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Key Points:
- Real-time data of CO_2 content and $\delta^{13}C$ in atmospheric/volcanic gases
- This study opens new perspective for the community for volcanic surveillance

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Real-time measurements of the concentration and isotope composition of atmospheric and volcanic CO_2 at Mount Etna (Italy)

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Abstract We present unprecedented data of real-time measurements of the concentration and isotope composition of CO_2 in air and in fumarole-plume gases collected in 2013 during two campaigns at Mount Etna volcano, which were made using a laser-based isotope ratio infrared spectrometer. We performed approximately 360 measurements/h, which allowed calculation of the $\delta^{13}C$ values of volcanic CO_2. The fumarole gases of Torre del Filosofo (2900 m above sea level) range from $-3.24 \pm 0.06‰$ to $-3.71 \pm 0.09‰$, comparable to isotope ratio mass spectrometry (IRMS) measurements of discrete samples collected on the same dates. Plume gases sampled more than 1 km from the craters show a $\delta^{13}C = -2.2 \pm 0.4‰$, in agreement with the crater fumarole gases analyzed by IRMS. Measurements performed along ~17 km driving track from Catania to Mount Etna show more negative $\delta^{13}C$ values when passing through populated centers due to anthropogenic-derived CO_2 inputs (e.g., car exhaust). The reported results demonstrate that this technique may represent an important advancement for volcanic and environmental monitoring.

1. Introduction

CO_2 is the most important greenhouse gas and plays a critical role in global climate change [e.g., *Keeling et al.*, 1995] due to the continuous increase in its atmospheric concentration recorded since before the Industrial Revolution [e.g., *Ciais et al.*, 2013]. It is also one of the major species degassing from volcanoes worldwide [e.g., *Shinohara*, 2013], and its study is critical for determining the activity state of volcanoes [e.g., *Aiuppa et al.*, 2007] as well as for estimating the impact of volcanic gases on the global carbon budget [e.g., *Aiuppa et al.*, 2008]. The isotope composition of CO_2 is a powerful complementary tool for investigating complex environmental processes such as the exchange of CO_2 isotopes in forests due to photosynthesis [e.g., *Flanagan et al.*, 1997; *Bowling et al.*, 1999; *Battipaglia et al.*, 2013] or for detecting changes that are directly or indirectly due to magmatic activity at depth [e.g., *Rizzo et al.*, 2009; *Hilton et al.*, 2010; *Paonita et al.*, 2012]. However, the most common technique used to make these kinds of measurement is still conventional isotope ratio mass spectrometry (IRMS), which requires that gases are manually collected in the field in glass flasks and then returned to a laboratory for processing and analysis. For example, at Mount Etna the only calculations of the $\delta^{13}C$ value of volcanic CO_2 in plume gases emitted from the craters were performed using the IRMS technique [e.g., *Chiodini et al.*, 2011]. Even if this method provides a good understanding of carbon isotope behavior in active volcanic systems, it suffers the limitation that only a small number of samples can be collected in the field and analyzed over time, making the detection of any high-frequency variations of carbon isotopes impractical.

New techniques aimed at overcoming this limitation have been developed in the last decade involving the use of laser-based isotope ratio infrared spectrometer (IRIS), aiming at high-frequency measurements of $\delta^{13}C_{CO2}$ [e.g., *Gagliardi et al.*, 2002; *Castrillo et al.*, 2006; *Jost et al.*, 2006; *Kerstel and Gianfrani*, 2008, and references therein]. *Murnick and Peer* [1994] demonstrated that using an IRIS could represent a useful alternative to IRMS for allowing real-time measurements directly in the field. Some of the applications of an IRIS have concerned the study of ecosystem respiration and diurnal to seasonal variations in CO_2 sources at high altitude [*Bowling et al.*, 2003; *Mohn et al.*, 2008; *Sturm et al.*, 2013]. Moreover, geothermal and volcanic gases have been investigated by *Richter et al.* [2002] and *Kassi et al.* [2006] but only for the CO_2 concentration. *Castrillo et al.* [2004] performed concentration and isotope measurements of CO_2 in volcanic gases at Solfatara di Pozzuoli

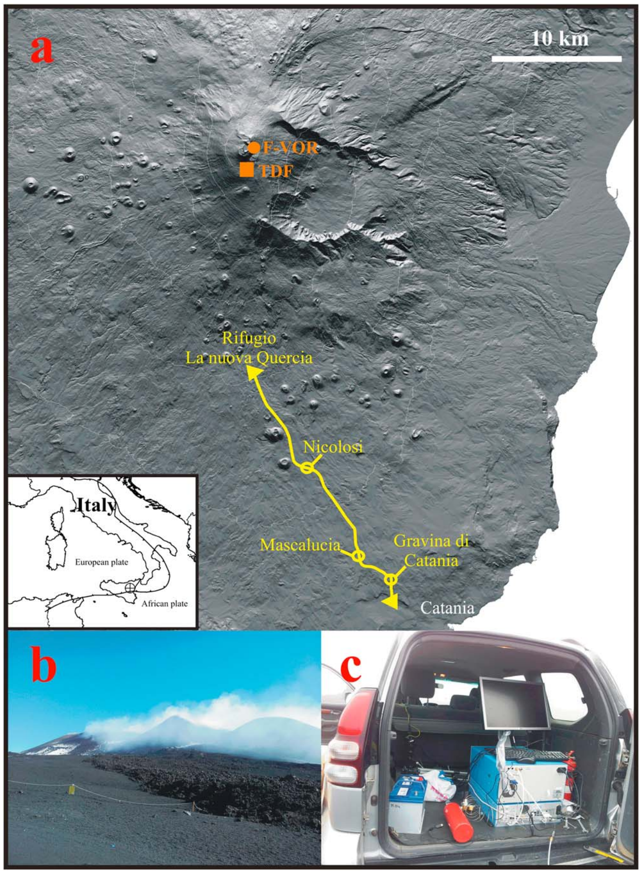

Figure 1. (a) Map of Mount Etna (Italy) displaying the location of sampling sites (TDF, Torre del Filosofo, orange square; F-VOR, Voragine crater fumaroles, orange circle) and the route followed by the car (called the Catania-Etna route) during the laser-based Delta Ray IRIS data acquisition (yellow line), from Catania (37°33′03.98″N, 15°04′03.38″E) to Rifugio La nuova Quercia (37°40′10.11″N, 14°59′17.77″E). (b) View of the degassing plume from the central craters. (c) Photograph taken at TDF of the Delta Ray IRIS setup in an all-wheel-drive car provided by INGV-Palermo.

(Naples, Italy), but the $\delta^{13}C_{CO2}$ values obtained typically had a standard deviation of >1‰. Such a high uncertainty level makes it impossible to distinguish variations of the natural system, which are generally associated with changes in $\delta^{13}C$ of <1‰ [e.g., *Paonita et al.*, 2012].

In this article we present results obtained using the first field application at Mount Etna volcano (Italy) of a new laser-based IRIS (Delta Ray™, Thermo Fisher Scientific) that is capable of performing real-time measurements of the concentration and isotope composition of CO_2 in air. We chose Mount Etna because it is the most active volcano in Europe and one of the largest emitters of CO_2 into the atmosphere globally [e.g., *Aiuppa et al.*, 2008]. Also, the geochemical characteristics of fluids discharged at Mount Etna have been studied in detail for many years [e.g., *Paonita et al.*, 2012, and references therein], and due to the challenging weather and environmental conditions, we propose that the success of this test would indicate that the technique has worldwide applicability. Indeed, while all volcanic systems are characterized by acidic gases, the barometric, wind, temperature, and overall seasonal conditions are particularly extreme at Mount Etna. Our findings during the field deployment are compared to those obtained from discrete sampling performed for regular volcano monitoring purposes by Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo (INGV-Palermo) and therefore can be considered in the context of geochemical observations. Here we demonstrate that the Delta Ray IRIS instrument is robust against adverse weather and environmental conditions (e.g., 2900 m above sea level (asl) and air temperatures around 0°C) and is capable of making accurate measurements under these conditions. We therefore believe that the method described herein could be adapted to diverse environmental settings.

2. Sampling and Methods

We performed two measurement campaigns at Mount Etna volcano on 11 July and 5 and 6 September 2013. During the former campaign we continuously measured atmospheric CO_2 at Torre del Filosofo (TDF), which is located on the southern side of the summit area at 2900 m asl (Figures 1a and 1b). Additionally, we performed real-time measurements of volcanic CO_2 emitted into the atmosphere from the TDF fumarole field (hereafter F-TDF) by moving the car with the analyzer several times inside and away from the plume of steam generated by those fumaroles. The main purpose of this procedure was to test the laser-based IRIS over a range of CO_2 concentrations (<1500 ppm) that is comparable to that of plume gases emitted from the main craters and collected next to the crater rims [e.g., *Aiuppa et al.*, 2007, 2008]. Following this test, we made continuous measurements of CO_2 and $\delta^{13}C$ inside and away from the plume consisting of gases emitted from the main craters and transported to the TDF area by the northwestern wind (Figure 1b) by placing the analyzer downwind in a safe location that was more than 1 km from the craters. At this distance the impact of corrosive volcanic gases is reduced because some of them are removed by adsorption to aerosols. We also performed discrete sampling of the Voragine crater fumaroles (here named F-VOR) (Figure 1a) as part of the periodic volcanic surveillance performed by INGV-Palermo (for further details see *Paonita et al.* [2012, and references therein], in which the same fumarole field is named F8-F9).

In September 2013 we replicated the measurements performed in July at the top of Mount Etna and additionally performed real-time measurements of the air along the ~17 km driving-track from Catania to Mount Etna (henceforth referred to as the “Catania-Etna route”) (Figure 1a). A discrete sampling of F-TDF to be analyzed by IRMS and compared to the IRIS data set was also performed by leaving three Vacutainer glass tubes exposed to the steam of the fumarole in order for the concentration and isotope composition of CO_2 to be comparable to that measured by the Delta Ray IRIS. Measurements of plume gases from central craters were not possible on 5 and 6 September due to unfavorable wind conditions.

Real-time measurements of the concentration and isotope composition of CO_2 in air, fumarole gases, and plume gases were performed using the Delta Ray IRIS, which has been developed over the last few years. The analyzer employs a tunable diode laser operating at 4.3 μm to simultaneously determine $\delta^{13}C$ and $\delta^{18}O$ in CO_2 at ambient concentrations (200–3500 ppm). It requires a power supply of $<$300 W, measures 59 cm × 43 cm × 43 cm, and weighs 37 kg. It is based on direct absorption spectroscopy, employing a discrete multipass cell with a path length of 5 m that is highly insensitive to mirror contamination (e.g., loss in reflectivity due to impact of particles or corrosive gases). No decrease in performance was noticed during the observation period. A precision in the measured $\delta^{13}C$ value of $<$0.05‰ was achieved during our tests involving typical 1 min periods of static data acquisition. This performance is a key requirement in order to perform measurements in a dilute plume ($CO_2 < 1500$ ppm Vol; hereafter reported as ppm) at a distance from the crater rim where the environmental conditions are much less challenging. The high temporal resolution yields sufficient data points to allow statistical fitting of mixing lines (volcanic fluids versus atmosphere) and calculation of the nonatmospheric end-member. The Qtegra™ Intelligent Scientific Data Solution software (Thermo Fisher Scientific) used to acquire the data allows for unattended operation for days and supports periodic calibration and referencing workflows as well as data visualization. The isotope composition of carbon is determined relative to a working standard, which in our case was the Vienna Pee Dee Belemnite (VPDB) standard, and is reported as delta (δ) per mil (‰) values. Regular referencing is performed during data acquisition with an internal Thermo Fisher Scientific standard having $\delta^{13}C = -25$‰. The accuracy of the acquired data has been verified by measuring air at a site with no (or negligible) anthropogenic pollution or volcanic gases, or using an internal INGV-Palermo calibrated standard ($\delta^{13}C = -40.3$‰ versus VPDB). The modular design makes the analyzer portable and field deployable, so it was set up in an all-wheel-drive car provided by INGV-Palermo (Figure 1c) and powered in the field by the car’s electrical system. Due to the required power supply, the car needed to be running while using the device, in which case the immediate environment might be contaminated by the car exhaust. This could only have affected the measurements when the car was stationary or in adverse wind conditions.

Gases from F-TDF and F-VOR were collected discretely following commonly used procedures [e.g., *Paonita et al.*, 2012]. Analyses were performed by the IRMS technique at INGV-Palermo laboratory using an internal reference calibrated with a Carrara Marble certified standard ($\delta^{13}C = 2.45$‰ versus VPDB). The standard deviation values were generally $<$0.2‰.

3. Results and Discussion

3.1. Air CO_2 Measurements Over Time

Most of our measurements of background atmospheric air were performed at TDF, and generally showed $CO_2 \sim 380$ ppm and $\delta^{13}C \sim -8$‰, in agreement with similar investigations performed at Jungfraujoch (Switzerland, 3580 m asl) [*Sturm et al.*, 2013], but slightly lower than the values obtained by the Global Monitoring Division of NOAA/Earth System Research Laboratory ($CO_2 \sim 395$ ppm). We adopted our values as the background reference in the subsequent processing.

In Figure 2a we report the results of the temporal data of the concentration and isotope composition of $\delta^{13}C_{CO2}$ in air obtained on 5 September 2013 using a Delta Ray IRIS. The measurements were made along the

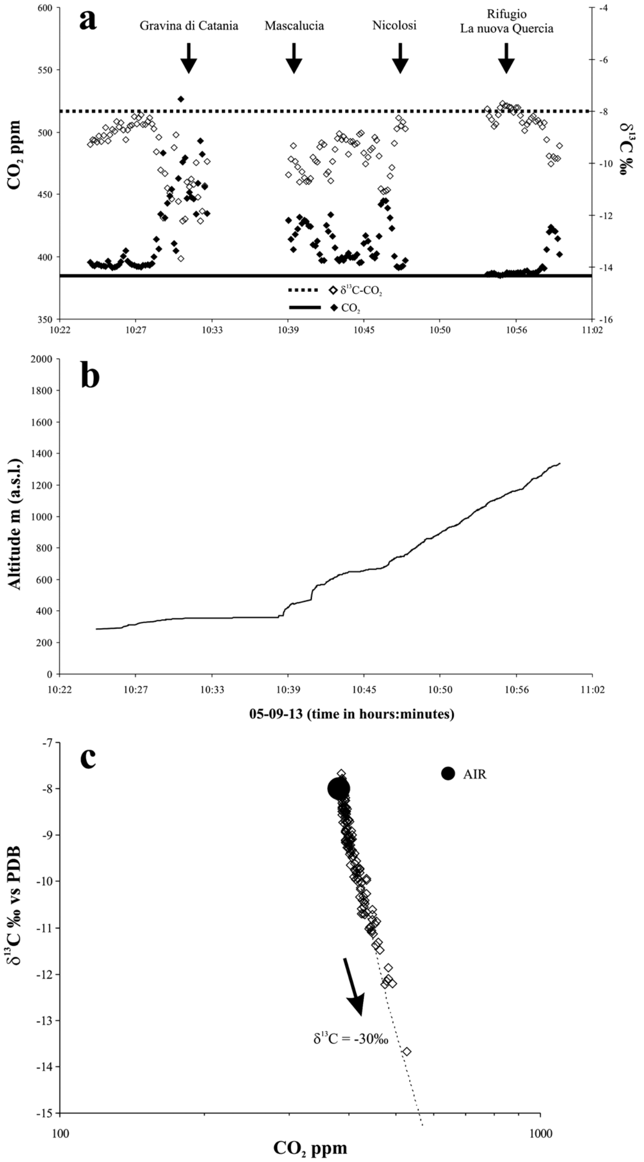

Figure 2. (a) Temporal variations of CO$_2$ (filled symbols) and δ^{13}C (open symbols) while the car was moving along the Catania-Etna route. Time is reported in hours and minutes local time (UT + 2 h) on 5 September 2013. The arrows indicate the times at which the corresponding populated centers were crossed. Continuous and dotted horizontal lines are atmospheric CO$_2$ concentration and δ^{13}C, respectively. (b) Altimetric profile during the Catania-Etna route. (c) Plot of δ^{13}C versus CO$_2$ concentration for data acquired along the route. The dotted line is for binary mixing between air (black full circle, CO$_2$ = 380 ppm and δ^{13}C = −8‰) and an end-member representing pollution from the gasoline car exhaust (CO$_2$ = 119,500 ppm [*Tastan et al.*, 2013] and δ^{13}C = −30‰ [*Zimnoch*, 2009]).

Catania-Etna route (Figure 1a) while the car was moving, starting from 280 m asl (Catania) and reaching an altitude of 1300 m asl (Rifugio La nuova Quercia). The corresponding altimetric profile is reported in Figure 2b. The two gaps in the plot data are due to periodic automatic calibration of the Delta Ray IRIS programmed before starting data acquisition. The CO$_2$ concentration varied between 385 and 527 ppm, while δ^{13}C varied from −7.7‰ to −13.7‰. It is noteworthy that even small variations of the CO$_2$ concentration (i.e., a few tens of ppm) were accompanied by significant changes in δ^{13}C (Figures 2a and 2c), notwithstanding the vibrations due to the moving car that could affect the precision and the stability of data acquisition, demonstrating the high sensitivity and robustness of the Delta Ray IRIS. We did not observe any drift over time or any correlation between the recorded variations of the CO$_2$ concentration and δ^{13}C values or changes in barometric pressure during data acquisition (Figures 2a and 2b).

The most significant variations of the CO$_2$ concentration and δ^{13}C were observed while passing through the small towns of Gravina di Catania, Mascalucia, and Nicolosi (Figure 2a), which are along the main southern part of the Catania-Etna route (i.e., local roads SP10 and SP92; Figure 1a). The variation observed at the end of our monitoring (from 10:56 to 11:02 A.M. local time, Figure 2a) is attributable to the exhaust gas of our car when it was parked for a few minutes with the engine running. In detail, during this period we noticed a simultaneous increase in CO$_2$ concentration and decrease in δ^{13}C relative to the "pure air" signature measured by the Delta Ray IRIS (i.e., CO$_2$ ~ 380 ppm; δ^{13}C ~ −8‰). We infer that all these variations of δ^{13}C can be explained by a variable extent of pollution-derived CO$_2$ in the air surrounding the small towns, for example, with Rifugio La nuova Quercia located far from inhabited centers in a traffic-free area, thus showing the typical atmospheric values. The CO$_2$ emitted from anthropogenic sources has three different isotope signatures all tending toward highly negative values of the carbon isotope composition [e.g., *Zimnoch*, 2009]: δ^{13}C ~ −24‰ (from coal burning), δ^{13}C ~ −30‰ (from car traffic, irrespective of the type of engine), and δ^{13}C ~ −52‰ (from methane burning). Figure 2c shows a plot of δ^{13}C versus CO_2 concentration for data acquired along the Catania-Etna route in order to evaluate the signature of pollution-derived CO_2. All the data are aligned along a trend line and are well fitted by assuming a binary mixing between an atmospheric end-member, having $CO_2 \sim 380$ ppm and $\delta^{13}C \sim -8‰$, and a source of CO_2 from gasoline car traffic, having $CO_2 = 119{,}500$ ppm [*Tastan et al.*, 2013] and $\delta^{13}C = -30‰$ [*Zimnoch*, 2009]. Even considering data from air monitoring performed at TDF on 11 July and 5 September 2013 (Figure 3a), which were partially contaminated by our car exhaust due to wind turbulence, we observe the same behavior as reported above.

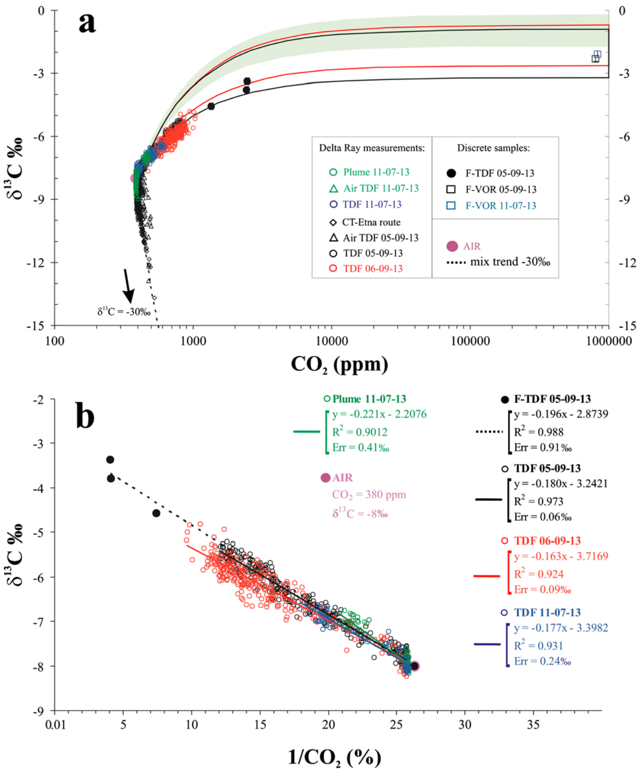

Figure 3. (a) Plot of δ^{13}C versus CO_2 concentration showing the entire data set (air, fumarole gases, and plume gases) obtained using the Delta Ray IRIS and discrete sampling, both of which were performed during the campaigns on 11 July and 5 and 6 September 2013. The dotted line is as in Figure 2c. The area within the black line is for binary mixing between air ($CO_2 = 380$ ppm and $\delta^{13}C = -8‰$) and a volcanic end-member having pure CO_2 (i.e., 1,000,000 ppm) and δ^{13}C values between $-2‰$ and $-3.5‰$, which corresponds to the range of values measured at the TDF fumarole field (F-TDF) by *Pecoraino and Giammanco* [2005]. Similarly, the area within the red line is for binary mixing with a volcanic end-member having pure CO_2 and δ^{13}C values between $-1‰$ and $-3‰$, which is the range of values measured at F-VOR by previous discrete investigations [*Liotta et al.*, 2010; *Chiodini et al.*, 2011; *Paonita et al.*, 2012]. The light green area is for binary mixing with a volcanic end-member having pure CO_2 (i.e., 1,000,000 ppm) and δ^{13}C values between $-0.5‰$ and $-2.5‰$, corresponding to the range of values measured in plume gases by *Liotta et al.* [2010] and *Chiodini et al.* [2011]. (b) Plot of δ^{13}C versus $1/CO_2$ (%) for the data set of fumarole gases and plume gases measurements performed by the Delta Ray IRIS and by discrete sampling (black full circles). The equation of linear regression, coefficient of determination (R^2), and associated standard error (95% confidence interval) are also reported for F-TDF and plume gases. Note that the intercept of the best fit equation essentially corresponds to the δ^{13}C value of the volcanic end-member.

3.2. Measurements of Volcanic CO_2

After we assessed the precision, accuracy, and robustness of the Delta Ray IRIS measurements made on Mount Etna, we measured the concentration and isotope composition of CO_2 emitted from F-TDF (Figure 1a). The results of the two measurement campaigns are reported in the plot of δ^{13}C versus CO_2 concentration shown in Figure 3a. The isotope composition varied from $-8.1‰$ to $-4.8‰$, while the concentration varied between 380 and 1030 ppm. All the data from F-TDF overlap and are aligned along a trend line corresponding to binary mixing between air and a volcanic end-member, the latter characterized by pure CO_2 and δ^{13}C values between $-3.2‰$ and $-3.7‰$ (Figure 3a; see also section 3.3). It is worth noting that the gases collected at F-TDF on 5 September 2013 (Figure 3a) and subsequently analyzed in the INGV-Palermo laboratory by IRMS fall on the same trend line. Additionally, data acquired by the Delta Ray IRIS and by discrete sampling fall within the range of δ^{13}C values found for gases collected from the same fumarole field during previous studies [e.g., *Pecoraino and Giammanco*, 2005, and references therein] (Figure 3a, area depicted by the black line). This confirms that also in a volcanic environment, which is characterized by an air-dominated gas containing water vapor and possibly acidic species (e.g., sulfur), the measurements made using the Delta Ray IRIS can be precise and accurate, allowing calculation of the volcanic end-member. This is consistent with the preliminarily findings obtained by *Castrillo et al.* [2004], who applied a laser-based system to gases obtained from Solfatara di Pozzuoli (Italy).

On 11 July 2013 we also performed a short period of measurements of plume gases emitted by the central craters (Figure 1b). These gases were brought southeastward by the wind toward TDF, which is more than 1 km from the craters, and it was possible to capture them using the Delta Ray IRIS for only a few tens of minutes. The CO_2 concentration varied between 385 and 481 ppm, while $\delta^{13}C$ values varied from −8.1‰ to −6.8‰. As shown in Figure 3a, the data for the plume gases imply the presence of significant dilution by air (i.e., volcanic CO_2 at <100 ppm), being rather close to the values for an atmospheric end-member. Nevertheless, they are consistent with a binary mixing trend between air and a calculated volcanic end-member having pure CO_2 (i.e., 1,000,000 ppm) and $\delta^{13}C$ values between −2‰ and −2.5‰. This can be observed more clearly and quantitatively in Figure 3b (see also section 3.3). This calculation partially overlaps the range of values obtained for the Etnean plume by discrete sampling (i.e., between −0.5‰ and −2‰) [*Liotta et al.*, 2010; *Chiodini et al.*, 2011] (Figure 3a, light green area). The wind conditions did not allow us to collect discrete samples of the plume at the central craters. Therefore, in order to validate the plume measurements made using the Delta Ray IRIS, we analyzed the carbon isotope composition of F-VOR, given that previous investigations have demonstrated that the $\delta^{13}C$ values of F-VOR generally reflect those of plume gases [*Liotta et al.*, 2010; *Chiodini et al.*, 2011; *Paonita et al.*, 2012] (Figure 3a, area within the red line). The obtained results indicated average values of −2.1‰ and −2.3‰ on 11 July and 5 September, respectively (Figure 3a), in agreement with the values obtained using the Delta Ray IRIS.

3.3. Perspective for Volcano Monitoring

The measurements of the concentration and isotope composition of CO_2 made using the Delta Ray IRIS in gases emitted from Mount Etna, as discussed above, are indicative of mixing between atmospheric and volcanic CO_2. The results therefore cannot be directly used to detect temporal variations due to magma degassing, for example. A mathematical modeling approach allows calculation of volcanic $\delta^{13}C$ end-members. By assuming mixing between two components, a simple linear regression can be applied to obtain the equation describing the fit (i.e., $y = mx + b$), the volcanogenic $\delta^{13}C$ (in practice, the b term in the equation), the coefficient of determination (R^2), and the associated standard error with a 95% confidence interval. Figure 3b displays results obtained by applying this mathematical procedure to data acquired from F-TDF on 11 July and 5 and 6 September, from the plume on 11 July, and by the discrete sampling of F-TDF on 5 September; note that the last is based on only four measurements (inclusive of the air value). Data from F-TDF obtained on 11 July and 5 and 6 September mostly overlap each other and result in calculated values for $\delta^{13}C$ of -3.24 ± 0.06‰ and -3.71 ± 0.09‰ (mean ± standard error), respectively. We point out that the most negative values of volcanic $\delta^{13}C$ calculated for TDF data obtained on 6 September could be affected by a slight contribution of CO_2 from the car exhaust due to strong winds generating turbulence around the car. Also, we cannot exclude that the variability observed in the data set is related to high-frequency variations of the natural system that has not been detected previously due to the inability to perform continuous measurements. Further investigations are necessary to address this possibility. As discussed above with reference to Figure 3a, data acquired by the discrete sampling of F-TDF shows a fit that is comparable to those of Delta Ray IRIS measurements acquired on the same date, leading to a computed $\delta^{13}C$ value for volcanic CO_2 of -2.9 ± 0.9‰. Plume data show $\delta^{13}C = -2.2 \pm 0.4$‰, in agreement with the less negative values found for gases emitted in the crater area and with F-VOR measurements made on the same date (Figure 3a).

Considering that the ultimate aim of using the Delta Ray IRIS is to perform temporal monitoring of $\delta^{13}C$, the values for the volcanic end-members calculated as described above are plotted in Figure 4 and compared to previous discrete measurements made at F-VOR by *Paonita et al.* [2012]. The figure employs a type of graphical representation that volcanologists commonly use for volcano monitoring. It is well known [e.g., *Holloway and Blank*, 1994] that the $\delta^{13}C$ value for vapor CO_2 degassed from a melt decreases during the course of magma degassing, with the amount of fractionation depending on the type of degassing (in an open or closed system) and its extent. This property may be used to obtain information about processes of progressive melt degassing and/or mixing between melts stored at different pressures. *Paonita et al.* [2012] used $\delta^{13}C$ values to infer magma dynamics at Mount Etna volcano during the 2008–2009 eruption (Figure 4). The ability to perform $\delta^{13}C$ measurements with a high temporal resolution could provide new insights into the type of CO_2 degassing, with implications for volcanic surveillance as described below. In the present study we did not intend to assess the activity level of Mount Etna, instead focusing on demonstrating the new perspective that the Delta Ray IRIS provides for volcano monitoring. Considering the importance of $\delta^{13}C$ monitoring for comprehending magma

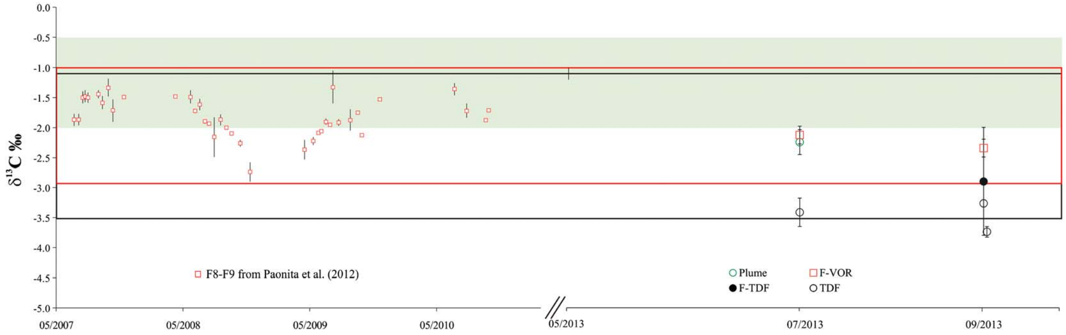

Figure 4. Volcanogenic δ^{13}C values calculated and reported in Figure 3b for each measurement campaign plotted on a temporal scale and compared to previous discrete measurements made at F-VOR by *Paonita et al.* [2012]. The light green area and the red and black lines are as in Figure 3a.

dynamics at depth, we expect that continuous measurements made using an IRIS will provide a major step forward in volcanic surveillance. The next goal is to perform longer field tests of a volcanic system involving the monitoring of complementary geochemical and geophysical parameters, such as CO_2/SO_2 ratio, SO_2 flux, $^3He/^4He$ ratio, noble gas ratios, seismic tremors, and ground deformations.

4. Conclusions

Real-time data of the concentration and isotope ($\delta^{13}C_{CO2}$) composition of CO_2 in air and in volcanic gases (fumarole and plume) from Mount Etna (Italy) have been presented herein. The measurements were made during two campaigns performed in July and September 2013 using a portable and field deployable laser-based IRIS (Delta Ray). The main results can be summarized as follows:

1. Data acquired in air along the Catania-Etna route and at TDF (2900 m asl) showed an excess of CO_2 due to pollution produced by car exhaust gases having $\delta^{13}C_{CO2} \sim -30‰$.
2. The carbon isotope composition of volcanic gases collected from F-TDF varied between –3.2‰ and −3.7‰. These values are in agreement with IRMS measurements made of gases collected on the same date and fall within the range of previous measurements.
3. The first real-time measurements of $\delta^{13}C_{CO2}$ for diluted plume gases, collected more than 1 km from the craters, made it possible to calculate a volcanic signature of $-2.2 \pm 0.4‰$, which is comparable to data from crater fumaroles sampled on the same date and is within the range of previous measurements.

The Delta Ray IRIS performed well in the extreme weather and environmental conditions of Mount Etna, which demonstrates that this new technique is sufficiently robust, precise, and accurate to be used by the scientific community for volcanic surveillance and for investigating both natural and anthropogenic emissions of greenhouse gases into the atmosphere.

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