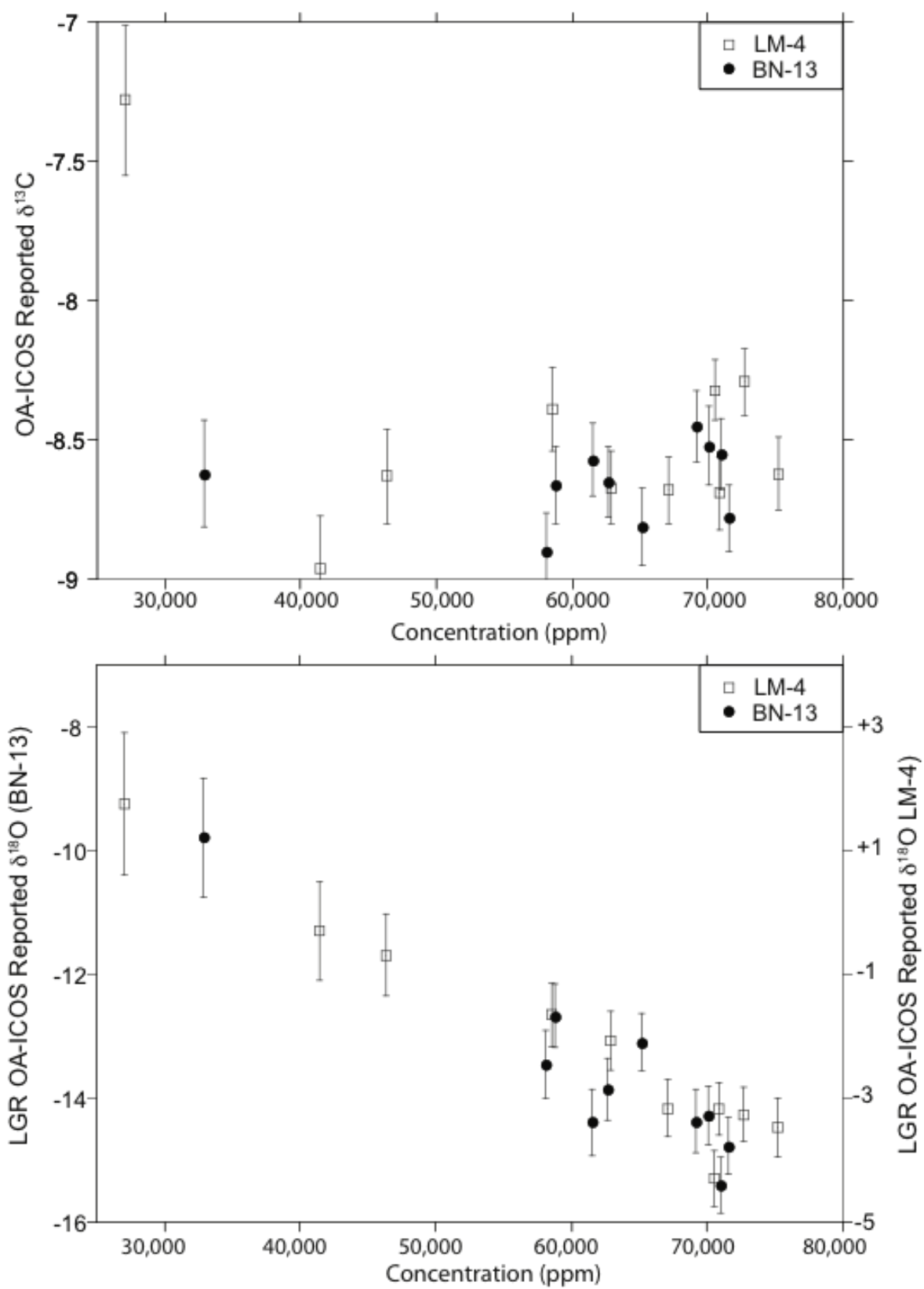
| # | Sample | Press | T_°C | [$^{12}\text{CO}_2$] | [$^{13}\text{CO}_2$] | [$^{12}\text{C}^{16}\text{O}^{18}\text{O}$] | [CO_2] | $\delta^{13}\text{C}$ | s.e. | $\delta^{18}\text{O}$ | s.e. | Corr $\delta^{18}\text{O}$ |
|----|--------|-------|-------|------------------------|------------------------|---|-------------------|-----------------------|------|-----------------------|------|----------------------------|
| 1 | LM4 | 39.13 | 25.14 | 62527 | 698 | 251 | 63523 | -6.3 | 0.2 | 0.8 | 0.7 | 1.3 |
| 2 | LM4 | 39.05 | 25.57 | 77108 | 861 | 309 | 78336 | -6.6 | 0.1 | -0.4 | 0.3 | 1.9 |
| 3 | BN13 | 39.04 | 25.96 | 57155 | 637 | 226 | 58061 | -7.3 | 0.1 | - | 0.2 | -12.1 |
| 4 | LM4 | 39.05 | 26.30 | 55111 | 614 | 221 | 55987 | -7.5 | 0.1 | -0.5 | 0.2 | -1.0 |
| 5 | BN13 | 39.09 | 26.60 | 61589 | 687 | 244 | 62566 | -7.7 | 0.1 | - | 0.2 | -11.8 |
| 6 | LM4 | 39.05 | 26.86 | 69130 | 771 | 276 | 70229 | -8.0 | 0.1 | -2.6 | 0.2 | -1.4 |
| 7 | BN13 | 39.07 | 27.16 | 57335 | 639 | 227 | 58243 | -8.0 | 0.2 | - | 0.8 | -12.6 |
| 8 | LM4 | 39.07 | 27.34 | 63107 | 703 | 252 | 64110 | -8.2 | 0.1 | -2.0 | 0.5 | -1.5 |
| 9 | BN13 | 39.10 | 27.50 | 57598 | 642 | 228 | 58511 | -8.4 | 0.1 | - | 0.5 | -12.7 |
| 10 | LM4 | 39.06 | 27.63 | 60611 | 675 | 242 | 61573 | -8.3 | 0.1 | -3.1 | 0.5 | -2.9 |

Table 4: Concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 gas generated from standards BN13, BN83-2, H6M and Merck. 85% H_3PO_4 was used for all samples.

| Sample | Press | T_°C | [$^{12}\text{CO}_2$] | [$^{13}\text{CO}_2$] | [$^{12}\text{C}^{16}\text{O}^{18}\text{O}$] | [CO_2] | $\delta^{13}\text{C}$ | s.e. | $\delta^{18}\text{O}$ | s.e. | Corr $\delta^{18}\text{O}$ | $\delta^{13}\text{C}$ | $\delta^{18}\text{O}$ |
|--------|-------|-------|------------------------|------------------------|---|-------------------|-----------------------|------|-----------------------|------|----------------------------|-----------------------|-----------------------|
| BN13 | 39.12 | 29.09 | 65428 | 729 | 259 | 66465 | -7.8 | 0.1 | -14.1 | 0.4 | -13.3 | 2.2 | 13.7 |
| BN13 | 39.11 | 29.14 | 66637 | 743 | 263 | 67693 | -8.2 | 0.1 | -14.6 | 0.4 | -13.6 | 1.8 | 13.4 |
| BN83 | 39.09 | 29.07 | 66457 | 742 | 264 | 67513 | -5.6 | 0.1 | -8.4 | 0.4 | -7.5 | 4.4 | 19.5 |
| BN83 | 39.19 | 29.16 | 61742 | 690 | 246 | 62723 | -5.8 | 0.1 | -7.7 | 0.5 | -7.3 | 4.2 | 19.7 |
| H6M | 39.13 | 29.11 | 68147 | 757 | 266 | 69221 | -10.9 | 0.1 | -24.5 | 0.4 | -23.4 | -0.9 | 3.6 |
| H6M | 39.15 | 29.15 | 61151 | 679 | 239 | 62115 | -11.2 | 0.1 | -23.4 | 0.5 | -23.1 | -1.2 | 3.9 |
| Merck | 39.13 | 29.10 | 71171 | 764 | 281 | 72268 | -45.1 | 0.1 | -15.4 | 0.4 | -13.9 | -35.1 | 13.1 |
| Merck | 39.22 | 29.15 | 65632 | 704 | 259 | 66644 | -45.3 | 0.1 | -14.2 | 0.4 | -13.3 | -35.3 | 13.7 |

Table 5: Isotopic ratios (average $\pm 1 = \sigma$) determined by OA-ICOS (and accepted isotopic values determined by IRMS) for 4 different standard materials over a three month period using a universal (rather than daily) calibration.

| Standard | $\delta^{13}\text{C}$ (OA-ICOS) | $\pm 1 \sigma$ | Accepted $\delta^{13}\text{C}$ (IRMS) | $\delta^{18}\text{O}$ (OA-ICOS) | $\pm 1 \sigma$ | Accepted $\delta^{18}\text{O}$ (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 |



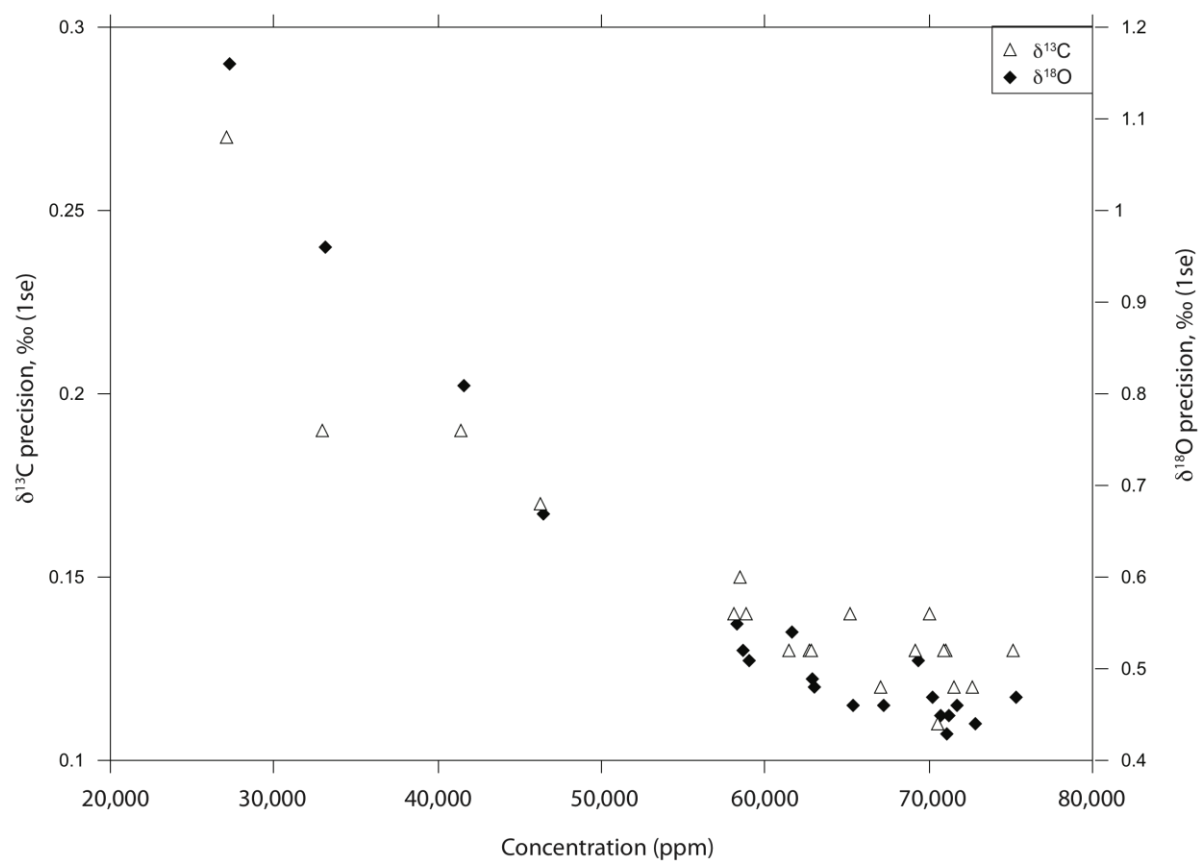


Figure 2

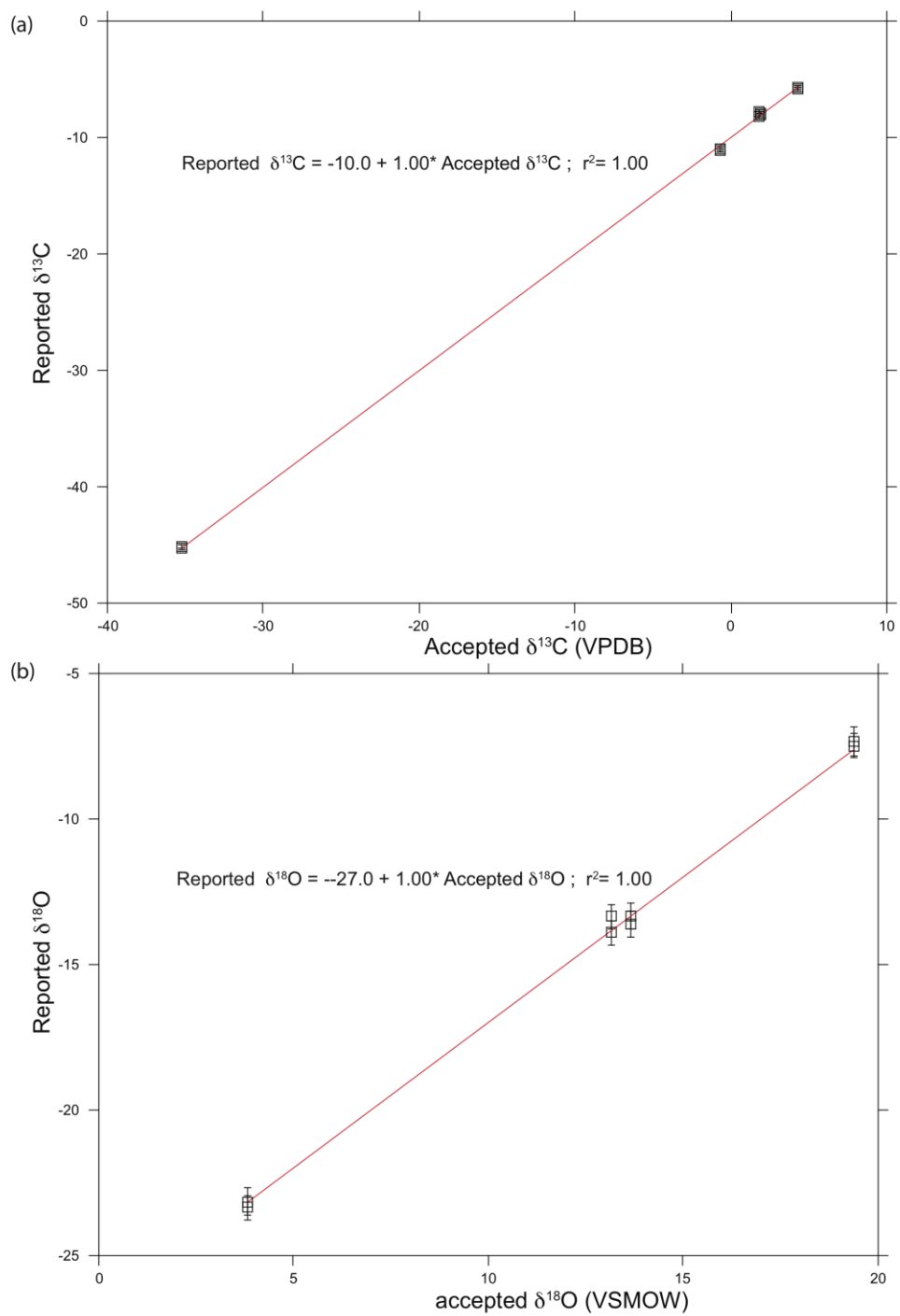


Figure 4