ACCESS TO RESEARCH INFRASTRUCTURES

Emission in atmosphere of Natural gases and TEmporal variations Related to volcanic activity

ENTER

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1. Introduction and motivation

Many studies on volcanic emissions (especially CO_2) in the atmosphere as well as atmospheric gas/aerosol dispersion already exist (e.g., Bobrowski et. al. 2015; Roberts et al., 2009; von Glasow and Crutzen, 2014), but lacks of isotope measures and of multidisciplinary approach. Measurements of the isotope composition of the volcanic CO_2 emitted in atmosphere has been limited due the detection limit of most common analytical methods (Rizzo et al., 2014, 2015 and references therein). Due to its frequent eruptions, Piton de la Fournaise (PdF) volcano (Reunion island) represents an unique occasion to deepen this knowledge, to evaluate the temporal variability of $\delta^{13}C$ due to changes of magmatic activity study, and to estimate the impact of CO_2 onto the atmosphere. The attempt of making in the field real-time measurements of the isotope composition of CO_2 represents a total novelty for the scientific community and a promising way to better evaluating the degassing of the volcano and its impact into atmosphere. The primary aim of ENTER project is the improvement of knowledge on the origin of volcanic gases (mainly CO_2) emitted from PdF and their incidence in the local atmosphere.
In detail, ENTER project focuses on the study of concentration and $\delta^{13}C$ values of CO_2 emitted from the soil of Gite degassing area that is the closest anomalous degassing site from the central active area of Piton de la Fournaise (PdF) and the comparison with data regularly acquired from the multidisciplinary volcanic monitoring network of the Observatoire Volcanologique du Piton de la Fournaise (OVPF) (Fig. 1). A second area of investigation was Cilaos, located on Piton des Neige (PdN) volcano (Fig. 1), well know site on the island to be an important CO_2-rich thermal spring, which is in contrast with the low passive degassing of PdF. In this project, we also aimed at investigating short-term variations due to volcano-tectonic activity and/or environmental conditions, to be compared with geophysical and geochemical data of the OVPF and chemical and environmental parameters recorded by the Maïdo Observatory.
The ENVRIplus TNA project represented an important opportunity for close collaboration and sharing of ideas and expertise between members of the Observatoire Volcanologique du Piton de la Fournaise (OVPF), the Maïdo Observatory, and the Istituto Nazionale di Geofisica e Vulcanologia of Palermo (INGV-Palermo, Italy). The access period was from the 1st to the 13th October 2018, when it was possible to visit the OVPF Observatory and the University of La Reunion. During access period there was an ongoing eruption at Piton de la Fournaise (Fig. 2),

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which represented a great opportunity to test model and real-time variations of geochemical tracers strictly related to magmatic activity, as well as the influence of volcanic gases in atmosphere.

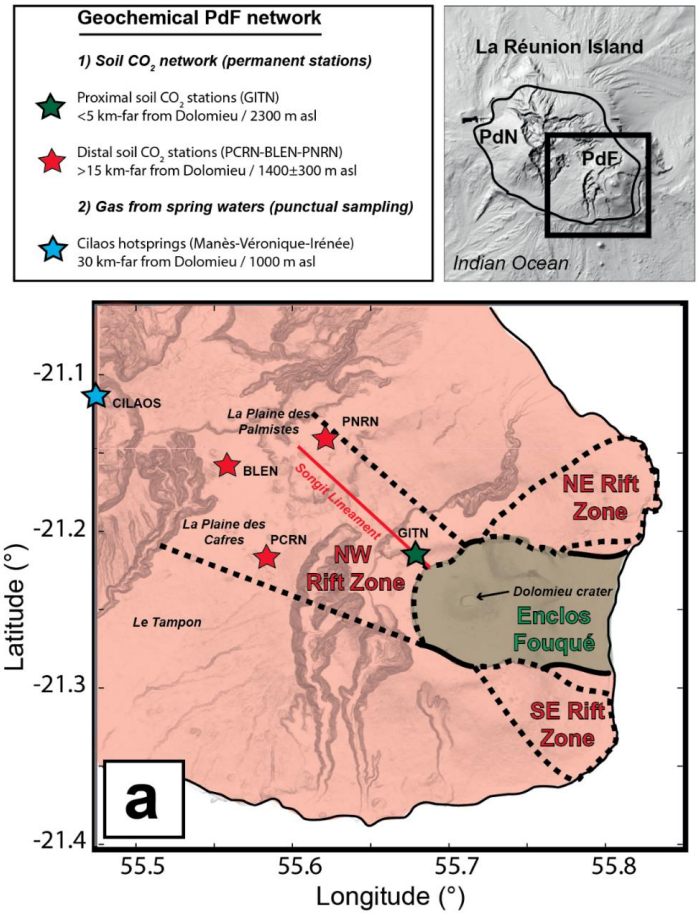

Fig. 1: Map of La Reunion Island showing the location where measurements of gas were taken during the TNA visit at La Reunion. Grey area indicates the PdF caldera where eruptive activity occurs at present. GITN indicates the area of Gite where a permanent station of soil CO_2 emission was recently installed and where we conducted part of our fieldwork. The blue star indicates the area of Cilaos, sited on Piton des Neige, where the thermal establishment is located.

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Fig. 2: Photo of eruptive fracture at PdF during initial phases of September-October 2018 eruption. Photo credit by Andrea Di Muro.

2. Multidisciplinary approach

To achieve the scientific goals, we planned some field surveys in the areas of Gite (on PdF) and Cilaos (on PdN) (Fig. 1) in order to: a) define the concentration and $\delta^{13}C$ of CO_2 emitted from these areas; b) investigate possible short-term variations related to eruptive activity; c) compare our measures with existing data from OVPF monitoring and Maïdo Observatory; d) evaluate the influence of CO_2 degassing in the local atmosphere. To validate our approach, we also planned a collection of gas samples from soil and thermal gases for later chemical and isotope analyses at INGV-Palermo, for a better comprehension of the volcanic gases contribution into the atmosphere.

The obtained data, currently under analysis and modelling, will be finally available in Open Data format for the ENVRIplus community.

3. Scientific objectives

In this project we intended to address the existing gap in knowledge by 1) defining the chemical and isotopic characteristics of magmatic fluids (CO_2, SO_2 and noble gases) either at source or in distal areas; 2) quantifying the amount of volatiles emitted from the volcano and their evolution in the atmosphere; 3) evaluating the impact of volcanic emissions in the local atmosphere.

The ENTER project aimed at improving the knowledge on the isotope composition ($\delta^{13}C$) of CO_2 emitted on La Réunion island, focusing in two key degassing areas: the first is in Gite,

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which is proximal to the PdF central caldera where most of the present eruption occur; the second is in Cilaos, which is located on PdN and represents an important source of CO_2 degassing where clues on the probable connection of Cilaos degassing regime and the deeper magmatic activity at PdF are arising (Fig. 1). We plan to better define the origin of CO_2 and evaluate possible short-term variations due to volcano-tectonic activity and environmental conditions.

4. Methodology and experimental set-up

The survey on Piton de la Fournaise was carried out while September-October 2018 eruption at PdF was ongoing (Fig. 2). Although it was not possible to access the eruptive fracture for direct field measurements, the ongoing eruption represented a great opportunity to investigate the behaviour of soil degassing in the proximal area of Gite and compare with phases of quiescent activity monitored by OVPF.

As above reported, our field surveys were performed in the degassing areas of Gite and Cilaos. The fieldwork benefited of the use of different instrumentations: 1) a specific instruments entirely designed and assembled at INGV-Palermo, able to measure simultaneously CO_2 gas from the soil in combination with others physical parameters; 2) an analyser of CO_2-CH_4-H_2O concentration in atmosphere; 3) a laser for real-time measures of concentration of CO_2 and $\delta^{13}C$. This laser was installed for 1 day at Gite and for a few weeks in a CO_2 -rich thermal spring (Cilaos) for testing temporal variability.

The obtained data will be integrated with other geophysical and geochemical monitoring data of the OVPF and chemical and environmental parameters recorded by the Maïdo Observatory.

5. Preliminary results and conclusions

As above reported, our field survey was performed in the anomalous degassing areas of Gite and Cilaos (Fig. 1). The surveys were carried out while the September-October 2018 eruption at PdF was ongoing (Fig. 2). In Fig. 3, we report the main results achieved until now. We selected two points of measure (P0 and P5) of CO_2 concentration and isotope composition from the soil of Gite, because periodic monitoring performed by OVPF revealed that these are key points of anomalous degassing related to the state of activity variations of the volcano. In fact, as can be observed in Fig. 3, important variations occur almost simultaneously at the two points, especially while eruptive activity is ongoing. The opportunity of to use the laser directly on the island during the ENTER project allowed to make high frequency measurements of CO_2 concentration and isotope composition that seem strongly correlated. This preliminary finding will allow us validating the hypothesis that changes of degassing regime induce also variations of the isotope composition of CO_2. Next step will be to deepen this aspect with further measures coupled to the continuous monitoring of CO_2 concentration in the soil, now possible thank to the recent installation by OVPF of an automatic station devoted for this purpose.

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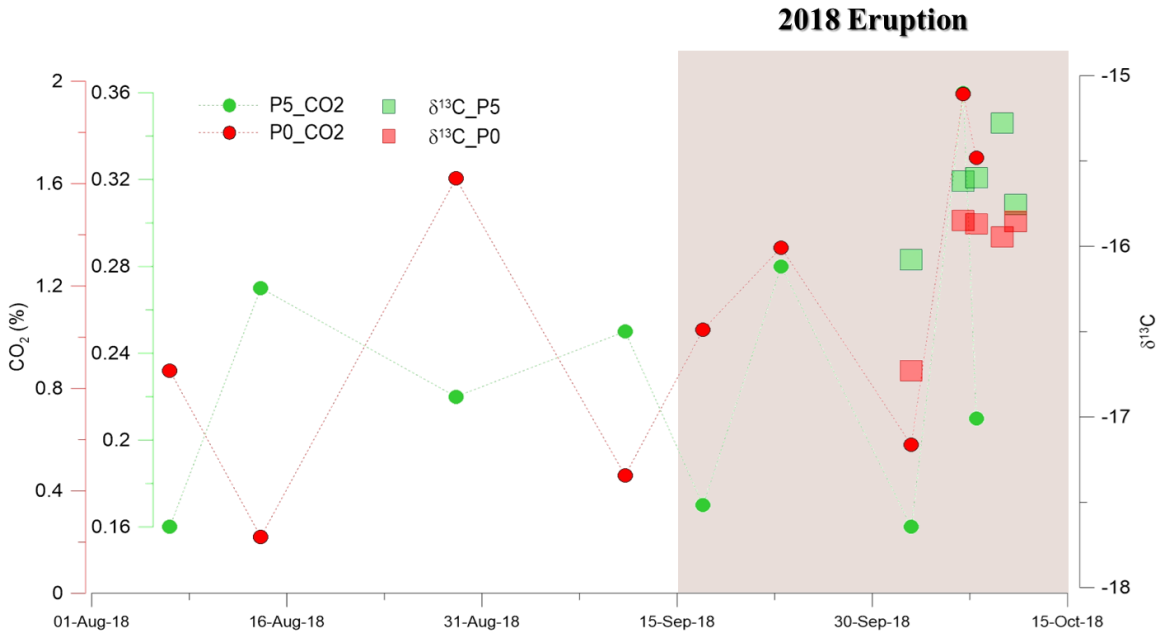

Fig. 2 : Time series of the CO_2 concentration and isotope ratio ($\delta^{13}C$) measured in Gite area, proximal to PdF during the September-October 2018 eruption (grey rectangle).

The second part of access period was carried out in the area of Cilaos, and regarded in particular the installation in the thermal spring of Irénée of the laser previously used at Gite (Fig. 4). This study starts from the findings obtained during 3 years of periodic sampling by OVPF, in which we noticed that gases emitted from Cilaos thermal springs have a clear magmatic signature in terms of $^3He/^4He$ (expressed normalized to the same ratio in atmosphere and corrected for the atmospheric contamination, as Rc/Ra) and $\delta^{13}C$ (Fig. 3). Furthermore, the isotope ratios measured in the thermal springs vary in the same range of the same measurements carried out in mineral fluid inclusions of rocks erupted at PdF (Furi et al., 2011; Boudoire et al., 2018). This clearly implies that these gases could have the same source, therefore opening a crucial question on the state of activity of PdN and its possible relations with eruptions at PdF. Finally, but not least important, the relevant degassing rate of CO_2 from Cilaos thermal spring needs an evaluation on its possible impact on the local atmosphere, because it remains an open question.

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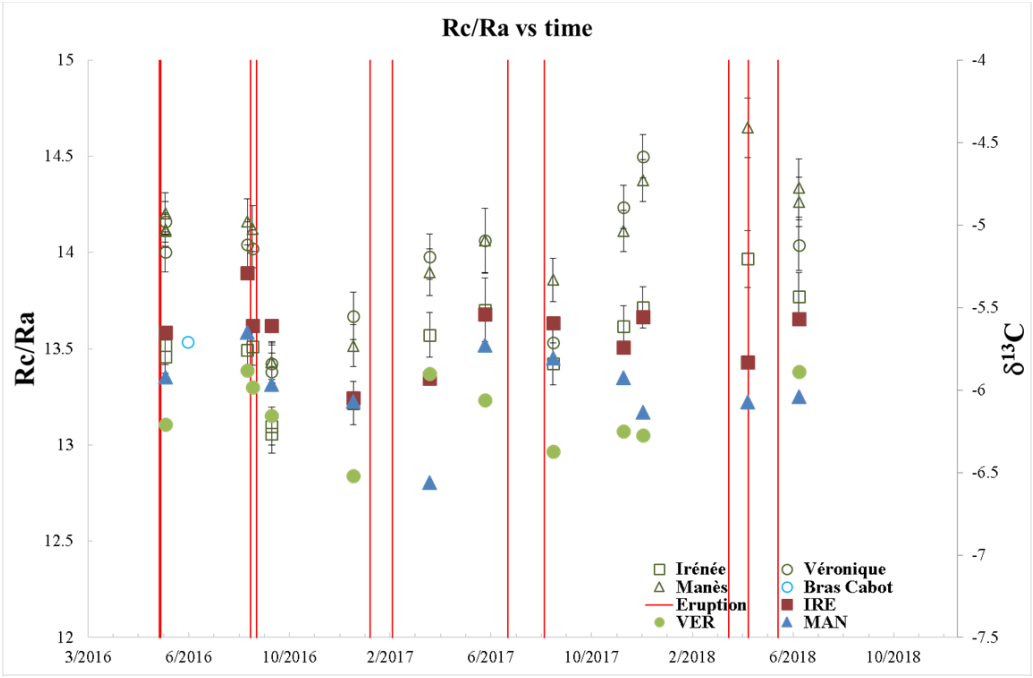

Fig. 3: Noble gas and carbon isotopic signature from three different water springs at Cilaos hydrothermal area. Full symbols are plotted on the right axis ($\delta^{13}C$); empty symbols are plotted on the left axis (Rc/Ra).

In Fig 5, we report the real-time measurements of $\delta^{13}C$ conducted at Irénée thermal spring. In the figure, we also reported the range of values measured by periodic samplings and isotope ratio mass spectrometry analyses in several labs (between horizontal orange lines) and the theoretical $\delta^{13}C$ ratio in air. The main findings of these preliminary data reveal that laser measurements are within the expected range of values, confirming the reliability of this instrument. Apart some gaps of data due to technical issues and to the fact that the instrument was in the same period used for measuring the samples collected at Gite site, it is noteworthy to observe some sharp variations that occurred during the short time span. We exclude that these variations can be related to technical aspects, so next step will be to inter-compare these data with other geophysical and volcanological data acquired from the OVPF monitoring network. This is a preliminary confirmation that Cilaos is an area of La Reunion that holds much potential for the recording of geochemical variations that may correlate with volcanic activity.

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Fig. 4: Installation of laser at Irénée thermal spring of Cilaos hydrothermal area.

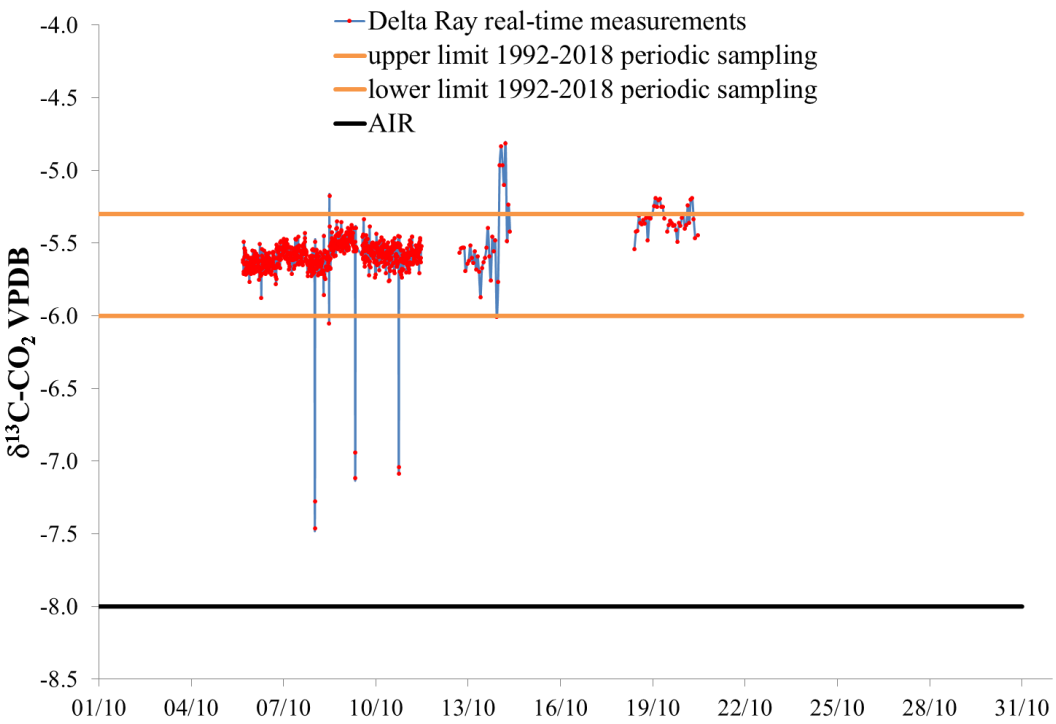

Fig. 5: Real-time measurements of CO_2 isotope composition from Irénée therm spring at Cilaos. The horizontal black line represents the theoretical $\delta^{13}C$ in air, while the two orange horizontal lines indicate the range of $\delta^{13}C$ values measured in 1992 and 2014-2018.

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The final part of access period regarded a day of discussion and inter-calibration with colleagues of University of La Reunion, who work in the atmosphere domain. This day was useful to calibrate different analysers (Picarro and Los Gatos) we used for fieldwork and by the University of La Reunion for precise and accurate measurements of CO_2 concentration in atmosphere in the framework of ICOS project (Fig. 6). In detail, we firstly calibrated the analysers with same reference gas stored in one tank available at the OSUR. Afterwards, we measured the concentration of CO_2 and CH_4 of the atmosphere above the OSUR building and in two different bags where we stored gas collected from the anomalous degassing area of Gite and Cilaos (Fig. 7). The results of the inter-comparison reveal a good reproducibility of the measurements made by Picarro and Los Gatos analysers (Fig. 7) that confirmed the reliability of our measurements in the field. One sample in the bag revealed an atmospheric pollution during measurement with the LGR analysers due to a possible leak of the valve of that bag.

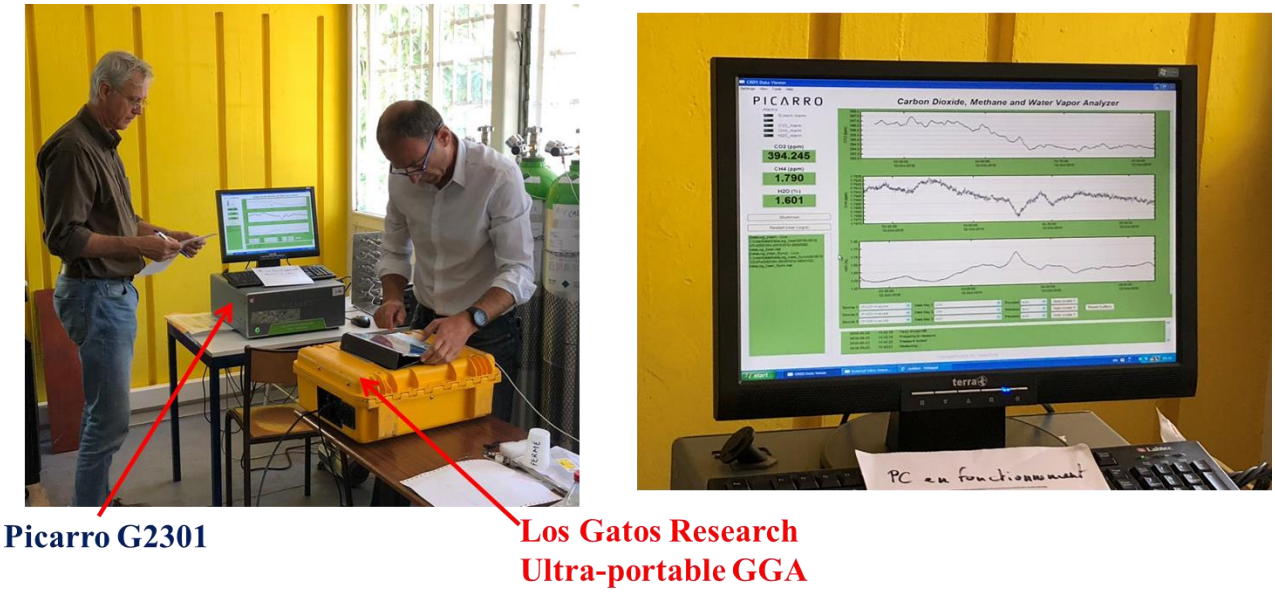

Fig. 6: Interdisciplinary activity between Atmospheric and Solid Earth domains by comparing measures of CO_2 and CH_4 concentration between two different analysers.

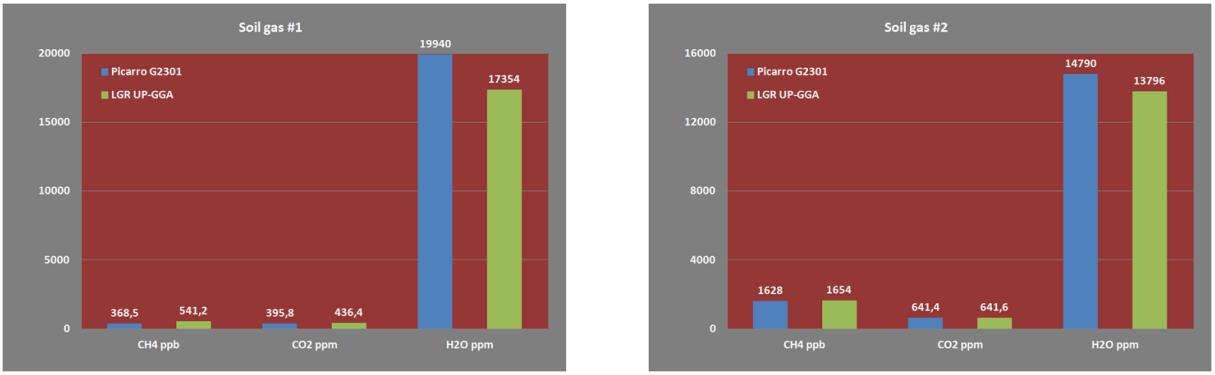

Fig. 7: Results from analyses of different bags where we stored variable amounts of CO_2 emitted from the soil of Gite area. Blue colour indicate the results obtained with Picarro analyser from University of La Reunion, while the green ones indicate those obtained with a Los Gatos analyser provided by INGV-Palermo.

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These data are preliminary and need further and more careful interpretation, after integration with other multidisciplinary information from OVPF and Maido observatory.
However, it is noteworthy that the variations of CO_2 concentration measured in the soil of Gite appear related with the state of activity of the volcano and accompanied by variations of CO_2 isotope composition. The use in the field of a laser that allows real-time measurements it proved to be fundamental to track short-term variations that may occur in proximal area, especially while eruptive activity is ongoing. Finally, the application of the laser at Cilaos thermal spring was important as for Gite, because showed sharp and sudden variations of $\delta^{13}C$ that could be related to magmatic dynamics in the mantle somehow related to PdF eruptions.
Unfortunately, during the eruption period, at proximal areas such as Gite and at the caldera rim of the PDF, CO_2 contents above the atmospheric background were not detected likely because the volcanic plume was always at higher altitudes. . Therefore, on this front, further investigations are needed in order to include within the existing framework the impact of carbon dioxide in the atmosphere from volcanic eruption at Piton de la Fournaise.

6. Outcome and future studies

Outcomes from the present campaign of study include:

- Soil CO_2 concentration and isotope composition measurements at Gite area
- $\delta^{13}C$ isotopic signature of Iréneé gases from Cilaos thermal spring waters
- Helium and carbon isotopic ratios and concentration from free gases of thermal spring waters
- Calibration and inter-comparison of different analysers at University of La Reunion

Future studies will aim:

- To extend the comparison to other eruptive cases between geochemical datasets and atmospheric measurements provided by Maïdo Observatory.
- To re-evaluate the impact in the atmosphere of carbon dioxide emitted from volcanic eruptions of Piton de la Fournaise.
- To extend the analysis of the volcanic gases also to other gas species (CO_2, CO, CH_4, H_2S) released from or related to the Piton de la Fournaise, by using a microGC analyzer, and to evaluate their impact in atmosphere.
- To make real-time measurements of CO_2 concentration and isotope ratios in the soil and in the air above to evaluate the impact of anomalous soil degassing in the first meters of atmosphere

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