

Near real-time field measurements of $\delta^{13}\text{C}$ in CO_2 from volcanoes

John Stix, Gregor Lucic², and Kalina Malowany³

Department of Earth and Planetary Sciences, McGill University, 3450 University Street,
Montreal, Quebec H3A 0E8, Canada. Email: stix@eps.mcgill.ca

²Now at: Picarro Inc., 3105 Patrick Henry Drive, Santa Clara, CA 95054, USA

³Now at: Core6 Environmental, 777 Hornby Street, Suite 1410, Vancouver, BC V6Z 1S4,
Canada

Abstract

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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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_2O 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 SO₂ 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 CO₂/SO₂ 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 CO₂. 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., $^{12}\text{C}^{16}\text{O}_2$). 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. CO₂ 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 CO₂ 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 $\delta^{13}\text{C}$, 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 CO₂ concentrations from 400 to 3000 ppm are also accounted for when δ¹³C 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 δ¹³C signal (Malowany et al. 2015). In essence, the presence of H₂S imparts a strongly negative value to δ¹³C as a result of H₂S interference primarily upon the ¹³C isotope (Fig. 4). As a result, the CRDS δ¹³C measurement is strongly dependent upon both H₂S and CO₂ concentrations, being most severe at low CO₂ and high H₂S. For example, at 1000 ppm CO₂ and ~30 ppb H₂S, the negative δ¹³C shift is ~ -1 per mil. This isotopic shift is observed over the entire operating range of the instrument (400 – 3000 ppm CO₂) and for H₂S 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 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 H₂S 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 H₂S. This can be assessed visually, as the copper turns black during reaction with H₂S. Using this approach ensures that the gas is free of hydrogen sulfide during isotopic analysis of the CO₂. In volcanic environments that typically have H₂S 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 CO₂ concentration using a portable infrared CO₂ instrument. If the gas exceeds 3000 ppm CO₂, it is too concentrated for the CRDS, so we dilute it in the field. For example, if the gas is 100% CO₂, we inject 1 ml of the gas into a sampling bag prefilled with 1000 ml air that has been scrubbed of CO₂ by passing it through an ascarite filter in the lab or hotel room (Fig.

7). This dilution produces a gas with ~1000 ppm CO₂, suitable for analysis by the CRDS. In this situation, we run all our samples including unknowns and standards at 1000 ppm CO₂ for maximum consistency. If the gas is less than 3000 ppm CO₂, 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 HgCl₂ to prevent any bacterial production that might affect the δ¹³C 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 CO₂ 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 CO₂ 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 CO₂ gas standard is run after 5-10 samples, always at similar CO₂ 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 CO₂. Studying soil gases in calderas can be particularly fruitful, as magmatic or hydrothermal CO₂ 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 CO₂ 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 CO₂ emissions, we also needed to identify other sources of CO₂, 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 CO₂ 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 CO₂. 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ value of -2.9 ± 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 ($\geq 480^\circ \text{C}$) 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.

$\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ signal. Furthermore, diurnal variations of CO_2 concentration and $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$, and thus is highly advantageous for detailed studies addressing the interaction of multiple carbon components.

7. Future directions

300 The isotopic character of CO₂ at a volcano is a useful measurement that can now
301 be done on a routine basis during field deployments. Characterizing the carbon isotopic
302 character of a volcano provides a basis and baseline to understand its CO₂ emissions and
303 source or sources. The isotopic signal may vary with time, and this could signify a
304 change in the volcano's condition and state of activity. For example, $\delta^{13}\text{C}$ values that
305 become increasingly negative could signify a progressively degassing magma, a
306 decreasing hydrothermal and increasing magmatic component, and/or an increased
307 biogenic component. Isotopic values which become more positive could be indicative of
308 an increasing crustal component or the arrival of new magma rich in CO₂ (see Malowany
309 et al. 2017). Such variations are potentially useful for volcano monitoring.

310 A particularly interesting application well suited for CRDS instruments is the
311 measurement of volcanic plumes, as we have done at Turrialba. Such measurements hold
312 promise for monitoring purposes. It is possible that isotopic shifts occur in open systems,
313 such as when CO₂ is transported from deep crustal or mantle environments into the
314 shallow plumbing system of a volcano. Coupled with Multi-GAS measurements of C/S,
315 determining the carbon isotopic composition of the plume on a regular or continuous
316 basis could reveal significant variations with time that correlate with eruptive activity.
317 For such isotopic measurements to be robust and useful, it is essential that (a) plume
318 samples are accurately and precisely measured for both CO₂ concentration and $\delta^{13}\text{C}$, and
319 (b) the atmospheric end-member is well characterized, especially if its CO₂ concentration
320 and $\delta^{13}\text{C}$ value are not constant as a function of time.

321 Chiodini et al. (2008) pioneered the integration of CO₂ fluxes and isotopes in soil
322 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 CO₂ (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 CO₂ flux measurements. This field-based approach is the ideal means of fully characterizing the CO₂ output of a volcano, providing crucial information on both the strength and the source of the CO₂ signal. The data which are collected are nearly real-time, allowing a rapid and highly detailed characterization of the CO₂ 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 CO₂ 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 $\delta^{13}\text{C}$ 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 CO₂ measurements, these additional isotopic systems can provide more detailed insight regarding sources and degassing mechanisms. We are excited about exploiting these new opportunities.

Acknowledgements

We are most grateful to the staff at Picarro Inc. for their continued assistance and interest in our applications, most notably Aaron Van Pelt, Mike Ahern, Danthu Vu, and Linda Huynh. Aaron has been a steadfast and enthusiastic supporter of using this technology for applications on active volcanoes. Maarten de Moor has provided crucial scientific and logistical advice at Turrialba. Boswell Wing of McGill University has helped us considerably in a number of ways, extending his extensive isotopic knowledge and perceptive insight to help us resolve a variety of issues. Barbara Sherwood Lollar, Georges Lacrampe-Couloume, and Katrina Chu of the University of Toronto have provided fundamentally important scientific and technical input into cross-calibration of our Picarro CRDS with their gas source mass spectrometers. We thank one anonymous reviewer, Taryn Lopez, and the editor Toby Fischer for helpful comments and suggestions that improved the paper. We acknowledge ongoing support from the Natural Sciences and Engineering Research Council of Canada for this research through Discovery, Accelerator, and Create grants to JS.

References cited

368 Aiuppa A, Moretti R, Federico C, Giudice G, Gurrieri S, Liuzzo M, Papale P, Shinohara
 369 H, Valenza M (2007) Forecasting Etna eruptions by real-time observation of volcanic
 370 gas composition. *Geology* 35:1115-1118
 371 Bergfeld D, Evans WC, Howle JF, Farrar CD (2006) Carbon dioxide emissions from
 372 vegetation-kill zones around the resurgent dome of Long Valley Caldera, eastern
 373 California, USA, *J Volcanol Geotherm Res* 152:140–156
 374 Chiodini G, Caliro S, Cardellini C, Avino R, Granieri D, Schmidt A (2008) Carbon
 375 isotopic composition of soil CO₂ efflux, a powerful method to discriminate different
 376 sources feeding soil CO₂ degassing in volcanic-hydrothermal areas. *Earth Planet Sci*
 377 *Lett* 274:372–379
 378 Chiodini G, Caliro S, Aiuppa A, Avino R, Granieri D, Moretti R, Parello F (2011) First
 379 ¹³C/¹²C isotopic characterization of volcanic plume CO₂. *Bull Volcanol* 73:531–542
 380 Conde V, Bredemeyer S, Duarte E, Pacheco JF, Miranda S, Galle B, Hansteen TH (2014)
 381 SO₂ degassing from Turrialba volcano linked to seismic signatures during the period
 382 2008-2012. *Int J Earth Sci* 103:1983-1998
 383 Cuntz M (2011) Carbon cycle: a dent in carbon's gold standard. *Nature* 477:547-548
 384 Daag AS, Tubianosa BS, Newhall CG, Tuñgol NM, Javier D, Dolan MT, Reyes PJD,
 385 Arboleda RA, Martinez MML, Regalado MTM (1996) Monitoring sulfur dioxide
 386 emission at Mount Pinatubo. In: Newhall CG, Punongbayan RS (eds) *Fire and mud,*
 387 *eruptions and lahars of Mount Pinatubo, Philippines.* Philippine Institute of
 388 *Volcanology and Seismology,* Quezon City, University of Washington Press, Seattle,
 389 pp 409-414

390 De Moor JM, Aiuppa A, Avarð G, Wehrmann H, Dunbar N, Muller C, Tamburello G,
 391 Giudice G, Liuzzo M, Moretti R, Conde V, Galle B (2016) Turmoil at Turrialba
 392 volcano (Costa Rica): degassing and eruptive processes inferred from high-frequency
 393 gas monitoring. *J Geophys Res* 121:5761-5775, doi:10.1002/2016JB013150
 394 Edmonds M, Herd RA, Galle B, Oppenheimer CM (2003) Automated, high time
 395 resolution measurements of SO₂ flux at Soufrière Hills volcano, Montserrat. *Bull*
 396 *Volcanol* 65:578-586
 397 Fischer TP, Lopez TM (2016) First airborne samples of a volcanic plume for $\delta^{13}\text{C}$ of CO₂
 398 determinations. *Geophys Res Lett* 43:3272-3279, doi:10.1002/2016GL068499
 399 Galle B, Oppenheimer C, Geyer A, McGonigle AJS, Edmonds M, Horrocks L (2003) A
 400 miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: A new tool for
 401 volcano surveillance. *J Volcanol Geotherm Res* 119:241–254
 402 Global Volcanism Program (2015) Report on Turrialba (Costa Rica). In: Wunderman R
 403 (ed) *Bulletin of the Global Volcanism Network*, Smithsonian Institution 40:4
 404 Horton KA, Williams-Jones G, Garbeil H, Elias T, Sutton AJ, Mougini-Mark P, Porter
 405 JN, Clegg S (2006) Real-time measurement of volcanic SO₂ emissions: validation of a
 406 new UV correlation spectrometer (FLYSPEC). *Bull Volcanol* 68:323-327
 407 Lloyd J, Kruijt B, Hollinger DY, Grace J, Francey RJ, Wong SC, Kelliher FM, Miranda
 408 AC, Farquhar GD, Gash JH, Vygorskaya NN (1996) Vegetation effects on the
 409 isotopic composition of atmospheric CO₂ at local and regional scales: theoretical
 410 aspects and a comparison between rain forest in Amazonia and a boreal forest in
 411 Siberia. *Funct Plant Biol* 23:371–399

412 Lucie G, Stix J, Sherwood Lollar B, Lacrampe-Couloume G, Muñoz A, Ibarra C M
 413 (2014) The degassing character of a young volcanic center: Cerro Negro, Nicaragua.
 414 Bull Volcanol 76:850, doi:10.1007/s00445-014-0850-6
 415 Lucie G, Stix J, Wing B (2015) Structural controls on the emission of magmatic carbon
 416 dioxide gas, Long Valley Caldera, USA. J Geophys Res 120:2262-2278,
 417 doi:10.1002/2014JB011760
 418 Malowany K, Stix J, Van Pelt A, Lucie G (2015) H₂S interference on CO₂ isotopic
 419 measurements using a Picarro G1101-i cavity ring-down spectrometer. Atmos Meas
 420 Tech 8:4075-4082
 421 Malowany K, Stix J, de Moor M, Sherwood Lollar B, Chu K, Lacrampe-Couloume G
 422 (2017) Carbon isotope systematics of Turrialba volcano, Costa Rica, using a portable
 423 cavity ring-down spectrometer. Geochem Geophys Geosyst, in press
 424 Moussallam Y, Peters N, Ramírez C, Oppenheimer C, Aiuppa A, Giudice G (2014)
 425 Characterisation of the magmatic signature in gas emissions from Turrialba volcano,
 426 Costa Rica. Solid Earth 5:1341–1350, doi:10.5194/se-5-1341-2014
 427 Oppenheimer C, Bani P, Calkins JA, Burton MR, Sawyer GM (2006) Rapid FTIR
 428 sensing of volcanic gases released by strombolian explosions at Yasur volcano,
 429 Vanuatu. Appl Phys B 85:453-460
 430 Oremland RS, Miller LG, Whiticar MJ (1987) Sources and flux of natural gases from
 431 Mono Lake, California. Geochim Cosmochim Acta 51:2915-2929
 432 Picarro Inc. (2015) Cavity ring-down spectroscopy (CRDS). Picarro
 433 Inc. http://www.picarro.com/technology/cavity_ring_down_spectroscopy. Accessed
 434 15 July 2015 2015

- Rella CW, Chen H, Andrews AE, Filges A, Gerbig C, Hatakka J, Karion A, Miles NL, Richardson SJ, Steinbacher M, Sweeney C, Wastine B, Zellweger C (2013) High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air. *Atmos Meas Techn* 6:837–860, doi:10.5194/amt-6-837-2013
- Rizzo A, Jost H, Caracausi A, Paonita A, Liotta M, Martelli M (2014) Real-time measurements of the concentration and isotope composition of atmospheric and volcanic CO₂ at Mount Etna (Italy). *Geophys Res Lett* 41:2382-2389, doi:10.1002/2014GL059722
- Rizzo AL, Liuzzo M, Ancellin MA, Jost HJ (2015) Real-time measurements of $\delta^{13}\text{C}$, CO₂ concentration, and CO₂/SO₂ in volcanic plume gases at Mount Etna, Italy, over 5 consecutive days. *Chem Geol* 411:182-191
- Shinohara H (2005) A new technique to estimate volcanic gas composition: plume measurements with a portable multi-sensor system. *J Volcanol Geotherm Res* 143:319-333
- Vogel FR, Huang L, Ernst D, Giroux L, Racki S, Worthy DEJ (2013) Evaluation of a cavity ring-down spectrometer for in situ observations of ¹³CO₂. *Atmos Meas Techn* 6:301-308
- Zapata G JA, Calvache V ML, Cortés J GP, Fischer TP, Garzon V G, Gómez M D, Narváez M L, Ordóñez V M, Ortega E A, Stix J, Torres C R, Williams SN (1997) SO₂ fluxes from Galeras volcano, Colombia, 1989-1995: progressive degassing and conduit obstruction of a Decade volcano. *J Volcanol Geotherm Res* 77:195-208

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 CO₂ gas standard measured in the field. The CO₂ 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 H₂S on the $\delta^{13}\text{C}$ value. A 1000 ppm CO₂ gas standard with $\delta^{13}\text{C}$ 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 H₂S is added to the CO₂ standard at ~21 minutes, the $\delta^{13}\text{C}$ 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 H₂S gas prior to isotopic analysis of CO₂ 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 CO₂ if the concentration is less than 3000 ppm, or if concentrated, the CO₂ can be diluted to concentrations appropriate for analysis.

Figure 7: Apparatus used to remove CO₂ from air in the field. The canister is filled with ascarite which removes the CO₂ by the reaction $\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$. 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 HgCl₂ 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 CO₂ gas standards in the field.

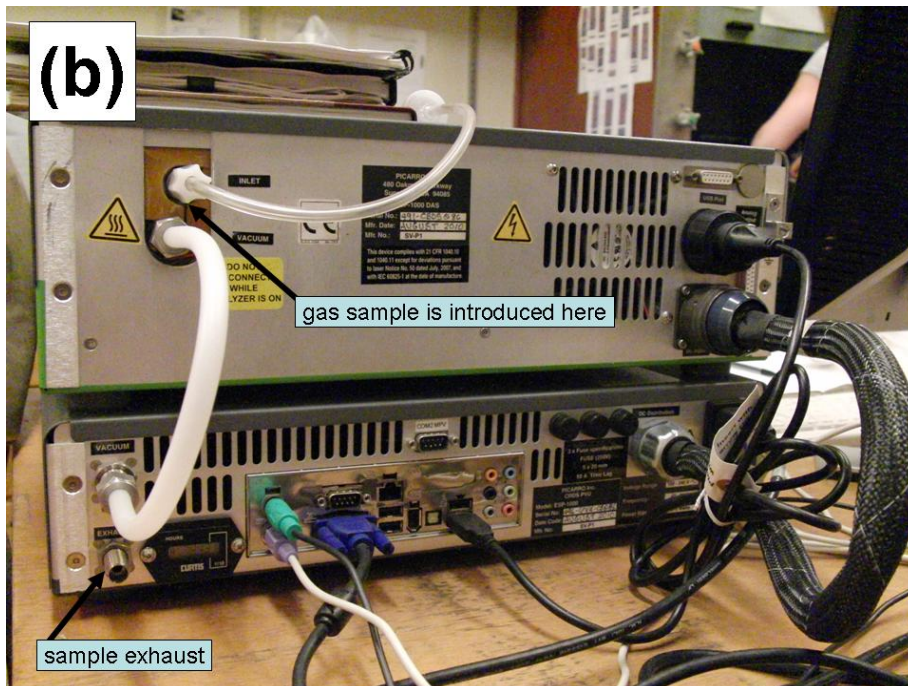
Figure 9: Screen grab showing a sample being analyzed from 1436 to 1445 hours. The first several minutes of the analysis are not used, as the CO₂ is shifting from background room air to the sample. The sample is analyzed from 1438 to 1445 hours. The lower noise level of the sample relative to the background results from the higher CO₂ concentration of the sample.

504



505

506



507

508

509

Figure 1

510

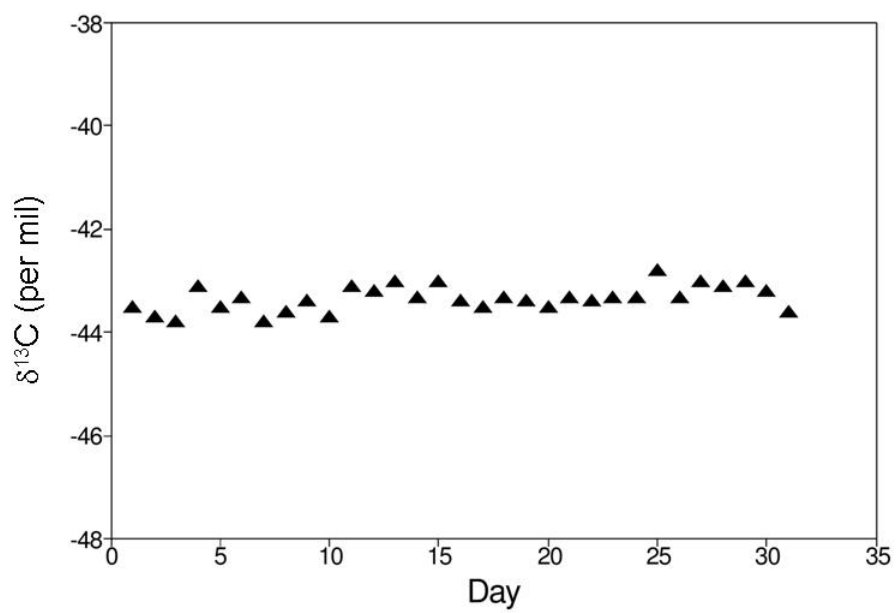
511

512

513

514

515



516

517

518

Figure 2

519

520

521

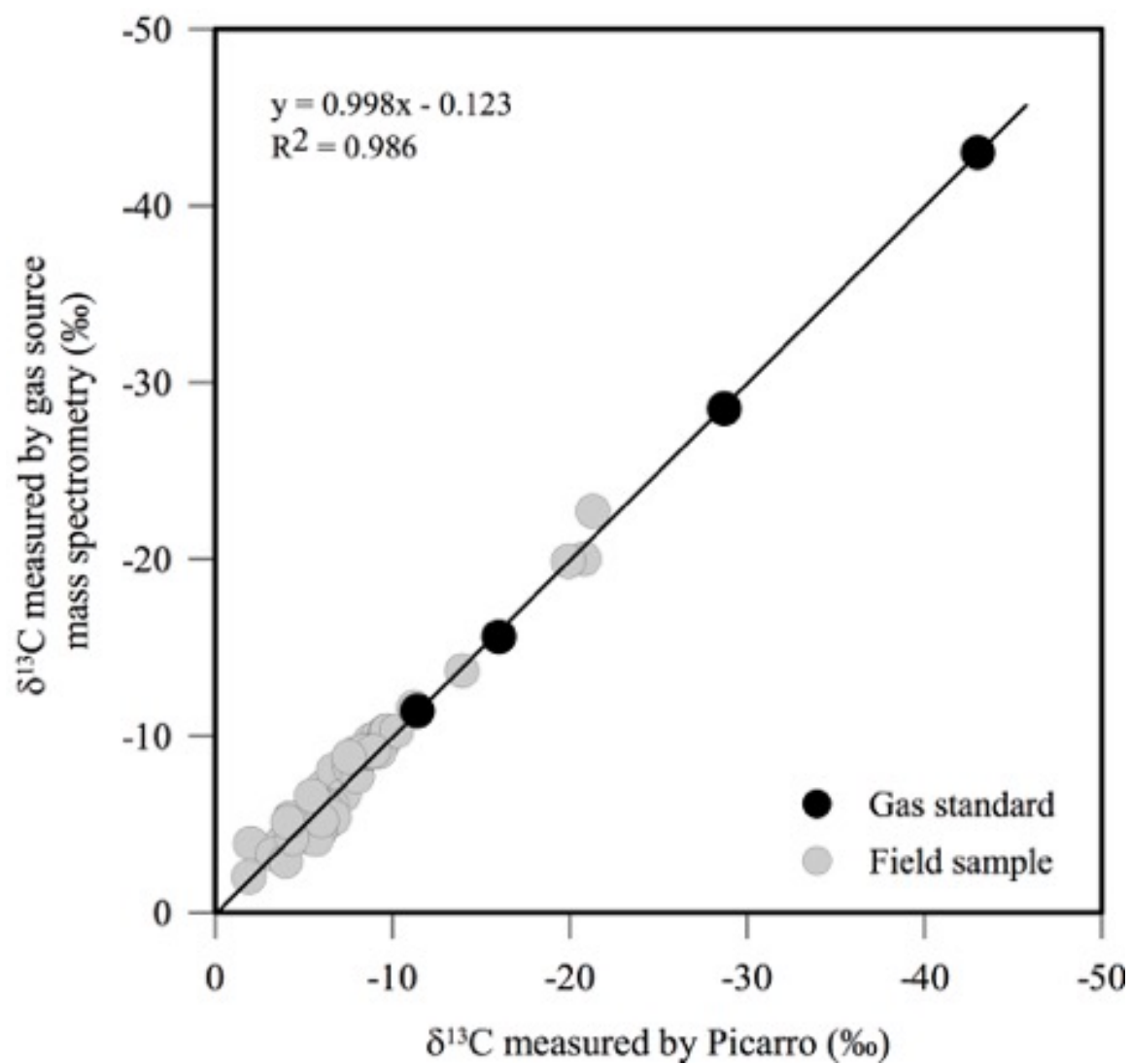
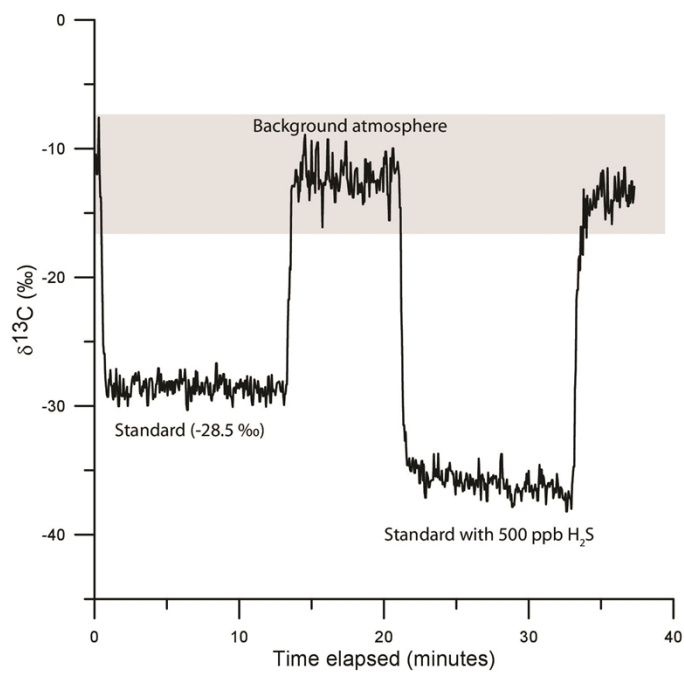


Figure 3

531



532

533

Figure 4

534

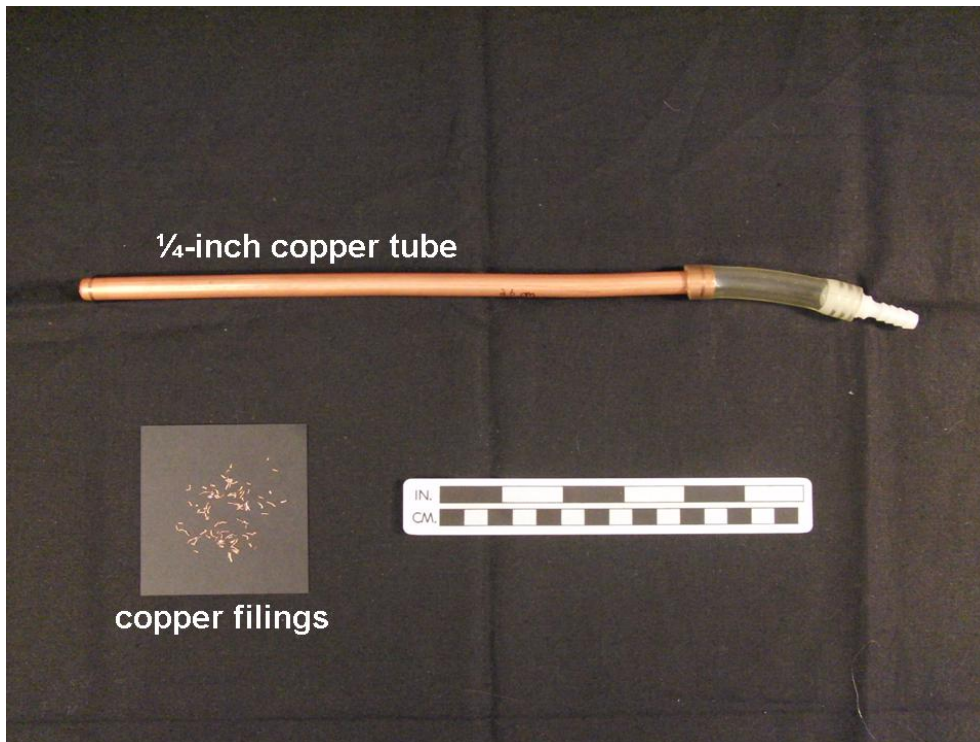
535

536

537

538

539



540

541

542

543

544

545

Figure 5

546

547

548

549

550

551

552

553

554



555

556

557

558

559

Figure 6

560

561

562

563

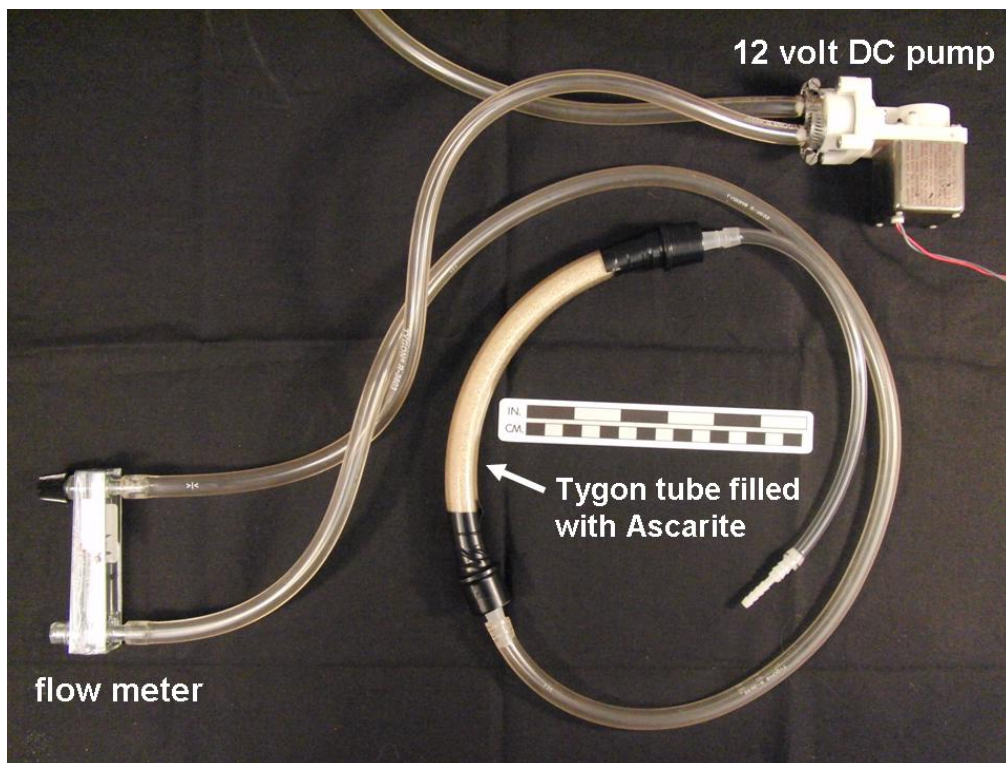
564

565

566

567

568



569

570

571

572

573

574

575

576

Figure 7

577

578

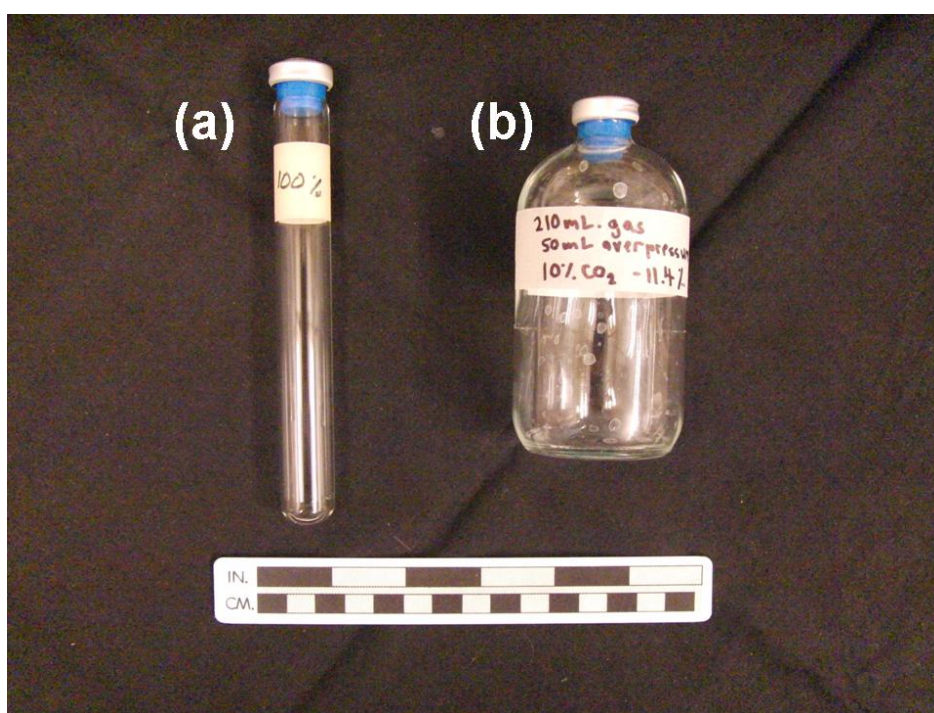
579

580

581

582

583



584

585

586

587

588

589

590

Figure 8

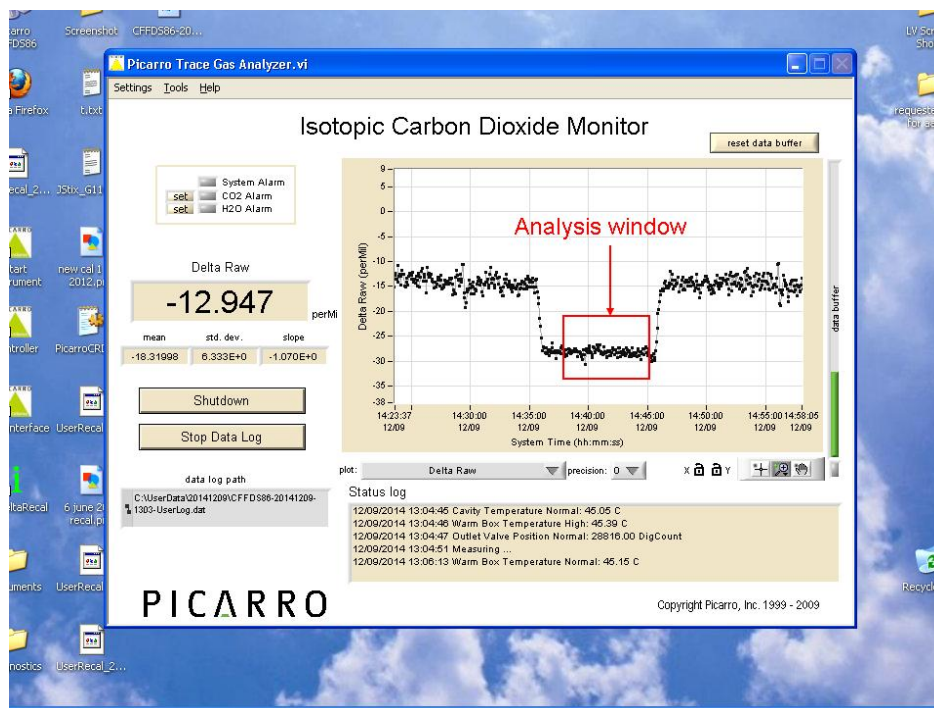


Figure 9