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Measurement of δ^{18}O and δ^2H values of fluid inclusion water in speleothems using cavity ring-down spectroscopy compared with isotope ratio mass spectrometry

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RATIONALE: The hydrogen and oxygen isotopic analyses (δ^2H and δ^{18}O values) of water trapped within speleothem carbonate (fluid inclusions) have traditionally been conducted utilizing dual-inlet isotope ratio mass spectrometry (IRMS) or continuous-flow (CF)-IRMS methods. The application of cavity ring-down spectroscopy (CRDS) to the δ^2H and δ^{18}O analysis of water in fluid inclusions has been investigated at the University of Miami as an alternative method to CF-IRMS.
METHODS: An extraction line was developed to recover water from the fluid inclusions consisting of a crusher, sample injection port and an expansion volume (either 100 or 50 cm^3) directly connected to the CRDS instrument. Tests were conducted to determine the reproducibility of standard water injections and crushes. In order to compare results with conventional analytical methods, samples were analyzed both at the University of Miami (CRDS method) and at the Vrije Universiteit Amsterdam (CF-IRMS method).
RESULTS: The analytical reproducibility of speleothem samples crushed on the Miami Device demonstrates an average external standard deviation of 0.5 and 2.0 ‰ for δ^{18}O and δ^2H values, respectively. Sample data are shown to fall near the global meteoric water line, supporting the validity of the method. Three different samples were analyzed at Vrije Universiteit Amsterdam and the University of Miami in order to compare the performance of each laboratory. The average offset between the two laboratories is 0.7 ‰ for δ^{18}O and 2.5 ‰ for δ^2H.
CONCLUSIONS: The advantage of CRDS is that the system is a low-cost alternative to CF-IRMS for fluid inclusion isotope analysis. The CRDS method demonstrates acceptable precision and good agreement with results from the CF-IRMS method. These are promising results for the future application of CRDS to fluid inclusion isotope analysis.

The δ^2H and δ^{18}O analyses of waters obtained from fluid inclusions are able to provide additional insights into the conditions prevailing at the time of mineral formation when combined with conventional δ^{18}O analysis of the solid phase. For example, determining the δ^{18}O values of both the trapped fluid and the accompanying mineral, and assuming that the δ^{18}O value of the trapped water represents that of the fluids at the time of formation, allows the temperature of mineral formation to be determined.[1]

The δ^2H and δ^{18}O measurement of fluid inclusions is a two-step process: (i) the extraction of water from the sample and (ii) the actual O and H isotopic analysis. The first step can be achieved either through thermal decrepitation or by crushing the sample. Thermal decrepitation releases trapped water by heating the fluid bearing sample to a high temperature.[2] While this method has proven to be effective in speleothem studies,[3] there are limitations to this technique including inter-laboratory offsets[2,4] arising from variations in the extraction temperature,[4] isotopic exchange at high temperature and fractionation during the thermal decrepitation process. Crushing of the sample under vacuum or a flow of a carrier gas, such as He, also allows the H_2O to be released and is considered to be the preferred method, as it potentially avoids some of the problems associated with thermal decrepitation.[5,6]

For the isotopic analysis of the released water, previous speleothem fluid inclusion isotopic studies relied first on dual-inlet isotope ratio mass spectrometry[2,4,5] and, more recently, on continuous-flow isotope ratio mass spectrometry (CF-IRMS).[7–9] Both methods require conversion of the water vapor into molecular species suitable for O and H isotopic analysis. The development of CF-IRMS allowed for faster analysis on smaller samples and a precision similar to that achieved using dual-inlet methods.[7,9,10] One of the first successful systems which combines crushing with CF-IRMS was developed by Vonhof *et al.*[9] at the Vrije Universiteit (VU) in Amsterdam. The Amsterdam Device consists of a crusher, cold trap and a flash heater to heat the trapped water, subsequently directed by the carrier gas to the inlet of a Finnigan TC-EA furnace (High-Temperature Conversion-Elemental Analyzer, Thermo Scientific, Bremen, Germany). Within the TC-EA, the water vapor is converted into CO

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and H_2 by reaction with glassy carbon and the products are then separated using a packed gas chromatographic column before analysis using IRMS.[10] A similar method was employed by Dublyansky and Spötl[7] also using CF-IRMS and both laboratories are capable of analyzing small amounts of water (0.1–0.2 μL) with typical standard deviations of 0.5 ‰ for δ^{18}O values and 1.5 ‰ for δ^2H values.[8] Although these systems have been applied to paleoclimate studies,[7,8,11,12] there is an observed inter-laboratory offset of 1 ‰ for δ^{18}O values and 3 ‰ for δ^2H values.[8]

This paper describes the first application of cavity ring-down spectroscopy (CRDS) to fluid inclusion isotopic analysis. We have constructed a fluid inclusion water extraction device (Miami Device) based on the Amsterdam Device and interfaced to a model L2130-i water isotope analyzer (Picarro, Inc., Santa Clara, CA, USA). The important difference between the IRMS method and the CRDS method is that the latter does not require conversion of the water into other molecular species; rather the CRDS technique utilizes the absorption of a specific wavelength of laser light corresponding to the vibrational frequency of the $H_2^{16}O$, $^2H^1H^{16}O$ and $H_2^{18}O$ molecules. The precision of water isotopic analysis utilizing the CRDS systems has been demonstrated to be superior to that of traditional IRMS systems.[13] The motivation to conduct fluid inclusion isotopic analysis by CRDS is driven by the potential that this system offers for faster analysis, less maintenance arising from simpler sample processing, and comparable precision.

DESIGN OF THE SYSTEM

The Miami Device

The Miami Device consists of a piston to crush the calcite and release the water from within the sample, a stainless steel line and a volume reservoir which is connected to the CRDS instrument. This design utilizes aspects of the Amsterdam Device as outlined in Vonhof *et al*.[9] as well as a Picarro vaporizer unit (A0211), which consists of a heated 150 cm^3 volume reservoir through which N_2 gas has been flushed. The liquid water sample is directly injected into the volume. After injection the volume is opened to the CRDS analyzer and the water enters the instrument. The large volume provides a continuous stable signal of water on which the δ^{18}O and δ^2H values can be measured.

The Miami Device extraction line is constructed entirely of stainless steel 1/8" external diameter tubing (SS-T2-S-6ME, Swagelok, Mulberry, FL, USA), with the exception of 1/4" stainless steel tubing (Swagelok SS-T4-S-6ME) connecting the volume to the crusher. The entire extraction line is heated with nickel-chromium resistance heating wire with fiberglass sleeving (NI80-015, FBGS-N-22, OMEGA Engineering, Stamford, CT, USA) which ensures that there are no cold spots where water vapor can condense. Heating of the crusher unit is accomplished by a 100 W cartridge heater inserted into a base plate on which the crusher valve rests. The temperature is monitored throughout the line and at the crusher unit to ensure uniform heating throughout. The temperature is maintained at 115 °C during analysis which represents the ideal temperature to limit adsorption of fluid inclusion water on calcite directly after crushing.[7,9]

Crusher

The crusher consists of a modified 3/8" Nupro vacuum valve (Swagelok SS-6BG) (Fig. 1(b)) with the valve seat replaced by a steel piston, which slides into a customized valve body milled to accommodate it. In order to crush the sample, the valve stem is turned to lower the piston to crush the sample and release the water within the calcite. A 0.5 μm pore size (Swagelok SS-2 F-05) in-line filter is located adjacent to the crusher to prevent particles of the crushed calcite sample from contaminating the downstream line and potentially entering the CRDS analyzer.

Water injection port

An injection port consisting of a septum (Swagelok SS-4-T) is fitted before the crusher and allows for the introduction of 0.1 to 1.2 μL standard water from a 5 μL syringe (Fig. 1).

Expansion volume

In order to mimic the design of the Picarro vaporizer, a 100 cm^3 or 50 cm^3 stainless steel expansion volume (Quality Float Works, Inc., Schaumburg, IL, USA) (Fig. 1(c)) is placed downstream of the crusher. The volume can be isolated from the CRDS instrument and the crusher utilizing two Swagelok Nupro SS-4H valves (valves 4 and 5, Fig. 1).

Vacuum and vent connections

Between the crusher and the expansion volume a vacuum pump connection (KNF 84.4, KNF Neuberger, Inc., Trenton, NJ, USA) allows residual water vapor to be removed from the extraction line between crushed samples or injections of standard waters. The carrier gas can be isolated during line maintenance using a Swagelok SS-2P4T valve (valve 1, Fig. 1) and the carrier gas can be vented to prevent excess pressure from entering the CRDS instrument (valve 2, Fig. 1).

PROTOCOL FOR ANALYSIS

For a typical analysis, the sample (in the case of this study, a stalagmite specimen) is subsampled utilizing a diamond band saw producing a calcite chip typically between 0.2 and 0.8 g, with the size being dependent on the amount of water present in the sample (ideally between 0.3 and 1.0 μL). The calcite chip is then loaded and the crusher is connected to the N_2 supply. A crush is initiated once the temperature of the extraction line reaches 115 °C and the background water concentration in the CRDS isotope analyzer is <150 ppm. The sample is then crushed to a fine powder. After the crush, water is carried to the expansion volume and into the L2130-i analyzer (Picarro). Once the concentration reaches 1000 ppm H_2O as measured using the CRDS instrument, the valve between the volume and the crusher (valve 4, Fig. 1) is closed. Water vapor continues to enter the analyzer from the expansion volume, and the concentration rises to values between 4000 and 20, 000 ppm depending on the size of the sample being crushed and its water concentration. If valve 4 is closed when the concentration of H_2O exceeds 1000 ppm, the sample would flush through the CRDS water isotope analyzer too quickly and a stable measurement would not be attained. After at least 250 s of measurement, the valve

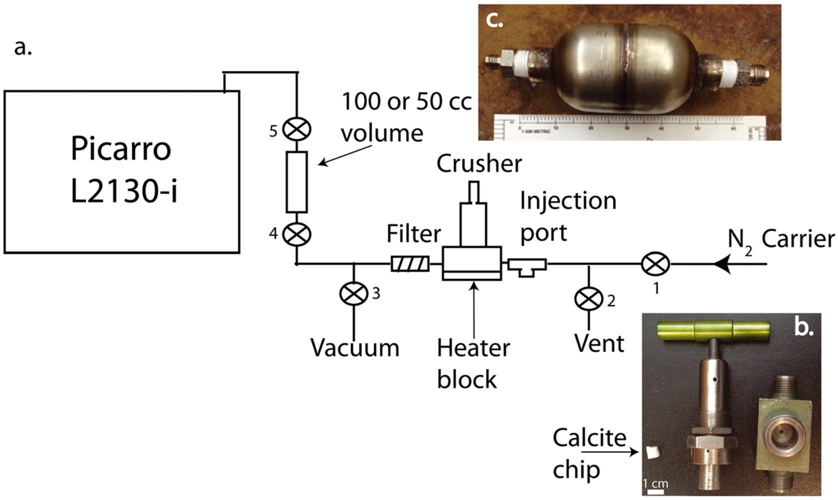

Figure 1. The design of the Miami Device. (a) Schematic of the 'Miami Device'. The entire line is heated (~115 °C) to minimize absorption of water. Alternative designs which were tested are presented in the Supporting Information. (b) Photograph of the modified valve unit showing the steel piston and the valve body which has been drilled to accommodate the piston. The piston is raised and lowered using the valve stem. Also shown is a typical calcite cube to be crushed, the sample weighed 0.4 g. The crusher assembly can accommodate samples up to 1.3 cm^3 and can be disconnected for sample exchange. (c) Photograph of the 100 cm^3 volume, made by Quality Float Works, Inc. The 50 cm^3 volume is similar in shape and length.

closest to the CRDS analyzer is closed (valve 5, Fig. 1), the valve between the crusher and the volume (valve 4) is opened and the N_2 gas isolated (valve 1). This allows the crusher and volume to be evacuated to remove residual water vapor between samples. After pumping the line for approximately 60 s, the extraction line and the CRDS instrument are purged with the carrier gas. The next injection or crush can start once the background reaches <150 ppm H_2O, thereby allowing for five or six individual analyses per hour.

For standard water injections, water is injected through the water injection port (Swagelok SS-4-T) allowing for the introduction of 0.1 to 1.2 μL standard water through a septum (Fig. 1). The procedure for a standard water injection is the same as that described above for a sample crush.

For each individual rock sample analyzed there is a set protocol involving a series of standard injections before and after the rock is crushed. Prior to crushing the sample, the extraction line is first conditioned with 2 to 4 standard water injections (0.5 μL) with the isotopic compositions of the waters ideally not being too far from that expected in the crushed sample. The sample is then crushed, followed by two or more standard water injections in which the injection amount matches that released by the crush. This is because, as observed in other systems, the raw δ^2H and δ^{18}O values vary with the amount of water introduced, with a marked decrease in δ^2H and δ^{18}O values for smaller samples (Figs. 2(a) and 2(b)).[7] In the case of oxygen and hydrogen, for both the 100 and 50 cm^3 volumes, a decrease in isotopic value is associated with smaller sample size (Fig. 2), although the decrease is not as pronounced for δ^{18}O values. Plotting the δ^2H or δ^{18}O values versus 1/concentration, the data falls on a linear relationship (Figs. 2(c) and 2(d)), as has been observed for other CRDS instruments.[14] In order to correct for the size offset, directly after a crush, between two and four standard waters close in size to that of the crush are injected. The isotope crush data are then corrected for any offset as a result of size. In addition, this procedure allows us to assess whether any water adhered to the freshly crushed calcite.[9] This correction method is similar to that followed at VU. In total, with two to four injections prior to the crush, followed by the crush and two or more injections after the crush, the entire process takes between 1 and 2 h.

After the measurement cycle, the crusher is removed from the line, the contents are exchanged for a new sample, and the crusher reconnected to the extraction line. The line is purged with dry N_2 for approximately 30 to 60 min to remove adhered water vapor before the next measurement cycle.

Calibration

Calibration is conducted utilizing a series of four laboratory standard waters, previously calibrated using the Vienna Standard Mean Ocean Water scale (VSMOW), Greenland Ice Sheet Precipitation (GISP), and Standard Light Antarctic Precipitation (SLAP). An injection size of 0.5 μL was chosen because smaller samples exhibit a larger standard deviation in their δ^2H and δ^{18}O values (Fig. 2). Johnson *et al*. noted a significant increase in measurement errors below 2500 ppm, corresponding to approximately 0.1 μL for the Picarro water vapor analyzer, similar to what has been observed with the Miami Device.[14]

DATA REDUCTION

The Picarro software continually collects data when the instrument is operating regardless of whether there is a sample being measured and hence data reduction consists

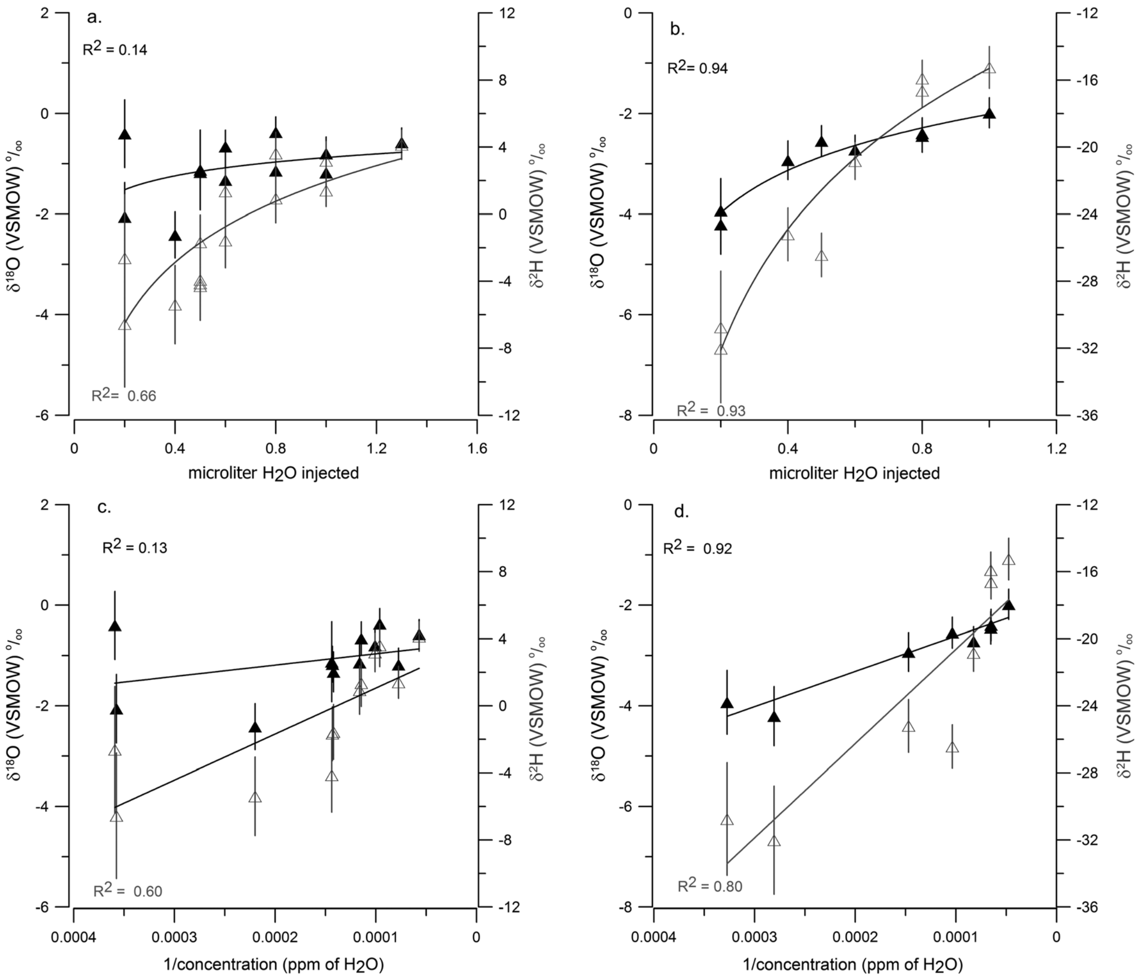

Figure 2. Standard water injections at variable injection amounts. For information on the standard waters, see Supporting Information. (a) Oxygen (filled black triangles) and hydrogen (grey open triangles) isotope ratio values for standard water LS at variable water injection amounts using the 100 cm^3 volume. (b) Oxygen (filled triangles) and hydrogen (grey open triangles) isotope ratio values for standard water LS4 at variable water injection amounts using the 50 cm^3 volume. Regression lines are logarithmic fit to the data with R^2 values. Grey R^2 values correspond to hydrogen isotope data, black R^2 values correspond to oxygen isotope data. (c) Oxygen (filled triangles) and hydrogen (grey open triangles) isotope ratio values for standard water LS using the 100 cm^3 volume plotted versus 1/concentration of water in ppm. (d) Oxygen (filled triangles) and hydrogen (grey open triangles) isotope ratio values for standard water LS4 using the 50 cm^3 volume plotted versus 1/concentration of water in ppm. Regression lines are linear fit to the data with R^2 values. Grey R^2 values correspond to hydrogen isotope data, black R^2 values correspond to oxygen isotope data. All isotope ratios are relative to VSMOW. Vertical error bars represent standard deviation associated with the sample isotopic value.

of accessing the appropriate data file and averaging the signal for each crush or injection. A typical output from the data file of the concentration of water and the corresponding δ^{18}O and δ^{2}H signal is shown in Fig. 3. For the purposes of this paper, data (H_2O ppm, δ^{18}O and δ^{2}H values) are averaged 2 min after the crushed or injected sample is introduced, as this is the amount of time required for the sample to reach the water analyzer and then stabilize. Integration continues up to 1 min before the sample is flushed away. Integration of data over longer periods produced no significant change in the δ^{18}O and δ^{2}H values (the results are provided in Supplementary Fig. S4 and Supplementary Table S2, Supporting Information). This data reduction scheme has been compared with that of a water injection introduced through the Picarro vaporizer unit in Supplementary Fig. S3 (Supporting Information) and demonstrates similar results for the Picarro vaporizer unit and the Miami Device. Raw data are then corrected to VSMOW using the calibration line established between known and measured values of the injected waters. In the case of a crush, the data have been corrected for any size effects (see previous discussion).

RESULTS

Results for standard water injections and crushed samples for both the 100 and the 50 cm^3 volume are presented. In addition, data are presented of an inter-laboratory comparison based on the same speleothem samples analyzed at the University of Miami utilizing CRDS (UM) and at Vrije Universiteit Amsterdam utilizing IRMS (VU).

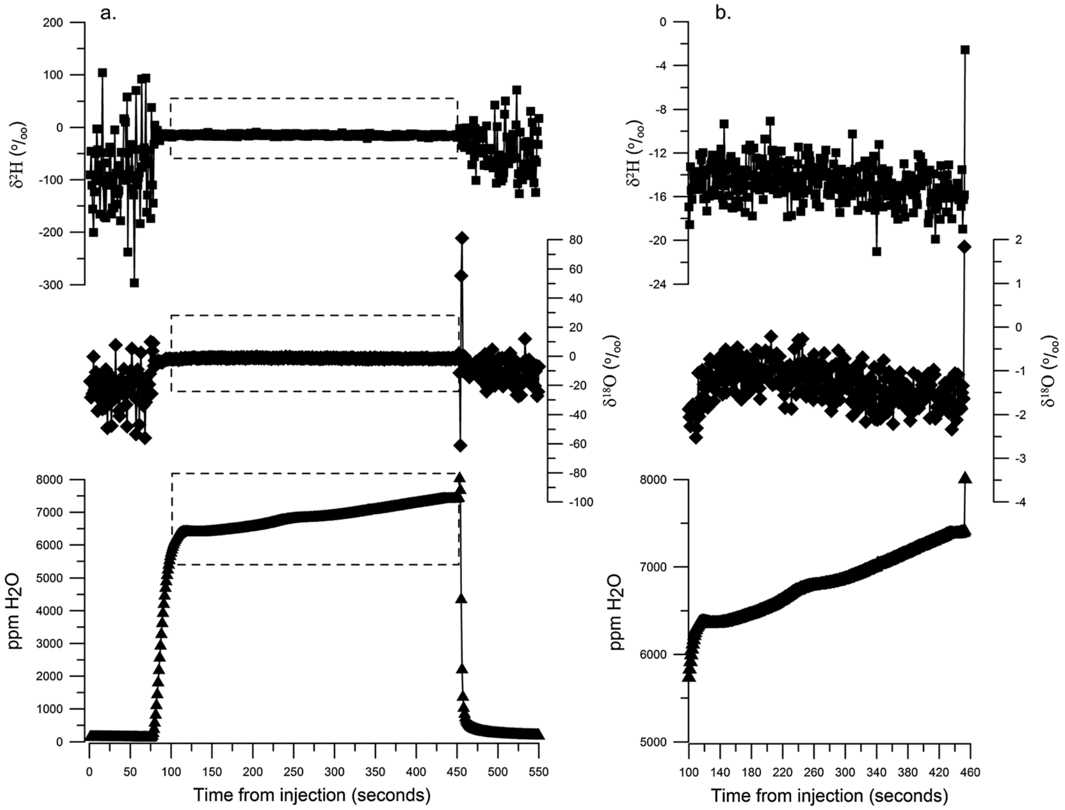

Figure 3. Water concentration, oxygen and hydrogen isotopes from a typical injection. (a) The concentration of water (black triangles) with the corresponding $\delta^{18}O$ values (black diamonds, instrument scale) and $\delta^{2}H$ values (black squares, instrument scale) from a typical injection, demonstrating the time for the sample to reach the water isotope analyzer, stabilize and be pumped out using the method outlined in the text. Time represents seconds since injection. (b) Close up of the water concentration, $\delta^{18}O$ and $\delta^{2}H$ data from the dashed square in (a). The standard deviation of the concentration of H_2O during the analysis is ~150 ppm, which is close to that expected in this instrument.

Reproducibility

Injections

For calibration, four standard waters with a range of $\delta^{18}O$ and $\delta^{2}H$ values are each injected two or three times. The average standard deviations for all injections are 0.4 ‰ for $\delta^{18}O$ values and 1.1‰ for $\delta^{2}H$ values (see Supporting Information). Injection sizes are approximately 0.5 µL, yielding an apparent concentration of ~6000 and 9000 ppm of water in the 100 and 50 cm^3 volumes. Similar results are obtained for the raw $\delta^{18}O$ and $\delta^{2}H$ values using the two volumes. As a result of the higher concentration of water using the 50 cm^3 volume, better precisions are achievable in the case of smaller samples (0.1–0.3 µL) for both $\delta^{18}O$ and $\delta^{2}H$ values (Fig. 2).

Crushes

In order to determine the precision of fluid inclusion isotopic analyses, repeated crushes have been conducted for both the 100 and the 50 cm^3 volumes using the samples described in Table 1. Although all the samples analyzed in this study are calcite speleothems, the method can also be applied to aragonite materials. For the 100 cm^3 volume, samples DCF and HBC2 were analyzed. The average $\delta^{18}O$ and $\delta^{2}H$ values for these samples are similar, not unexpectedly considering that the samples were collected from closely situated islands on the Bahamas platform (Table 2(a)). On average, for 0.5 g of calcite analyzed, the samples yielded about 0.4 µL of H_2O.

Table 1. Description of speleothem samples analyzed for fluid inclusion isotopes. Samples chosen for this study are from a range of localities and are both stalagmites and flowstones

Sample ID	Type of speleothem	Cave	Location
DCF	Flowstone	Dan's Cave	Abaco, Bahamas
HBC2	Flowstone	Hatchet Bay	Eleuthera, Bahamas
SCF	Flowstone	Scladina	Belgium
DC-S	Stalagmite	Dan's Cave	Abaco, Bahamas
HS	Stalagmite	Huagapo	Peruvian Andes

Table 2. (a) Reproducibility tests of repeated analysis of fluid inclusion isotopes from two flowstones (DCF and HBC2) utilizing the 100 cm^3 volume. The δ^{18}O and δ^2H values are corrected to VSMOW and have been corrected for size as outlined in the text. The DCF sample analyzed on 2/13/2013 is an outlier due to low water content. The amount of water released from the sample was 0.1 μL. (b) Reproducibility tests of repeated analysis of fluid inclusion water from three speleothems (DCF, HS and SCF) utilizing the 50 cm^{3}volume. The δ^{18}O and δ^2H values are corrected to VSMOW and have been corrected for size. Also shown are averages and standard deviations for each sample, sample size and water content

(a)

Date	Sample ID	Sample size (g)	δ^{18}O (‰)	δ^2H (‰)	outlier δ^{18}O (‰)	outlier δ^2H (‰)	Water content (μL/g $CaCO_3$)
1/21/2013	DCF	0.7	–3.6	–13.7			0.9
1/22/2013	DCF	0.6	–3.8	–11.8			1.0
1/30/2013	DCF	0.5	–3.8	–18.6			1.3
2/7/2013	DCF	0.4	–3.1	–13.6			0.6
2/13/2013	DCF	0.4			–3.5	–10.7	0.2
2/12/2013	DCF	0.5			–4.6	–27.3	0.3
	Average	*0.5*	*–3.6*	*–14.4*			*0.7*
	SD		*0.4*	*2.9*			
1/21/2013	HBC2	0.8	–4.8	–10.2			0.6
1/24/2013	HBC2	0.5	–4.2	–18.4			0.5
1/28/2013	HBC2	0.6	–3.2	–16.3			0.8
2/6/2013	HBC2	0.5	–4.4	–11.9			1.2
2/8/2013	HBC2	0.3	–4.0	–13.7			1.0
2/13/2013	HBC2	0.5	–5.3	–16.3			0.8
2/18/2013	HBC2	0.3	–4.2	–15.7			1.0
	Average	*0.5*	*–4.3*	*–14.7*			*0.8*
	SD		*0.7*	*2.9*			

(b)

Date	Sample ID	Sample size (g)	δ^{18}O (‰)	δ^2H (‰)	outlier δ^{18}O (‰)	outlier δ^2H (‰)	Water content (μL/g $CaCO_3$)
2/19/2013	DCF	0.6	–3.5	–16.1			0.8
2/23/2013	DCF	0.4	–4.6	–19.8			0.3
2/27/2013	DCF	0.5	–3.3	–15.5			0.6
	Average	*0.5*	*–3.8*	*–17.1*			*0.6*
	SD		*0.7*	*2.4*			
2/23/2013	HS	0.4	–14.8	–105.2			3.0
2/25/2013	HS	0.3	–14.5	–104.9			3.2
2/28/2013	HS	0.3	–14.7	–105.9			3.9
5/8/2013	HS	0.2	–13.8	–105.3			3.5
	Average	*0.3*	*–14.5*	*–105.3*			*3.4*
	SD		*0.5*	*0.4*			
2/19/2013	SCF	0.5	–9.4	–56.4			2.0
2/20/2013	SCF	0.3	–8.3	–57.5			1.1
2/20/2013	SCF	0.3	–9.8	–61.0			1.2
2/26/2013	SCF	0.3	–8.5	–60.5			0.9
2/27/2013	SCF	0.5			−10.4	−70.6	0.9
2/28/2013	SCF	0.4	–9.0	–58.6			0.8
4/28/2013	SCF	0.3	–8.6	–59.2			1.0
5/8/2013	SCF	0.3	–8.9	–59.4			1.0
	Average	*0.4*	*–8.9*	*–58.9*			*1.1*
	SD		*0.5*	*1.6*			

For the 50 cm^3 volume, DCF, Scladina, and Huagapo samples were analyzed. The average δ^{18}O and δ^2H values for the DCF sample agree within error of the results from the 100 cm^3 volume for the same sample (Table 2(b)). The average δ^{18}O and δ^2H values for sample HS are –14.5 ‰ (±0.5 ‰) and –105.3 ‰ (±0.4 ‰) ($n = 4$), respectively (Table 2(b)), with an average sample size of 0.3 g yielding approximately 1.1 μL of H_2O. The SCF fluid inclusion average value for δ^{18}O is –8.9 ‰ (±0.5 ‰) and –58.9 ‰ (±1.6‰) for δ^2H ($n = 7$). The water content per crush is calculated from the amount of water released and the weight of the sample, demonstrating that the amount of water varied per sample (Table 2).

Table 3. Comparison of fluid inclusion isotopic results between speleothems measured both at UM and VU. Results are for speleothems DC-S, HS and SCF. Average $\delta^{18}O$ and $\delta^{2}H$ values for both laboratories corrected to VSMOW. Also shown is the number of analyses conducted per sample and the average amount of water extracted

	Measured at VU Amsterdam				Measured at UM					
SAMPLE ID	Average O ‰	Average H ‰	n	Average water µL/g	Average O ‰	Average H ‰	n	Average water µL/g	Difference O UM-VU	Difference H UM-VU
DC-S 10	–1.3	–2.1	2	0.7	–1.3	–6.9	1	2.1	0.0	–4.9
DC-S 12	–1.3	–6.3	1	0.2	–2.5	–12.0	1	1.3	–1.2	–5.7
DC-S 14	–1.5	–6.0	2	0.9	–1.3	–5.0	2	1.4	0.2	1.1
DC-S 18	–1.8	–4.2	2	0.7	–1.6	–7.2	1	2.0	0.2	–3.0
DC-S 24	–2.1	–7.4	2	1.4	–2.2	–8.4	2	1.8	0.0	–1.0
DC-S 27	–2.3	–6.4	3	2.1	–1.8	–8.0	1	3.0	0.6	–1.6
DC-S 28	–2.0	–8.1	2	2.7	–3.3	–12.1	1	1.0	–1.3	–3.9
DC-S 30	–1.7	–4.6	2	1.5	–1.8	–5.5	1	3.6	–0.1	–0.9
DC-S 33	–1.0	–0.6	2	0.8	–2.3	–8.2	1	2.6	–1.3	–7.6
DC-S 36	–2.2	–5.1	2	3.1	–1.5	–7.1	2	3.1	0.7	–2.0
DC-S 38	–1.5	–8.2	1	0.3	–2.5	–12.5	2	1.5	–1.0	–4.3
DC-S 39	–1.6	–5.4	3	1.2	–2.5	–9.0	1	1.4	–0.9	–3.5
DC-S 42	–1.7	–5.7	2	1.3	–2.0	–11.8	2	1.6	–0.3	–6.1
HS	–14.0	–105.0			–14.5	–105.3	4	3.4	–0.5	–0.3
SCF	–7.5	–55.0			–8.9	–58.9	7	1.1	–1.4	–3.9
Average offset (UM-VU)					*–0.7*	*–2.5*				

Comparison between laboratories

In order to compare the Amsterdam and Miami Devices a series of samples were crushed and analyzed in both laboratories (Table 3). The offsets were found to be 0.7 and 2.5 ‰, respectively, for $\delta^{18}O$ and $\delta^{2}H$ values with the Miami data being more negative in both $\delta^{18}O$ and $\delta^{2}H$ values than the VU data.

DISCUSSION

We have demonstrated the precision and accuracy of the Miami Device as well as its versatility in analyzing a range of sample types and sizes. Through repeated analysis of cave calcites, average standard deviations of ±0.5 and ±2.0 ‰ for $\delta^{18}O$ and $\delta^{2}H$ values, respectively, in waters from fluid inclusions were determined.

Difference between the Amsterdam and Miami Devices

Inter-laboratory offsets of 1‰ for $\delta^{18}O$ values and 3‰ for $\delta^{2}H$ values were previously observed between the VU and Innsbruck University (IU) results, with the IU results giving lower $\delta^{18}O$ and $\delta^{2}H$ values.[8] The average offset between the Amsterdam and Miami laboratories was found to be similar, with the data from the Miami Device also giving lower $\delta^{18}O$ and $\delta^{2}H$ values.

Possible fractionation during injection and crushing

Although it is possible that some fractionation might have taken place during crushing (or injection) and subsequent expansion, it was observed that once a stable concentration of gas was attained within the analyzer, the $\delta^{18}O$ and $\delta^{2}H$ values both did not vary significantly (Fig. 3) indicating that little fractionation occurred during this process. Furthermore, all samples analyzed with the Miami Device fall within 5‰ of the Global Meteoric Water Line (GMWLL), the exception being sample HBC2 (Fig. 4), suggesting that the $\delta^{18}O$ and $\delta^{2}H$ values have not been affected by fractionation and that the data therefore reflect a value representative of the original meteoric water composition.

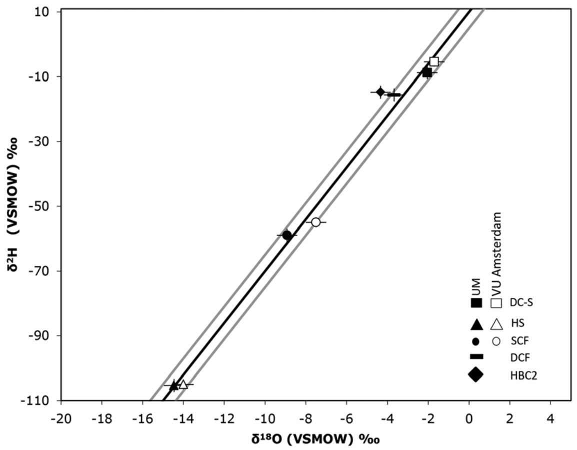

Figure 4. Average oxygen and hydrogen isotope ratios (VSMOW) plotted for all fluid inclusion isotope sample data. Black line represents the global meteoric water line and grey lines are ±5 ‰ $\delta^{18}O$. Open data symbols are sample data from VU, while black data symbols represent results from UM. Squares are DC-S data, triangles are HS data, circles are SCF results, black rectangle is DCF sample data and the black diamond is from HBC2.

As two of the samples (DCF and the HBC2) were collected from Pleistocene aged material in the Bahamas, it is possible to compare modern cave temperatures and $\delta^{18}O$water ($\delta^{18}Ow$) values of drip waters with values obtained from fluid inclusion isotopic analysis. The oxygen isotope values of the calcite (+26.8 ‰ VSMOW for DCF; +25.8 ‰ VSMOW for HBC2) were determined and temperatures were calculated using the water-calcite oxygen isotope fractionation equation from Tremaine *et al*.[15] Although it is not possible to know the precise δ^{18}Ow value and the temperature of formation as these samples are Pleistocene in age, the derived temperatures (+20.9 °C and +22.9 °C) and the measured δ^{18}Ow values of the fluid inclusions (–3.7 ‰ VSMOW for DCF and –4.3 ‰ VSMOW for HBC2) are close to those which we have observed in a modern cave in the Bahamas where stalagmites are currently forming (average annual temperature = 23.2 °C and drip water = –3.8 ‰ for δ^{18}Ow VSMOW). These data further support the accuracy of the analyses.

Possible interferences using CRDS

One of the potential drawbacks of utilizing CRDS is the possibility of interferences over the range of wavelengths used for measurement. In particular, interferences have been observed in the presence of ethanol and methanol[13] and dissolved organic carbon (DOC), such as organic contaminates from leaf[16,17] and soil extracts.[17] Offsets as high as 15.4 ‰ for δ^{18}O values and 46 ‰ for δ^{2}H values have been observed when comparing CRDS and IRMS data; however, lower offsets have also been observed.[16,17] The offset driven by these contaminants does not appear to be linear, and therefore is difficult to correct for.[16,17] Although in an IRMS system such contaminants have the potential to be converted into either CO or H_2 gas, the concentrations are usually insignificant relative to the amount of water present and therefore their importance is minor and does not significantly affect the results.[16] In order to alleviate the issues of interferences in CRDS systems, Picarro now offers a post-processing software, Chemcorrect™, that flags samples for contamination. The software detects contaminations by monitoring the wavelength spectrum of the instrument for irregularities and comparing with known spectral features of water contaminates; the software also monitors the spectral baseline and the slope of the spectral baseline, which are also indicators of potential contamination.[18] Another potential solution from Munksgaard *et al*.[19] is to diffuse the water through porous PTFE tubing which is shown to reduce the interferences from DOC.[19] For stalagmites, organic matter, which is typically comprised of humic and fulvic acid compounds,[20] can be trapped in the speleothem calcite and can be useful for identifying environmental change through UV fluorescence.[21] Dissolved organic carbon is found in cave drip waters,[22] but it is not known if this extends to fluid inclusions and whether this is a potential source of contamination for fluid inclusion isotopic analysis. Future work combining UV fluorescence and fluid inclusion isotope analysis may shed light on these questions. Through careful observation of sample data, the use of correction software and the analysis of sample spectra, it is possible to identify samples which are affected by interferences.

CONCLUSIONS

Cavity ring-down spectroscopy is a lower cost and mechanically simpler alternative to the continuous flow IRMS method for the measurement of δ^{18}O and δ^{2}H values in fluid inclusions. For water extraction, we have developed a hybrid system utilizing aspects of the Amsterdam Device and the Picarro vaporizer unit. Through repeated crushes of cave calcites, the standard deviation of fluid inclusion isotope data from the Miami Device is shown to be comparable with errors reported by Dublyansky and Spötl[7,8] and Vonhof *et al*.,[8,9] both of whom utilized IRMS-based systems. Comparison of fluid inclusion isotope data between the Amsterdam Device and the Miami Device demonstrates that the Miami Device measurements accurately reflect the values of the water trapped in the mineral. In addition, the samples analyzed with the Miami Device fall near the GMWL, further supporting this conclusion. While we do observe offsets between the data from VU and UM, we attribute this offset to differences in the laboratory setup, considering that similar inter-laboratory offsets have been observed between IRMS systems. As more fluid inclusion work is conducted, the ability to correct for inter-laboratory biases must be addressed through the development of standards.

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