



## RESEARCH ARTICLE

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## Carbon isotope systematics of Turrialba volcano, Costa Rica, using a portable cavity ring-down spectrometer

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## Key Points:

- Spatial heterogeneity in the  $\delta^{13}\text{C}$  of volcanic gases imply hydrothermal modification of volcanic  $\text{CO}_2$  at Turrialba
- The hyperbolic mixing model for predicting volcanic end-member compositions is preferred to the Keeling method
- Diurnal changes in  $\delta^{13}\text{C}$  can impact volcanic plume measurements in densely vegetated areas

## Supporting Information:

- Supporting Information S1
- Table S1

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**Abstract** Over the past two decades, activity at Turrialba volcano, Costa Rica, has shifted from hydrothermal to increasingly magmatic in character, with enhanced degassing and eruption potential. We have conducted a survey of the  $\delta^{13}\text{C}$  signatures of gases at Turrialba using a portable field-based CRDS with comparison to standard IRMS techniques. Our  $\delta^{13}\text{C}$  results of the volcanic plume, high-temperature vents, and soil gases reveal isotopic heterogeneity in the  $\text{CO}_2$  gas composition at Turrialba prior to its recent phase of eruptive activity. The isotopic value of the regional fault system, Falla Ariete ( $-3.4 \pm 0.1\text{‰}$ ), is in distinct contrast with the Central crater gases ( $-3.9 \pm 0.1\text{‰}$ ) and the 2012 high-temperature vent ( $-4.4 \pm 0.2\text{‰}$ ), an indication that spatial variability in  $\delta^{13}\text{C}$  may be linked to hydrothermal transport of volcanic gases, heterogeneities in the source composition, or magmatic degassing. Isotopic values of  $\text{CO}_2$  samples collected in the plume vary from  $\delta^{13}\text{C}$  of  $-5.2$  to  $-10.0\text{‰}$ , indicative of mixing between atmospheric  $\text{CO}_2$  ( $-9.2 \pm 0.1\text{‰}$ ), and a volcanic source. We compare the Keeling method to a traditional mixing model (hyperbolic mixing curve) to estimate the volcanic source composition at Turrialba from the plume measurements. The predicted source compositions from the Keeling and hyperbolic methods ( $-3.0 \pm 0.5\text{‰}$  and  $-3.9 \pm 0.4\text{‰}$ , respectively) illustrate two potential interpretations of the volcanic source at Turrialba. As of the 29 October 2014, Turrialba has entered a new eruptive period, and continued monitoring of the summit gases for  $\delta^{13}\text{C}$  should be conducted to better understand the dominant processes controlling  $\delta^{13}\text{C}$  fractionation at Turrialba.

## 1. Introduction

The isotopic composition of  $\text{CO}_2$  gas being emitted from volcanoes is a well-established tool for understanding their degassing character [Taylor, 1986; Gerlach and Taylor, 1990; Carapezza et al., 2004]. Previous studies have tried to link temporal variations in carbon isotopes to the eruptive potential of a volcano by inferring periods of magma replenishment from variations in the isotopic signature [i.e., Paonita et al., 2002; Hilton et al., 2010; Vaselli et al., 2010; Paonita et al., 2013; Fischer et al., 2015]. Measurements of the  $\delta^{13}\text{C}$  composition of volcanic plumes provide a link to the isotopic composition of magmatic gas without necessitating direct sampling from fumaroles or vents [Chiodini et al., 2010; Liotta et al., 2010], which is hazardous during periods of enhanced eruptive potential. The recent development of portable instruments capable of measuring isotope compounds in near real time [O'Keefe and Deacon, 1988] presents the possibility of using isotopic measurements of plume gases as a monitoring tool at active volcanoes.

Cavity-enhanced absorption spectroscopy was originally developed for isotopic measurements of atmospheric gas and recently has been adapted for volcanic environments [Lucic et al., 2015]. The successful application of isotope ratio infrared spectrometers to measure the  $\delta^{13}\text{C}$  composition of  $\text{CO}_2$  in a volcanic plume demonstrates the ability of these instruments to resolve the isotope composition of the magmatic source [Rizzo et al., 2014, 2015]. In this paper, we use a cavity ring-down spectrometer (CRDS) to characterize the magmatic isotope composition of a volcanic plume by adapting the Keeling method [Keeling, 1958], and comparing it to a commonly used binary mixing model [Chiodini et al., 2010; Liotta et al., 2010]. The Keeling approach was originally formulated to derive the biogenic component of atmospheric  $\text{CO}_2$  using a two-component mixing model characterized by  $\delta^{13}\text{C}$  composition and  $\text{CO}_2$  concentration. Here we use it to represent the mixture between the volcanic source and ambient atmosphere as

manifested in a volcanic plume. This approach is more sensitive to small isotopic changes and is easy to implement in near real time, thereby facilitating the future application of cavity-enhanced spectrometers as forecasting tools.

Portable spectrometers permit a broad characterization of magmatic gases with minimal sample preparation and analysis time [Lucic *et al.*, 2015], which was advantageous for gas sampling at Turrialba volcano, Costa Rica. We performed isotope analyses on a variety of gas types at Turrialba, including the volcanic plume, the 2012 high-temperature vent, fumaroles, and soil gases. Previous carbon and helium isotope data suggest that Turrialba may have short time scale variations in magmatic volatile sources linked to tectonic-scale processes over the period of several months [Hilton *et al.*, 2010]. However, the major gas compositions have suggested that high-temperature vents are related to a single magmatic composition, and that local variation in the CO<sub>2</sub>/SO<sub>2</sub> ratio and the SO<sub>2</sub> flux result from the drying of the hydrothermal system with increasing magmatic activity [Moussallam *et al.*, 2014; Conde *et al.*, 2014; de Moor *et al.*, 2016]. We apply our  $\delta^{13}\text{C}$  characterization of the Turrialba gases to assess heterogeneity in carbon isotope compositions and link spatial and temporal trends to the observed activity at Turrialba.

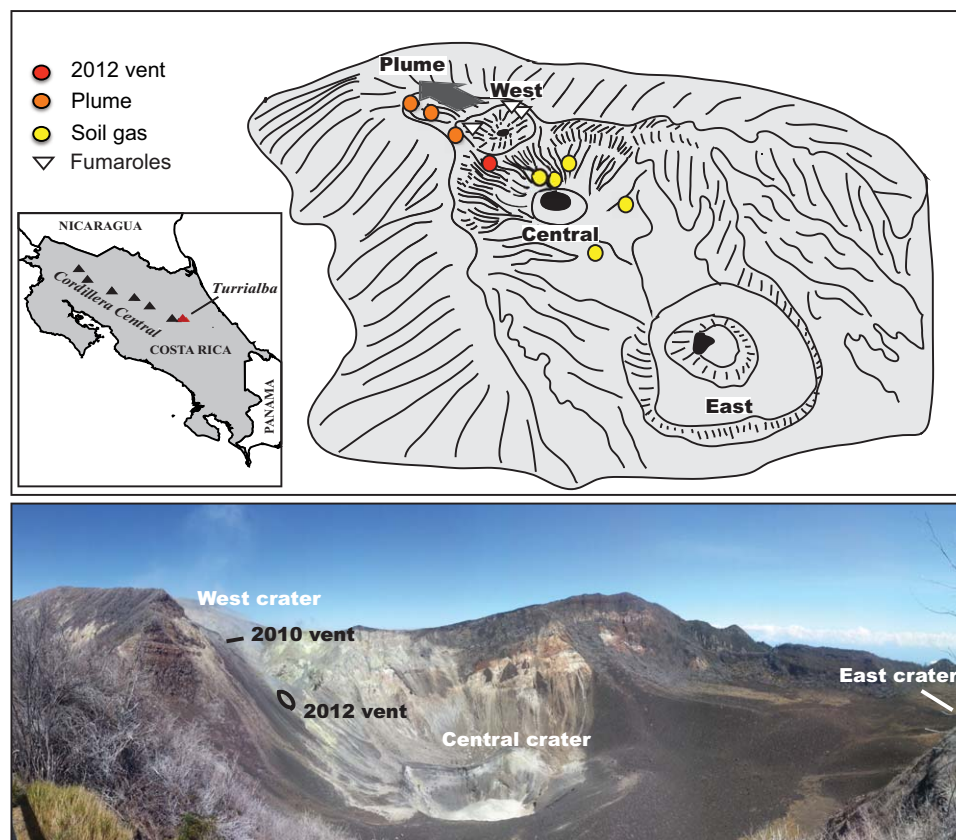
### 1.1. Geologic Setting

Turrialba is a basaltic andesite arc volcano in Costa Rica, formed as part of the Central American Volcanic Arc (CAVA), an expression of the Cocos Plate subducting beneath the Caribbean plate [Reagan *et al.*, 2006; Freundt *et al.*, 2014]. Turrialba shares a plumbing system with its neighboring volcano, Irazú, and together they compose the largest stratovolcano complex in Central America [Carr *et al.*, 1990]. CAVA extends from Guatemala to Costa Rica, and substantial variation in gas chemistry and magma composition has been observed resulting from differences in the along-arc structural and magmatic character [Carr *et al.*, 1990; Protti *et al.*, 1995; Shaw *et al.*, 2003; Zimmer *et al.*, 2004; Aiuppa *et al.*, 2014]. Turrialba is upwind of the Central Valley in Costa Rica, ~20 km from the country's densest population center of San Jose, and ~30 km from the international airport. Eruptions from Turrialba are of concern for their direct impact on local farmland and urban centers [Reagan *et al.*, 2006]; recent eruptions commencing on 29 October 2014 have had substantial impact on the local community and have resulted in local evacuations and airport closures [de Moor *et al.*, 2016; Alvarado *et al.*, 2016; Rizzo *et al.*, 2016]. Turrialba has had six major phreatic and phreatomagmatic eruptions in the past 3400 years, with the last major period of activity ending in 1866 [Reagan *et al.*, 2006]. The active edifice has three visible craters, East, Central, and West, which were formed consecutively from east to west (Figure 1). The West crater was formed during the eruptive event in 1864–1866 and is the site of the recent eruptive activity.

### 1.2. Recent Activity

Turrialba experienced over a century of quiescence since its last major eruptive period from 1864 to 1866. In 1996, seismic activity and increased fumarolic activity at the summit signified a reawakening [Barboza *et al.*, 2003]. Geochemical [Tassi *et al.*, 2004; Vaselli *et al.*, 2010; Martini *et al.*, 2010] and geophysical [Conde *et al.*, 2014; Martini *et al.*, 2010; Barboza *et al.*, 2003] indicators suggest a progressive shift from hydrothermal-dominated to magmatic-dominated activity at Turrialba from 2001 to 2007 [Vaselli *et al.*, 2010]. Vent forming eruptions from 2010 to present have opened fractures that emit high-temperature (>500°C) gases [Campion *et al.*, 2012; Moussallam *et al.*, 2014; Vaselli *et al.*, 2010]. Increasing levels of degassing from the vents and fumaroles in the Central and West craters have produced sulfur deposits and generated a large visible plume [Conde *et al.*, 2014]. The gas plume is occasionally visible up to 2 km above the rim and follows the dominant windward direction to the west-southwest (Figure 1). As a result, the western flank of Turrialba has an extensive area of tree kill, where vegetation has been subjected to elevated levels of acid gases [Conde *et al.*, 2014]. A regional fault system, the Falla Ariete, trends northeast-southwest and transects the central edifice [Rizzo *et al.*, 2016]. The most prominent surface expression of this fault zone is a steep canyon on the southern flank of the volcano where fumarolic activity has been observed since 2005 [Vaselli *et al.*, 2010].

A shift from hydrothermal activity to magmatic activity dominating the gas composition at Turrialba occurred around 2007, culminating in the opening of the 2010 vent (Figure 1), after which time the activity declined temporarily [Moussallam *et al.*, 2014; Vaselli *et al.*, 2010; Conde *et al.*, 2013]. In 2012, a second episode occurred in late January, producing the 2012 vent and bringing high-temperature gases (~800°C) to



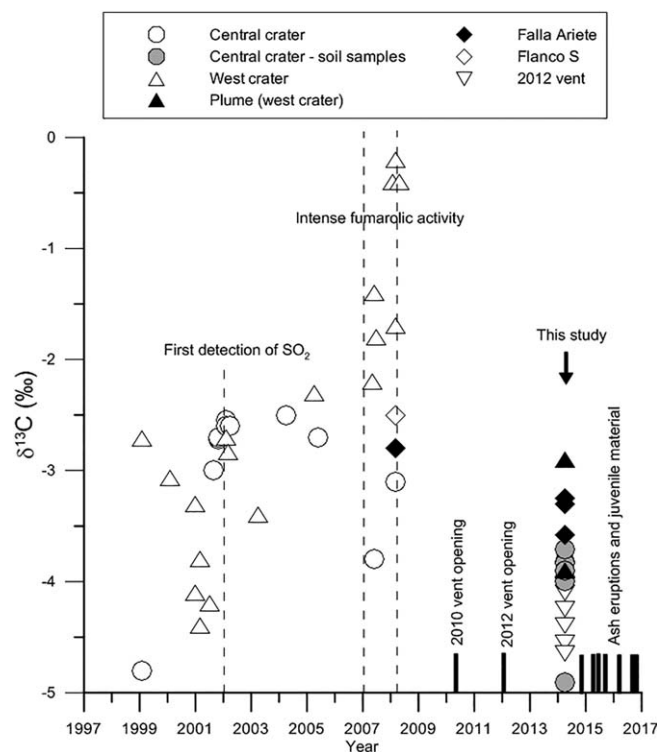
**Figure 1.** Turrialba is the southernmost volcano of the Central Cordilleran volcanic chain, a subsidiary of the Central American Volcanic Arc that extends north into Guatemala. There are three craters which constitute its edifice: East, Central, and West.

the surface. On 29 October 2014, an energetic summit eruption occurred at the West crater, eradicating the most recent vent (2012 vent) and producing ash dominated by hydrothermally altered clasts with a minor component of juvenile magmatic material [de Moor *et al.*, 2016; Rizzo *et al.*, 2016; Alvarado *et al.*, 2016]. Since this point, Turrialba has entered an active phase of frequent ash eruptions, which have continued until the present time (June 2017).

### 1.3. Geochemistry and Carbon Isotopes

Previous geochemical studies suggest a hydrothermal-magmatic origin of the gases at Turrialba volcano [Martini *et al.*, 2010; Hilton *et al.*, 2010; Vaselli *et al.*, 2010; Tassi *et al.*, 2004; Shaw *et al.*, 2003; de Moor *et al.*, 2016]. The transition between hydrothermally dominated and magmatically dominated conditions at Turrialba occurred between 2001 and 2007 as shown by large increases in the  $S_{\text{tot}}/\text{CO}_2$  and  $(\text{HCl} + \text{HF})/\text{CO}_2$  ratios [Vaselli *et al.*, 2010]. Hilton *et al.* [2010] reported a time series of  $\text{CO}_2/{}^3\text{He}$  and  $\delta^{13}\text{C}$  measurements and interpreted the data as variable slab contributions with time. More recent models suggest a similar magmatic source for the high-temperature vent gases (2012 and 2010 vents), which are causing a progressive “drying-out” of the local hydrothermal system [Campion *et al.*, 2012; Moussallam *et al.*, 2014; de Moor *et al.*, 2016]. This work builds on these geochemical studies to ascertain the processes governing the  $\delta^{13}\text{C}$  signature of  $\text{CO}_2$  at Turrialba in the months preceding its most recent eruptive period.

Isotopic measurements made during the hydrothermal stage from 2001 to 2007 [Vaselli *et al.*, 2010, Hilton *et al.*, 2010; Shaw *et al.*, 2003] were taken at fumaroles in the Central and West craters. Isotopic values of  $\text{CO}_2$  are variable between  $-3.8$  and  $-0.2\text{‰}$  with substantial differences between the Central and West craters (Figure 2). Temperatures of the reported gas samples generally did not exceed boiling temperature ( $\sim 92^\circ\text{C}$ ) except for a few samples taken at the West crater during a period of vigorous fumarolic activity in 2007, where temperatures reached upward of  $200^\circ\text{C}$ . Carbon isotopes in the fumarolic gases show temporal



**Figure 2.** Carbon isotope measurements made on Turrialba since its reawakening in 1996 [Shaw *et al.*, 2003; Vaselli *et al.*, 2010; Hilton *et al.*, 2010]. The detection of SO<sub>2</sub> in late 2001 is the first indication of magmatic degassing [Vaselli *et al.*, 2010]. Vigorous fumarolic activity in the West crater from 2007 to 2008 results in very enriched  $\delta^{13}\text{C}$  values ( $-0.2\text{‰}$ ), while Central crater values remain depleted ( $-3.3\text{‰}$ ). Our measurements record the most depleted values since its reawakening, only 6 months prior to the onset of the eruptive period starting on 29 October 2014.

tion for the current period of activity on 29 October 2014. Plume samples were collected on the rim of the West crater and on the western flank of the volcano. Soil gas samples were collected at the Central crater fumaroles, near the 2012 vent and along the Falla Ariete, to serve as a comparison to the plume gases. The 2012 vent was sampled directly with the aid of a 3 m titanium tube, and fumaroles from Falla Ariete were sampled with a soil gas probe. Ambient atmosphere measurements were made on the southern and eastern flanks of the volcano, away from regions impacted by volcanic gases. Sampling locations are indicated in Figure 3.

Gas samples were collected in duplicate, with at least one sample collected in a Tedlar gas bag for same-day analysis with the CRDS and another collected in a 30 mL evacuated vial for laboratory analysis with the IRMS. The vials were evacuated to 150 mTorr and were pretreated with 0.2  $\mu\text{L}$  of HgCl<sub>2</sub> to prevent bacterial respiration and isotopic fractionation during storage and transport. Both the plume and atmospheric samples were collected using a low flow pump built into a Crowcon CO<sub>2</sub> meter. The gas was pumped through several meters of Tygon tubing upwind of the pump to avoid capturing biogenic CO<sub>2</sub> from our respiration. The line was first purged with the sample by pumping gas for several minutes before samples were taken. Each Tedlar bag was also purged twice before being filled with approximately 1 L of gas for analysis. A 60 mL syringe was used to sample gas from the line while maintaining positive gas flow. A total of 50 mL of gas was injected into the 30 mL evacuated vial to create an overpressure. Soil gas samples were taken using a stainless steel probe coupled with the Crowcon pump or a hand pump to extract gas in the pore spaces and were then sampled using bags and vials as described above.

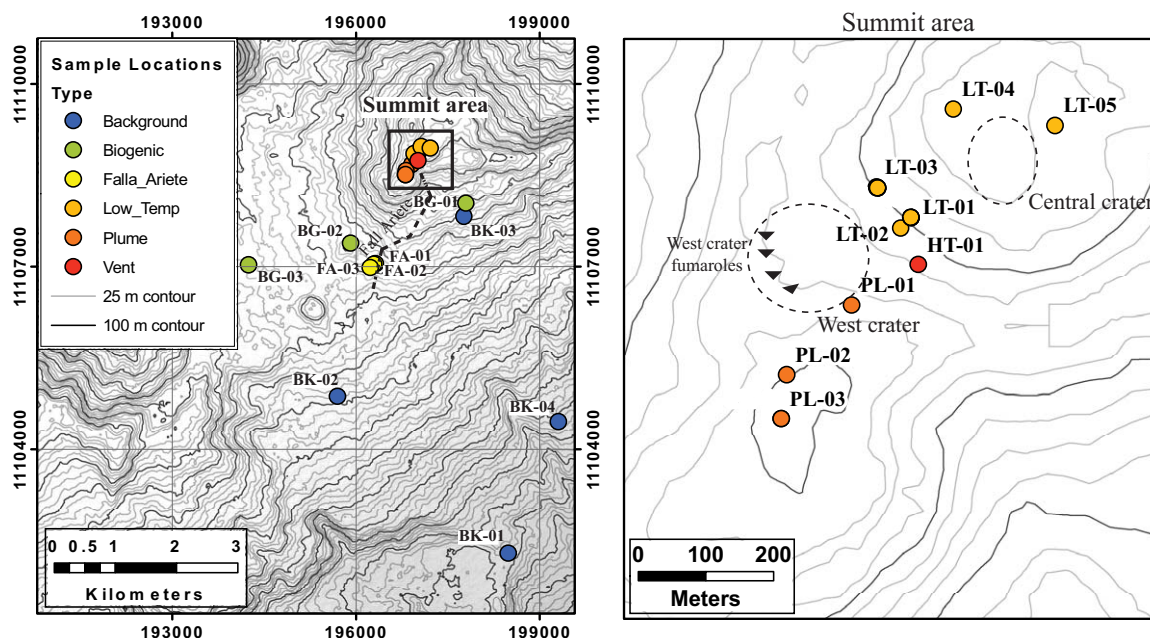
Recent work has illustrated that the spectral lines of the G1101-i CRDS have an inherent interference with large (greater than ambient) quantities of H<sub>2</sub>S [Malowany *et al.*, 2015; Lucic *et al.*, 2015]. Turrialba has H<sub>2</sub>S concentrations exceeding 20 ppm, which can cause large spectral interferences with the CRDS. A copper trap was employed to eliminate H<sub>2</sub>S from all samples prior to analysis, thereby removing any potential

variation since the reawakening in 1996, but sporadic measurements make it difficult to observe large scale changes in the volcanic system. Spatial variations in isotopic values among the Central crater, the West crater, and the Falla Ariete are evident from these studies, especially during periods of vigorous degassing. However, the limited data sets of C-isotopes have not been adequate to resolve the spatial and temporal trends at any one time on Turrialba. Increased sample density and shorter analysis times are required to establish the degassing trends related to the activity level of the volcano.

## 2. Methodology

### 2.1. Sample Collection

This study combines field measurements with a Picarro G1101-i CRDS and laboratory measurements with an isotope ratio mass spectrometer (IRMS) to evaluate the CO<sub>2</sub> isotopic composition of Turrialba gases. Our measurements were made from 1 to 6 April 2014 during a period of active degassing preceding the first eruption



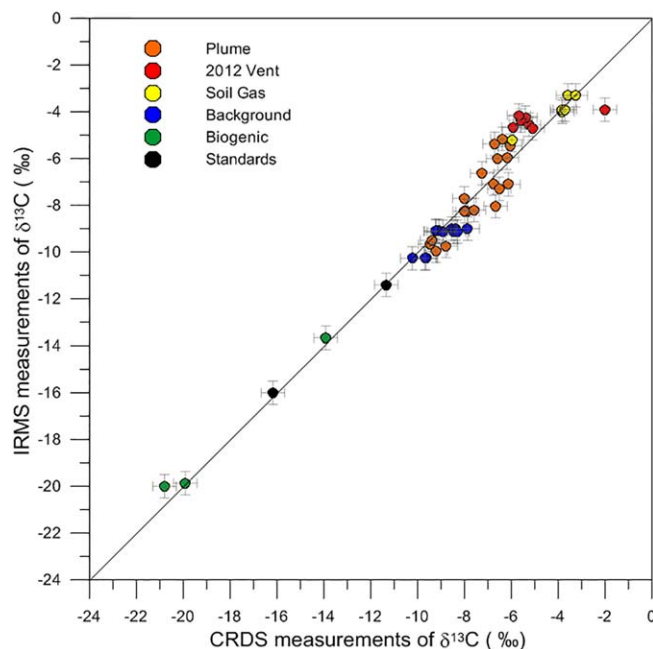
**Figure 3.** Sample locations at Turrialba volcano from 1 to 6 April 2014. Soil gas samples were taken at the low temperature, biogenic, and Falla Ariete locations. Air samples were collected at the 2012 vent, plume, and background locations. All background samples were collected at locations unaffected by the volcanic plume, automobile combustion, and crop burning. DEM source data: ASTER GDEM, a product of METI and NASA.

interference [Malowany *et al.*, 2015]. Samples collected from the plume and crater were first passed through a copper tube 30 cm long filled with copper filings to remove  $\text{H}_2\text{S}$ . The copper scrub was changed daily and monitored for visible signs of reaction by  $\text{H}_2\text{S}$  forming  $\text{CuS}$ .

## 2.2. Field-Based Isotopic Measurements

The Picarro G1101-i CRDS for isotopic analysis of  $\text{CO}_2$  was stationed  $\sim 5$  km west of the summit at Turrialba Lodge (2650 m asl), where there was a reliable power source to which we added an uninterruptible power supply in order to maintain a stable voltage for the instrument. The CRDS was operated continuously during sample analysis in the evenings at temperatures of  $0$ – $10^\circ\text{C}$  and an average relative humidity of 65% for the month of April. The G1101-i performs gas phase analysis for  $^{12}\text{CO}_2$  (ppm),  $^{13}\text{CO}_2$  (ppm), and  $\delta^{13}\text{C}$  over a concentration range of 300–6000 ppm  $\text{CO}_2$  with a nominal precision of  $\pm 0.85\text{‰}$  ( $1\sigma$ ) at 500 ppm [Lucic *et al.*, 2015]. The precision is concentration dependent and can vary by  $0.6\text{‰}$  over a concentration range of 500–5000 ppm  $\text{CO}_2$  [Lucic *et al.*, 2015]. To eliminate such variations, all samples and standards were diluted to  $\sim 1000$  ppm with  $\text{CO}_2$ -free air, except for the atmospheric and plume samples whose concentrations were generally less (400–1000 ppm). The soil gas samples had concentrations of 58–81 vol %  $\text{CO}_2$  and needed to be diluted. To do this, we removed  $\text{CO}_2$  from the ambient air using an ascarite (NaOH) scrub to produce  $\text{CO}_2$ -free air ( $< 10$  ppm  $\text{CO}_2$  as determined on the Picarro CRDS) in the Tedlar bags with which to dilute high concentrations of  $\text{CO}_2$ .

We brought three in-house gas standards ( $-11.5\text{‰}$ ,  $-16.0\text{‰}$ , and  $-43.0\text{‰}$ ) to use for in-field instrument calibration. The standards have been analyzed against international standards using a Finnigan-MAT IRMS at the University of Toronto, and the CRDS is able to reproduce a 1:1 match on the standards with the Finnigan MAT. All gas samples collected during the day in the Tedlar gas bags were analyzed the same evening, for near real-time analysis. Each set of samples was bracketed with a set of standards at the beginning and end of analysis to monitor and correct for instrumental drift. The total analysis time for each sample set did not exceed 3 h, and the instrumental drift during this period was negligible. Standards were reproduced within error each day, with root-mean-squared (RMS) values of  $0.1\text{‰}$  and  $0.5\text{‰}$  for the  $-11.5\text{‰}$  and  $-16.0\text{‰}$  standards, respectively. This illustrates that the CRDS has accuracy similar to that of the IRMS (RMS =  $0.4$ – $0.5\text{‰}$ ). The instrument was operated continuously during the evenings while samples were analyzed. The CRDS measured ambient  $\text{CO}_2$  in the field lab, which was variable (450–800 ppm  $\text{CO}_2$ ) due to our respiration.



**Figure 4.** Comparison of  $\delta^{13}\text{C}$  values from the Picarro G1101-i cavity ring-down spectrometer (CRDS) and the Finnegan MAT isotope ratio mass spectrometer (IRMS). CRDS values of 2012 vent gases are slightly depleted with respect to the IRMS values, suggesting that the composition of the 2012 vent gases are causing a potential interference with the CRDS values.

For analysis, a sample bag was attached to the inlet of the instrument, separated by a 1  $\mu\text{m}$  Acrodisc CR 25 mm syringe filter to remove particulate matter, registering an increase or decrease in  $\text{CO}_2$  and establishing a stable signal. The instrument used a flow-through system, taking one measurement every 10 s at a flow rate of 40 mL/min. An individual gas bag ( $\sim 1$  L) was analyzed for 15–20 min, a period which produced sufficiently precise measurements for statistical analysis. The statistical toolkit of the G1101-i was used to calculate the average  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  concentrations and the  $\delta^{13}\text{C}$  value relative to Vienna Pee Dee Belemnite, which are reported here.

### 2.3. Laboratory Analysis

The 30 mL evacuated vials containing 50 mL of sample were analyzed at the University of Toronto on a continuous flow Finnigan MAT gas source mass spectrometer with a Varian gas chromatograph.

The reported precision for  $\delta^{13}\text{C}$  is  $\pm 0.1\text{‰}$ , but lower concentration samples ( $< 1000$  ppm) have a higher uncertainty of up to  $\pm 0.5\text{‰}$ . Each sample was analyzed in duplicate, and an in-house standard was analyzed every 10 samples to monitor instrument drift. Samples with high  $\text{H}_2\text{S}$  concentrations were sufficiently separated by the gas chromatograph so as to not interfere with the  $^{12}\text{C}$  and  $^{13}\text{C}$  peaks. There is excellent agreement between the CRDS measurements and the Finnigan MAT (Figure 4), except for a small deviation for the samples of the 2012 vent where the values differ by  $\sim 1\text{‰}$ .  $\text{CO}_2$  and  $\text{H}_2\text{S}$  concentrations were analyzed using gas chromatography. Large ranges in the  $\text{CO}_2$  concentrations (380–88,000 ppm) necessarily generate the need for a linearity correction. Two in-house standards were used for this comparison, one with a concentration of 1996 ppm for the low concentration samples and one at 10,000 ppm for the high concentration samples. All samples were run in triplicate, and the reported values include the mean and standard deviation for the three measurements.  $\text{H}_2\text{S}$  was only measured for the 2012 vent samples where we had observed an anomalous response from the CRDS.  $\text{H}_2\text{S}$  had previously been removed from all other samples using a copper tube as described above.

### 2.4. Hyperbolic Mixing Model

The  $\delta^{13}\text{C}$  and  $\text{CO}_2$  composition of the volcanic plume can be represented as a binary mixture between the volcanic and atmospheric end-members as

$$\delta^{13}\text{C}_p[\text{CO}_2]_p = f \delta^{13}\text{C}_v[\text{CO}_2]_v + (1-f)\delta^{13}\text{C}_a[\text{CO}_2]_a \quad (1)$$

where  $f$  refers to the relative contribution of the volcanic source, and the subscripts  $p$ ,  $v$ , and  $a$  refer to the plume, volcanic source, and ambient air compositions, respectively. This equation can be rewritten as a hyperbolic function (2), whereby the slope of the mixing line (3) and the intercept (4) can be calculated accordingly. Assuming that the volcanic source has a molar concentration of 1, then the  $b$  value is thus a computation of the  $\delta^{13}\text{C}$  at the source:

$$\delta^{13}\text{C}_p = b + \frac{a}{[\text{CO}_2]_p} \quad (2)$$

$$a = [\text{CO}_2]_v [\text{CO}_2]_a \frac{\delta^{13}\text{C}_a - \delta^{13}\text{C}_v}{[\text{CO}_2]_v - [\text{CO}_2]_a} \quad (3)$$

$$b = \frac{\delta^{13}\text{C}_a [\text{CO}_2]_a - \delta^{13}\text{C}_v [\text{CO}_2]_v}{[\text{CO}_2]_v - [\text{CO}_2]_a} \quad (4)$$

Chiodini *et al.* [2010] applied a similar method in his computations of the volcanic sources from plume measurements on three Italian volcanoes. Following this example, we applied the Monte Carlo method to subsample our data set and generate a hyperbolic fit which minimizes quadratic differences between the selected data points. This was reiterated 10,000 times to develop a modal distribution of the *a* and *b* parameters from equation (2).

### 2.5. Keeling Mixing Model

The Keeling method [Keeling, 1958] was originally used to estimate the biogenic source composition of plant respiration and photosynthesis using mixtures with background air. For our purposes, the source value is volcanic instead of biogenic, and we are measuring the mixture of volcanic gas and background atmosphere in the form of the volcanic plume. This method previously has been presented by Fischer and Lopez [2016] during airborne measurements of the plume at Kanga volcano, and by Rizzo *et al.* [2015] for determining the plume composition at Etna volcano. It has excellent potential to be applied in future monitoring efforts due to the relative ease of the calculation.

The Keeling method is a linearization of the hyperbolic curve from equation (2), accomplished by plotting  $\delta^{13}\text{C}$  versus  $1/\text{CO}_2$  as per equation (5) below, where the subscripts *p*, *v*, and *a* refer to the plume, volcanic source, and air compositions, respectively.

$$\delta^{13}\text{C}_p = \delta^{13}\text{C}_v + \frac{(\delta^{13}\text{C}_a - \delta^{13}\text{C}_v) * [\text{CO}_2]_a}{[\text{CO}_2]_p} \quad (5)$$

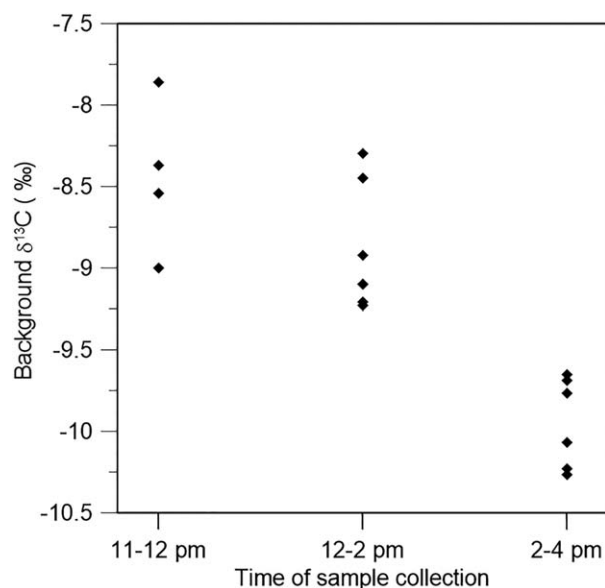
A linear regression then permits the determination of the *y*-intercept at a molar ratio of 1, and in our case, predicts the volcanic end-member  $\delta^{13}\text{C}$  composition at the source. This method is a fast way to predict the magmatic source composition and is easily adaptable to both small and large data sets.

A standard least squares regression (LSR) is the most widely applied regression for predicting end-member compositions using the Keeling plot [Zobitz *et al.*, 2006] and is the regression applied in our analysis. To enhance the statistical significance of the regression outcome, we have again employed the Monte Carlo method to the Keeling least squares approach in order to account for variability in the data. To apply the Monte Carlo method, we selected a subset of 10 plume samples and performed a regression as per the Keeling method (described above). This is reiterated 10,000 times to produce a statistically significant outcome from the data set.

## 3. Results

### 3.1. Ambient Atmosphere

Carbon isotope values are reported in with associated  $\text{CO}_2$  concentrations,  $\text{H}_2\text{S}$  concentrations, and temperature measurements for each. Reported isotopic compositions agree well with typical values for fumaroles, ambient atmosphere, and biogenic soil gases. Concentrations of  $\text{CO}_2$  in the ambient atmosphere averaged  $405 \pm 26$  ppm  $\text{CO}_2$ , slightly above the global average of 401.33 ppm (Scripps/NOAA, Mauna Loa  $\text{CO}_2$ ; April 2014, www.co2now.org). The background samples had  $\delta^{13}\text{C}$  of  $-8.3\text{‰}$  to  $-10.2\text{‰}$ , within the range of atmospheric values previously observed in rainforest environments [Keeling, 1958; Lloyd *et al.*, 1996; Trolier *et al.*, 1996]. We observed slightly more negative background values from samples taken later during the day ( $-9.7\text{‰}$  to  $-10.2\text{‰}$ ), compared to those taken near midday ( $-7.8\text{‰}$  to  $-8.5\text{‰}$ ; Figure 5). Diurnal variations in the background  $\text{CO}_2$  isotopic composition have been attributed to photosynthetic activities of plants, where the preferential uptake of  $^{12}\text{C}$  results in a peak ambient  $\delta^{13}\text{C}$  value at midday and a corresponding  $\text{CO}_2$  minimum [i.e., Lloyd *et al.*, 1996]. Our measurements were made following this midday isotopic maximum. Figure 5 illustrates the observed decrease in  $\delta^{13}\text{C}$  values from noon to late afternoon, resulting from an increase in the cellular respiration of plants and a decline in photosynthetic activity following the midday  $\delta^{13}\text{C}$  maximum. To determine the appropriate atmospheric composition to compare with



**Figure 5.** Variations in ambient atmosphere  $\delta^{13}\text{C}$  values illustrate a temporal change resulting from photosynthetic activity. Plant respiration maintains an atmospheric composition close to  $-10\text{‰}$  but photosynthetic activity during daylight hours enriches the isotope values. This can cause diurnal variations in the  $\delta^{13}\text{C}$  signature in regions with abundant vegetation (i.e., rainforest environments) [Lloyd *et al.*, 1996; Keeling, 1958]. At Turrialba, we observe a diurnal range of  $\sim 2\text{‰}$  with a maximum occurring near midday ( $-8.6\text{‰}$  avg. value BK-04). We have used late afternoon values ( $-9.6\text{‰}$  avg. of BK-02 and BK-03) to compare with the volcanic plume because they reflect the atmospheric composition at the time that the plume samples were taken.

(see Figure 4). The reason for this discrepancy is still being evaluated, but we hypothesize the presence of an interferent in the 2012 vent gas composition which is altering the compositional reading of the CRDS. Since the 2012 vent was the only location where IRMS and CRDS values varied by more than the reported errors, further study needs to be done regarding the performance of CRDS in high-temperature vents and their associated gas compositions. We have thus adopted the IRMS value as the reported composition for the 2012 vent.

Relative to  $\delta^{13}\text{C}$  measurements previously reported for fumaroles at Turrialba volcano, the 2012 vent samples (IRMS values) are the lowest  $\delta^{13}\text{C}$  values reported since its reactivation in the mid-late 1990s, except for one value in 1999 from the Central crater (Figure 2). The values for these high-temperature samples from a high gas flux vent range from  $-4.2\text{‰}$  to  $-4.7\text{‰}$  and are the most mantle-like carbon isotope compositions observed for magmatic gases on the Central American Arc [Shaw *et al.*, 2003]. These high-temperature gases are more enriched than MOR basalt that has an isotopic signature of  $-6.5\text{‰} \pm 1.5\text{‰}$  [Javoy *et al.*, 1986]. The observed enrichment in  $^{13}\text{C}$  could be the result of isotopic heterogeneity in the mantle, carbonate input from the subducted slab (carbonate  $\delta^{13}\text{C} = 0\text{‰}$ ), or fractionation during melt degassing as the heavy isotope of carbon preferentially partitions into the gas phase [Javoy *et al.*, 1986, 1978]. High-temperature open vent volcanic gases, such as those derived from the 2012 vent, are the most likely volcanic products to represent source volatile isotopic compositions [de Moor *et al.*, 2013]. We attribute the fact that our high-temperature samples from Turrialba have  $\delta^{13}\text{C}$  compositions heavier than MORB to the input of subducted carbonate in the source region [Shaw *et al.*, 2003, Hilton *et al.*, 2010].

### 3.3. Soil Gases

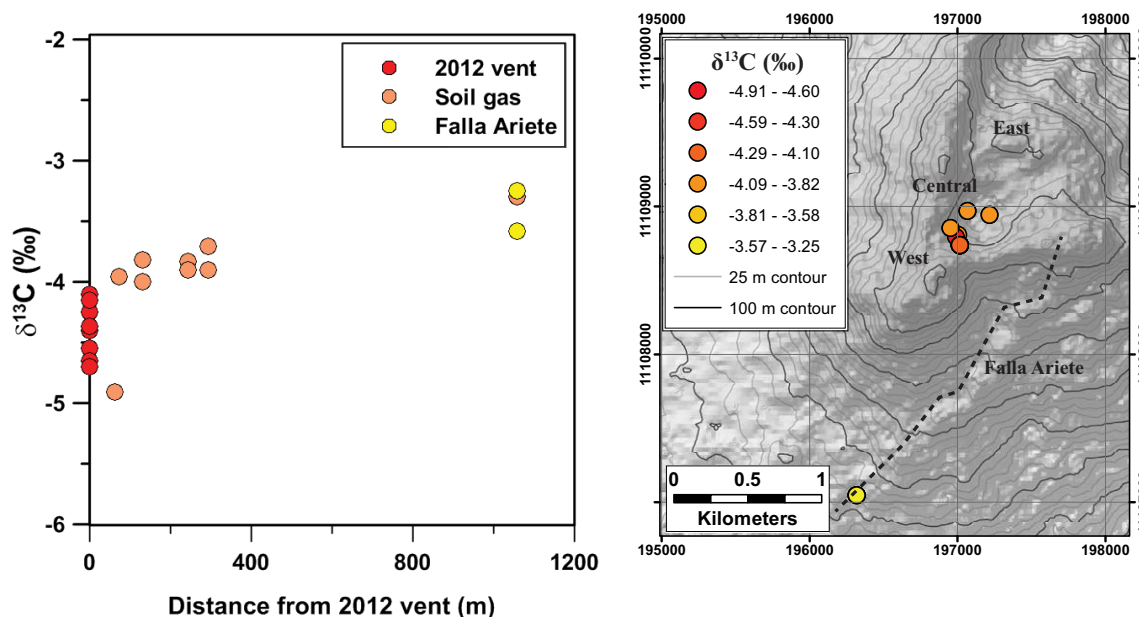
Low-temperature soil gas samples from the Central crater had a range of  $-3.7\text{‰}$  to  $-4.9\text{‰}$  and an average value of  $-4.0\text{‰} \pm 0.4\text{‰}$ . The soil samples show a spatial correlation with distance from the 2012 vent (Figure 6). Gases sampled close to the 2012 vent had higher temperatures and lower  $\delta^{13}\text{C}$ , approaching the composition of the 2012 vent ( $-4.4\text{‰}$ ). For example, sample LT-01 was closest to the 2012 vent (62 m) and

the plume compositions for our mixing calculations, we averaged background values taken during early afternoon ( $-9.2 \pm 0.1\text{‰}$ ), the period during which the plume samples were also collected.

### 3.2. High-Temperature (2012) Vent

The difficult access, high gas flux, and high temperatures of the 2012 vent made sample collection challenging at this locality. Gases were sampled using a 3 m titanium tube inserted into the vent opening ( $\sim 4$  m in diameter).  $\text{CO}_2$  measured by CRDS had concentrations  $> 5$  vol %  $\text{CO}_2$ , suggesting that a major component of volcanic gas was being captured. Temperature readings using a thermocouple had a maximum temperature of  $480^\circ\text{C}$  for the measured gases; however, the actual volcanic gas temperatures could be higher due to the mixing with air. Initial results from the CRDS showed little variability and a reported  $\text{CO}_2$  isotopic composition of  $-5.5\text{‰} \pm 0.3\text{‰}$ . By contrast, IRMS measurements returned isotopic values of  $-4.4\text{‰} \pm 0.2\text{‰}$  for the 2012 vent gases, suggesting that there is a  $\sim 1.1\text{‰}$  discrepancy between the two measurement types





**Figure 6.** Increase in the measured isotope values with increasing distance from the 2012 vent. The extrapolated plume composition portrays values significantly more enriched in  $^{13}\text{C}$  than those from either the 2012 vent or the soil gases. Gases emitted along the Falla Ariete regional fault system are likely derived from the local hydrothermal system and represent a hydrothermal end-member for gases at Turrialba volcano. DEM source data: ASTER GDEM, a product of METI and NASA.

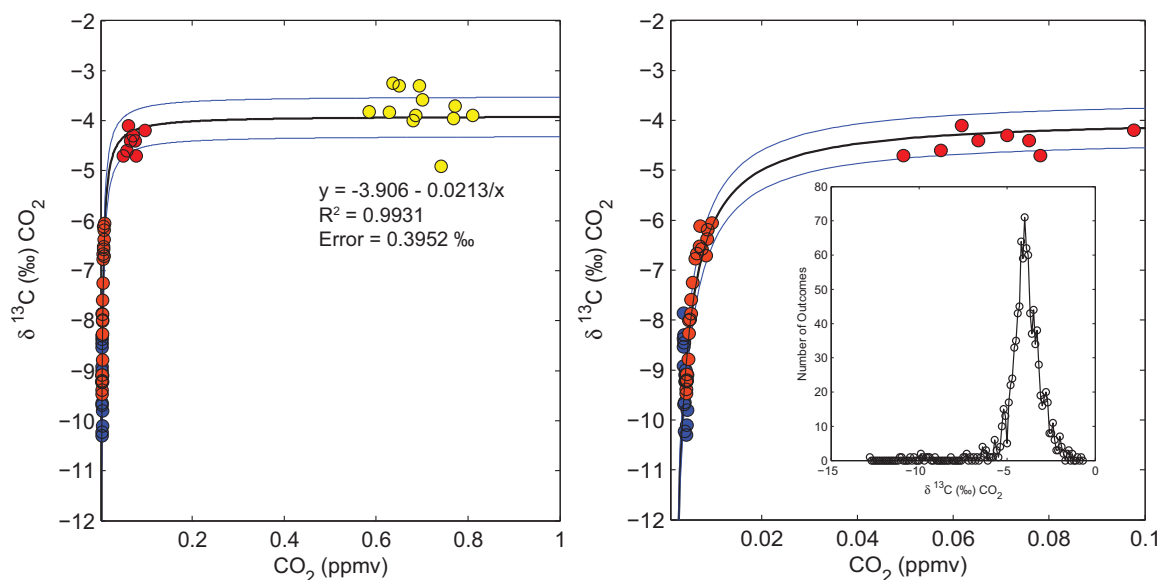
had the most depleted isotopic values measured ( $-4.9\text{‰}$ ). By contrast, soil gases at a distance of 294 m from the 2012 vent (sample LT-05) exhibited  $\delta^{13}\text{C}$  of  $-3.7\text{‰}$ .

A series of soil gas samples also were taken along the Falla Ariete, approximately 1 km outside the Central crater. At this location, the fault is expressed as a gully  $\sim 50$  m wide. Soil gases were sampled near fumaroles along the east side of the gully (FA-01) and have a narrow isotopic composition of  $-3.4\text{‰} \pm 0.1\text{‰}$ . Sample FA-02 was taken at the base of the gully, where there was evidence of tree kill from extremely high  $\text{CO}_2$  concentrations ( $>79$  vol %  $\text{CO}_2$ ), but no visible degassing. The isotopic composition of this sample was slightly depleted ( $-5.6\text{‰}$ ) compared to those from the nearby fumaroles. Vegetation on the gully floor may be contributing to the negative values at this location relative to the soil samples at FA-01. For comparison with FA-02, a soil gas sample was taken outside the gully on the west side of the fault (FA-03); this sample had a  $\delta^{13}\text{C}$  of  $-13.8\text{‰}$ , indicating a mixture between magmatic and biogenic  $\text{CO}_2$ . On the flank of the volcano where there was no evidence of volcanic gases being emitted, soil gas samples BG-01, BG-02, and BG-03 have an average value of  $-20.3\text{‰} \pm 0.6\text{‰}$ , representative of the typical isotopic composition of organic soil in equatorial climates, which is a mixture of respired  $\text{CO}_2$  from C3 and C4 plants [Cerling and Quade, 1993; Cerling 1984].

### 3.4. Volcanic Plume

Both ground-based [Rizzo *et al.*, 2014, 2015] and airborne [Fischer and Lopez, 2016] surveys of  $\delta^{13}\text{C}$  in a volcanic plume have been made recently using an isotope ratio infrared spectrometer (IRIS). Here we present measurements of plume gas samples taken at proximity ( $<500$  m) to a volcanic vent and fumaroles; the samples were then analyzed by a cavity ring-down spectrometer (CRDS). At sampling locations P-01, P-02, and P-03, we collected a range of samples whose concentrations decreased from 1036 to 435 ppm  $\text{CO}_2$  with increasing distance from the crater. Plume samples at near atmospheric concentrations (e.g., PL-01 and PL-03) range in isotopic composition from  $-6.6$  to  $-10.0\text{‰}$ , whereas higher plume  $\text{CO}_2$  concentrations ( $>750$  ppm) taken at PL-02 had more enriched isotopic signatures ( $-6.0\text{‰}$  to  $-5.2\text{‰}$ ). It has been assumed that plume samples represent mixing between atmospheric and volcanic end-members. All the following calculations have included only the volcanic plume data, with the atmospheric, fumarolic and 2012 vent samples plotted for comparison only.

Using the hyperbolic mixing function (2) and a regression which minimized quadratic differences of the plume data, the  $\delta^{13}\text{C}$  of the volcanic source was estimated to be  $-3.9 \pm 0.4\text{‰}$ , as illustrated in Figure 7. The reiteration procedure produced a series of  $y$ -intercept values from the fit-function, from which the mean ( $x = -3.9\text{‰}$ ) and standard error ( $\sigma = 0.4\text{‰}$ ) were computed. A volcanic source composition of  $-3.9\text{‰}$



**Figure 7.** Binary mixing curve defined by the plume measurements take at Turrialba volcano. Mathematical modeling of the hyperbolic function (2) using  $\delta^{13}\text{C}$  versus  $\text{CO}_2$  was performed 10,000 times using randomly selected subsamples of the plume data. The best fit model is defined by a hyperbolic curve with a  $y$ -intercept at a  $\text{CO}_2$  molar ratio of 1. The distribution of predicted  $y$ -intercept values is expressed as a histogram. The best fit model was generated using the mean  $a$  and mean  $b$  values from the Monte Carlo estimation and is expressed in the above plots (plot on the right is a close up of the plume and 2012 vent data). The plot depicts a good agreement with the soil gas (yellow), the 2012 vent (red), and the background air (blue) compositions. We report the equation for the curve ( $y = a/x + b$ ), the coefficient of determination (i.e.,  $R^2$ ), and the standard error with a 95% confidence interval for evaluation. The upper and lower bounds of the confidence interval are plotted for reference (in blue).

reflects mixing from a single source that is also linked to both the 2012 vent and Central and West crater fumaroles, as they plot within the 95% confidence interval.

In Figure 7, the isotopic values from the 2012 vent, the summit soil gases, and the background atmosphere have been overlain on the model to illustrate the contextual fit with the predicted volcanic end-member. The model links the plume, the 2012 vent and the soil gases to a single volcanic source composition. A few points which plot above the 95% confidence interval represent a heavier isotopic composition at the Falla Ariete ( $-3.4\text{‰}$ ), suggesting that additional processes or sources are affecting the  $\delta^{13}\text{C}$ - $\text{CO}_2$  composition at this site. The fumaroles along the Falla Ariete are likely dominated by a hydrothermal system which is transmitting deep gases along the fault. Previous isotopic measurements at this location [Tassi *et al.*, 2003; Vaselli *et al.*, 2010] have consistently shown enriched  $\delta^{13}\text{C}$  in  $\text{CO}_2$  compared to the summit gases.

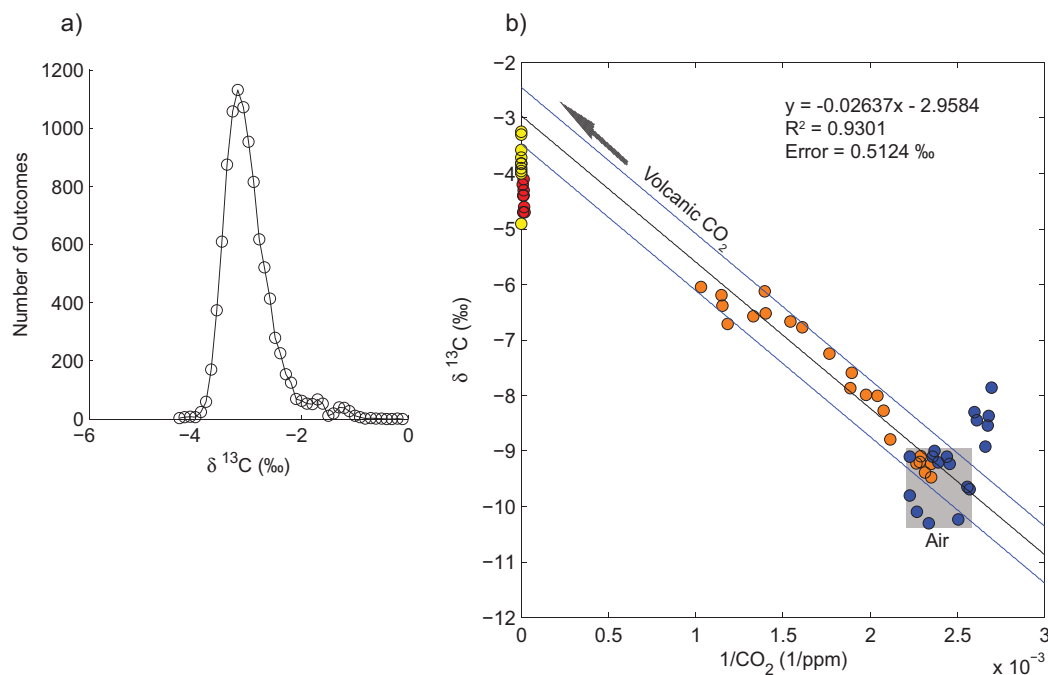
For comparison with the hyperbolic method, the volcanic source end-member was estimated using the Keeling method [Keeling, 1958], which produces a linearization of the hyperbolic curve and permits analysis by linear regression (Figure 8). To reduce the impact of outliers, we have subsampled the plume data, performing 10,000 different regressions. Figure 8a illustrates the distribution of the predicted volcanic composition from each regression and produces a peak mode at  $-3.0\text{‰} \pm 0.5\text{‰}$ . This deviates from the single regression outcome ( $-2.6 \pm 1.4\text{‰}$ ) but provides a more robust illustration of the plume data set by extracting a trend that is less heavily influenced by data variability resulting from diurnal changes in atmospheric composition.

As illustrated in Figure 8b, the predicted  $\delta^{13}\text{C}$ - $\text{CO}_2$  value for the volcanic source from the plume data is neither representative of the 2012 vent nor of the soil gas from the Central crater, but rather predicts a heavier source composition of  $-3.0 \pm 0.5\text{‰}$ . The predicted volcanic end-member composition by the Keeling method suggests a distinct isotopic signal originating from the West crater fumaroles (see Figure 4), in contrast to the hyperbolic mixing method, which can explain all of the data as mixing between a single volcanic source and air.

## 4. Discussion

### 4.1. Background $\delta^{13}\text{C}$ Variations in Tropical Environments

Daily variations in the atmospheric  $\delta^{13}\text{C}$  composition make comparison of plume measurements taken at different times of day challenging. Diurnal variations in photosynthesis and plant respiration can cause



**Figure 8.** A linear model ( $y = mx + b$ ) of  $\delta^{13}\text{C}$  versus  $1/\text{CO}_2$  was fit using a least squares technique and reiterated 10,000 times. The resulting  $b$  values are illustrated in (a) and show the histogram from which the mean values is  $-3.0\text{‰}$  ( $2\sigma = 0.45\text{‰}$ ). (b) The resulting linear regression is illustrated in a plot of  $\delta^{13}\text{C}$  versus  $1/\text{CO}_2$ . We report the equation for the curve, the coefficient of determination (i.e.,  $R^2$ ) and the standard error with a 95% confidence interval for evaluation. The upper and lower bounds of the confidence interval are plotted for reference (in blue).

relatively large isotopic variations in the background compositions of up to  $2\text{‰}$  in areas where vegetation is abundant. The magnitude of these isotopic variations is dependent upon the degree of biogenic influence in a particular region [Lloyd *et al.*, 1996; Keeling, 1958]; therefore, we anticipate that these fluctuations should be greater in rainforest areas (e.g., Costa Rica) and negligible in semiarid or desert regions. The daily variations in background composition affect the plume compositions throughout the day, generating depleted values in the mornings and evenings, and enriched compositions at noon when photosynthesis is most efficient. When collecting repeated measurements from a volcanic plume, they should be made at the same time of day as the atmospheric measurements, or the two should be taken simultaneously. This is especially important for concentrations within 200 ppm of the background atmospheric concentration that are most sensitive to this ambient atmospheric variability. Our plume measurements were taken daily between 13:00 and 15:00 local time, when background compositions were  $-9.2 \pm 0.1\text{‰}$ . This allows measurements from multiple days to be compared. The plume compositions were collected over a large range in  $\text{CO}_2$  concentration (400–1000 ppm  $\text{CO}_2$ ), which minimizes effects from small variations in background composition during this time. Monitoring the changes in isotopic composition of the magmatic source using plume measurements is a promising tool for volcano monitoring. In regions with dense vegetation, however, a careful background characterization should be conducted before plume measurements are compared on a daily basis.

#### 4.2. Comparison of the Keeling and Hyperbolic Methods for Volcanic Monitoring

In principle, the Keeling method and the hyperbolic regression should return the same results for the predicted volcanic end-member. However, our results demonstrate that there is a difference in the predicted outcomes of each method when applied to the same data set. The Keeling method returned a  $y$ -intercept value that was biased toward heavier values ( $-3.0\text{‰}$ ) compared to that predicted by the hyperbolic mixing curve ( $-3.9\text{‰}$ ). This bias appears to result from a stronger dependency on low concentration gas samples when using a linear style regression. Analytical uncertainty and daily and diurnal variations in the background air composition have resulted in a data set that deviates from a true binary mixture. These variations are magnified at low concentrations when fitting the Keeling curve. An initial characterization of the binary mixing in a volcanic plume should be carried out using the hyperbolic

method; once the system and uncertainties have been fully characterized, the Keeling method may still be applied, if it is a true binary mixture.

#### 4.3. Implications for the Volcanic Source at Turrialba

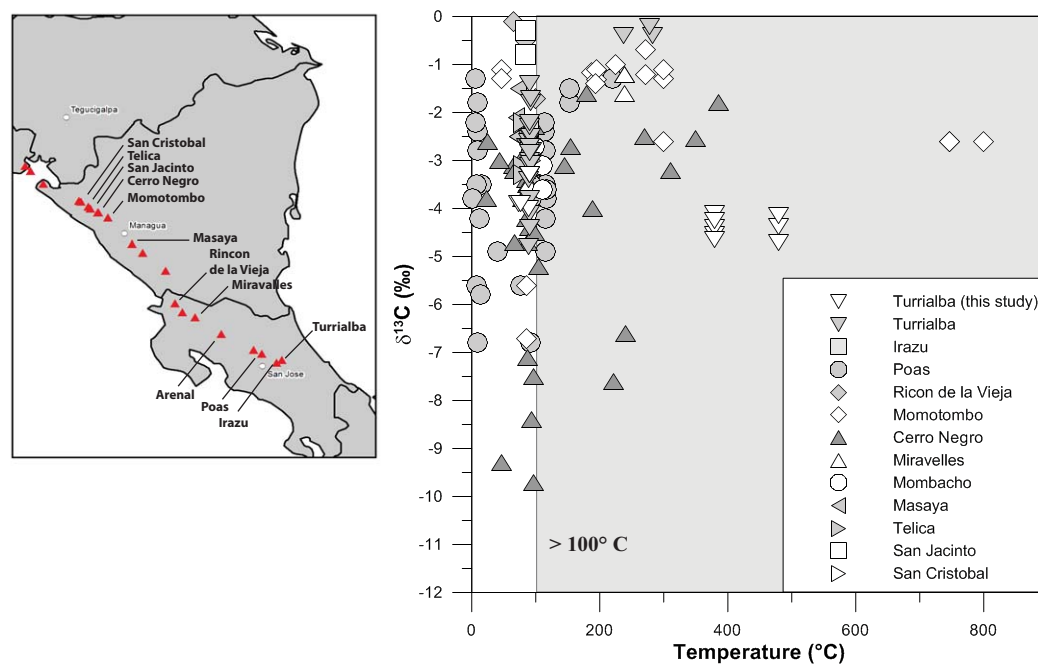
We have applied two different models for the evaluation of the volcanic source composition from the volcanic plume at Turrialba. First, the hyperbolic mixing model reveals a source composition of  $-3.9 \pm 0.4\text{‰}$ , which supports binary mixing between a single volcanic source and the background atmosphere, and is consistent with gas compositions from the Central crater as well as the 2012 vent. However,  $\delta^{13}\text{C}$ -CO<sub>2</sub> measurements from the Falla Ariete are slightly offset than this predicted source composition, illustrating the presence of a hydrothermal end-member that is heavier than the volcanic source dominating at the summit. Second, the volcanic  $\delta^{13}\text{C}$  composition predicted by the Keeling model was noticeably heavier ( $-3.0 \pm 0.5\text{‰}$ ), suggesting that the isotopic signature of the West crater fumaroles is hydrothermally controlled. This contrasts with the composition of the high-temperature 2012 vent ( $-4.4\text{‰}$ ) and the high CO<sub>2</sub> concentration soil gases in the Central crater ( $-4.0\text{‰}$ ), implying that the hydrothermal source was still active in the West crater in April 2014, producing compositions enriched in the heavy isotope, whereas a more negative magmatic signal was dominant at the Central crater.

Although both methods vary slightly in their interpretation, it is clear that the shallow hydrothermal system beneath Turrialba was still influential in April 2014, as evident by the isotopic variability between the summit gases and the Falla Ariete. However, it is unclear if the hydrothermal system was also dominating the composition of the West crater fumaroles, from which the volcanic plume is sourced. Ratios of H<sub>2</sub>S, SO<sub>2</sub>, and CO<sub>2</sub> reported by *de Moor et al.* [2016] for the volcanic plume indicate that the hydrothermal system was still influential before and after the first eruption on 29 October 2014. A shift toward a more magmatic gas signature in the plume (H<sub>2</sub>S/SO<sub>2</sub> < 0.05) occurred following the second eruptive period from March to May 2015, when there was a marked depletion in the hydrothermal system and dominance of open high-temperature conduits. Further evaluation of the Keeling method for its continued use as a predictive model should be undertaken to ensure that there is no inherent bias in the least squares technique before it is widely applied in lieu of traditional mixing models. The Keeling model appears to be sensitive to variations in atmospheric background carbon isotope composition; therefore, care must be taken to sample ambient air at the same time as the plume. Potential bias in the Keeling method could result in incorrect interpretations of data collected in volcanic plumes.

#### 4.4. Spatial and Temporal Variations of Carbon Isotopes at Turrialba

In both 2007 and 2014, dramatic differences have been observed spatially on Turrialba in the  $\delta^{13}\text{C}$ -CO<sub>2</sub> signature between the summit gases and the fumaroles at the Falla Ariete. In 2007, increased heat and gas output in the presence of an active hydrothermal system buffered the  $\delta^{13}\text{C}$  to more enriched values (up to  $-0.2\text{‰}$ ) as gas temperatures increased to near 282°C, while fumaroles at Falla Ariete retained a more hydrothermal composition ( $-2.8\text{‰}$ ) with temperatures near boiling ( $\sim 90^\circ\text{C}$ ). Conversely, our 2014 data show a depletion in  $\delta^{13}\text{C}$  of the CO<sub>2</sub> Central crater gases ( $-3.7\text{‰}$  to  $-4.9\text{‰}$ ), while fumaroles at the Falla Ariete had reported compositions of  $-3.4\text{‰}$ , similar to the compositions reported for Falla Ariete in 2007. Hence, it appears that there has been a strong shift in the isotopic signature of the summit gases relative to the Falla Ariete fumaroles between 2007 and 2014. The observed difference between the summit gases and the Falla Ariete fumaroles can be attributed to one of three different processes, including the following:

1. Temperature-dependent variations arising from fluid-gas exchange within the hydrothermal system on Turrialba. *Vogel et al.* [1970] illustrated experimentally that exchange of carbon between the fluid and gas phase can produce a temperature-dependent fractionation, where <sup>13</sup>C preferentially partitions into the gas phase. This could explain the enriched isotopic values from fumaroles and soil gases that are fed by the hydrothermal system, including those taken at the Falla Ariete. The fluid-gas fractionation of carbon isotopes at temperatures >120°C has not been determined experimentally, but low-temperature experiments suggest that the fractionation factor increases with temperatures [*Vogel et al.*, 1970; *Mook et al.*, 1974]. This would help explain the observed increase in  $\delta^{13}\text{C}$  to  $-0.2\text{‰}$  during periods when the fumarole temperatures exceeded 200°C, however, further experimental work is needed to support this interpretation.
2. Mixing between different sources may be the dominant process controlling the isotopic signature. The enriched signal measured in 2007 at the West crater fumaroles ( $-0.2\text{‰}$ ) is potentially a symptom of rapid



**Figure 9.** CO<sub>2</sub> isotope composition of gases from active volcanoes in Costa Rica and Nicaragua. A large range of values is observed at low temperatures. High-temperature samples are less common and generally show a narrower range of compositions. Overall, Turrialba has lower  $\delta^{13}\text{C}$  signature compared to the rest of the arc, suggesting more mantle C input. Data compiled from Snyder *et al.* [2001], Shaw *et al.* [2003], Sano and Williams [1996], Vaselli *et al.* [2010], Hilton *et al.* [2010], Fischer *et al.* [2015], Lucic *et al.* [2014], Allard [1983], and Tassi *et al.* [2004].

changes in the source composition. Troll *et al.* [2012] demonstrated the immediate impacts of stored crustal CO<sub>2</sub> on the  $\delta^{13}\text{C}$ -CO<sub>2</sub> gas composition during an ongoing eruption. Enrichments of up to  $-0.2\text{‰}$  could be attributed to mixing with an enriched end-member, such as limestone or crustal fluids. Conversely, the depleted values observed at the summit fumaroles may be indicative of increased input from a mantle source [Hilton *et al.*, 2010]. Further investigation of  $\delta^{13}\text{C}$  in conjunction with  $^3\text{He}/^4\text{He}$  is required to determine variations in source composition. Previous work by Shaw *et al.* [2003] and Hilton *et al.* [2010] have demonstrated that small variations in the  $\delta^{13}\text{C}$  composition at Turrialba could arise from differences in the mantle versus slab contributions over time. However, these changes should be reflected throughout the entire volcanic system and are unlikely to be expressed differently if volatiles are derived from the same source region.

- Magmatic fractionation of CO<sub>2</sub> gas can evolve to more negative  $\delta^{13}\text{C}$  as the degassing progresses, resulting in a signature that is progressively depleted as the system loses its volatiles. CO<sub>2</sub> gas exsolved from melt is enriched in  $^{13}\text{C}$  with respect to carbon dissolved in the melt. As open system degassing progresses, the system releases  $^{13}\text{C}$  preferentially, thereby becoming lighter and causing subsequent fluid compositions to evolve to lower  $\delta^{13}\text{C}$  values. Since the summit fumaroles in 2007 were enriched in  $^{13}\text{C}$  with respect to those measured at the Falla Ariete, it would imply that melt which had undergone little degassing was present at that time. Our measurements of the summit gases indicate that a much more depleted signature was present at the summit in 2014 than was measured in 2007. This would imply that the residual melt had even lower  $\delta^{13}\text{C}$  values than the gas in 2014, suggesting that the current melt feeding the summit fumaroles has experienced significant degassing.

Further investigation relating to the isotopic composition and gas speciation at both the summit fumaroles and the Falla Ariete is warranted to understand the dominant processes controlling  $\delta^{13}\text{C}$  fractionation at Turrialba. The three interpretations discussed above have different implications for the determining the future eruption potential at Turrialba and could help in developing a forecasting model for  $\delta^{13}\text{C}$  measured in the volcanic plume.

Currently, continued heat input is drying out the hydrothermal system [Moussallam *et al.*, 2014; de Moor *et al.*, 2016], and a magmatic SO<sub>2</sub> signature with negligible H<sub>2</sub>S is currently dominant. The high-temperature

vents (2012 and 2010) which have opened in the Central crater demonstrate the increasing gas flux and a much “drier” signal, without scrubbing of volatiles. Our isotopic measurements of the soil gases and the 2012 vent show the most depleted  $\delta^{13}\text{C}$  reported to date on Turrialba, ranging from  $-3.7\text{‰}$  to  $-4.9\text{‰}$  in the Central crater and  $-4.5\text{‰}$  from the 2012 vent. Overall, it appears that the  $\delta^{13}\text{C}$  composition of  $\text{CO}_2$  at Turrialba is progressively becoming isotopically lighter with time, toward a more mantle-like source. This conclusion is in agreement with the results of Vaselli *et al.* [2010] and de Moor *et al.* [2016], which show that the magmatic component of the gases in the summit region has progressively increased between 1996 and 2016. By comparing the  $\delta^{13}\text{C}$  measurements from this study with the rest of the Central American Volcanic Arc (Figure 9), we observe that Turrialba has some of the most depleted signatures, possibly attributed to increasing mantle contributions and decreasing contributions of carbonate from the subducting slab in Costa Rica.

Following Aiuppa *et al.* [2014], we emphasize that only high-temperature emissions should be used to distinguish deep carbon source variations observed in volcanic gases, especially if hydrothermal signals dominate low-temperature fumaroles (e.g., the Falla Ariete). Considering the variability of our low-temperature measurements on Turrialba, as well as the potential for modification by a hydrothermal system, it is important to identify the high-temperature and  $\text{SO}_2$ -rich sources when characterizing the contribution of slab elements at depth. Further monitoring of high-temperature magmatic gases is needed at Turrialba and other volcanoes to assess the effects of progressive magma degassing and changes in source contribution upon C-isotope compositions in volcanic gases.

## 5. Conclusions

Portable cavity-enhanced absorption spectrometers allow field analysis of isotopic compositions, enabling assessment of the data in near real time. We used a portable cavity ring-down spectrometer (CRDS) to evaluate the isotope composition of  $\text{CO}_2$  gas at Turrialba volcano in April 2014. Fortunately, this was 6 months prior to Turrialba’s first major eruption since its reawakening in 1996. We used two different methods to evaluate the volcanic source composition from  $\delta^{13}\text{C}$ - $\text{CO}_2$  volcanic plume measurements. The hyperbolic model yielded a volcanic source composition of  $-3.9 \pm 0.4\text{‰}$ , suggesting that the summit gases (including those from the 2012 vent) are derived from a single volcanic-end-member. In contrast, isotopic values for the West crater plume extrapolated using the Keeling method have a significantly heavier carbon isotope composition ( $-3.0 \pm 0.5\text{‰}$ ), indicating a significant but heterogeneous hydrothermal interaction at the summit. Variability in our low concentration plume and background samples has led us to select the hyperbolic method as a robust model for predicting the composition of the volcanic end-member. Our observations indicate that soil gas samples from the regional fault system ( $-3.4\text{‰}$ ) are distinct from summit gases ( $-4.0\text{‰}$ ) an indication that hydrothermal modification of the  $\delta^{13}\text{C}$  values is favoring the  $^{13}\text{C}$ -isotope. Modification of the magmatic carbon isotopic signature by the local hydrothermal system explains the heterogeneous signal observed at Turrialba; further monitoring is needed reveal if the hydrothermal system persists at the West crater fumaroles during the current eruptive phase. Overall, the C-isotope signature on Turrialba is becoming depleted in  $^{13}\text{C}$  over time and reflects increasing mantle input as the system becomes more active. Going forward, it will be important to characterize the magmatic value at Turrialba through continued monitoring of  $\delta^{13}\text{C}$ , especially for the high-temperature vents. Only then can comparisons be made to link changes in carbon isotope composition to degassing behavior or changes in the carbon source composition, as it pertains to eruption forecasting.

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