Recommendations and Protocols for the Use of the Isotope RatioInfrared Spectrometer (Delta Ray) to Measure StableIsotopes from CO2: An Application to Volcanic Emissions atMount Etna and Stromboli (Sicily, Italy)

Guillaume Boudoire, F. Grassa, G. Giuffrida, M. Liuzzo

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Recommendations and Protocols for the Use of the Isotope Ratio Infrared Spectrometer (Delta Ray) to Measure Stable Isotopes from CO_2: An Application to Volcanic Emissions at Mount Etna and Stromboli (Sicily, Italy)

G. Boudoire,[1,2] **F. Grassa**,[1] **G. Giuffrida**,[1] **and M. Liuzzo**[1]

[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy*
[2]*Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, 6 avenue Blaise Pascal, 63178 Aubière, France*

Correspondence should be addressed to G. Boudoire; guillaume.boudoire@uca.fr

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Among major volatiles released from the Earth's interior, CO_2 is an important target for the international community. The interest is keenly motivated by the contribution of CO_2 in the Earth's carbon budget and its role on past, current, and future climate dynamics. In particular, the isotopic signature of CO_2 is fundamental to characterize the source of this gas and its evolution up to the atmosphere. The recent development of new laser-based techniques has marked an important milestone for the scientific community by favoring both high-frequency and in situ stable isotope measurements. Among them, the Delta Ray IRIS (Thermo Scientific Inc., Waltham, USA) is one of the most promising instruments thanks to its high precision, its limited interferences with other gaseous species (such as H_2S and/or SO_2), and its internal calibration procedure. These characteristics and the relative easiness to transport the Delta Ray IRIS have encouraged its use on the field to analyze volcanic CO_2 emissions in recent years but often with distinct customized protocols of measurements. In this study, various tests in the laboratory and on the field have been performed to study the dependence of CO_2 isotope measurements on analytical, instrumental, and environmental conditions. We emphasize the exceptional ability of the Delta Ray IRIS to perform isotope measurements for a large range of CO_2 concentration (200 ppm–100%) thanks to a dilution system and to get a reliable estimation of the real CO_2 content from the diluted one. These tests lead to point out major recommendations on the use of Delta Ray IRIS and allow the development of adapted protocols to analyze CO_2 emissions like in volcanic environments.

1. Introduction

Carbon dioxide (CO_2) is a greenhouse gas present in the atmosphere known to play a major role on the Earth's climate dynamics [1, 2]. Among natural emissions of CO_2, volcanic and tectonic areas are the main contributors to the global carbon budget [3–5]. These natural CO_2 emissions may represent less than 2% of anthropogenic emissions, but the uncertainty remains high and is a hot debated topic for the scientific community [4, 6]. It has stimulated the creation of research initiatives such as the Deep Carbon Observatory to address the issues relative to the causes and consequences of variations in natural CO_2 emissions [7]. In particular, natural variations of CO_2 markers are fundamental to constrain the dynamics of the Earth's reservoirs [8, 9] but are also of peculiar interest to characterize the origin of volcanic gases [10–14], detect magma dynamic changes [15, 16], and detect hidden diffusive degassing zones [14, 17].

The recent development of new techniques involving the use of the laser-based isotope ratio infrared spectrometer (IRIS) has favored both high-frequency and in situ measurements with respect to more conventional isotope ratio mass spectrometry (IRMS) techniques [18–21]. First applications of IRIS were aimed at study ecosystem respiration and temporal variations of CO_2 sources in the atmosphere [9, 22, 23]. It is only recently that volcanic gases were

investigated with such technique [24–28]. IRIS measurements are based on the absorption of infrared photons by exciting a molecule's rotational and vibrational energy states. They may use different light sources (broadband light sources, mid- or near- infrared lasers) and different absorption cells (multipath, resonant). Among all these optical-based techniques (see [21] for a review), the Delta Ray IRIS (Thermo Scientific Inc., Waltham, USA) is one of the most relevant. It is based on the use of two tunable near-infrared diode lasers combined with a nonlinear crystal to produce a laser beam in the midinfrared region. It allows the use of a short effective pathlength due to an associated line strength that is approximately 8000 times stronger than the near-infrared region. This allows a higher precision that is crucial to deal with volcanic gases whose time variations of CO_2 markers are often <1‰ [16]. Moreover, the midinfrared region does not suffer of interferences with other species (e.g., H_2S) as observed with other instruments working in the near-infrared one [29]. Finally, the Delta Ray IRIS uses an unprecedented internal calibration procedure that takes into account the concentration dependency of isotopes when using optical-based techniques (see [9] for a review).

Many tests were performed to study the precision and the accuracy of Delta Ray IRIS measurements [9, 21]. But to our knowledge, no study focuses on the development of protocols for isotope analysis in the laboratory and on the field. Actually, previous results from volcanic gases were obtained with the use of various homemade protocols [13, 24–27]. In this study, we aim to provide recommendations to obtain precise and accurate measurements with the Delta Ray IRIS in order to develop standard protocols on its use for isotopic measurements of CO_2. Various tests have been performed on (i) the dependency on isotopic signatures and contents of analyzed CO_2, (ii) the analytical and instrumental conditions of use, and (iii) the environmental influence. Results bring new insights on the optimized acquisition time to perform accurate and precise measurements. In the case of punctual gas sampling, it allows to determine the minimum required volume of gas and thus to identify the most adapted gas sampler to use. In the case of (semi)continuous long-term measurements, it allows to optimize the monitoring procedure of CO_2 emissions. Finally, for the first time, the possibility to recalculate real CO_2 contents from diluted ones is evaluated.

2. Methods

In this study, we have used two Thermo Fisher Delta Ray IRIS instruments belonging to the Istituto Nazionale di Geofisica e Vulcanologia Sez. di Palermo (hereafter, INGV Palermo) (Figure 1(a)). Analysis may be performed between -10 and 45°C and within a pressure range of 700-1200 mbar (that can be accommodated with a choked device in altitude [27]). The analyzer operates in a midinfrared range (4.3294–4.3275 μm) to simultaneously measure the $\delta^{13}C$, $\delta^{18}O$ (measurements relative to a standard and reported as delta (δ) per mil (‰) values), and CO_2 content through 4 absorption lines of isotopologues ($^{12}C^{16}O^{16}O$ with two absorption lines, $^{13}C^{16}O^{16}O$, and $^{12}C^{16}O^{18}O$) at 500 Hz. Measurements may be performed over a CO_2 concentration range of 200-3500 ppm or for concentration up to 100% using an innovative dilution system with CO_2-free synthetic air (Figure 1(b)). The Delta Ray IRIS has the specificity to use an internal calibration procedure to (i) correct linearly the CO_2 content and (ii) correct the isotopic values from the concentration dependency [9]. Calibration is performed after the warm-up using two in-house references. We used two pure CO_2 gas tanks having different isotope signatures ($\delta^{13}C = -39.3$‰ and -1.3‰ and $\delta^{18}O = -40.3$‰ and -5.2‰, respectively, versus the V-PDB standard). Referencing is performed before and after each cycle of measurements (so-called "smart referencing" procedure suggested in the IRIS user's manual) using the one of the reference gases.

Table 1 summarizes the various tests performed in this study and related analytical and environmental conditions. For tests, we used three different gases with known isotope values ($\delta^{13}C = -39.3$‰, -11.3‰ and -1.3‰; $\delta^{18}O = -40.3$ ‰, -13.4‰ and -5.2‰). The stable carbon and oxygen isotopes ($\delta^{13}C$ and $\delta^{18}O$, respectively) in all of these three reference gases have been previously analyzed with a Thermo Delta Plus XP CF-IRMS (precision ± 0.15 δ‰) coupled to a Thermo Trace gas chromatograph (GC) and a Thermo GC/C III interface at the INGV Palermo [17]. Five sets of measurements were performed in the laboratory and available in Appendix 1:

(1) The first set of measurements (Appendix 1–Sheet 1) is dedicated to test the influence of analytical conditions on the precision and accuracy of the analyses. Here, pure CO_2 has been injected in 5 L Multi-Layer Foil gas sampling bags produced by Restek. This material presents a lower CO_2 permeability ($0.0078\ cm^3m^{-2}d^{-1}$) than Tedlar gas sampling bags by Restek ($172\ cm^3m^{-2}d^{-1}$). CO_2 contents from 100% down to 300 ppm were then obtained adding various extents of CO_2-free synthetic air (N57 POL, Air Liquide™). Results were obtained for (1a) different isotopic signatures of CO_2 ($\delta^{13}C = -39.3$, -11.3 and -1.3‰; $\delta^{18}O = -40.3$, -13.4 and -5.2‰, respectively); (1b) different fixed range dilution wires provided with the analyzer to cover the full range of CO_2 contents from 3500 ppm to 100% (orange, gray, blue, pink, and yellow); (1c) different $^{12}C^{16}O^{16}O$ integration peaks (i.e., high concentration peak at 4.3277 μm and low concentration peak at 4.3280 μm); (1d) different CO_2 contents to test the response of the analyzer either in the recommended range of use of the dilution wires or in the possible range defined by the manufacturer (Thermo Fisher documentation; Figure 1(c)); (1e) different protocols of measurements (Protocol 1, suggested by the manufacturer, refers to 60 s of flushing time of the analyzer to clean the absorption cell, 180 s of measurements of the reference gas whereas Protocol 2 refers to 40 s of flushing time and 20 s of measurements of the reference gas); and (1f) different Delta Ray IRIS instruments (called DR1 and DR2)

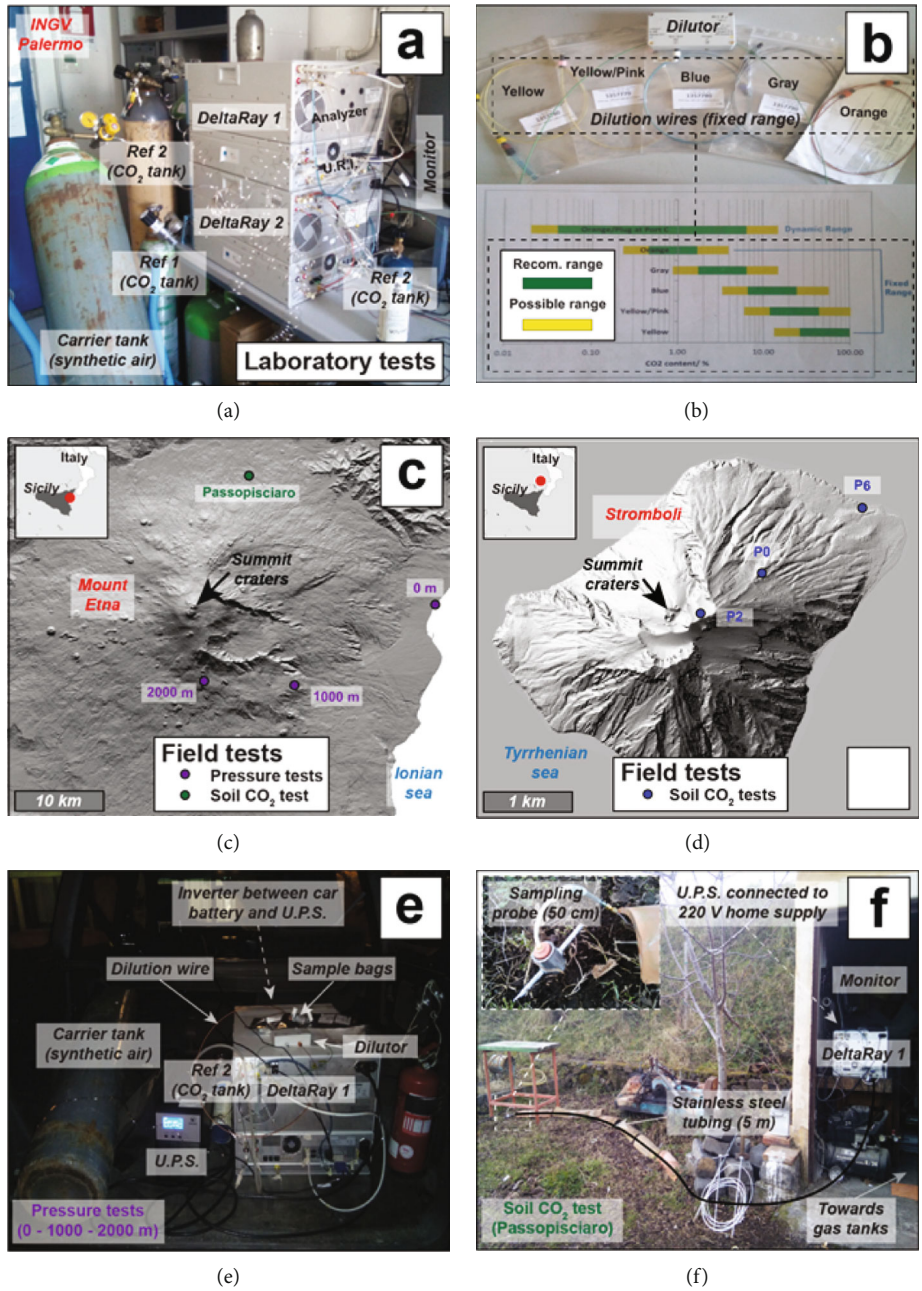


Figure 1: Description of deployed material and location of sample sites. (a) Deployment of the Delta Ray IRIS in the INGV Palermo laboratory. U.R.I.: Universal Reference Interface; Ref: reference gases (see text for explanations). (b) Delta Ray Xpand dilution system with the dilutor and the 5 fixed range dilution wires used in this study covering the full range of CO_2 content. (c) Location of the main field tests. Pressure tests were performed at 3 various altitudes (about 0, 1000, and 2000 m) on Mount Etna along the road with the Delta Ray IRIS embarked in an INGV Palermo car. The soil CO_2 test was performed at Passopisciaro with the Delta Ray IRIS deployed in a shed, less than 20 m far from the permanent soil CO_2 flux station of the EtnaGas network [42]. (d) Location of the sampling sites at Stromboli (P0, P2, and P6) where soil CO2 emissions were sampled within both Multi-Layer bags and Exetainer vials. (e) Deployment of the Delta Ray IRIS in the INGV Palermo car for the pressure tests. The power supply was provided by the car battery connected, adjusted with an inverter, and modulated with an Uninterruptible Power Supply (U.P.S.). (f) Deployment of the Delta Ray IRIS at Passopisciaro for semicontinuous measurements of soil CO_2 during 24 h. The power was provided by a 220 V home supply modulated with the U.P.S. Measurements were performed through a 5 m long stainless steel tubing connected to a 50 cm depth stainless steel probe to avoid adsorption of the CO_2 onto the internal tube [25].

(2) The second set of measurements (Appendix 1–Sheet 2) is obtained in the laboratory by simulating time variations of CO_2 isotopic signatures by switching each 10 minutes a valve between two gas samples ($\delta^{13}C = -39.3‰$ and -1.3‰ versus the V-PDB standard)

Table 1: Conditions of use for the 124 tests performed in this study in the laboratory and on the field. The isotopic composition of standard gases was subjected to slight natural variations during tank replacements (<1‰). Here, the most common values used in the tests are reported. Meanwhile, the accuracy described in this study always refers to the difference between the measurement and the real isotopic signature of the gas standard.

(a)

Test	Focus	Appendix	Sheet	Conditions of use															
				CO_2 (%)										Dilution wire					
				Nat.	100	40	20	10	4	1	0.4	0.3	0.1	Without	Orange	Gray	Blue	Pink	Yellow
Laboratory	Parameters	1	1		X	X		X		X		X	X	X	X	X	X	X	X
	Response to gas perturbation	1	2		X							X		X					X
	Stability (semicontinuous meas.)	1	3		X														X
	Stability (time storage in sampler)	1	4							X					X				
	Recalculated CO_2 contents	1	5		X	X	X	X	X	X						X	X	X	X
Field	P-T influence (semicontinuous meas.)	2	1		X														X
	P-T influence (punctual meas.)	2	2		X					X					X				X
	Protocol validity (punctual meas.)	2	3	X												X	X	X	
	Protocol validity (semicontinuous meas.)	2	4	X										X					

(b)

Conditions of use																	
$\delta^{13}C$(‰)			$\delta^{18}O$(‰)			Peak int.		Range of use		Protocol		Delta Ray		Pressure		Samplers	
-39.3	-11.3	-1.3	-40.3	-13.4	-5.2	High	Low	Recom.	Possible	1	2	DR1	DR2	Lab.	Field	Bags	Vials
X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	
X		X	X		X		X	X		X		X		X		X	
		X			X		X	X		X		X		X		X	
X		X	X		X		X	X		X		X		X		X	
X		X	X				X	X		X		X	X	X		X	
		X			X		X	X		X		X			X	X	
X			X				X	X		X		X		X	X	X	
							X	X		X		X		X		X	X
							X	X		X		X			X	X	

meas.: measurements; int.: integration; Recom.: recommended; Nat.: natural emissions.

(3) The third set of measurements (Appendix 1–Sheet 3) represents the results of 65 hours of measurements (1 Hz) averaged each 15 min (60 s of flushing time for both the reference and sample gases, 180 s of measurements of the reference gas, and 600 s of measurements of the sample gas)

(4) The fourth set of measurements (Appendix 1–Sheet 4) is aimed at evaluating the potential temporal drift in stable carbon isotopes related to the sampling method (Multi-Layer Foil gas sampling bags, Restek). Here, we have analyzed at different timescales the same sampling bags (from 1 day to more than 2 months to test the stability of the sampling bags) containing dry CO_2 (about 1%) in CO_2-free synthetic air

(5) Finally, the last set of measurements (Appendix 1–Sheet 5) is dedicated to test the ability to rebuild real CO_2 content from diluted ones, i.e., when the dilution system is used for CO_2 content between 3500 ppm and 100%. Real CO_2 contents were beforehand validated by the use of a micro module (MicroGC 3000) equipped with Poraplot U column (15 m) fluxed by He (detector TCD). Analytical precision ($\pm 1\sigma$) was always better than ±3%. The detection limit was about 100 ppm

Four kinds of test were performed in the field. Results from tests on Mount Etna (Figure 1(c)) and Stromboli (Figure 1(d)) are available in Appendix 2:

(1) After calibration at sea level, a first test (Appendix 2–Sheet 1) was performed to study the evolution of the accuracy of (semi)continuous carbon isotope measurements in function of the ambient pressure-temperature conditions. A pure CO_2 gas standard was injected in a Multi-Layer bag that was analyzed by the Delta Ray IRIS installed in a car which was traveling along a road on Etna (with variations of altitude between 0 and 2000 m above sea level). Measurements were performed using the "smart referencing" procedure (60 s of flushing time and 140 s of measurements for both the reference and sample gases). In the same sheet, instrument conditions, ambient conditions, and computed pressure gradients are also reported

(2) The second test (Appendix 2–Sheet 2) was aimed at determining the influence of ambient pressure-temperature conditions (e.g., altitude) of gas sampling on the accuracy of carbon isotope measurements. For such purpose, the Multi-Layer bags were filled at different altitudes (from 0 to about 2000 m above sea level) on Mount Etna (Sicily, Italy) with pure CO_2 and with a mixture CO_2/synthetic air (CO_2 concentration of about 1%) (Figure 1(e)). Sampling bags were then brought back and analyzed a second time after few days in the laboratory at quite constant atmospheric pressure and temperature (at sea level)

(3) The third test was aimed at validating the sampling strategy related to the minimum volume of gas required to obtain precise and accurate measurements from punctual gas samples. The tests were performed on some soil CO_2 gas samples collected at Stromboli in sampling bags and in screw caps of Exetainer glass vials (Appendix 2–Sheet 3)

(4) The last test (Appendix 2–Sheet 4) represents (semi)-continuous measurements of stable carbon isotopes from a soil CO_2 emission on the flank of Mount Etna during 24 h. Measurements were performed by inserting a stainless steel probe at 50 cm depth in the soil and connecting it to the Delta Ray with a 5 m long Aisi 316 stainless steel (O.D. 1/16 in.× I.D. 0.007 in.) tubing to avoid CO_2 adsorption onto the internal tube [25]. A time delay of less than 3 min related to the gas path from the sampling point to the analyses was computed by injecting pure CO_2 in the probe before measurements. No dilution system was used, and the soil CO_2 contents were also compared to hourly soil CO_2 contents from the Passopisciaro station from the EtnaGas network, located less than 20 m far from the Delta Ray sampling point (Figure 1(f))

3. Results

3.1. Precision and Accuracy of Measurements. The Allan overlapped deviation ($\sigma(\tau)$ in ‰ [9]) was used to estimate the precision of the Delta Ray IRIS analyses (values reported in Appendix 1–Sheet 1). Using the dilution system, 99% of the maximum precision (<0.12‰ and <0.04‰) is obtained after 93 s and 97 s for $\delta^{13}C$ and $\delta^{18}O$, respectively (median values). Without the dilution system, 99% of the maximum precision (<0.04‰ and <0.004‰) is obtained after 98 s and 99 s for $\delta^{13}C$ and $\delta^{18}O$, respectively (median values). The precision of Delta Ray IRIS measurements is similar to that previously reported [9, 24]. Meanwhile, a small discrepancy of the precision is observed when using the dilution system (Figure 2).

To study the accuracy of Delta Ray IRIS analyses, the measurements of each raw series were averaged on the time (τ) required to obtain 99% of the maximum precision. Using the dilution system, the median accuracy is of 0.9‰ (maximum of 17.8‰ for the higher dilution wire) and 0.8‰ (maximum of 7.7‰ for the higher dilution wire) for $\delta^{13}C$ and $\delta^{18}O$, respectively. Conversely, without the dilution system, a better accuracy is obtained with a median of 0.3‰ and 0.1‰, respectively (Figure 2). These last values are similar to those previously reported in other studies [9, 25, 26] and by the manufacturer (Thermo Fisher documentation). It is worth noting that previous studies are focused on the use of the Delta Ray IRIS without the dilution system. In our case, we document here that the use of the dilution system induces a longer time to stabilize the system (due to mixing in the tube and in the absorption cell [9]) and to avoid inaccurate and less precise measurements (Figure 2).

To discriminate mixed values from those representative of the targeted gas sample (i.e., contribution > 99%), we have adapted a homemade Python script to apply a maximum likelihood method based on the use of a Gaussian mixture model implementing an expectation-maximization algorithm [14, 30]. It allows to determine when measurements start to be accurate (Figure 3). We find that mixed values are dominant during the first 113-797 s depending on the dilution wire used (from the blue one to the yellow one; Figure 1). It means that the user needs to wait for this time before recording reliable values or to apply a longer flushing time to clean the tube and the absorption cell (Figure 3). Dilution with the orange and gray wires (without the dilution system) does not require to wait for such time interval, with mixed values being eliminated during the flushing of the system in 35-60 s (Thermo Fisher documentation and [9]). By eliminating the mixed values, the accuracy of isotopic measurements improves greatly and reaches, whatever the wire, a median of 0.4‰ (against 0.9‰ on raw data) and of 0.1‰ (against 0.8‰ on raw data) for $\delta^{13}C$ and $\delta^{18}O$, respectively (Figure 3). Furthermore, the precision becomes higher than previously reported: 99% of the maximum precision (<0.01‰ and <0.004‰) is obtained on average after 94 s and 97 s for $\delta^{13}C$ and $\delta^{18}O$, respectively (median values). Both obtained precision and accuracy are similar to those reported without the use of the dilution system (Figure 3).

Averaging each series on the time (τ) required to obtain 95% of the maximum precision (instead of 99%) leads globally to a slight discrepancy on the accuracy (Appendix 3). However, the resulting median accuracy does not differ strongly and favors analysis on shorter times ($\tau_{95\%} < 23$ s; $\tau_{99\%} < 139$ s) when the volume of the sample gas is limited. An attempt was made to estimate accurate values by using a simple linear regression in a plot of $\delta^{13}C$ or $\delta^{18}O$ versus $1/CO_2$ (e.g., "extrapolation") instead of averaging the series (e.g., "average") during the time (τ) [11, 13]. The "extrapolation" leads to a slight discrepancy in accuracy with respect to the "averaging." For this reason, in the following parts of this study, the accuracy will refer to values obtained by averaging series on the time (τ).

3.2. Analytical Factors Influencing Punctual Measurements. The effect of distinct analytical conditions on the precision and the accuracy of the Delta Ray IRIS (DR2) measurements was analyzed (see Methods; Appendix 4). In our study, we find that the minimum time required to obtain 99% of the maximum precision (e.g., $\tau_{99\%}$) is obtained when (Figure 4)

(i) The low concentration peak of the $^{12}C^{16}O^{16}O$ isotopologue is integrated whatever the CO_2 concentration between 200 and 3500 ppm. The high amplitude of this peak may favor a better integration

(ii) The dilution wire is used in its recommended range of CO_2 concentrations (Figure 1(c); Thermo Fisher documentation)

(iii) The isotopic composition of the reference gas used is close to that of the sample gas

(iv) A higher flushing time and reference time is applied (c.f. Protocol 1)

Meanwhile, differences observed on the precision by varying the analytical conditions remain limited (Figure 4). They only involve, on average, a shift of few seconds to obtain a similar precision.

Regarding the influence of analytical conditions on the accuracy, we note that the difference of isotopic signatures between the sample and reference gases does not generate a discrepancy. We find that the accuracy is more sensitive to (Figure 4)

(i) The choice of the integrated $^{12}C^{16}O^{16}O$ isotopologue peak. Like for the precision, a better accuracy is observed using the low concentration peak

(ii) The range of use of the dilution wires (Figure 1(c); Thermo Fisher documentation). Like for the precision, a better accuracy is obtained when the dilution wires are used in their recommended range of CO_2 concentrations

(iii) The choice of the protocol. Like for the precision, a better accuracy is obtained with Protocol 1

Regarding the last point, note that the use of Protocol 2 leads to more inaccurate values. This protocol is based on a flushing time of 40 s, i.e., in the range recommended by the manufacturer (35 s) and by other studies (60 s [9]). But, the 20 s of analysis of the reference gas (instead of 180 s in Protocol 1) is probably insufficient to have a precise analysis of the reference gas. In fact, we have documented above a time of about 100 s to reach 99% of the maximum precision. Such short analysis time of the reference gas could explain the observed discrepancy on both the precision and the accuracy of the values obtained with Protocol 2.

Importantly, comparable results are obtained on the two Delta Ray IRIS used in this study (DR1 and DR2; Appendix 5). However, a greater accuracy is obtained on DR1 than on DR2. It is worthy to note that the power of the laser signal is two times greater for DR1 (≈0.45 μW) than for DR2 (≈0.21 μW) and could generate distinct precision and accuracy. Anyway, such result highlights the need to lead a careful analysis of the precision and the accuracy each time that a distinct Delta Ray is used. With respect to the above considerations, the following tests described in this study were performed by using optimal conditions of measurements (Table 1).

3.3. Instrumental Conditions Influencing Continuous Measurements. One major advantage of IRIS techniques with respect to more traditional ones (e.g., IRMS) is the possibility to perform (semi)continuous measurements at high temporal resolution. The objective in performing such measurements is mainly to track variations of carbon and oxygen isotopes of CO_2 [9, 13]. However, the use of the dilution wires has demonstrated that an important time delay may exist (up to 797 s in our study with the yellow wire) before recording

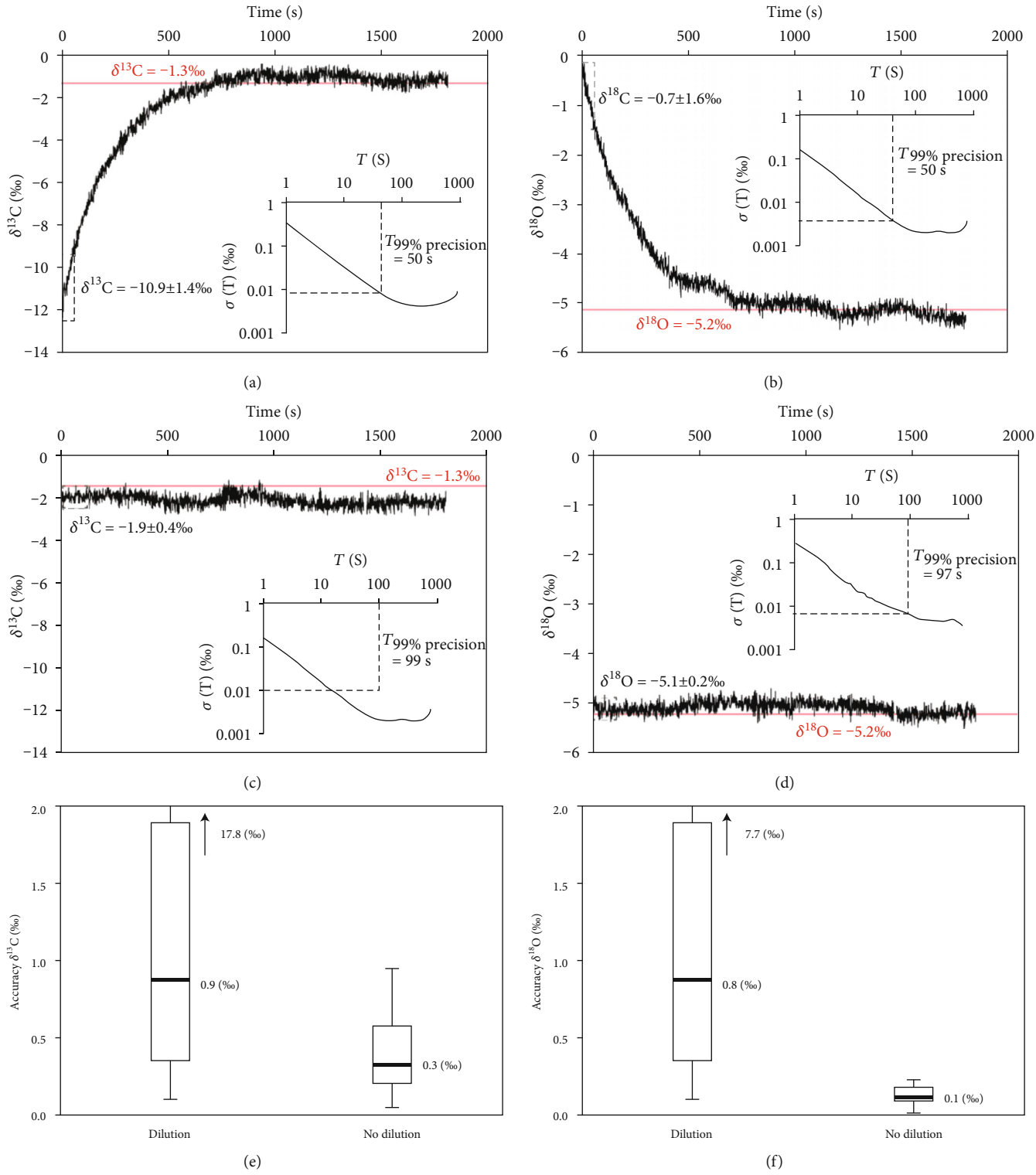


Figure 2: Raw signal (1 Hz) and overlapped Allan deviation obtained for 1800 s using a fixed range dilution system (yellow tube) for $\delta^{13}C$ (a) and $\delta^{18}O$ (b) and without a dilution system for $\delta^{13}C$ (c) and $\delta^{18}O$ (d). Red values and lines represent the theoretical signal expected from the analyzed sampling bag. Dashed square represents the subset of measurements (on a time τ required to obtain 99% of the precision) used to calculate the average value used for the test of accuracy. Box-and-whisker plots for the deviations of $\delta^{13}C$ (e) and $\delta^{18}O$ (f) measured values from theoretical values of reference gases used in this study (see Methods and Appendix 1).

accurate measurements. This point may be critical when dealing with (semi)continuous series.

The effect of gas mixing and potential induced time delay has been simulated in the laboratory by switching two reference gases isotopically distinct (Figure 5). Without dilution, a

good reproducibility between the theoretical curve and the measured one is observed (Figure 5(a)). Only a small time delay ($T \approx 39$ s in this test) is recorded between the moment when the valve is switched and the moment when accurate measurements are obtained. This time delay is consistent with the response time of the system (T) where $T = T_1 + T_2$, T_1 is the time took by the gas to start entering in the absorption cell (≈9 s), and T_2 is the time required to eliminate the mixing effect (≈30 s in this test). Similar time delay is reported by the manufacturer (35 s; Thermo Fisher) and by Braden-Behrens et al. [9] who estimated a time of about 47 s and 60 s to reach 99% and 99.9% of the maximum accuracy, respectively. This result sustains the need to apply a flushing time > 39 s, as documented in our study, and preferentially >47 s to reach 95% and 99% of the maximum accuracy, respectively. When using the dilution system, the response time is considerably greater (>600 s in this study with the yellow dilution wire; Figure 5(b)). In this case, it appears necessary to estimate the response time of the device deployed when using the dilution system to reach accurate values (Figure 3). It also evidences the inability of the system to determine the real $\delta^{13}C$ and $\delta^{18}O$ signatures of a gas generating a perturbation when the time between two successive perturbations of the system is lower than T (Figure 5(b)). Fortunately, even if delayed (T_1), the effect of a perturbation of the system will still be recorded (Figure 5(b)).

Applying long cycles of measurements appears thus necessary when performing continuous measurements based on the dilution system. On another hand, potential instabilities of the signal on some long time series acquired in the laboratory may occur (Figure 5(c)). There, a lost in precision for both the $\delta^{13}C$ and $\delta^{18}O$ measurements may appear after about 13 min if no referencing is performed and occurs independently of the analyzed CO_2 contents (Figures 5(c) and 5(d)). To investigate the origin of such discrepancy, a 65 h long time (semi)continuous series was obtained in the laboratory on a standard gas with a 15 min cycle of measurements (10 min of measurements and 5 min of flushing-referencing). This long time series of measurements reveals a slight dependence (correlations reported in Appendix 6) of CO_2 isotopes on the temperature/power of the laser signal ($R^2 < 0.3$) and on the internal pressure of the absorption cell ($R^2 < 0.15$) (Figure 5(e)). Fortunately, this dependency on instrumental conditions only leads to a limited variability of isotopic measurements ($\sigma = 0.1$‰). Conversely, measured CO_2 contents are much more dependent on the temperature/power of the laser signal ($R^2 > 0.5$) and on the internal pressure of the absorption cell ($R^2 \sim 0.5$) (Figure 5(f); Appendix 6).

3.4. Influence of Environmental Conditions. Potential dependence on internal pressure-temperature variations raises interrogations about the response of the Delta Ray IRIS when deployed on the field and thus when subjected to environmental pressure-temperature variations. To study this effect, the Delta Ray IRIS was brought on Mount Etna at distinct altitudes (i.e., distinct pressures and pressures; Figure 1(c)).

In the first experiment, the Delta Ray IRIS was calibrated at sea level pressure (1017 mbar). Then, Multi-Layer Foil gas sampling bags (Restek) were filled with a reference gas and analyzed at different altitudes (between 0 and 2000 m above sea level) while the Delta Ray IRIS was embarked in a car, i.e., under distinct external pressure (803-1018 mbar) and temperature (7-25°C) conditions. During the test, some inaccurate measurements were obtained (accuracy Δ differing from -1.6‰ to 0.7‰ of the real $\delta^{13}C$ value at -0.9‰) (Figure 6(a)). These inaccurate values are essentially present during the periods of car ascent and descent. Conversely, when the car was stabilized at constant altitude during complete reference-sample cycles of measurements (independently of the pressure-temperature), accurate measurements were recorded (Appendix 7). These important variations of the $\delta^{13}C$ accuracy are not directly correlated ($R^2 < 0.08$) with the instrumental conditions (e.g., temperature/power of the signal). In spite of important ambient pressure-temperature variations, the instrumental conditions remained broadly constant. The only exception is the internal pressure of the absorption cell that was strongly correlated ($R^2 > 0.98$) with the ambient pressure. Actually, the $\delta^{13}C$ accuracy and the gradient of the internal pressure of the absorption cell are slightly correlated ($R^2 > 0.15$). The most inaccurate $\delta^{13}C$ measurements ($\Delta = -1.6$‰) were obtained when the pressure gradient in the absorption cell was the most important, i.e., when the atmospheric pressure showed the largest variations ($\Delta P \approx 34$ mbar) during a reference-sample cycle of measurements (400 s). Additionally, Multi-Layer Foil gas sampling bags (Restek) were filled with reference gases in the field at distinct altitudes and then analyzed in the laboratory under the same pressure-temperature conditions than for the internal calibration procedure. Even if the ambient pressure-temperature conditions strongly differ between the sampling sites (up to 2000 m above sea level) and the laboratory, isotopic measurements remained accurate (Figure 6(a)). These experiences highlight that the dependence of Delta Ray IRIS measurements on environmental conditions (sampling and analysis) is mainly linked to the pressure gradient during a cycle of reference-sample measurements.

With respect to the above considerations, it could sometimes appear preferable to sample gases before analyzing them at constant environmental conditions, i.e., in a place where the environmental conditions (e.g., pressure) do not differ strongly between successive measurements. In this case, the time of gas storage may be an issue due to the suitability of gas sampling containers for isotopic measurements [31–33]. Consequently, in the second experience, Multi-Layer Foil gas sampling bags (Restek) were filled with gas mixtures of dry CO_2 ($\delta^{13}C = -1.3$ and -39.3‰) and CO_2-free synthetic air and regularly analyzed for about 3 months. No temporal discrepancy of isotopic measurements was observed during this period (Figure 6(b)). This result confirms that Multi-Layer Foil gas sampling bags (Restek) are suitable samplers for punctual gas sampling and storing for at least 3 months.

3.5. Estimations of Real CO_2 Contents from Diluted Ones. Determining the CO_2 content of gas samples analyzed for stable isotopes is often crucial to characterize the origin of volcanic gases and the concentration change in atmosphere

or in multicomponent mixing plots [11–13, 17, 34–36]. Conventional stable isotope analytical techniques such as the IRMS often require the use of an integrated gas chromatograph to obtain CO_2 contents [17, 36]. As most of the other laser-based instruments, the Delta Ray IRIS is able to measure stable isotopes from CO_2 content in the range 200-3500 ppm. But the instrument differs from the other by its ability to get measurements also at higher concentration (up to 100% CO_2) through an innovative dilution system. Meanwhile, to our knowledge, no test was performed in order to evaluate the possibility to rebuild the real CO_2 content from the diluted one displayed by the instrument. Here, we aim to study this possibility.

Multi-Layer Foil gas sampling bags (Restek) were filled with a gas mixture of dry CO_2 and synthetic air to obtain various CO_2 contents between 1 and 95%. Three distinct gas mixtures were analyzed for each dilution wire. Diluted CO_2 contents were then compared to CO_2 contents determined by a gas chromatograph (Figure 7). We document here a perfect correlation ($R^2 > 0.99$) between the diluted and real CO_2 contents opening the possibility to measure CO_2 contents in the full range of 200 ppm to ≈100% with the Delta Ray IRIS.

It is worth noting that even if this correlation is observed for the two Delta Ray IRIS, the coefficients of the linear regression strongly differ. It mirrors the dependence of measured CO_2 contents on the laser temperature/power, with the DR1 (≈0.45 μW) laser signal being two times more powerful than DR2 (≈0.21 μW). Actually, on the same instrument (e.g., DR1), the coefficients show also a significant variability when tests were performed at distinct dates, i.e., under distinct instrumental state of use (Figure 7(a)).

4. Discussion

Tests performed in this study have allowed to identify and evaluate the influence of various instrumental and environmental conditions on both the precision and the accuracy of the Delta Ray IRIS. Based on these results, we here discuss induced recommendations and protocols to perform isotopic measurements from either (i) punctual or (ii) (semi)continuous volcanic CO_2 emissions.

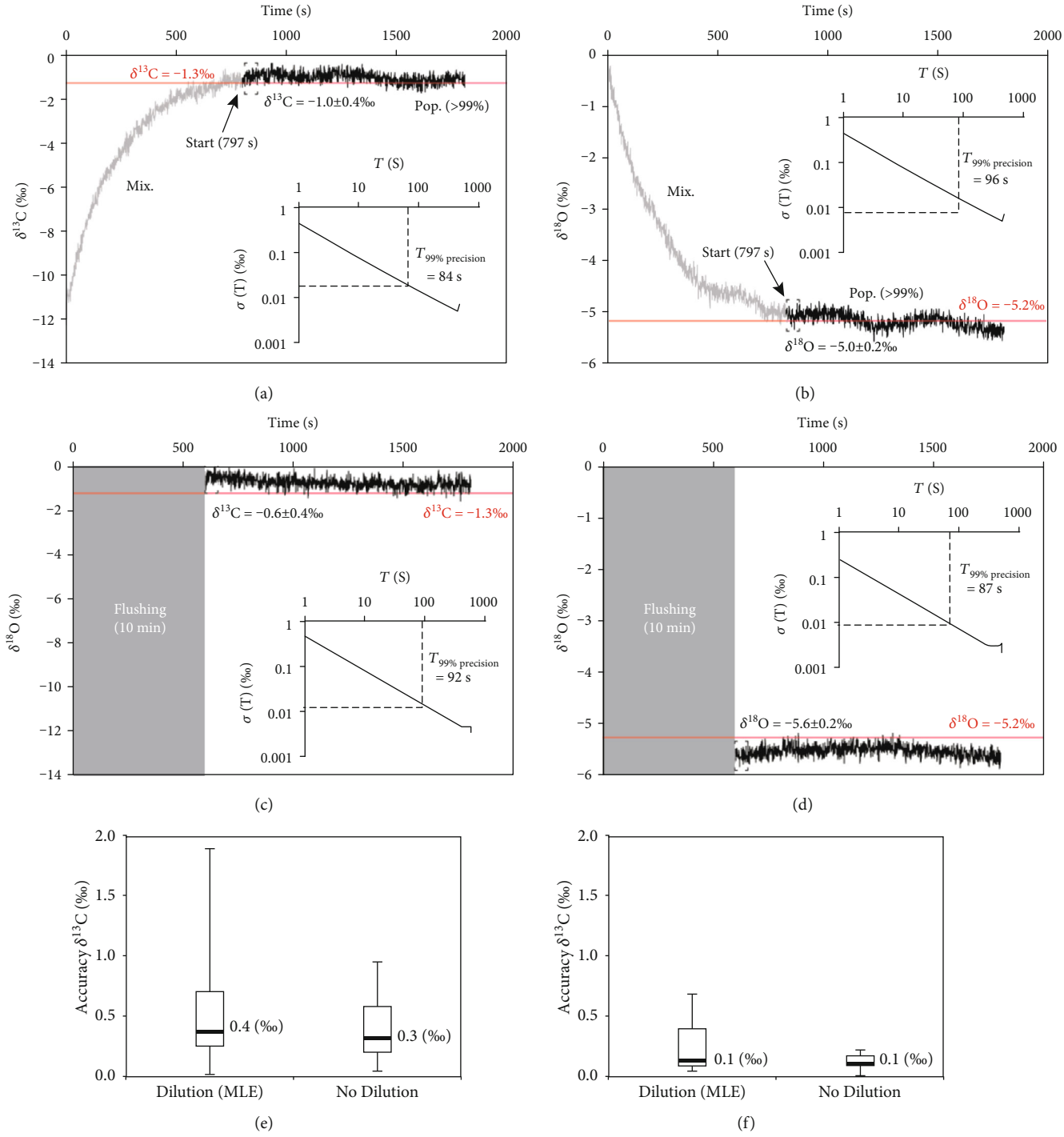
4.1. Punctual Gas Sampling. Tests performed with two distinct protocols (Table 1) on the flushing time and on the time of analysis of the reference gas have demonstrated that better precision and accuracy are obtained using 60 s of flushing time with 180 s of analysis of the reference gas. It is consistent with (i) calculations made by Braden-Behrens et al. [9] showing that 99% of the maximum accuracy is reached after 47 s without the use of the dilution system and (ii) our results showing that, in all our measurements, 99% of the maximum precision is obtained after 135 s. Consequently, we recommend to define protocols using at least 47 s of flushing time and 135 s of sample and reference gas analysis to reach 99% of the maximum precision and accuracy. Similarly, at least 39 s of flushing time and 23 s of sample and reference gas analysis should lead to 95% of the maximum precision and accuracy. In particular, we pointed out here that evoked times of 135 s and 23 s represent the maximum times in our dataset required to obtain 99% and 95% of the maximum precision, respectively, whatever the instrumental configuration used. Consequently, they allow to cover any potential discrepancy on the precision documented in our study linked to the choice of the peak integration, the range of use of the dilution tube (recommended or possible), and the choice of the isotopic signature of the reference gas (Figure 4). Furthermore, when adapting the dilution system on the Delta Ray IRIS, we have documented in our study the need to consider additional mixing times depending on the dilution wire used. These mixing times (maximum of 113 s to 797 s depending on the wire) have to be taken into consideration by increasing the flushing time of the sample gas before the analysis (Figure 3). It leads us to a median accuracy of

(i) 0.37‰ and 0.16‰ on $\delta^{13}C$ and $\delta^{18}O$, respectively, using 99% of the maximum precision

(ii) 0.39‰ and 0.20‰ on $\delta^{13}C$ and $\delta^{18}O$, respectively, using 95% of the maximum precision

These values are consistent with those obtained from other studies around 0.25-0.30‰ [25, 26]. In any case, we recommend the use of the integrated $^{12}C^{16}O^{16}O$ isotopologue peak at 4.3280 μm (i.e., low concentration peak) to obtain a better accuracy (Figure 4) even if the user's manual recommends to use "low" integration only for samples with CO_2 contants < 1500 ppm.

Based on the total minimum time required by each connection wire to obtain accurate and precise measurements (summed from the previous paragraph) and the corresponding flow rate documented by the manufacturer (Thermo Fisher documentation), the minimum volume of gas that has to be sampled to perform precise and accurate analysis with the Delta Ray IRIS may be estimated (Figure 8). We found that filling conventional volcanic gas samplers (e.g., 1 L Multi-Layer bags, ≈100 mL stainless steel samplers, ≈50 mL glass samplers, or 12 mL Exetainer vials) at 1 bar and with a CO_2 content exceeding 0.35% is sufficient for analysis of the stable isotopic composition of CO_2 using the Delta Ray IRIS. Tests performed on soil CO_2 gas samples collected at Stromboli in 1 L Multi-Layer bags and in 12 mL Exetainer vials and analyzed using our proposed protocols (Figure 8) show an accuracy better than 0.25‰ on $\delta^{13}C$ and a median accuracy of 0.11‰ that is similar to that obtained from IRMS (e.g., 0.15‰) (Appendix 8). Without the dilution system, i.e., for CO_2 content < 0.35%, filling 1 L Multi-Layer bags allows also to perform isotopic measurements. For such CO_2 contents, measurements from stainless steel samplers or glass samplers may be considered through few adaptions of the system as (i) taking replicates or (ii) diluting gas sample with CO_2-free synthetic air in order to increase the volume. In the last case, the user has to take care to reach a final CO_2 content above the lower limit of use of the instrument (200 ppm). Without the dilution system, the analysis of Exetainer vials appears compromised and requires the use of other more traditional techniques such as the IRMS. A similar recommendation is also available for gas



1 FIGURE 3: Raw signal (1 Hz) and overlapped Allan deviation using a fixed range dilution system (yellow tube) obtained for 1800 s of measurements for $\delta^{13}C$ (a) and $\delta^{18}O$ (b) and with an additional flushing time of 600 s before the measurements of $\delta^{13}C$ (c) and $\delta^{18}O$ (d). Red values and lines represent the theoretical signal expected from the analyzed sampling bag. "Pop." represents the gas population defined by the sample gas targeted (with 99% of confidence) whereas "Mix." represents the gas mixture within the cell and the tubes measured at the beginning of the acquisition (see text for explanations). Dashed square represents the subset of measurements (on a time τ required to obtain 99% of the precision) used to calculate the average value used for the test of accuracy. Box-and-whisker plots for the deviations of $\delta^{13}C$ (e) and $\delta^{18}O$ (f) measured values from theoretical values of reference gases used in this study (see Methods and Appendix 1). "MLE" refers to the accuracy of the subset of measurements (with the dilution system) belonging to the population of interest (Pop.) obtained using the maximum likelihood estimator.

released by crystal crushing whose CO_2 concentrations are generally <2000 ppm in a 16 mL glass tube [37, 38].

Finally, this study has revealed that long time cycles (>13 min) of Delta Ray IRIS measurements may generate a

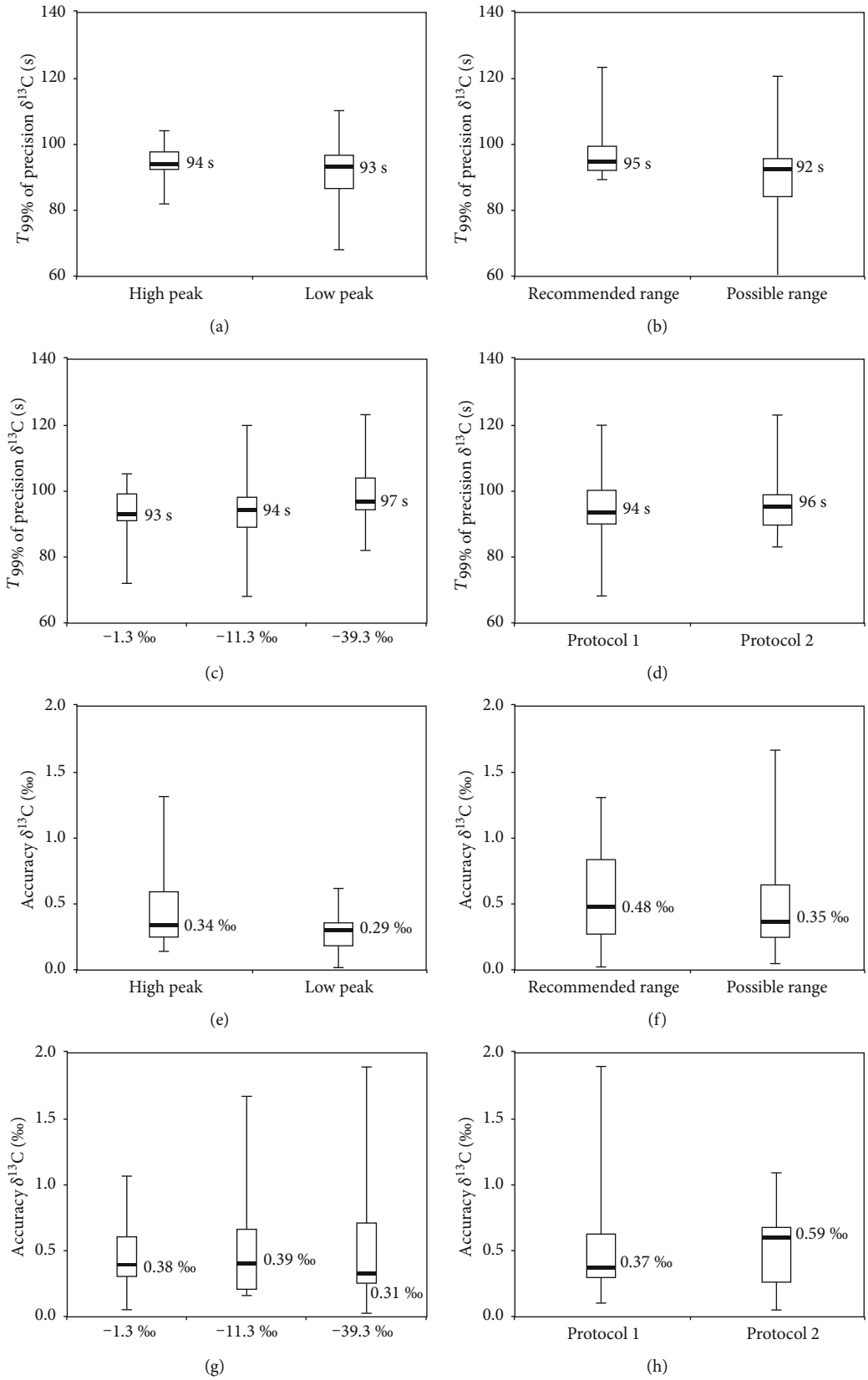


Figure 4: Box-and-whisker plots for (a–d) the time required to reach 99% of the maximum precision and (e–h) the accuracy of δ^{13}C. Precision and accuracy are studied in function of the peak integration (a, e), the range of use of the dilution tube (b, f), the isotopic signature of the reference gas (c, g), and the kind of protocol applied for the flushing and reference analysis time (d, h). Details provided in the text and in Methods.

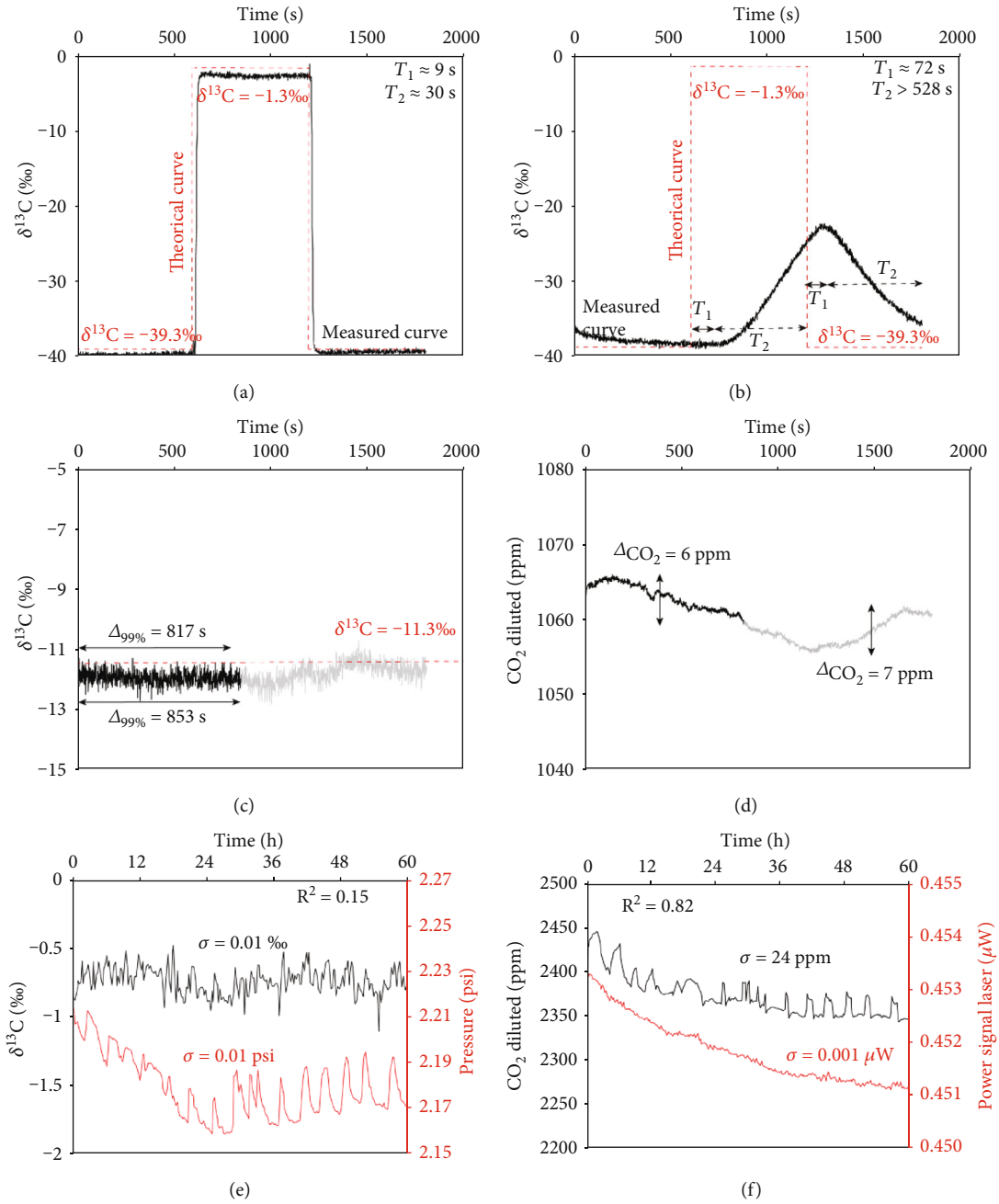


Figure 5: Raw signal (1 Hz) of simulated mixing between two gas samples (δ^{13}C = −39.3‰ and -1.3‰, respectively) by switching the valve each 10 min without the dilution system (a) and with the dilution (yellow) system (b). T_1 is the time required for the gas to start entering in the absorption cell. T_2 is the time required to eliminate the effect of gas mixing in the tube and the absorption cell. Red values and lines represent the theoretical signal expected from the analyzed sampling bag. (c) Example of potential long-term δ^{13}C instability of the raw signal (1 Hz) for 30 min of measurements of a reference sampling bag. $\Delta_{99\%}$ and $\Delta_{95\%}$ are, on average, the maximum time for which the precision is better than 99% and 95% of the maximum precision, respectively (Appendix 1). (d) Synchronous variability of measured CO_2 contents. (e) Long time acquisition (65 h) of δ^{13}C values (averages on 15 min cycles in black) of a standard gas with a fixed isotopic composition. Synchronous variations of the internal Delta Ray IRIS cell pressure are reported (in red). (f) Synchronous long time acquisition (65 h) of diluted CO_2 contents (averages on 15 min cycles in black; yellow wire) of a standard gas with a fixed CO_2 amount. Synchronous variations of the power of the laser signal are reported (in red).

variability in the analysis of CO_2 isotopes and contents (Figure 5). It is mainly linked to laser temperature/power and internal pressure fluctuations. This instrumental dependence suggests two main recommendations to increase the precision and the accuracy of the measurements:

(i) Delta Ray IRIS measurements have to be performed without fast ambient pressure variations. In our test performed on Mount Etna by embarking the Delta Ray IRIS in a car, we have noted that a better accuracy is obtained when the car was stopped,

independently of the pressure-temperature shift between the calibration and analysis sites. However, fast ambient pressure variations during a cycle of reference-sample analysis may lead to inaccurate measurements. In our case, we calculated that the accuracy of $\delta^{13}C$ measurements is on average better than 0.3‰ when the pressure gradient does not exceed 0.5 mbar/min (≈4 m/min of vertical ascension) and 0.5‰ when the pressure gradient does not exceed 2.5 mbar/min (≈20 m/min of vertical ascension). We thus recommend to take care of the ascension speed when the Delta Ray IRIS is embarked in a car or helicopter during the measurements

(ii) Instrumental stability has to be regularly monitored in a similar way that for other laser-based technics as Raman spectrometry for instance [39]

(iii) In the case of recalculations of CO_2 contents from diluted ones, in addition to the monitoring of the instrumental stability, we recommend during a session of measurements to frequently analyze at least two concentration reference gases with distinct known CO_2 contents under the same diluting condition (e.g., the same wire) in order to evaluate the variability affecting the coefficients of the equation of linear regression

4.2. Continuous Gas Sampling. Analyzing volcanic gases directly on the field with Delta Ray IRIS has led to the development of a plethora of homemade protocols with different integration times, analysis times, and referencing and flushing times [13, 27]. Based on the results of the study, we have deployed on Mount Etna (Sicily, Italy) during 24 hours Delta Ray IRIS (DR1) to measure the isotopic composition of soil CO_2 emissions (Figure 1). The following protocol was used:

(i) No fast ambient pressure variations (>0.5 mbar/-min) were recorded during the test

(ii) Flushing and analysis times of the reference gas were fixed at 60 s and 180 s to obtain more than 99% of the maximum precision and accuracy

(iii) Flushing time of the gas sample was fixed at 180 s to take into account the time delay of about 3 min related to the gas path (5 m long stainless steel tubing). Measurements were performed without the dilution system (CO_2 contents < 3500 ppm) and thus do not require extra flushing time

(iv) Analysis time of the gas sample was fixed at 480 s. This time is greater than the 135 s threshold required to reach more than 99% of the maximum precision and lower than 13 min to limit the effect of instrumental deviations. This time allows to perform, each hour, a 15 min cycle including the analysis of the reference and gas samples followed by 45 minutes of standby

(v) Instrumental conditions were monitored. The 24 h of acquisition was performed under stable instrumental conditions with a relative variability of the laser temperature/power and of the internal pressure of the absorption cell lower than 2%

In these conditions, soil CO_2 content measured by the Delta Ray IRIS varies from 1179 to 2225 ppm during the 24 h of data acquisition. At the same time, soil CO_2 content from the Passopisciaro station of the EtnaGas network (less than 20 m far) varies from 1357 to 1933 ppm and shows a similar signal trend (Figure 9(a)). It reflects changes in the soil CO_2 flux and is not linked to instrumental variations. On the same interval of time, the carbon isotopic signature of CO_2 varies from -16.9‰ to -21.2‰ (Figure 9(b)). On the basis of both CO_2 and related $\delta^{13}C$, three periods may be discriminated (Figure 9(b)):

(i) The first one (P1) is marked by low CO_2 contents (1179-1781 ppm) and the most positive $\delta^{13}C$ values (>-19.0‰)

(ii) The second period (P2) shows variable CO_2 contents (1340-2215 ppm) with quite constant $\delta^{13}C$ values ranging between -19.4 and -19.9‰

(iii) The third period (P3) is characterized by the highest CO_2 contents (1704-2225 ppm) together with the lowest $\delta^{13}C$ values ranging between -20.1 and -21.2‰

It is now well established that soil CO_2 flux may be subjected to the influence of environmental conditions such as pressure, temperature, and windspeed for the main ones [40–42]. In the short dataset presented in this study, correlations between either CO_2 contents or $\delta^{13}C$ values and environmental parameters acquired by the Passopisciaro soil CO_2 flux station are limited to $R^2 < 0.3$ (Appendix 9). However, considering only the periods P2 and P3, a greater correlation between $\delta^{13}C$ values and the temperature is observed ($R^2 > 0.5$). Actually, higher CO_2 contents and $\delta^{13}C$ values observed during P3 with respect to P2 occur at higher temperatures, i.e., during the day between 11:00 and 17:00 (local time) (Figures 9(a) and 9(b)).

To figure out this variability of CO_2 contents and $\delta^{13}C$ values, data were reported in a mixing plot between 3 components (magmatic, organic, and air; Figure 9(e) and related caption for details on the end-members). At a large scale, measurements are well represented ($R^2 > 0.6$; Appendix 9) by a mixing curve between the air ($\delta^{13}C = -8$‰; $CO_2 = 380$ ppm) and an end-member ($\delta^{13}C = -23.5$‰; $CO_2 = 100\%$) very close to the organic end-members (Figure 9(e)). The detail in Figure 9(f) shows the variability of the isotopic signature and CO_2 contents aforementioned, where the mixing plot confirms the greater contribution of air during P1. This period could correspond to the progressive emptying of the gas mixture between air and soil CO_2 contained in the stainless steel probe inserted at 50 cm depth. Higher CO_2 contents with the low $\delta^{13}C$ signature measured during P3 are consistent with a greater contribution of the organic component

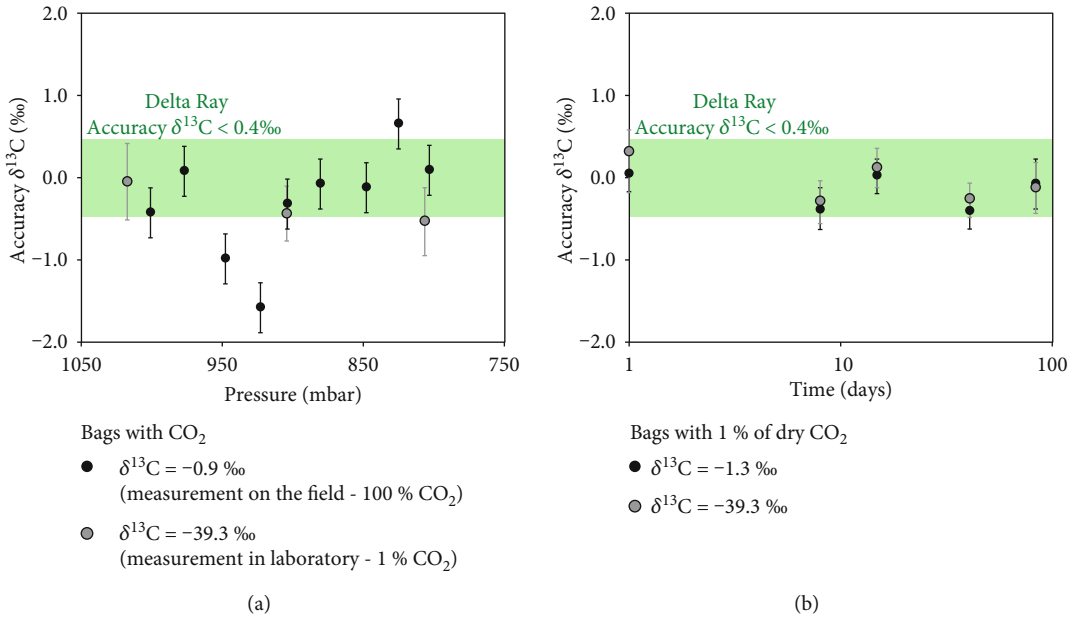


Figure 6: Dependence of $\delta^{13}C$ measurements on environmental conditions. (a) Accuracy of $\delta^{13}C$ measurements of CO_2 in function of the pressure of (i) analysis (in black; each 25 mbar) or of (ii) gas sampling (in gray). (b) Accuracy of $\delta^{13}C$ measurements of CO_2 in function of the time of gas storage in Multi-Layer Foil gas sampling bags (Restek). Green fields show the fields of accuracy of $\delta^{13}C$ measurements determined in this study (DR1 and DR2).

during the day when the temperature increases [43, 44]. Regarding the P2 period, it is interesting to notice how some measurements are characterized by higher CO_2 contents but without a decrease of $\delta^{13}C$ values (orange arrows on Figure 9(f)) and may reflect a greater contribution of ^{13}C-rich component. Even if the dataset presented in this study covers a very short time period and we cannot exclude that the observed changes are linked to a small modification in the isotope signature of the organic end-member (from -23.5 to -22.1‰), the results appear to be promising and could reflect high-frequency variations of soil CO_2 emissions related to a magmatic contribution. In fact, if we assume the Etnean magmatic component having a $\delta^{13}C = -2.2$‰ and $CO_2 = 100\%$ [24]; thus, the deep inorganic contribution would increase from ~5% to ~12% with respect to the organic end-member (Figure 9(e)). It is worth to note that during the same time, similar increases of the soil CO_2 content were also recorded at the Passopisciaro station. This station belongs to the EtnaGas network where some variations of soil CO_2 flux are known to be directly linked to the change of magmatic activity of Mount Etna [42]. This feature opens exciting prospects regarding volcano monitoring, and we strongly encourage further studies to focus on longer time series.

5. Conclusion

For few years, the development of the isotope ratio infrared spectrometer (IRIS) has opened new prospects on the isotopic analysis of CO_2 emissions directly on the field and/or at high frequency. In this study, we suggest technical and analytical protocols for the use of the Delta Ray IRIS (Thermo Scientific Inc., Waltham, USA), currently one of the most used IRIS techniques, by testing the influence of analytical, instrumental, and environmental conditions on the precision and accuracy of CO_2 isotope measurements.

Our results show that the choice of the integrated $^{12}C^{16}O^{16}O$ isotopologue peak, the range of use of dilution wires, flushing/analysis times, and the pressure gradient have the major influence on the precision and the accuracy of the measurements. More precise and accurate measurements are obtained when

(i) integrating the CO_2 concentration peak at 4.3280 μm

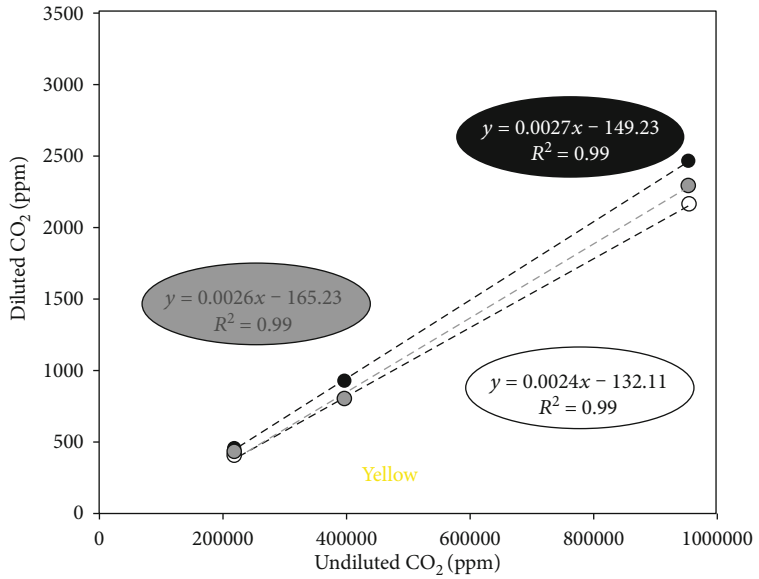
(ii) using the dilution wires in their recommended range

(iii) the ambient pressure gradient is lower than 0.5 mbar/min during a cycle of reference-sample analysis

Our results emphasize also the ability of the Delta Ray IRIS to perform isotope measurements for a large range of CO_2 concentration (200 ppm–100%) thanks to a dilution system. They show that a reliable estimation of the real CO_2 content may be obtained from the diluted one.

Performance tests have demonstrated that the volume of gas stored in traditional gas samplers (e.g., Multi-Layer bags, stainless steel sampler, glass sampler, or Exetainer vials) is theoretically sufficient to obtain precise and accurate measurements of CO_2 isotopes for contents above 3500 ppm, i.e., with the use of the dilution system. Conversely, lower CO_2 contents (200-3500 ppm) require a higher volume of gas favoring the use of Multi-Layer bags that were tested to be suitable for a gas storage time up to at least 100 days.

Like other laser-based techniques such as Raman spectrometry, it appears fundamental to monitor the conditions



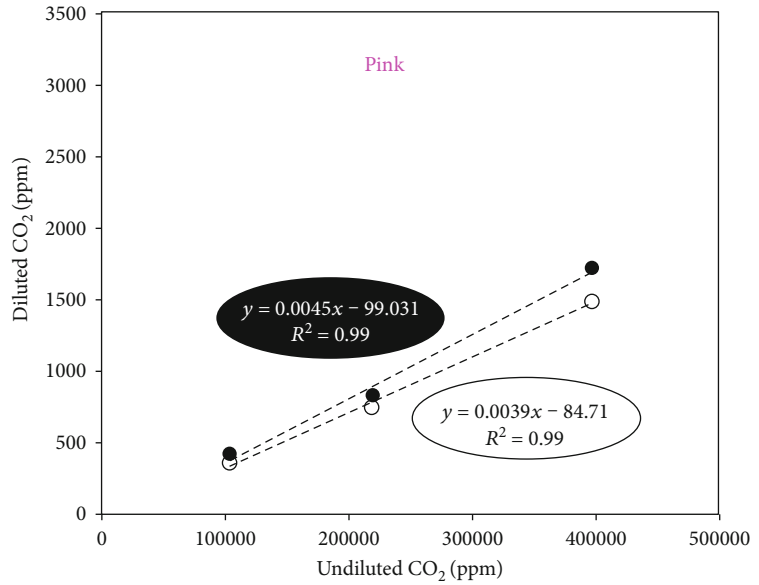
Delta Ray 1

- January 18, 2019
  Power (laser signal = 0.4541 μW)
- February 28, 2019
  Power (laser signal = 0.44535 μW)

Delta Ray 2

- January 18, 2019
  Power (laser signal = 0.2134 μW)

(a)



Delta Ray 1

- January 18, 2019
  Power (laser signal = 0.4541 μW)
- February 28, 2019
  Power (laser signal = 0.44535 μW)

Delta Ray 2

- January 18, 2019
  Power (laser signal = 0.2134 μW)

(b)

Figure 7: Continued.

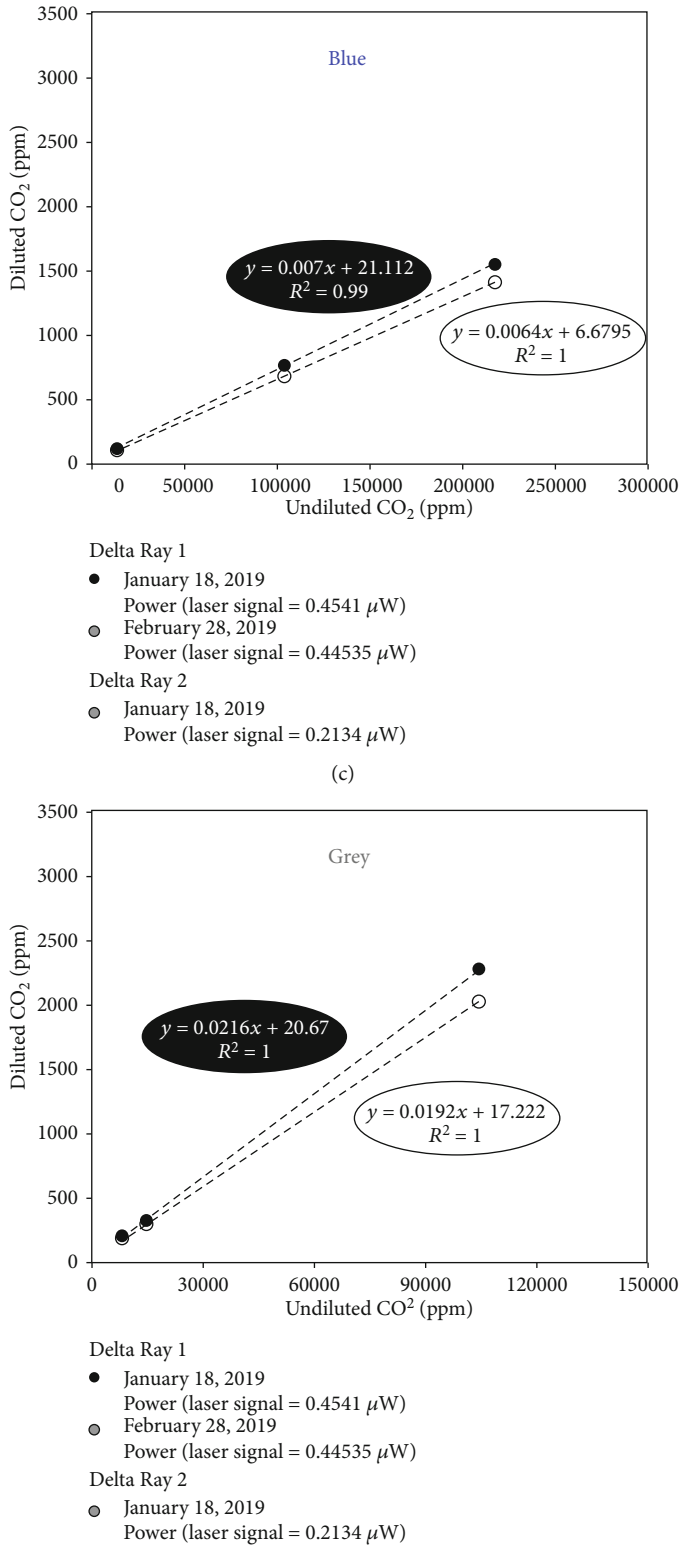
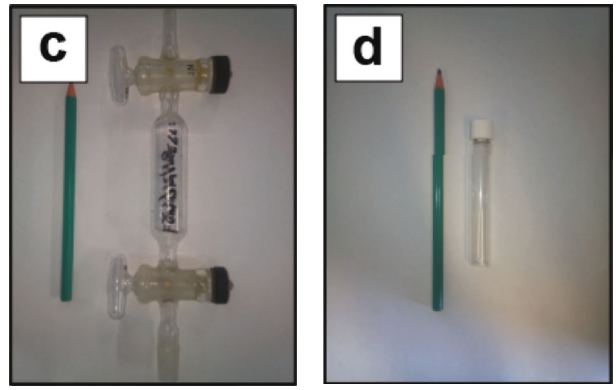


Figure 7: Comparison between real CO_2 contents and measured diluted ones from Delta Ray IRIS with either the (a) yellow, (b) pink, (c) blue, or (d) gray dilution wires. The two Delta Ray IRIS instruments available at the INGV Palermo (DR1 and DR2) were used for this test leading to distinct coefficients for the equation of linear regression. CO_2 contents of reference gases varying from 1 to 95% (see Appendix 1).

of use of the Delta Ray IRIS, such as the power/temperature of the laser signal, to guarantee long-term precise and accurate measurements. This point is crucial for the recalculation of CO_2 contents from diluted ones or in the prospects of

(a) (b)



(c) (d)

	99% of the maximum precision						95% of the maximum precision					
	Dilution (CO_2 content > 0.35%)					Without Dilution	Dilution (CO_2 content > 0.35%)					Without Dilution
	Yellow	Yellow/pink	Blue	Gray	Orange		Yellow	Yellow/pink	Blue	Gray	Orange	
Sample volume required												
Flow (mL/min)	0.12	0.27	0.48	1.85	7.06	80	0.12	0.27	0.48	1.85	7.06	80
Flushing time (s)	47	47	47	47	47	47	39	39	39	39	39	39
Mixing time max (s)	797	420	113	0	0	0	797	420	113	0	0	0
Precision time max (s)	135	135	135	135	135	135	23	23	23	23	23	23
Total min time (s)	979	602	295	182	182	182	859	482	175	62	62	62
Total min volume (mL)	2.0	2.7	2.4	5.6	21	243	1.7	2.2	1.4	1.9	7	83
Sampler compatibility												
(a) Multi layer bag (>1L)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
(b) Stainless steel sampler (100mL)	✓	✓	✓	✓	✓	$x^{(3)}$	✓	✓	✓	✓	✓	✓
(c) Glass sampler (50mL)	✓	✓	✓	✓	✓	$x^{(5)}$	✓	✓	✓	✓	✓	$x^{(2)}$
(d) Exetainer vials (12mL)	✓	✓	✓	✓	$x^{(2)}$	$x^{(21)}$	✓	✓	✓	✓	✓	$x^{(7)}$

(e)

Figure 8: Assumption on the use of distinct gas samplers to perform analysis with the Delta Ray IRIS: (a) Multi-Layer bag (>1 L), (b) stainless steel sampler (≈100 mL), (c) glass sampler (≈50 mL), and (d) Exetainer vials (12 mL). (e) Estimation of the minimum volume of gas required to obtain precise (99% and 95% of the maximum precision) and accurate measurements in function of the dilution tube (or without) for the full range of CO_2 contents from 200 ppm to 100%. Green-filled cells for accurate gas samplers. Red-filled cells for inaccurate gas samplers. In the last case, the reported exposant highlights either the number of similar gas samplers required to perform the analysis (see text for explanations).

(semi)continuous monitoring of volcanic CO_2 emissions. In particular, we recommend a regular analysis of known CO_2 content standards to cover the uncertainty linked to the variability of instrumental conditions on the equations of calibration of real/diluted CO_2 contents. Through an adapted protocol to the use of the Delta Ray IRIS instrument available at the INGV Palermo, we have shown that hourly monitoring of CO_2 contents and isotopes from peripheral soil gas emissions on Mount Etna presents a real variability that open exciting prospects for volcano monitoring.

Data Availability

It is not possible to add more than one appendix as supplemental material. Consequently, all appendixes in .png are compiled in a Word file. The Appendix 1 and Appendix 2 that are .xlsx files are available upon request to the corresponding author for the moment.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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Supplementary Materials

There are 9 appendixes in the Supplemental Material (3 tables and 6 figures). Appendix 1: results from tests performed on stable isotopes from CO_2 ($\delta^{13}C$ and $\delta^{18}O$) in the laboratory. Details provided in the text and in Methods. Appendix 2: results from tests performed on stable isotopes from CO_2 ($\delta^{13}C$ and $\delta^{18}O$) on the field. Details provided in the text and in Methods. Appendix 3: box-and-whisker plots for the accuracy obtained with either 95% or 99% of the maximum precision on (a) $\delta^{13}C$ and (b) $\delta^{18}O$. Box-and-whisker plots for the accuracy of (c) $\delta^{13}C$ and (d) $\delta^{18}O$ values obtained either using an average or by extrapolation ($\delta^{13}C$ versus $1/CO_2$ [11, 25]). Appendix 4: box-and-whisker plots for (a–c) the time required to reach 99% of the maximum precision and (d–f) the accuracy of $\delta^{18}O$. Precision and accuracy are studied in function of the peak integration (a, d), the range of use of the dilution tube (b, e), and the kind of protocol applied for the flushing and reference analysis time (c, f). Details provided in the text and in Methods. Appendix 5: comparison between the results obtained with Delta Ray 1 and Delta Ray 2. Box-and-whisker plots for the time required to reach 99% of the maximum precision of $\delta^{13}C$ with (a) Delta Ray 2 and (b) Delta Ray 1 using either Protocol 1 or Protocol 2 (see Methods). Box-and-whisker plots for the accuracy of $\delta^{13}C$ measurements with (c) Delta Ray 2 and (d) Delta Ray 1 using either Protocol 1 or Protocol 2 (see Methods). Box-and-whisker plots for the accuracy of (e) $\delta^{13}C$ and (f) $\delta^{18}O$ measurements with either Delta Ray 1 or Delta Ray 2. Appendix 6: correlations (R^2) between measurements of $\delta^{13}C$, $\delta^{18}O$, and CO_2 contents and Delta Ray IRIS instrumental conditions (e.g., power, inner pressure/temperature). Analysis performed during a 65 h long acquisition in the laboratory at 1 Hz with a 15 min cycle, i.e., with one averaged measurement each 15 min. In bold, the most important correlation for either $\delta^{13}C$, $\delta^{18}O$, or CO_2 contents. In bold italic, second-order correlations, if >0.5. Appendix 7: (semi)continuous measurements of dry CO_2 (100%) injected in a Multi-Layer bag with the Delta Ray IRIS embarked in a car driving on Mount Etna between 0 and 2000 m above sea level (after calibration at sea level). (a) Evolution of the accuracy $\delta^{13}C$ measurements during car ascent (in red), descent (in blue), or stop (in gray). (b) Correlation ($R^2 > 0.98$) between the atmospheric pressure and the internal cell pressure of the Delta Ray IRIS. (c) Evolution of the internal cell pressure during the track. (d) Evolution of the gradient of pressure in the internal cell pressure during the track. Appendix 8: the $\delta^{13}C$ signature of punctual samples of soil CO_2 emissions at Stromboli (see Figure 1 for the location of samples sites). Gas was sampled in bags and vials. Appendix 9: (a) correlations between molar CO_2 from soil measured with the Delta Ray IRIS (CO_2_DR), the permanent station from the EtnaGas network at Passopisciaro (CO_2_S), $\delta^{13}C$ values, and meteorological records during 24 hours on January 29 and 30, 2019 (frequency of 1 hour). The first table shows the correlations during the whole period (P1+P2+P3). The second table shows the correlations during the period (P2 +P3) without the initial phase of air contamination. Correlations with a $R^2 > 0.1$ are highlighted in green. (b) Plot of $\delta^{13}C$ versus $1/CO_2$ measured with the Delta Ray IRIS. (c) Plot of $\delta^{13}C$ versus $1/CO_2$ measured with the Delta Ray IRIS for anomalous values reported during the P2 period (orange arrows on Figure 9; see text for explanations). The intercepts of the best fit equation give the $\delta^{13}C$ values extrapolated to pure CO_2 ([11, 25]). *(Supplementary Materials)*

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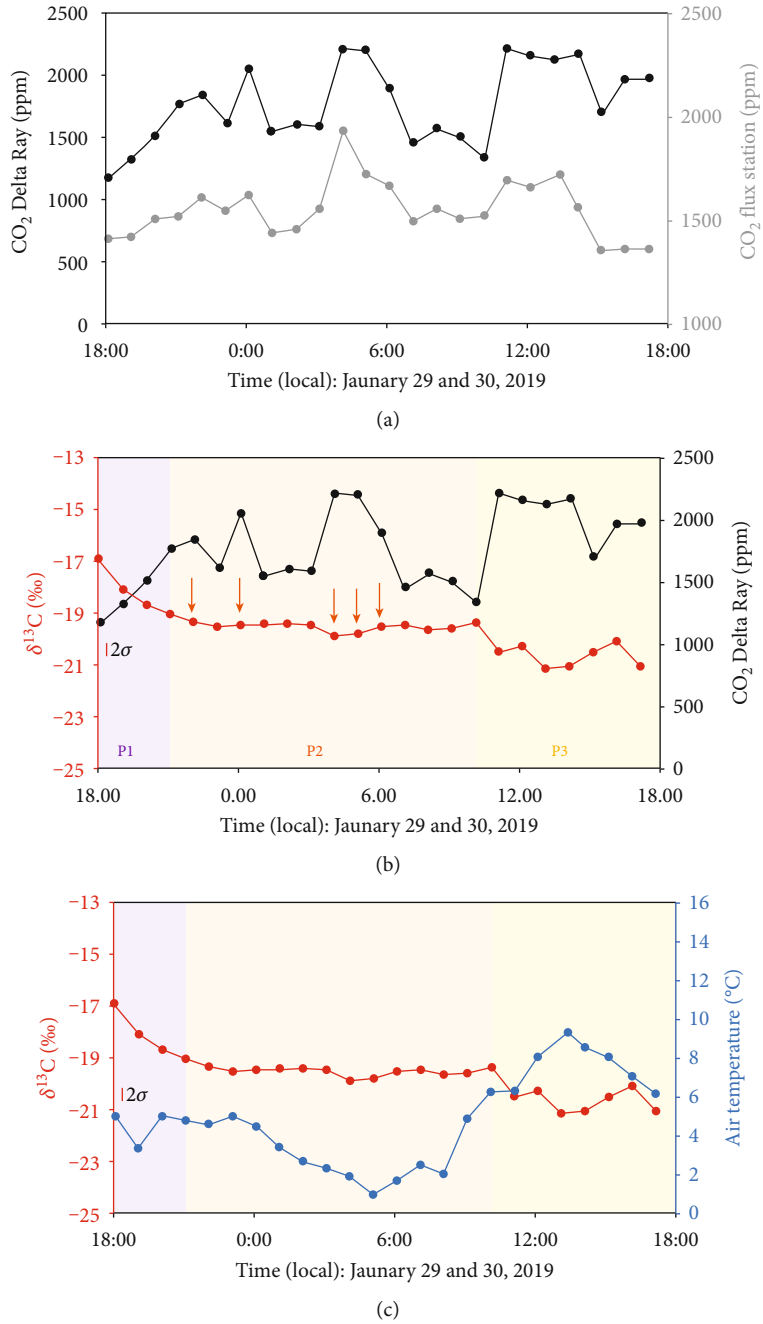

Figure 9: Continued.

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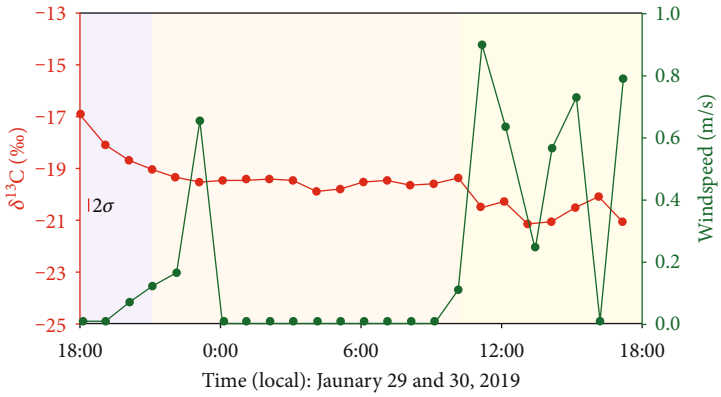

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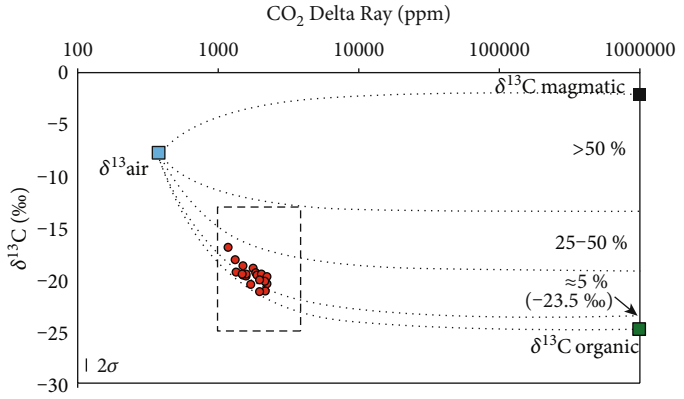

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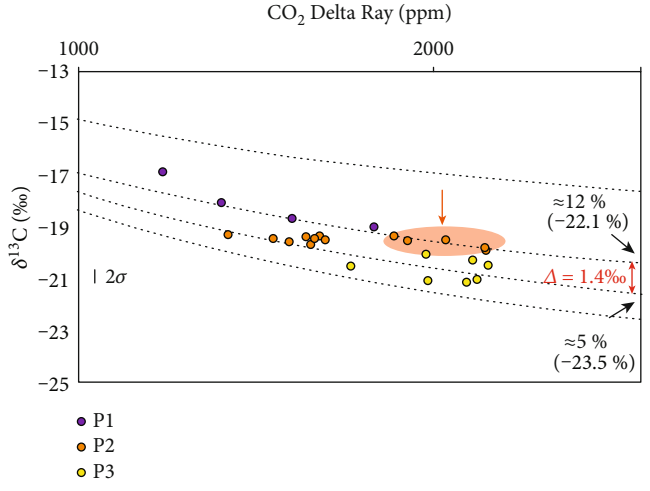

(f)

Figure 9: Time series of semicontinuous $\delta^{13}C$ measurements from soil CO_2 flux at Passopisciaro during 24 hours on January 29 and 30, 2019. (a) Comparison between molar CO_2 content in soil measured with the Delta Ray IRIS (black) and from the permanent station of the EtnaGas network less than 20 m far. (b) Comparison between molar CO_2 content in soil (black) and related $\delta^{13}C$ values (red) measured with the Delta Ray IRIS. Comparison between $\delta^{13}C$ values from soil CO_2 (red) measured with the Delta Ray IRIS and (c) the air temperature (blue) and (d) the windspeed (green) from the Passopisciaro permanent station. (e) Plot of $\delta^{13}C$ versus CO_2 concentration obtained from soil CO_2 using the Delta Ray IRIS. Magmatic end-member ($\delta^{13}C = -2.2‰$; $CO_2 = 1000000$ ppm) for Mount Etna, air values ($\delta^{13}C = -8.0‰$; $CO_2 = 380$ ppm), and biogenic end-member ($\delta^{13}C = -24.7‰$; $CO_2 = 1000000$ ppm) from [17, 24]. (f) Zoom of the plot of $\delta^{13}C$ versus CO_2 concentration. P1 (purple) for the period marked by air mixing in the probe. P2 (orange) for the night period. P3 (yellow) for the day period. "Anomalous" $\delta^{13}C$ values during the P2 period diverging from the main air-biogenic mixing line highlighted with orange arrows.

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