Supporting Information for

# Large isotopic shift in volcanic plume $CO_2$ prior to a basaltic paroxysmal explosion

**Fiona D'Arcy[1], Alessandro Aiuppa[2], Fausto Grassa[3], Andrea Luca Rizzo[4,5], John Stix[1]**

[1] McGill University, Montreal, Canada
[2] Dipartimento DiSTeM, Università degli Studi di Palermo, Palermo, Italy
[3] Istitutio Nazionale di Geofisica e Vulcanologia, Palermo, Palermo, Italy
[4] Department of Earth and Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 4, 20126, Milan, Italy
[5] Istitutio Nazionale di Geofisica e Vulcanologia, Sezione di Milano, Via Alfonso Corti 12, Milan, Italy

## Contents of this file

Text S1 to S7
Figures S1 to S8
Caption for Dataset S1
Caption for Dataset S2

## Additional Supporting Information (Files uploaded separately)

Dataset S1
Dataset S2

## Introduction

The Supporting Information contains details of the methods including sampling instrumentation (Text S1), fractionation tests (Text S1), isotopic analysis and calibration (Text S1 -S4 and Figures S1-S5), comparison of regression methods of calculating the volcanic source (Text S5-S6 and Figures S6-S8), and modelling parameters and equations for the pressure- depth-carbon isotope model (Text S7). We also include captions for datasets S1 and S2 which are uploaded as separate files.

**Text S1. Sampling techniques and methodology**

2018 UAS and non-automated pump

This was the first attempt to capture volcanic gas samples, which was used at Stromboli in 2018. This first approach was a simple combination consisting of a 1.2 L/minute TD-3LS Brailsford® pump powered by a USB battery. The pump and battery were contained in a lightweight plastic container, with tygon tubing leading from the outlet to a 15 cm copper tube filled with copper filings to eliminate $H_2S$ gas from being sampled, in order to reduce interference with subsequent carbon isotopic analysis as described in (Malowany et al., 2015). From the copper tube, short segments of tubing <20 cm were connected in series to two to ten 600 ml gas bags. This payload was placed into a mesh drawstring bag and suspended from a 2 metre long paracord, inspired by similar designs to capture volcanic crater water samples while keeping the UAS above the corrosive gases. This cord was attached with a carabiner to the lower frame of a TurboAce Matrix I quadcopter with a flight time of ~10 minutes. The pump was manually turned on with a switch just before take-off and turned off just after landing.

2019 UAS and CARGO 4.0

Building upon the challenges of the first test in 2018, we decided to build a new custom gas sampling system integrated with telemetry functions for the 2019 sampling campaign at Stromboli. The UAS was maneuvered with one remote controller by the pilot, while the gas sampling unit was controlled by a second person using a secondary remote controller to switch the pump on and off. The Compact Aerial Receiver-initiated Gas-sampling operation (CARGO 4.0) did not include copper tubes in order to limit excess weight for longer flight times. The other main difference is that the pump switch and $SO_2$ sensor were mapped to channels on a remote controller for the drone, allowing the pilot to use two-way telemetry to read the voltage of the $SO_2$ sensor and turn the pump on and off for sampling.  The payload (700 grams) consisted of a pump (micropump®, model d3k, 2.5 L/minute) connected to an electronic switch (Turnigy 10A/30V) which utilized an empty standard port on the UAS receiver. An $SO_2$ sensor (Citicell 0-200 ppmv range) was included with a voltage sensor (Futaba SBS-01V) connected to the SBUS2 port of the receiver and one of the inlet tubes of the pump. A portable USB-powered charger supplied power to the pump while a 9 volt battery powered the $SO_2$ sensor.
The assembly was deployed with two different UAS over the course of the fieldwork; a DJI Matrice 100 on June 17-18 and a DJI Inspire on June 20. The DJI Matrice 100 (UAS #1, figure 1) had a flight time of ~20 minutes and a payload comprising the gas sampling configuration attached on top of the UAS body which was secured with bungee cords, while two to four gas sample bags were attached directly below the drone. The DJI Inspire 1 (UAS #2, figure 1) had a flight time of ~10 minutes with the payload comprising the CARGO 4.0 as a separate unit suspended 1.5 metres below the UAS in a mesh bag.

Fractionation test of the CARGO 4.0

While the first sampling technique in 2018 involved a simple tubing and pump system, the multicomponent assemblies used in 2019 required that the gas pass through an $SO_2$ sensor before being drawn through the pump and into sample bags (Figure 1c and 1d).

We performed a simple test to evaluate possible fractionation from gas flowing through the $SO_2$ sensor in the 2019 CARGO. We analyzed a gas standard (-15.6 ‰ $\delta^{13}CO_2$) before passing it through the 2019 sampling assembly and collecting the gas for subsequent measurement (supplementary material). The measured value of the standard ranged from -15.77 ± 0.44 ‰ to -15.82 ± 0.38 ‰ $\delta^{13}CO_2$ before passing through the system and from -15.66 ± 0.35 ‰ to -15.83 ± 0.43 ‰ $\delta^{13}CO_2$ after passing through the $SO_2$ sensor and pump. This is a difference of 0.04 ‰ between the medians of the two sets of samples, indicating that isotopic fractionation due to passage through the $SO_2$ sensor is negligible or non-existent, as has been shown in other similar systems (Schipper et al., 2017)

Ground-based plume sampling
Ambient plume samples were taken from the crater rim by placing the inlet tube on top of a hiking stick 1 metre above the ground and connected to a mulltiGAS sensor with continuous pumping. When the multiGAS indicated high $SO_2$ readings, a 600ml sample bag was connected to the outlet tube and filled.

**Text S2. Isotopic analysis**
The gold standard for $\delta^{13}C$ analysis is Isotope Ratio Mass Spectrometry (IRMS); however, these instruments must be kept in a stable lab environment due to their sensitivity. Rizzo et al. (2014) demonstrated that $\delta^{13}C$ studies of volcanic plumes with laser-based isotope ratio infrared spectrometers (IRIS) are feasible for harsh environments and provide comparable isotopic results to those measured by IRMS. Similarly, Malowany et al. (2017) demonstrated that a Cavity Ring-Down Spectrometer (CRDS) could be used for near real-time $^{13}C$ analysis of volcanic plumes. In our study, we used both an IRIS (Delta Ray from Thermo Scientific) and a CRDS (G2201-i from Picarro). We analyzed a subset of samples on each instrument by connecting sample bags to the Picarro instrument until a stable $\delta^{13}C$ signal was achieved, then detaching the bag and immediately measuring the same bag on the Delta Ray instrument. A series of standard gases was used to calibrate the Picarro instrument in 2018, and both the Picarro and Delta Ray in 2019. In 2018, the two instruments were in good agreement, with standard deviations between the same sample bag measured on each instrument never exceeding 0.4 ‰. In 2019, the standard deviations of individual measurements between the two instruments did not exceed 0.7‰, with a maximum difference of 1 ‰ between analysis of the same sample on each instrument.

All samples were analyzed within 12 hours on a Picarro G2201-i CRDS and a Thermo Scientific Delta Ray IRIS at the field station. A copper tube filled with fine copper wire cuttings was used to remove any interference from $H_2S$, and three in-house standards (-43.15‰, -15.6‰, and -11.4‰) were used to define a calibration curve (supplemental info). A standard was run every 5 to 12 samples at concentrations ranging from 450 to 1050 ppmv $CO_2$ to monitor instrumental drift. Stable carbon isotopes were calculated using delta notation, where:

$$\delta^{13}C \ (‰) = \left( \frac{\left( {}^{13}C/{}_{12}C \right)_{sample}}{\left( {}^{13}C/{}_{12}C \right)_{standard}} - 1 \right) \cdot 1000 \qquad [1]$$

Carbon isotopic results are reported using the per mil notation which provides values relative to the Vienna Pee Dee Belemnite (VPDB) reference standard. Repeat analysis of 8 standards shows that uncertainties are ~0.3 ‰.

Our data is unique in that we were able to perform the usual calibrations with standards brought into the field in overpressured Wheaton gas bottles, as well as compare our isotopic results across the two portable instruments (Picarro and Delta Ray) in the field. In the following section we explain how we corrected the data.

**Text S3. Standards for calibration of isotopic data**

The 2018 Picarro data were calibrated with 18 individual standard measurements (Figure S1). The standards were measured at the beginning of the field campaign on May 12, as well as each day before and after samples were analyzed. The standards used were -15.6 per mil, -43.15 per mil, and -11.4 per mil. The Delta Ray analyses were corrected internally by the system which uses an intake of two reference gases from gas cylinders. The difference between the corrected Picarro and Delta Ray data was less than 0.5 per mil with a standard deviation of 0.16 per mil.

The 2019 data, being a larger dataset than that of 2018 as well as having standards analyzed on both the Picarro and Delta Ray instruments, underwent an extensive calibration (Figure S2). The Picarro data were calibrated with 15 individual standard measurements. The standards were measured at the beginning of the field campaign on June 17 as well as each day before and after samples were analyzed. In addition to an internal calibration, the Delta Ray underwent a calibration with 6 standards. For both Delta Ray and Picarro, the standards used were -15.6 per mil and -43.15 per mil, while the Picarro also used three additional standards for manual calibration of -11.4 per mil, -3.88 per mil, -39.98 per mil, and -0.63 per mil. The difference between the corrected Picarro and Delta ray values was less than 1.0 per mil with a standard deviation of 0.35 per mil.
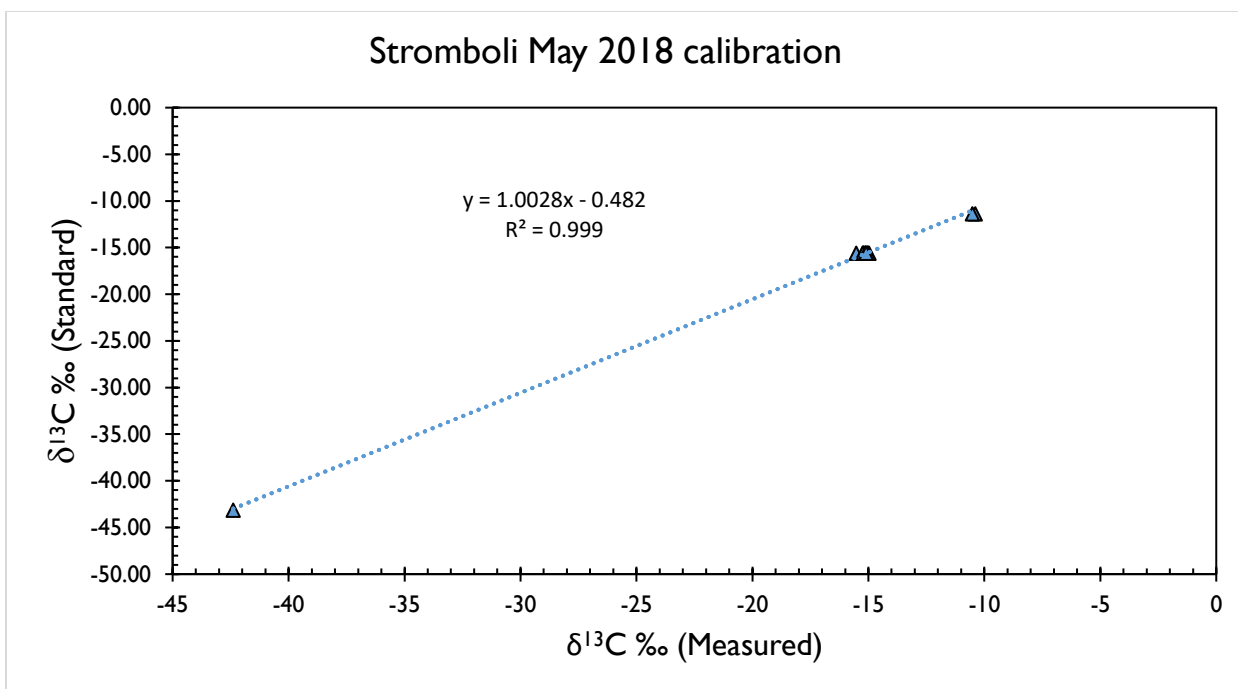
## Stromboli May 2018 calibration

$$y = 1.0028x - 0.482$$
$$R^2 = 0.999$$

**Figure S1.** Calibration of 2018 standards measured on the Picarro instrument versus known standard values. The line of best fit is used to correct all Picarro data from the 2018 field campaign. The correction brought the carbon isotopic value 0.75 per mil lighter, on average.
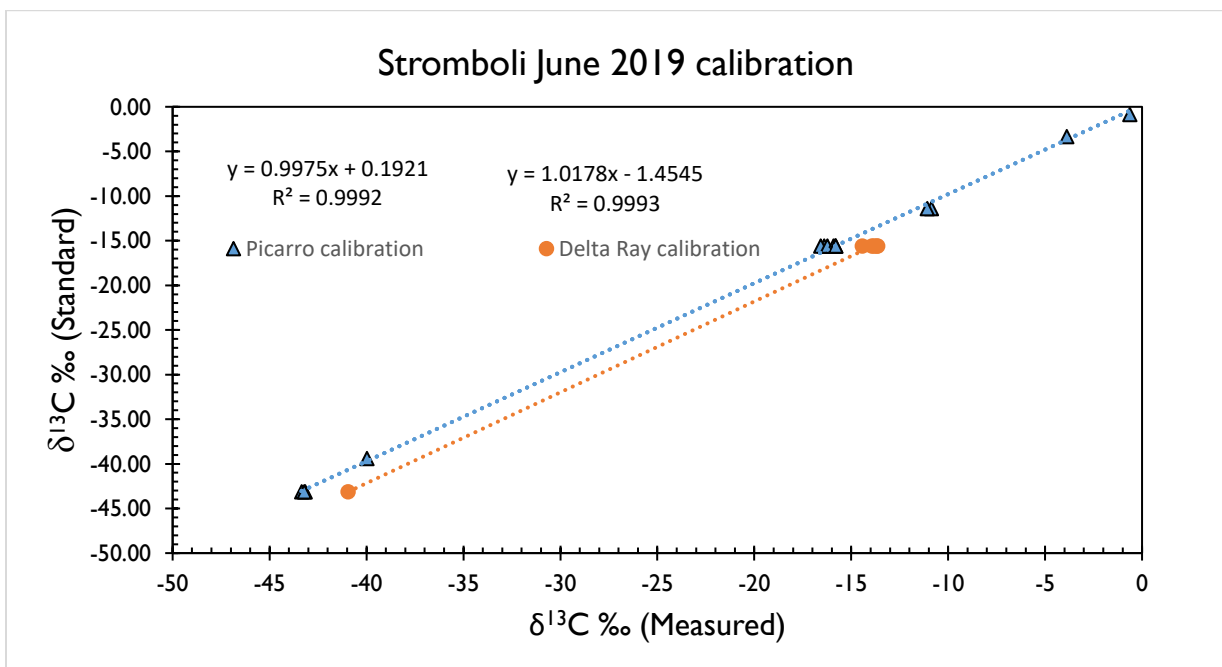
## Stromboli June 2019 calibration

$$y = 0.9975x + 0.1921$$
$$R^2 = 0.9992$$

△ Picarro calibration

$$y = 1.0178x - 1.4545$$
$$R^2 = 0.9993$$

● Delta Ray calibration

**Figure S2:** Calibration of 2019 standards measured on the Picarro and Delta Ray instruments versus known standard values. The orange line of best fit is used to correct all Delta Ray data and the blue line of best fit is used to correct all Picarro data from the

2018 field campaign. The correction brought the carbon isotopic value 0.2 per mil heavier for Picarro and 1.6 per mil lighter for Delta Ray, on average.

## Text S4. Calibration for concentration

We also performed a test to determine if a correction for the $CO_2$ concentration between the two instruments was necessary. After plotting concentration for matching analyses from both instruments against each other (Figures S3, S4), we applied a correction to the Picarro dataset based on the Delta Ray concentrations. While the 2018 concentrations of equivalent samples on each instrument was a 20ppm difference on average, the correction brought the difference down to less than 4ppm. However, as we had a smaller subset of samples on the Delta Ray, this led to a coefficient of regression less than 0.5. The 2019 concentrations of equivalent samples on each instrument was a 13ppm difference on average, and the correction brought the difference down to 1ppm. Finally, when the Picarro values which were corrected for concentration were plotted together with the Delta Ray data, each dataset deviated from the other in that the intercepts were different by 4 per mil or more (Figure S5).  Since we could not ascertain which instrument has more accurate concentrations, we decided to omit the correction for concentration to avoid over-processing the data. In future work, we would perform a calibration with standards of known concentration in the same way that the isotopic values were calibrated.
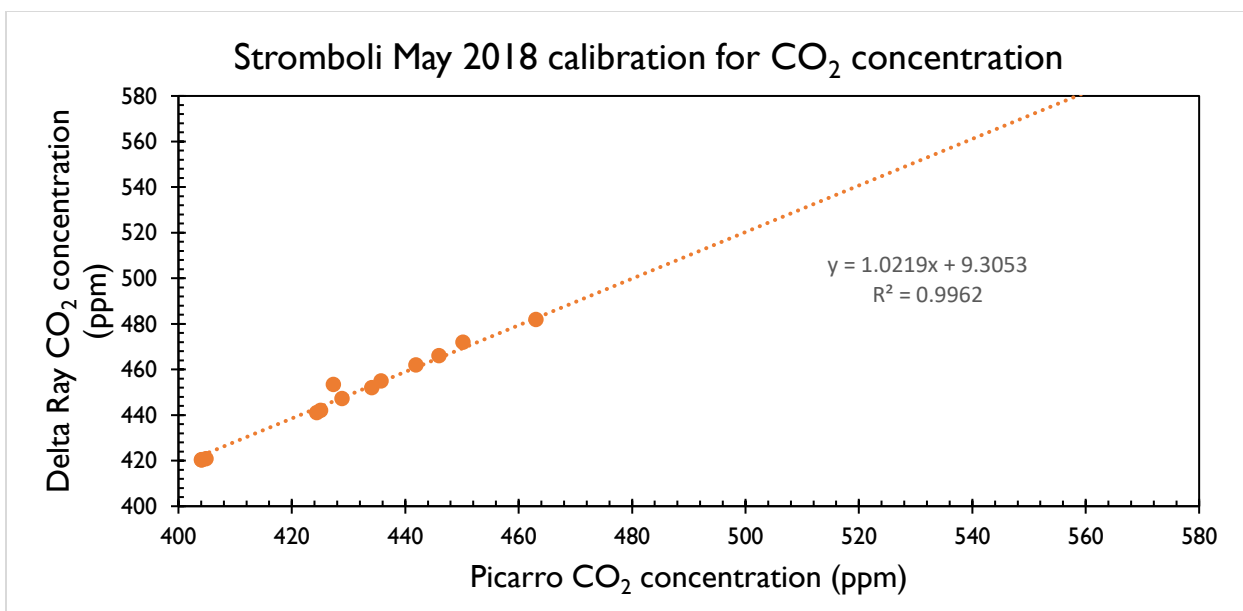
**Stromboli May 2018 calibration for $CO_2$ concentration**

$y = 1.0219x + 9.3053$
$R^2 = 0.9962$

Delta Ray $CO_2$ concentration (ppm)

Picarro $CO_2$ concentration (ppm)

**Figure S3:** The Picarro versus Delta Ray concentration data for the 2018 field campaign.

**Stromboli June 2019 calibration for $CO_2$ concentration**

$y = 0.9887x + 26.721$
$R^2 = 0.9949$

CO2 concentration (Delta Ray)

Picarro $CO_2$ concentration (ppm)
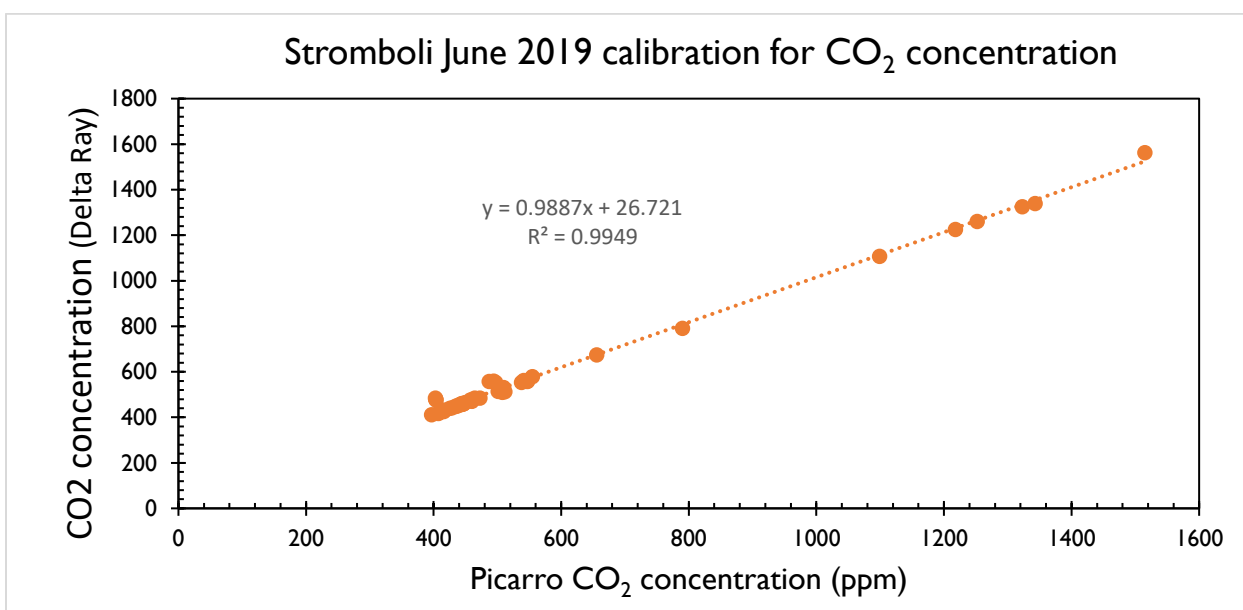
**Figure S4**: The Picarro versus Delta Ray concentration data for the 2019 field campaign.
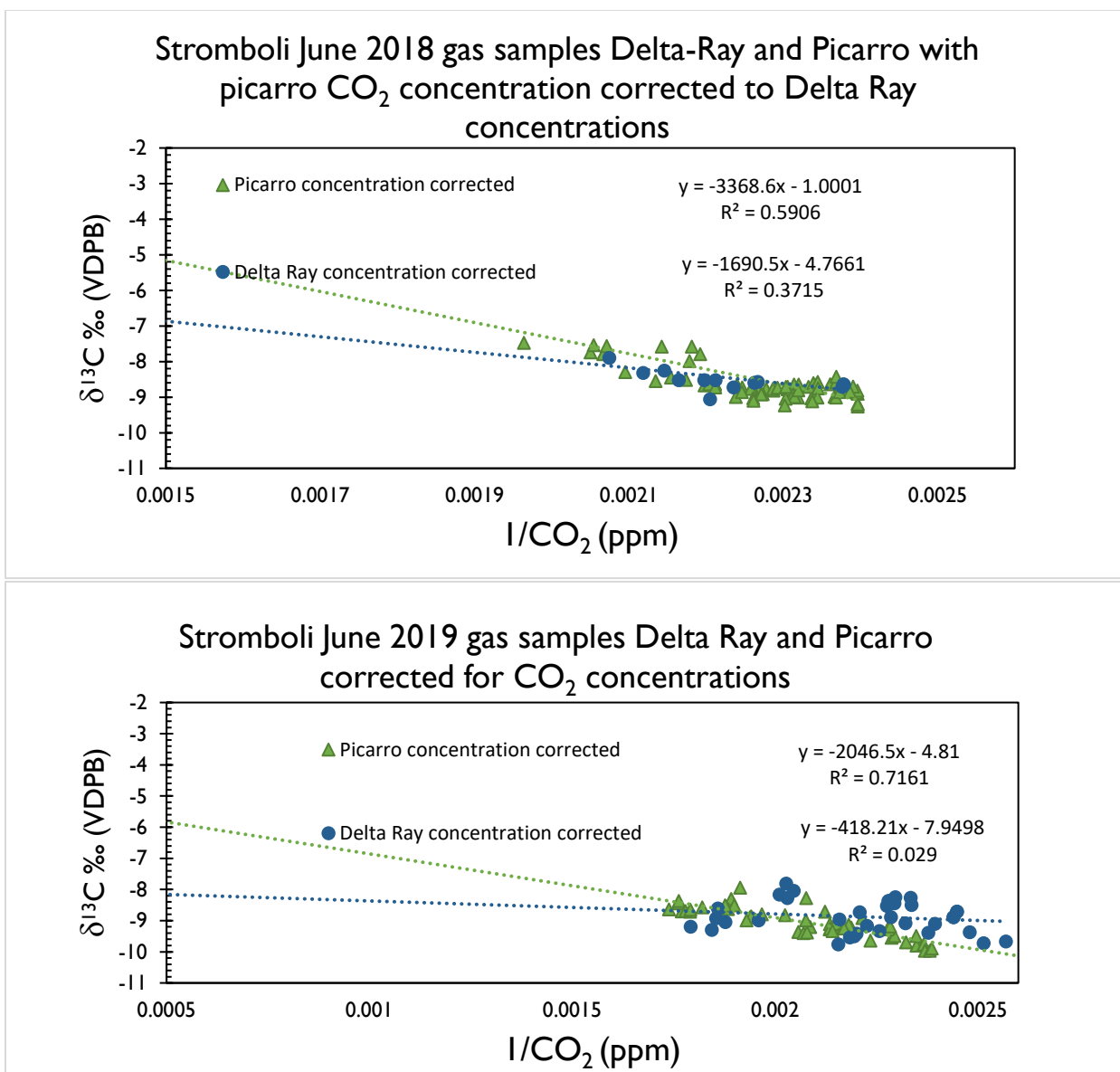
**Figure S5**: The Picarro and Delta Ray corrected concentration data for the 2018 (top) and 2019 (bottom) field campaigns.

**Text S5. Cross calibration of regression analysis between Delta Ray and Picarro**

In order to assess whether the difference between 2018 and 2019 data is significant, i.e. whether it represents a true volcanic variation in signature rather than being an artifact of the data processing, we were able to perform many tests to cross-calibrate the data between the two instruments to check the accuracy of each dataset. After calibration, differences between the two samples sets remained, which we discuss below.

The discrepancy between 2018 Delta Ray and Picarro data is likely due to the limited number of samples for a single day of measurements for the Delta Ray. This reduces the accuracy of the dataset, as can be seen by the low coefficient of regression for delta ray in

figure S6 (R2=0.37). It is possible that there were spatial and/or temporal variations at play as well. Unlike 2019, in 2018 we flew from two different take-off points to capture the samples and these flights were vent-specific. On 15 May, we flew from the pizzo targeting the C vent, which coalesces into a bulk plume at around 100 m height where plumes from several vents in the central and south crater merge. On 16 and 17 May, we flew from the helipad targeting the NE vent. While the Picarro collected samples on 15 to 17 May, the Delta Ray collected data only on 16 May. The lower intercept of the Delta Ray data (-4.8‰) is consistent with the 16 May Picarro data (Figure S7), which has a much lower intercept (-3.8‰) compared to the full Picarro dataset (-0.36‰). Furthermore, the combined Picarro and Delta Ray data for 2018 (Figure S6) shows a lower intercept (-2.0‰) than the Picarro data alone (-0.36‰), since the 16 May data are weighted towards lighter values from the additional Delta Ray samples.

The overall intercept for 2019 with Picarro data is -5.0 ‰ and a high $R^2$ value of 0.7, while the Delta Ray intercept is -7.8 ‰ with a $R^2$ of 0.03 (Figure S8). The combined data yield an intercept of -5.9 ‰ (R2= 0.3). Again, the 2019 differences between Delta Ray and Picarro are likely due to fewer analyses performed by the Delta Ray as well as a larger spread of data in the Delta Ray results.
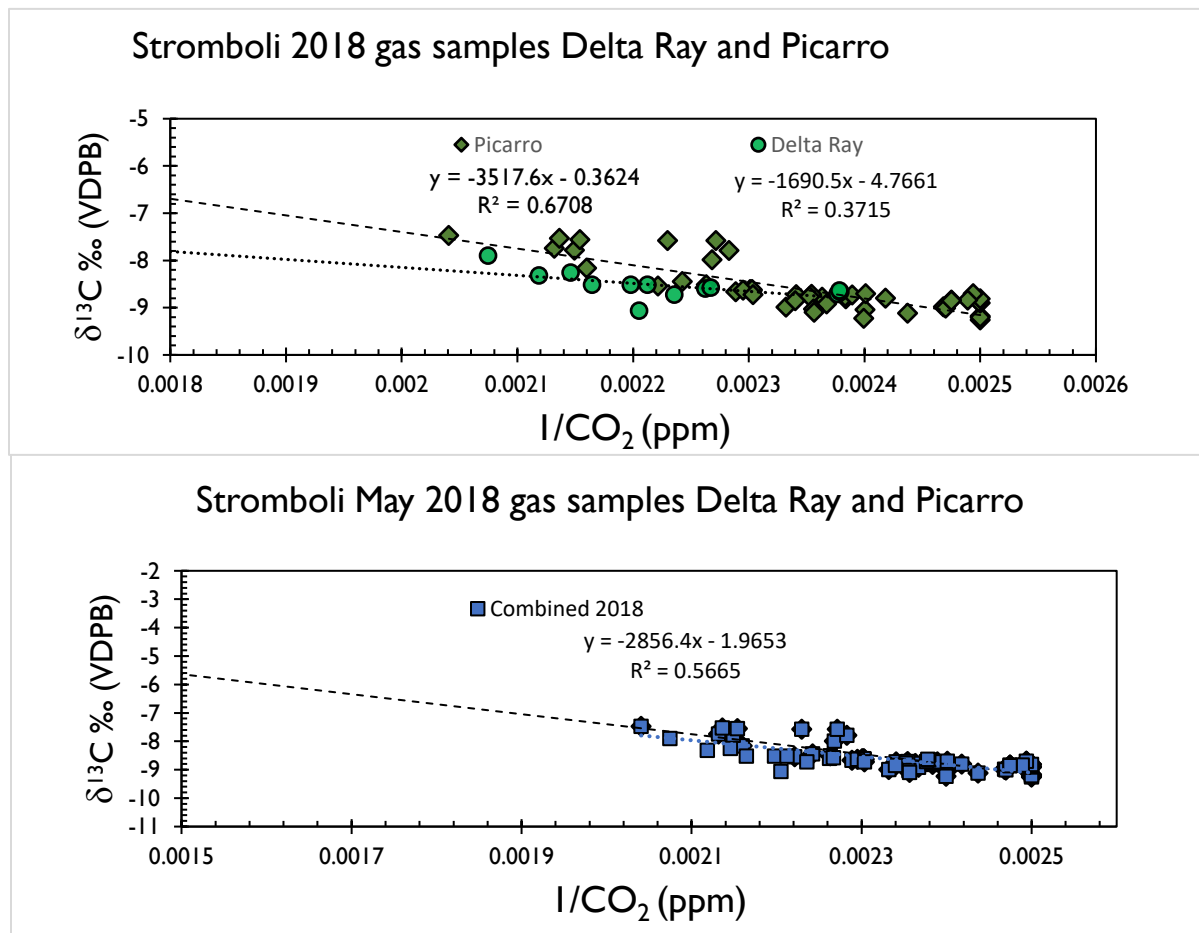


**Figure S6**: The Picarro and Delta Ray data for 2018 showing the datasets from both instruments plotted separately (top) and combined (bottom).
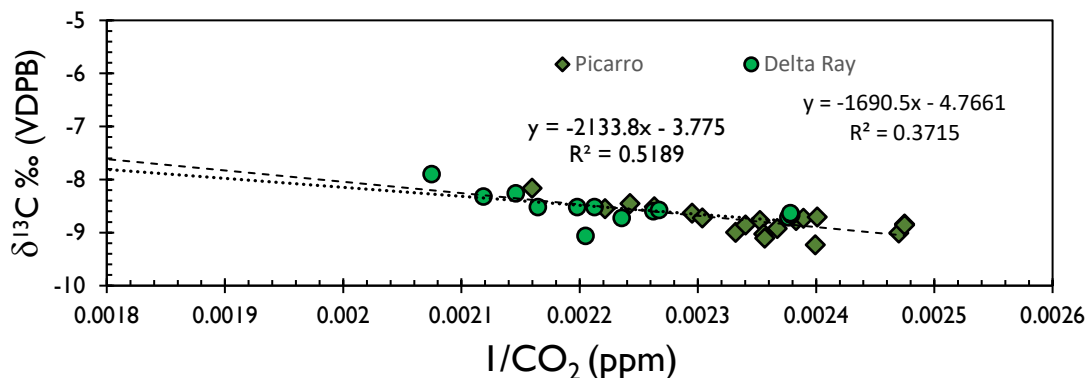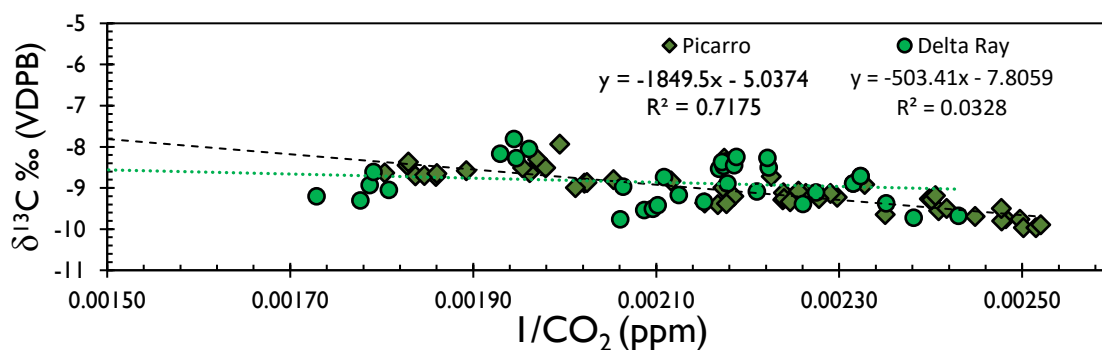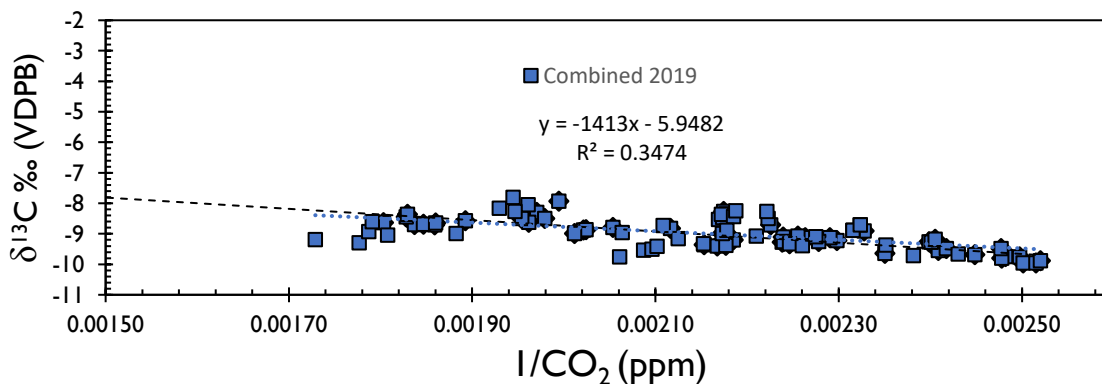
**Figure S7**: The Picarro and Delta Ray data for May 16 2018 showing the datasets from both instruments plotted separately. These include background, UAS flights, and ground-based plume samples.



**Figure S8:** The Picarro and Delta Ray data for 2018 showing the datasets from both instruments plotted separately (top) and combined (bottom).
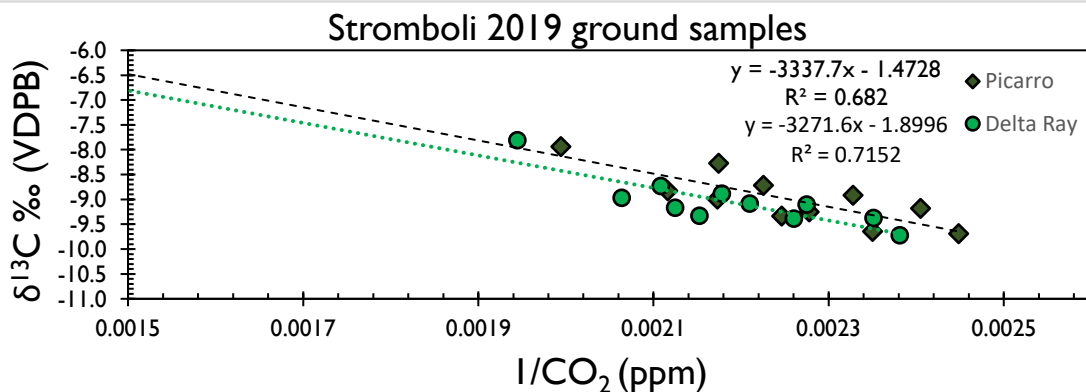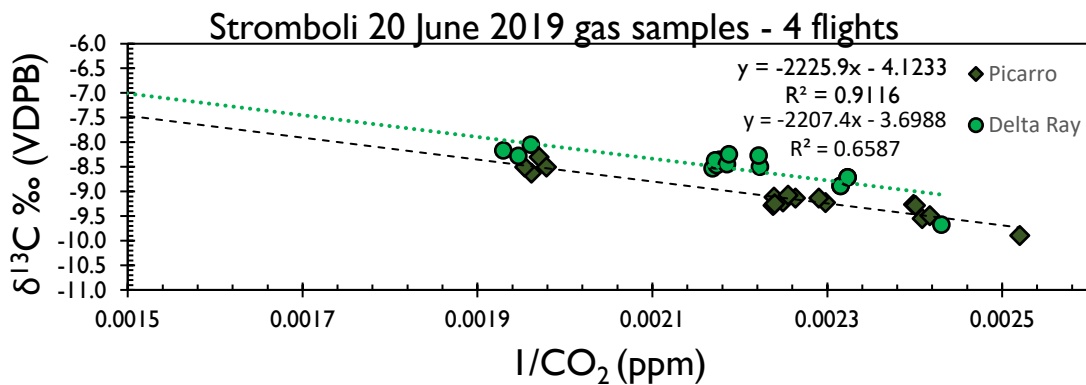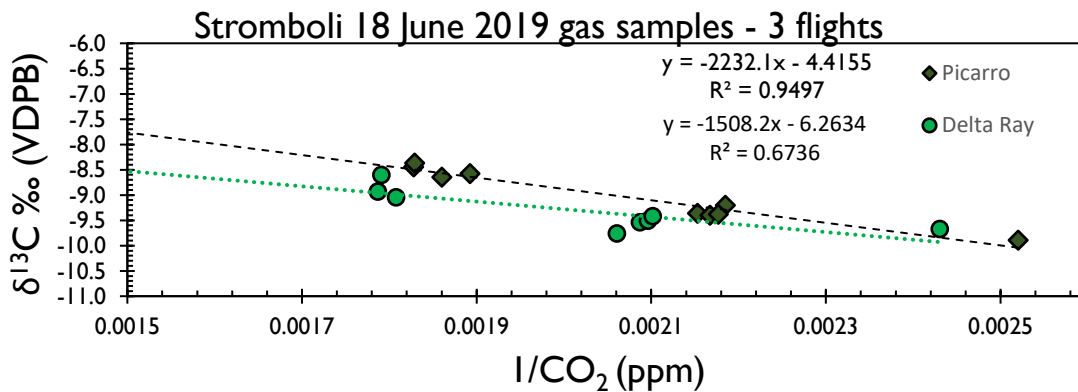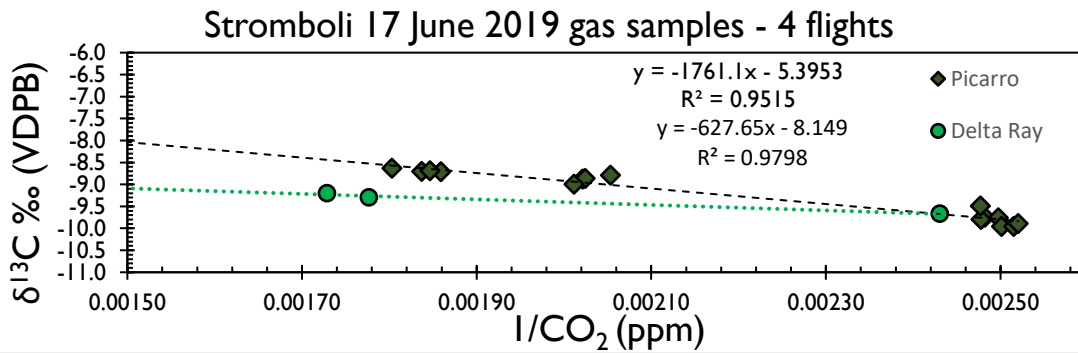
**Figure S9:** Picarro and Delta Ray data for 2019 UAS flights and ground samples.

**Text S6. Comparison of Picarro and Delta Ray results for individual days in 2019**

In 2019, Picarro data spans June 17, 18, and 20, while the Delta Ray data has just three datapoints from June 17 with most data from June 18 and 20. In 2019, we always flew from the pizzo and targeted the plume emanating from the central and south craters. One factor to consider here is that the plume emanations varied from one day to the next, so we plotted the individual days of data for the 2019 campaign (Figure S9). Of the four individual plots, the intercept on the 17 June is the most negative and the only plot where Delta Ray data comprises just three data points. This may explain the more negative (-8.1 ‰) intercept of the Delta Ray compared to the Picarro (-5.4‰) which has 13 data points. Interestingly, the ground samples for 2019 are much less negative than the UAS data, indicating that the ground samples may have a component of diffuse soil gas from the shallow hydrothermal system that the UAS samples directly above the plumes do not. It is notable that for all individual days of UAS flights, the data regress very well with $R^2$ values above 0.9 for Picarro and 0.6 for Delta Ray. It is unclear why the $R^2$ is so low for delta ray for the entire 2019 campaign, except that due to the large correction required to calibrate the data, the resulting values became scattered, leading to greater residuals when a linear regression was performed. Even though the combined dataset for Picarro and Delta Ray has significantly different intercepts in 2018 (-1.97 ‰) and 2019 (-5.95 %), we used the Picarro data because of the greater number of samples which were analyzed by the Picarro instrument compared to the Delta Ray. The intercomparison between the two instruments was used to examine small differences and to verify the overall consistency of our data.

**Text S7. Modelling**

We use a model which calculates the fraction of $CO_2$ remaining in the melt as a magma body rises and degasses, with starting parameters of 1000MPa, 2 wt % $CO_2$, NNO=0 (oxidation state). This is based on the Chosetto model of Moretti and Papale, 2004. We couple the output of this model with the closed and open degassing equations to determine the carbon isotopic signature of the melt and gas at each step of the model (Gerlach and Taylor, 1990). Heavier carbon is preferentially exsolved from a melt into the gas phase, with the gas-melt fractionation factor ranging from +2 to +4.5)(Javoy et al., 1978; Mattey, 1991). Here, we use a value of +3.5 as is common practice in recent studies (e.g., (Aubaud, 2022 and references therein). Accordingly,

$$\delta^{13}C_{gas} = \delta^{13}CO_{melt} + \Delta^{13}C_{gas-melt} \qquad [5]$$

The equation for closed-system degassing we use is:
$$\delta^{13}C_{gas(residual)} = \delta^{13}CO_{melt(primordial)} - (1-F)\Delta^{13}C_{gas-melt} \qquad [6]$$

The equation for open-system degassing is:
$$\delta^{13}C_{pm} = \delta^{13}CO_{res} + 1000(1-F^{\alpha-1}) \qquad [7]$$

**Data Set S1. Carbon isotopes from Stromboli volcano summit, 2018-2019**

The calibrated data for the 2018 and 2019 $CO_2$ concentrations and carbon isotopes from Stromboli volcano

**Data Set S2. Calculations of discrete carbon isotopes from Stromboli volcano summit, 2018-2019**

The calibrated data and calculations using the weighted means method for the 2018 and 2019 $CO_2$ concentrations and carbon isotopes from Stromboli volcano. The weighted means calculations use only plume samples with volcanic $CO_2$ greater than 50 ppm above background as in Schipper et al. 2017