Near real-time field measurements of $\delta^{13}$C in CO$_2$ from volcanoes

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This paper describes the operation and application of a portable cavity ring-down spectrometer (CRDS) designed to measure the isotopic composition of carbon dioxide. The instrument is capable of measuring $\delta^{13}C$ for CO$_2$ concentrations ranging from atmospheric (400 ppm) to 100%, at precisions and accuracies that are comparable to laboratory-based gas source mass spectrometers. This flexibility and portability are ideal for applications on active volcanoes, and it is now possible to obtain isotopic measurements on a near real-time basis. We show applications of the CRDS for soil gases on volcanoes and in calderas, for characterizing the isotopic composition of a volcanic plume, and for measuring the temporal variability of $\delta^{13}C$ in the atmosphere. Future directions hold the potential to use volcanic gas isotopes for monitoring purposes, and to combine different isotopic systems to reveal the source or sources of gas.

1. Introduction

Volcanic gases provide important clues to volcanic activity. Not only can gases indicate the state of unrest of an active volcano, they also reveal the ultimate source or sources of the gas. In this regard, both gas concentrations and stable isotope signatures of species such as H$_2$O and CO$_2$ play an important role. Coupled with other monitoring tools such as seismic and geodetic monitoring, gas data yield important insights into a volcano’s activity, including whether the system is accelerating or decelerating in terms
of restlessness. Sometimes anomalous emanations of gas are the first signs that a volcano is reawakening, and both increases and decreases in gas output, e.g., sulfur dioxides fluxes, have been documented prior to explosive eruptions (Daag et al. 1996; Zapata G et al. 1997; Conde et al. 2014).

In the past 20 years, significant advances have been made in studying and monitoring volcanic gases. Small, inexpensive mini-DOAS and FLYSPEC instruments have replaced the COSPEC for SO$_2$ flux measurements, which can be made from a variety of mobile and stationary configurations including automated data collection on a real-time basis (e.g., Galle et al. 2003; Edmonds et al. 2003; Horton et al. 2006). FTIR remote sensing measurements of plumes and craters have successfully characterized multiple gas species; in favorable circumstances a full spectrum of gas species can be identified and quantified (e.g., Oppenheimer et al. 2006). Similarly, Multi-GAS instruments are able to measure a variety of gas species in situ (Shinohara 2005); gas ratios can be easily derived from these measurements, with the CO$_2$/SO$_2$ ratio proving especially useful in tracking unrest (e.g., Aiuppa et al. 2007; de Moor et al. 2016).

Here we report on a new field-based approach for measuring the isotopic concentration of carbon dioxide emanating from volcanoes. The instrument deployed is a cavity ring-down spectrometer (CRDS) with precisions and accuracies that are comparable to conventional laboratory mass spectrometers. The principal advance is that we are able to make isotopic measurements on a near real-time basis in the field, allowing us to rapidly identify and map zones of magmatic CO$_2$. Typically, gas samples are collected and isotopic measurements made the same day, thereby decreasing the wait time for analysis and allowing sampling flexibility during a field campaign. The
instrument can be deployed in a number of configurations, and together with isotope ratio infrared spectrometry (IRIS) (Rizzo et al. 2014, 2015; Fischer and Lopez 2016), it is the only practical means of measuring the carbon isotopic composition of a degassing plume.

2. Principle of operation

The Picarro G1101-i CRDS exploits the near-infrared absorption of carbon’s two isotopologues ($^{13}$C and $^{12}$C). A single frequency laser diode produces a beam that enters the vacuum filled cavity with a unique wavelength that corresponds to the vibrational frequency of the target isotopologue. Within the cavity, the beam is reflected among three mirrors over an effective pathlength of $>$ 20 km, increasing in intensity over time. When a threshold is reached, the sample gas is introduced and the intensity of the light decreases with time due to the resonant absorption of energy by the target molecule (e.g., $^{12}$C$^{16}$O$_2$). The ‘ring-down’ time is the time required for the light intensity to drop to starting levels. Isotope concentrations are reported every ten seconds and are derived by comparing the difference in ring-down times between a sample-filled cavity and an empty one. This comparative method produces precise and robust quantitative measurements, independent of fluctuations in laser intensity and absolute laser power (Picarro Inc. 2015).

In practical terms, our CRDS comprises two components, one a data acquisition module (DAS) which houses the cavity and the other a power supply and vacuum pump module (CPVU). More recent versions comprise a single module. Together, the two
components weigh ~34 kg, and their footprint is similar to that of a large desktop computer (Fig. 1). The unit needs only electricity with a maximum power requirement of 375 watts. We generally run the instrument with an uninterruptible power supply (UPS) attached to house current, to ensure stable power and avoid any cuts in electricity to the instrument.

3. Calibration

Under controlled laboratory conditions, our Picarro instrument can easily achieve sub-per mil precision. CO$_2$ gas standards run in the lab at 1000-3000 ppm concentration levels show nominal reproducibilities on the order of 0.3-0.5 per mil, but multiple analyses of individual samples show that the true reproducibility can approach 0.1 per mil. The nominal reproducibility is simply the standard deviation on the average of multiple measurements of a single sample, while the true reproducibility is based on averaging multiple samples of a standard. During field deployments, 0.5 per mil or better reproducibility at 1000-3000 ppm CO$_2$ is achievable. At atmospheric conditions (~400 ppm), the nominal error is typically ~1 per mil, but repeat analyses of standards demonstrate that the actual error is again better than this.

Prior to a field deployment, the instrument is calibrated in the lab using a series of four in-house standard gases with various isotopic compositions from -43‰ to -11.4‰ that have been calibrated independently by gas source mass spectrometry using a series of gas standards referenced to internationally accepted reference materials. For greatest
precision and accuracy, we try to maintain a similar CO₂ concentration whenever possible for both standards and samples. This is because there can be a small concentration-dependent variation for δ¹³C, even though this effect is corrected by the Picarro algorithm. We generally do our calibrations at 1000 ppm CO₂ for good reproducibility, but concentrations of 2000 or 3000 ppm also can be used (Fig. 2). To maintain similar CO₂ concentrations, we do sample dilutions using air in which the CO₂ has been removed by an ascarite (NaOH) filter. Calibrations also can be done at atmospheric levels, i.e., 400 ppm, but the reproducibility is slightly degraded at these lower concentrations. In the field prior to commencing measurements, we check the lab calibration with our standards and redo the calibration if required with three of our four gas standards. Thereafter we run our -15.6 per mil standard interspersed with our unknown samples. The standard is always run at the same concentration (e.g., 1000 ppm) as the samples. Typically, these calibrations are stable for days to weeks at a time. If the standard differs by more than 1 per mil from the accepted value, we redo the full calibration.

In the early stages of development and deployment, we were cognizant of the need to demonstrate accuracy and precision of our CRDS measurements. Hence we took special care to measure selected standards and samples on both our Picarro instrument and also on a Finnigan MAT gas source mass spectrometer paired to a gas chromatograph combustion interface with a continuous flow-through system at the University of Toronto. Figure 3 is a plot showing measurements of the same samples made by the two different types of measurements; the correspondence is excellent, demonstrating the viability of the CRDS technique.
4. Interferences

Under normal atmospheric conditions, the only interferences that the CRDS experiences are those from water vapor (Rella et al. 2013) and methane (Vogel et al. 2013), which are accounted for and corrected by the instrument’s hardware and software. Variable CO$_2$ concentrations from 400 to 3000 ppm are also accounted for when $\delta^{13}$C is being measured. Nevertheless, we generally make our measurements at a fixed concentration value, as explained above, to minimize any residual concentration-dependent effects.

In gases containing hydrogen sulfide, we have observed a significant effect of this species upon the $\delta^{13}$C signal (Malowany et al. 2015). In essence, the presence of H$_2$S imparts a strongly negative value to $\delta^{13}$C as a result of H$_2$S interference primarily upon the $^{13}$C isotope (Fig. 4). As a result, the CRDS $\delta^{13}$C measurement is strongly dependent upon both H$_2$S and CO$_2$ concentrations, being most severe at low CO$_2$ and high H$_2$S. For example, at 1000 ppm CO$_2$ and ~30 ppb H$_2$S, the negative $\delta^{13}$C shift is ~ -1 per mil. This isotopic shift is observed over the entire operating range of the instrument (400 – 3000 ppm CO$_2$) and for H$_2$S concentrations in excess of 1 ppb (Malownany et al. 2015).

The simplest and most effective way to deal with this interference is to remove it, and we do this by using a metal scrub, typically copper, which reacts with the hydrogen sulfide to form copper sulfide by the reaction $2\text{H}_2\text{S} + 2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuS} + 2\text{H}_2\text{O}$. In practical terms, we use a 10-20 cm length of $\frac{1}{4}$-inch diameter copper tubing that is filled
with copper filings in order to enhance reactivity by increased surface area (Fig. 5); our experiments suggest that not all H$_2$S is removed with only the copper tube or copper filings alone (Malowany et al. 2015) The copper tubes are utility grade, the copper filings are CHEM.57B grade “B”, and both contain small amounts of other metals. We use these copper tubes both in field sampling from vents and fumaroles, and also during the CRDS analysis, so that the gas has passed through this double set of filters before entering the instrument. The copper filters have no measurable effect on the carbon isotope composition or gas concentrations (Malowany et al. 2015). The tubes and filings need to be replaced periodically before they have reacted fully with the H$_2$S. This can be assessed visually, as the copper turns black during reaction with H$_2$S. Using this approach ensures that the gas is free of hydrogen sulfide during isotopic analysis of the CO$_2$. In volcanic environments that typically have H$_2$S present, this procedure is essential to obtain accurate and precise CRDS measurements.

5. Sampling and measurement

When sampling in the field, we pump the gas into 1000 ml ALTEF or Tedlar sampling bags (Fig. 6). As we pump the gas, we also measure its CO$_2$ concentration using a portable infrared CO$_2$ instrument. If the gas exceeds 3000 ppm CO$_2$, it is too concentrated for the CRDS, so we dilute it in the field. For example, if the gas is 100% CO$_2$, we inject 1 ml of the gas into a sampling bag prefilled with 1000 ml air that has been scrubbed of CO$_2$ by passing it through an ascarite filter in the lab or hotel room (Fig.
This dilution produces a gas with ~1000 ppm CO$_2$, suitable for analysis by the CRDS. In this situation, we run all our samples including unknowns and standards at 1000 ppm CO$_2$ for maximum consistency. If the gas is less than 3000 ppm CO$_2$, we can either sample and measure it without dilution, or do a small dilution to obtain 1000 ppm.

In general, it is a good idea to take duplicate samples from time to time for later analysis by conventional gas source mass spectrometry. This provides a further check of accuracy for the CRDS. To do this, we take a 50-ml sample from a gas bag, placing this volume in a pressurized 30 ml anaerobic culture tube containing 5 µl of HgCl$_2$ to prevent any bacterial production that might affect the $\delta^{13}$C value between sampling and analysis (typically several weeks to months) (Fig. 8a) (Oremland et al. 1987).

Our general protocol is to collect gas samples during the day, then analyze them in the evening. This protocol minimizes the time during which gas can diffuse into or out of the bag. In this manner, we process approximately 10 samples each day. Prior to analyzing our samples, we check the calibration of the CRDS by running 3-4 of our in-house CO$_2$ gas standards spanning a range of isotope compositions. If the calibration is accurate, we can analyze our samples; if it is not, we recalibrate the CRDS. We transport our standard gases to the field in 210-ml anaerobic media bottles (Fig. 8b). This method obviates the need for compressed gases and associated paraphernalia, and we have sufficient standard gas to run periodically, interspersed with our samples, as a check on accuracy and precision.

To analyze our samples is a straightforward procedure. We attach the gas bag directly to the instrument which pumps gas into the analyzer at a rate of ~0.1 l/min. An analysis time of ~10-15 minutes is generally sufficient; the data are normally averaged...
over this time period, except for the first several minutes which are not used because the
CO$_2$ concentrations entering the CRDS are changing from atmospheric to those of the
sampling bag (Fig. 9). Once the analysis is finished, the sample bag is disconnected from
the instrument, the CRDS re-equilibrates to atmospheric conditions for a few minutes,
and then the next sample bag is attached to the instrument for the subsequent analysis. A
CO$_2$ gas standard is run after 5-10 samples, always at similar CO$_2$ concentrations as the
samples, as a check of accuracy and precision.

6. Applications

Because the CRDS is portable, it can be easily used in the field to collect isotopic
data of high precision and accuracy. Its portability and field use are advantageous when a
field campaign needs to be adjusted or modified to a changing situation. For example, if a
particular location becomes inaccessible, samples can be collected elsewhere and
analyzed promptly. Below we summarize three useful applications of the CRDS at
volcanoes.

Isotopic characterization of soil gases

Soil gases in volcanic areas are commonly rich in carbon dioxide, and the gas is
typically a mixture of deep, biogenic, and atmospheric CO$_2$. Studying soil gases in
calderas can be particularly fruitful, as magmatic or hydrothermal CO$_2$ can reveal
subsurface fault structures which serve to focus gas flow. At Long Valley caldera our
goal was to extend the work of Bergfeld et al. (2006), in order to understand the role and
interplay of regional faults and caldera faults in influencing the release of magmatic CO$_2$
gas. To do this, we sampled soil gases and fumaroles in and around the caldera, targeting
key areas such as the caldera margin, the south moat of the caldera which is very active
seismically, and the resurgent dome which has been uplifted by nearly one meter since
the early 1980’s. In order to characterize the magmatic CO$_2$ emissions, we also needed to
identify other sources of CO$_2$, namely biogenic and atmospheric (Lucic et al. 2015). The
samples from the southern margin of the resurgent dome reveal a dominantly magmatic
character, consistent with the volcanic unrest in this sector of the caldera. A number of
these points plot in the mixing field, showing variable contributions of the three end-
members (Lucic et al. 2015). This example demonstrates the importance of conducting a
comprehensive characterization of the CO$_2$ budget of a particular site, so that subtle
differences in mixing can be identified and interpreted.

Isotopic characterization of volcanic plumes

Characterizing the isotopic character of a volcanic plume can yield significant
insight regarding the source of the CO$_2$. Monitoring the isotopic composition of the
plume over time can provide invaluable monitoring data in terms of processes such as
magma degassing and magma replenishment within or beneath the volcano. Chiodini et
al. (2011) pioneered this approach on a number of Italian volcanoes, and more recently
several studies used isotope ratio infrared spectrometry (IRIS) to isotopically characterize
plumes (Rizzo et al. 2014, 2015; Fischer and Lopez 2016). We applied the CRDS to measure $\delta^{13}$C in the plume of Turrialba volcano in Costa Rica. Turrialba has shown escalating activity since the late 1990’s, and the volcano is currently in a state of heightened unrest. Gases have become less hydrothermal and more magmatic over time (Moussallam et al. 2014; De Moor et al. 2016), and SO$_2$ fluxes are high and variable. In late 2014 and 2015, solid juvenile material was erupted for the first time (Global Volcanism Program, 2015). Our goal at Turrialba was to characterize the isotopic character of the CO$_2$ being emitted from the volcano through soil gases, fumaroles, and high-temperature vents. A primary objective was an attempt to characterize the volcano’s plume for its carbon isotopic signature. The CRDS is an ideal instrument for isotopic analysis of the plume for two reasons. First, a number of gas samples can be collected fairly quickly in the plume, then analyzed immediately afterward. Second, the sub per mil precision of the CRDS allows us to discriminate between samples with small isotopic differences. At Turrialba, this entailed taking multiple samples from within the plume at CO$_2$ concentrations of 400-800 ppm and then analyzing them on the CRDS. Because the plume is diluted significantly by atmospheric CO$_2$, it was necessary to conduct a detailed mixing model for the plume (Malowany et al. 2017). Extrapolation of the plume data from the atmospheric end-member through the data points from the plume reveals that the magmatic end-member has a $\delta^{13}$C value of $-2.9 \pm 0.5$ per mil, which is similar to other low-temperature fumaroles and soil gases in and around the crater. By contrast, the high-temperature 2012 vent ($\geq 480^\circ$ C) is offset to slightly lighter values ($-4.4$ per mil). These results reveal the complex and heterogeneous isotopic character of CO$_2$ emissions at Turrialba.
\( \delta^{13}C \) of atmospheric CO\(_2\)

The CRDS is effective at accurately measuring sub per mil variations in atmospheric CO\(_2\) concentrations and isotopic compositions (Vogel et al. 2013). Global atmospheric CO\(_2\) concentrations currently are around 400 ppm and rising, with isotopic concentrations of -8.2‰ and decreasing (Cuntz 2011). Anthropogenic pollution can influence the atmospheric CO\(_2\) concentration and \( \delta^{13}C \) signal. Furthermore, diurnal variations of CO\(_2\) concentration and \( \delta^{13}C \) arise from photosynthetic and respiratory activity of plants, causing variations in the isotopic signal from local vegetation (Lloyd et al. 1996). At Turrialba volcano, variations in the atmospheric isotopic composition were approximately 2 per mil due to photosynthesis of the surrounding rainforest (Malowany et al. 2017). The most enriched values occurred at mid-day, resulting from the preferential uptake of \( ^{12}C \) when photosynthetic activities were at their maximum. Characterizing and understanding these variations in ambient atmosphere are important for the implementation of mixing plots among atmospheric, volcanic and biogenic endmembers. The CRDS is well equipped to measure these subtle changes in atmospheric \( \delta^{13}C \), and thus is highly advantageous for detailed studies addressing the interaction of multiple carbon components.

7. Future directions
The isotopic character of CO₂ at a volcano is a useful measurement that can now
be done on a routine basis during field deployments. Characterizing the carbon isotopic
character of a volcano provides a basis and baseline to understand its CO₂ emissions and
source or sources. The isotopic signal may vary with time, and this could signify a
change in the volcano’s condition and state of activity. For example, δ¹³C values that
become increasingly negative could signify a progressively degassing magma, a
decreasing hydrothermal and increasing magmatic component, and/or an increased
biogenic component. Isotopic values which become more positive could be indicative of
an increasing crustal component or the arrival of new magma rich in CO₂ (see Malowany
et al. 2017). Such variations are potentially useful for volcano monitoring.

A particularly interesting application well suited for CRDS instruments is the
measurement of volcanic plumes, as we have done at Turrialba. Such measurements hold
promise for monitoring purposes. It is possible that isotopic shifts occur in open systems,
such as when CO₂ is transported from deep crustal or mantle environments into the
shallow plumbing system of a volcano. Coupled with Multi-GAS measurements of C/S,
determining the carbon isotopic composition of the plume on a regular or continuous
basis could reveal significant variations with time that correlate with eruptive activity.
For such isotopic measurements to be robust and useful, it is essential that (a) plume
samples are accurately and precisely measured for both CO₂ concentration and δ¹³C, and
(b) the atmospheric end-member is well characterized, especially if its CO₂ concentration
and δ¹³C value are not constant as a function of time.

Chiodini et al. (2008) pioneered the integration of CO₂ fluxes and isotopes in soil
gas. We took this approach at Cerro Negro volcano in Nicaragua. Samples with high CO₂
fluxes invariably had a magmatic isotopic character of -2 to -5 per mil, while lower-flux samples showed an increasing influence of biogenic CO$_2$ (Lucic et al. 2014). In this case we did our carbon isotope measurements by gas source mass spectrometry after the field campaign. However, this example illustrates the potential of simultaneous deployment of the CRDS coupled with CO$_2$ flux measurements. This field-based approach is the ideal means of fully characterizing the CO$_2$ output of a volcano, providing crucial information on both the strength and the source of the CO$_2$ signal. The data which are collected are nearly real-time, allowing a rapid and highly detailed characterization of the CO$_2$ emissions. Furthermore, specific zones can be targeted at high spatial and temporal resolutions.

An increasing number of manufacturers are producing CRDS and related instruments that are field-deployable to measure the isotopic character of CO$_2$ and other gases at active volcanoes. The procedures and applications that we have highlighted in this paper should be applicable for these new developments. Furthermore, this advance provides new possibilities for volcano monitoring. For example, a series of CRDS instruments could be installed permanently at a volcano, making continuous and automated $\delta^{13}$C measurements which are telemetered to an observatory on a true real-time basis. Since many volcanoes are dangerous to sample directly, this type of remote monitoring can be highly advantageous. Field-based approaches also can be taken using hydrogen and oxygen isotopes for fluids and gases. When coupled with the CO$_2$ measurements, these additional isotopic systems can provide more detailed insight regarding sources and degassing mechanisms. We are excited about exploiting these new opportunities.
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Figure captions

Figure 1: Photograph of our Picarro G-1101-i analyzer, showing the data acquisition module (DAS) on top and the power supply/vacuum pump module below. (a) Front end of instrument. (b) Rear view. Together the two modules weigh ~34 kg and are similar in size to a large desktop computer.

Figure 2. Daily variability of a CO$_2$ gas standard measured in the field. The CO$_2$ concentration range is 2000-2500 ppm, the reference isotopic value is 43.0 per mil, and the two-sigma standard deviation is 0.50 per mil.

Figure 3: A series of gas samples and standards analyzed by our Picarro CRDS and by gas-source mass spectrometry. The excellent agreement shows the high accuracy of the CRDS system. The line is a best-fit linear regression through the data points.

Figure 4: Interference of H$_2$S on the $\delta^{13}$C value. A 1000 ppm CO$_2$ gas standard with $\delta^{13}$C of -28.5 per mil is analyzed by the CRDS from ~1 to ~13 minutes elapsed time. The isotopic signal is stable and accurate. By contrast, when 500 ppb H$_2$S is added to the CO$_2$ standard at ~21 minutes, the $\delta^{13}$C value becomes more negative, ranging in value from -35 to -37 per mil. The baseline is not stable, becoming increasingly negative with time.

Figure 5: A ¼-inch diameter copper tube filled with copper filings that removes H$_2$S gas prior to isotopic analysis of CO$_2$ by the CRDS.
Figure 6: A 1000-ml ALTEF gas sampling bag used to collect gases in the field. The bag can be connected directly to the CRDS for isotopic analysis of the CO$_2$ if the concentration is less than 3000 ppm, or if concentrated, the CO$_2$ can be diluted to concentrations appropriate for analysis.

Figure 7: Apparatus used to remove CO$_2$ from air in the field. The canister is filled with ascarite which removes the CO$_2$ by the reaction CO$_2$ + 2NaOH $\rightarrow$ Na$_2$CO$_3$ + H$_2$O. Air is pumped through the canister at a rate of 0.5 l/min, monitored by a flowmeter.

Figure 8: (a) 30 ml anaerobic culture tube treated with 5 μl HgCl$_2$ to prevent bacterial growth (Oremland et al. 1987). A 50 ml gas sample is injected into the tube for later analysis by gas source mass spectrometry. (b) 210 ml anaerobic media bottle used for transporting CO$_2$ gas standards in the field.

Figure 9: Screen grab showing a sample being analyzed from 1436 to 1445 hours. The first several minutes of the analysis are not used, as the CO$_2$ is shifting from background room air to the sample. The sample is analyzed from 1438 to 1445 hours. The lower noise level of the sample relative to the background results from the higher CO$_2$ concentration of the sample.
Figure 1
Figure 2
Figure 3

\[ y = 0.998x - 0.123 \]

\[ R^2 = 0.986 \]
Figure 4
$\frac{1}{4}$-inch copper tube

copper filings

Figure 5
Figure 6
Figure 7
Figure 8
Figure 9