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ABSTRACT

This first year intermediate report describes the results achieved so far in task 3.2.1: - Progresses in multiparametric volcano observations. In the specific, the so-far reached results in three independent topics are discussed:

(i) An advancement report on a MultiGAS-coupled sampling system designed to sample high-temperature volcanic plumes First field tests have been carried out (Etna) to test/validate hardware for volcanic gas observations (e.g., telemetry and communication systems between gas sensing unit (datalogger) mounted on the drone and the base receiver);
(ii) The construction of a compact portable self-calibrated LIBS instrumentation with low weight and low power consumption (for elemental analysis of fine volcanic ashes for volcano monitoring and hazard assessment);
(iii) The setting up of novel automatic ash sampling system, is under test on Stromboli.

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4.Results obtained

4.1 A MultiGAS-coupled sampling system designed to sample high-temperature volcanic plumes.

Chemical characterization of high-temperature volcanic gases is paramount to our understanding of magmatic degassing at depth and offer crucial clues to forecast transitions between quiescent and explosive behaviour at active volcanoes. However, subaerial volcanic plumes are often inaccessible to traditional gas sampling techniques (e.g., direct sampling). Consequently, UAVs have become prominent in volcanic gas research by providing scientists with a safe and efficient mean of collecting data. Within the activities of RETURN, a new generation of drone-based volcanic gas real-time sensing unit has been designed, assembled and tested in the lab. This instrument allows for real-time airborne (e.g., while mounted on drones) measurement and sampling of volcanic gases, and will therefore revolutionize our ability to monitor volcanic gases during eruptions, or at remote, hardly accessible volcanoes. Its use will pave the way to improved eruption response, in Italy and elsewhere.

4.1.1 Technical specifications of drone-based MultiGAS unit

The MultiGAS instrument offers high-temporal resolution (1 Hz) readings of major volatile species, such as H_2O, CO_2, SO_2, and H_2S. In this project, a smaller version of this instrument has been developed to allow MultiGAS surveys to be carried out using UAVs (Fig. 4.1.1). Our field setup links the latter with a gas sampler in order to synchronously provide real-time measurements of in-plume gas concentrations and gas samples for laboratory analysis (Fig. 4.1.2a).

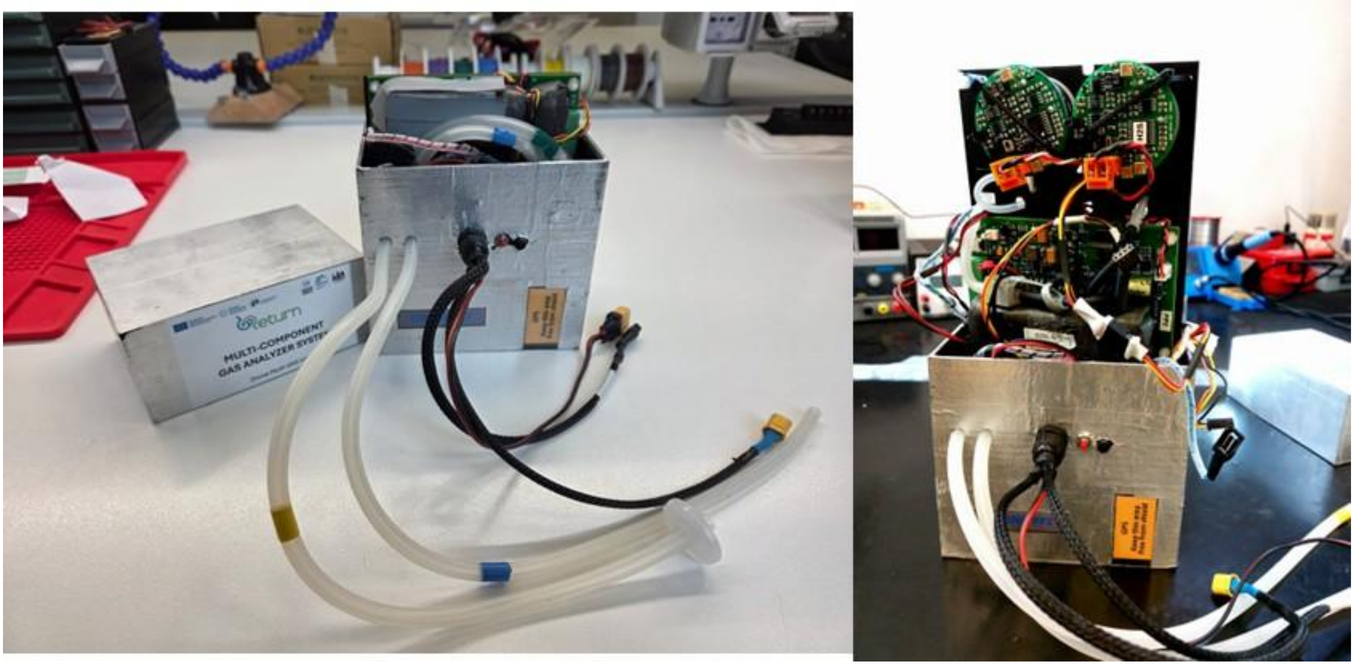


Figure 4.1.1: The drone-based Multi-GAS unit developed in RETURN

The drone-based MultiGAS unit developed (Fig. 4.1.1) is a miniaturised, multi-component gas analyser designed for in-situ measurements of volcanic plumes. The Drone Multi-GAS station represents a miniaturized evolution of volcanic gas analysis systems, specifically designed to be integrated as a payload on UAV (Unmanned Aerial Vehicle) platforms. This instrument was engineered to operate in critical environmental contexts, such as active volcanic areas, allowing for the sampling of plumes that are inaccessible through traditional methodologies while ensuring, at the same time, the safety of technical personnel. From a structural standpoint, the unit is distinguished by a contained mass of approximately 860 g and a reduced spatial footprint of 15.5 × 13.5 × 9.5 cm. The external frame is the result of a 3D printing process using thermoplastic polymers such as PLA, PETG, or ABS, realized via a Creality CR-10S Pro printer. Inside, a shaped platform allows for the organized housing of a complex technical setup that includes electrochemical, NDIR, and environmental (PTU) sensors for the detection of SO_2, H_2S, CO_2, pressure, temperature, and humidity, as well as essential pneumatic components such as the diaphragm micro-pump, tubing, and filters. The external operational interface is completed by a status LED for firmware monitoring and dedicated connectors for power supply and data transmission.

Air is drawn through a 1 µm particle filter exposed to ambient conditions, which prevents particulate contamination and ensures stable gas flow. Sampling is performed at a constant pump rate of 1.0–1.2 L min^{-1}, allowing near-real-time measurements at a frequency of 1 Hz. The analytical core of the instrument consists of integrated electrochemical and infrared sensors. Sulphur species (SO_2 and H_2S) are detected using electrochemical sensors (CiTiceL T3ST/F and T3H; City Technology), calibrated over ranges of 0–200 ppmv, with an accuracy of ±2% and a resolution of 0.1 ppmv. Cross-sensitivity between SO_2 and H_2S is determined during calibration and corrected in post-processing. Carbon dioxide concentrations are measured using a non-dispersive infrared (NDIR) spectrometer (e.g., Edinburgh Instruments Gascard ND or Microsensorik Smartgas Modul Premium2), calibrated between 0 and 10000, with ±2% accuracy and 1 ppmv resolution.

Temperature, pressure and relative humidity are monitored using integrated sensors (e.g., BME280 or Galltec thermo-hygrometers), which allow calculation of water vapour concentrations and correction of gas concentrations for variations in atmospheric conditions and measurement altitude. All sensors are synchronised within a single acquisition system, with data logged locally to micro-SD storage and telemetered in real time to a ground station via radio. This enables plume tracking during flight and allows the operator to identify high-concentration regions. The system is shielded from radio frequency interference to ensure stability of the electrochemical and infrared measurements. Calibration is performed using certified reference gases before and after each field campaign, and instrumental drift is evaluated through laboratory checks.

The technological heart of the system resides in the TEODORA motherboard, which integrates a Teensy® 3.5 Development Board based on an ARM Cortex-M4 120 MHz microcontroller. This architecture was selected for the optimal balance between computational capacity and compactness, offering high-resolution analog inputs (up to 13-bit) and multiple digital interfaces (UART, I²C, SPI, CAN) indispensable for communication with the PTU modules and the GPS system. The board also manages local storage on microSD and the connection with long-range radio modules for real-time telemetry.

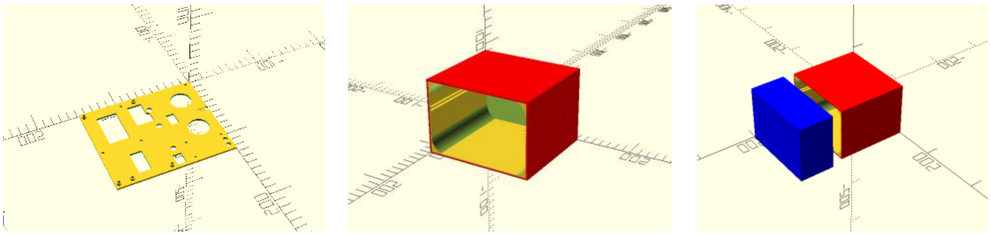


Figure 4.1.2: Dimensions and components of the drone-based Multi-GAS

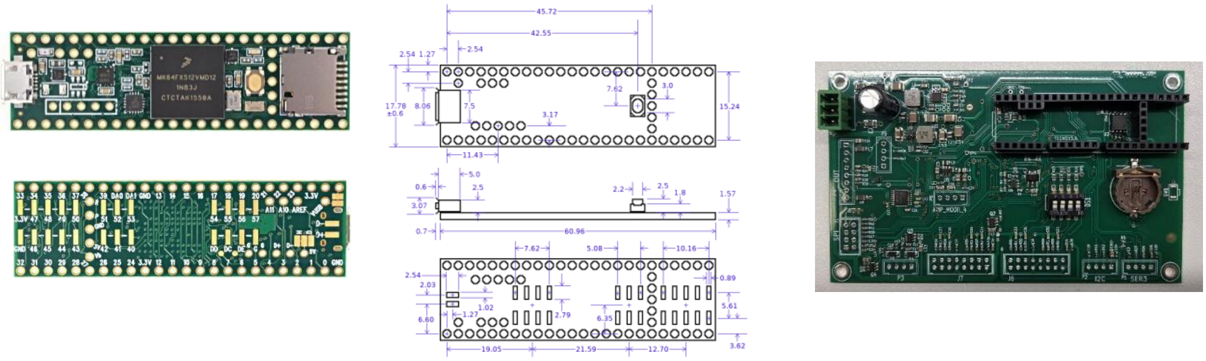
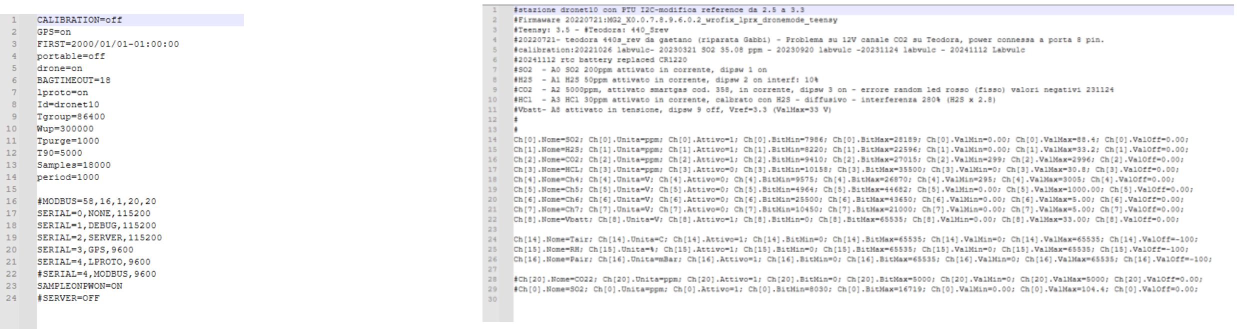


Figure 4.1.3: TEODORA motherboard and components

The operational management of the station is entrusted to dedicated firmware that automates the sampling and analysis procedures in "Drone Station" mode. The system configuration (Fig. 4.1.4) is stand-alone and occurs via simple text files saved on the microSD: the HEADER.TXT file establishes fundamental parameters such as, for example, the sampling frequency (standard 1 Hz), warm-up time, pump activation times, station ID, and communication port speeds and parameters (TTL, RS232). Another file on the microSD, CFG.TXT, contains the sensor calibration coefficients obtained in the laboratory with the aid of standard gases. These parameters are fundamental for accurately converting electrical signals into gas concentrations expressed in ppmv. Every operation and command executed by the system is recorded in a log file (LOG.TXT) saved on the microSD, which is fundamental for monitoring correct operation and for the analysis of any anomalies or malfunctions.



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GPS=on
FIRST=2000/01/01-01:00:00
portable=off
drone=on
BAGTIMEOUT=18
lproto=on
Id=dronet10
Tgroup=86400
Wup=300000
Tpurge=1000
T90=5000
Samples=18000
period=1000

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SERIAL=1,DEBUG,115200
SERIAL=2,SERVER,115200
SERIAL=3,GPS,9600
SERIAL=4,LPROTO,9600
#SERIAL=4,MODBUS,9600
SAMPLEONPWON=ON
#SERVER=OFF
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#stazione dronet10 con PTU I2C-modifica reference da 2.5 a 3.3
#Firmaware 20220721:MG2_X0.0.7.8.9.6.0.2_wrofix_lprx_dronemode_teensy
#Teensy: 3.5 - #Teodora: 440_Srev
#20220721- teodora 440s_rev da gaetano (riparata Gabbi) - Problema su 12V canale CO2 su Teodora, power connessa a porta 8 pin.
#calibration:20221026 labvulc- 20230321 SO2 35.08 ppm - 20230920 labvulc -20231124 labvulc - 20241112 Labvulc
#20241112 rtc battery replaced CR1220
#SO2  - A0 SO2 200ppm attivato in corrente, dipsw 1 on
#H2S  - A1 H2S 50ppm attivato in corrente, dipsw 2 on interf: 10%
#CO2  - A2 5000ppm, attivato smartgas cod. 358, in corrente, dipsw 3 on - errore random led rosso (fisso) valori negativi 231124
#HCl  - A3 HCl 30ppm attivato in corrente, calbrato con H2S - diffusivo - interferenza 280% (H2S x 2.8)
#Vbatt- A8 attivato in tensione, dipsw 9 off, Vref=3.3 (ValMax=33 V)
#
#
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Figure 4.1.4: Configuration text files

The acquired data are stored in CSV format, including for each record the timestamp synchronized via RTC, the geographic coordinates, and the values measured by the sensors. This structure guarantees total traceability of the measurements, allowing for the derivation of molar ratios during the post-processing phase, which are fundamental for interpreting magmatic degassing processes. The adoption of UAV carriers confers high mobility to the system, allowing for the execution of targeted transects within the regions with the highest concentration of the volcanic plume. Data transmission during flight is ensured by an RFD 868x-EU Long Range modem, operating on the 868 MHz band to establish a reliable bidirectional link between the drone and the ground station. This telemetric architecture allows the pilot to monitor geochemical parameters in real-time, optimizing flight trajectories based on plume dynamics.

Energy autonomy is guaranteed by a 1.2 Ah 4S LiPo battery pack, assisted by a Matek UBEC DUO step-down regulator that distributes stabilized voltages at 12 V and 5 V for the transmission systems, reducing the risks of electromagnetic interference. Finally, the accurate georeferencing of each measurement is entrusted to an Adafruit Ultimate GPS module (PA1616S chipset), the integration of which allows each chemical datum to be uniquely associated with its position in three-dimensional space, facilitating the subsequent mapping of emissions (Fig. 4.1.5 and 4.1.6).

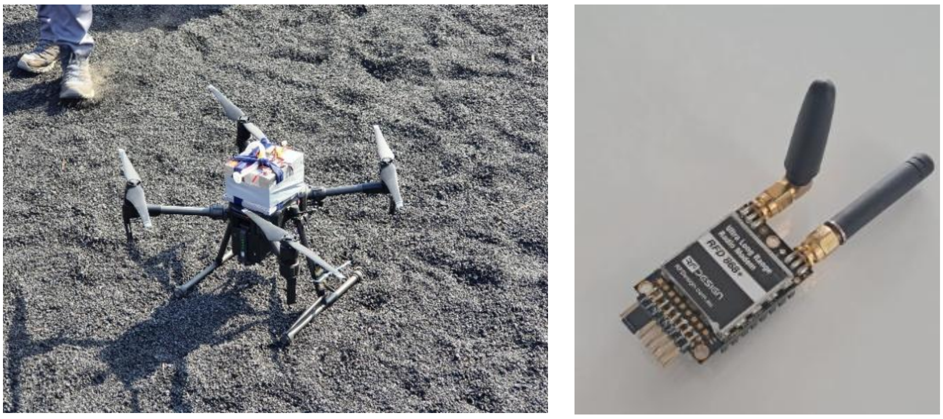


Figure 4.1.5: The drone and the transmission system

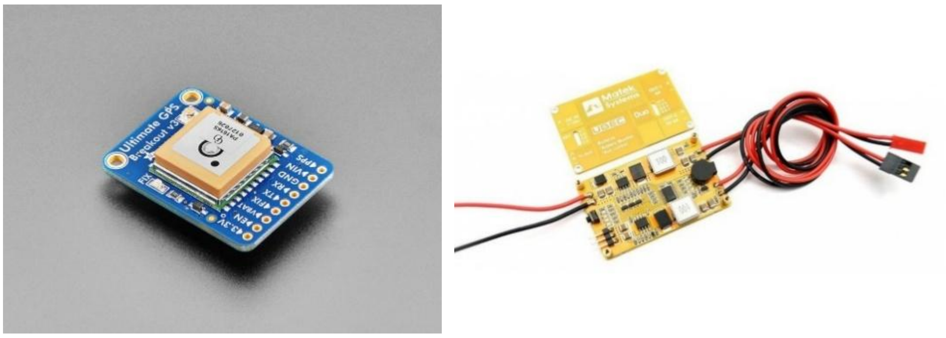


Figure 4.1.6: GPS module and components

4.1.2 Technical specifications of sampler unit for isotope analysis

The sampler (Fig. 4.1.6) combines two 1.8 L min^{-1} diaphragm pumps for a total flux of 3.6 L min^{-1}. These allow sampling approximately 800 ml of gas in an 18-second window, which is optimal to minimize drone exposure and potential loss of equipment due to vigorous volcanic activity. The gas sampler and the MultiGAS inlets are both connected to an external plastic container, from which both systems collect a mixture of volcanic and atmospheric gases simultaneously. The shared gas volume allows pairing volcanic gas compositions and the time window of bag collection in post-processing, and at a later stage, coupling analytical results (e.g., isotope compositions) with relative abundances of volatiles (e.g., CO_2/SO_2 ratios) in the plume. Two 1 L Tedlar bags connect directly to the sampling system (Fig. 4.1.6b).

4.1.3 Data

High-frequency acquisition of plume composition enables identification of rapid fluctuations in gas concentrations associated with turbulent mixing and plume heterogeneity. Gas concentration time series are processed to derive molar ratios such as CO_2/SO_2 and H_2S/SO_2, which are widely used as indicators of magma degassing processes and volatile saturation. Data are corrected for atmospheric dilution, sensor cross-sensitivity and variations in pressure, temperature and humidity.

Water vapour concentrations are calculated from temperature and relative humidity measurements using established thermodynamic relationships. Gas ratios are obtained by regression analysis of plume concentration peaks. This approach minimises the effects of background atmospheric variability and allows extraction of representative volcanic gas signatures. Synchronisation between real-time MultiGAS measurements and the time window of bag sampling enables accurate pairing between analytical results and plume composition. This provides a direct link between laboratory measurements and in situ gas ratios.

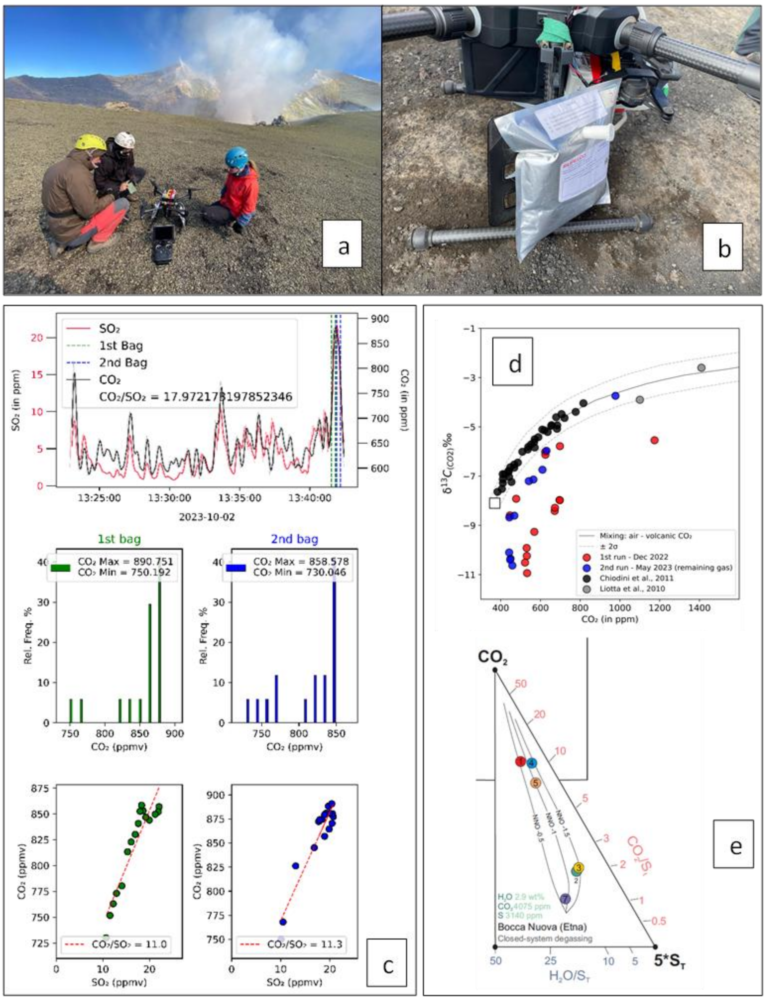


Figure 4.1.7: The gas sampling unit **a)** Instrument setup at Bocca Nuova carter (Mount Etna); **b)** Tedlar bag after sampling flight over the Bocca Nuova crater (Mount Etna); **c)** Real-time data visualization in the field after bag collection, showing continuous time series of SO_2 and CO_2 concentrations and data collected for each bag over an 18-second period; **d)** Preliminary $\delta^{13}C$ results from analytical runs performed in the Dec 2022 and May 2023 (see references in legend for literature data); **e)** Ternary plots showing degassing trends for Bocca Nuova samples collected in October 2022.

So far, this system is being used to investigate the fractionation behaviour of carbon upon magmatic degassing. The carbon stable isotope ratio ($^{13}C/^{12}C$ conventionally expressed as $\delta^{13}C$-values, $\delta^{13}C = ((^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{standard}) - 1) \times 1000$; see Fig. 4.1.7d), when coupled with in-tandem volatile ratios, may provide a window into the various stages of magma degassing, recharge and ascent, all crucial to eruption forecasting.

Our results from a field campaign in May 2023 (Fig. 4.1.7d) resemble those reported in the literature. These were obtained by running the Tedlar bags collected in the field through a Picarro near-infrared spectrometer (Department of Earth Sciences, University of Cambridge), a real-time, trace gas monitor capable of measuring isotopic ratios of carbon in CO_2 and total CO_2 concentration with parts-per-billion sensitivity. Through volatile saturation models (Fig. 4.1.7e), we can then calculate the pressure and estimate the depth of volatile exsolution for each sample, and ultimately track the carbon isotope fractionation path to the surface. A further campaign in October 2023 field campaign offered further insights into the isotope and chemical heterogeneity of Etna summit craters, and ultimately provided the proof of concept needed to further use this system at much more inaccessible volcanoes around the world.

4.1.4 Application

The compact size and reduced weight of aerial MultiGAS systems allow integration on multirotor UAV platforms, which are particularly suitable for plume investigations due to their hovering capability and manoeuvrability. This enables targeted measurements within high-concentration regions of volcanic plumes while maintaining safe stand-off distances from active vents. Compared to conventional ground-based or crewed aircraft surveys, UAV-mounted MultiGAS instruments provide improved spatial resolution, flexible deployment, and reduced operational costs.

Airborne measurements also enable close-range monitoring of gas composition in environments that are otherwise inaccessible or hazardous, such as active craters, eruptive vents and high-temperature fumaroles. The rapid deployment of UAVs allows frequent measurements during periods of volcanic unrest, providing robust time-series data and improving the detection of short-term variations in gas composition that may precede eruptive transitions. UAV systems also allow sampling of remote or difficult-to-access volcanoes, expanding observational capabilities to regions that were previously under-monitored.

Moreover, the integration of near real-time gas sensing with remotely triggered bag sampling represents a significant advancement in plume geochemistry. This approach enables laboratory-based isotopic and trace gas analyses to be directly coupled with plume composition and variability. The ability to synchronise sample collection with high gas concentrations improves the quality of isotopic measurements and reduces atmospheric contamination. This is particularly important for carbon isotope studies, where the combination of $\delta^{13}C$ values and volatile ratios provides constraints on magma recharge, mixing and degassing pathways.

4.1.5 Relevance and future advances

The use of UAV-based gas surveys significantly augments existing monitoring techniques by providing new opportunities in terms of access, resolution and timing of data collection. Remote measurements allow data acquisition from hazardous regions while reducing risks to personnel and equipment. Such systems complement satellite observations, which are often limited by spatial resolution, atmospheric interference and the detection of a restricted range of gas species. Only SO_2 is currently measurable with sufficient sensitivity by most satellite methods, whereas in situ measurements enable quantification of multiple volatile species, including CO_2 and H_2S, which are critical for interpreting magma dynamics.

Unoccupied aircraft systems offer rapid, responsive and high-resolution measurements of volcanic plumes, and support direct sampling from hostile environments. These capabilities facilitate the generation of dense time-series data and improve understanding of short-term and long-term changes in volcanic systems. As highlighted in recent developments, UAS are developing into fundamental tools for tackling key challenges in volcanology by enabling close-range observations and sampling from inaccessible environments. Our unit has already been successfully tested in field applications in the Canary (La Palma volcano) and in Iceland.

Future developments are expected to include further miniaturisation of sensors, improved autonomy, increased flight endurance and the integration of multiple analytical techniques. The coupling of gas sensing, isotopic sampling and remote sensing observations will allow more comprehensive monitoring of volcanic degassing and improved forecasting of eruptive behaviour. In addition, the deployment of UAV-based systems as part of integrated monitoring networks may enhance real-time hazard assessment and early warning capabilities at active volcanoes worldwide.

4.2 Development of MultiGAS monitoring networks

Recent advances in instrumental monitoring of volcanic gas compositions have markedly improved our ability to track pre-eruptive degassing of magmas and interpret transitions from quiescence to volcanic eruption. The advent of the Multi-component Gas Analyser System (MultiGAS) has enabled systematic, high temporal resolution measurements of volcanic plume compositions, representing a breakthrough for volcanic gas studies. In particular, the continuous and automated acquisition of CO_2/SO_2 ratios has emerged as a powerful tool for detecting changes in magmatic degassing regimes and identifying early warning signals of escalating volcanic activity.

Permanent MultiGAS networks have progressively been implemented at persistently degassing volcanoes, allowing long-term time series of plume compositions to be acquired in real time. These systems operate autonomously and are designed to function under harsh environmental conditions, including strong winds, high humidity, snow, and volcanic ash. Stations are typically equipped with telemetry systems that allow data streaming to monitoring observatories, where measurements can be stored, analysed and interpreted in near real time. This infrastructure enables continuous surveillance of volcanic degassing and facilitates integration with other geophysical and remote sensing datasets.

The temporal evolution of volcanic gas compositions recorded by MultiGAS networks has demonstrated that passive degassing regimes are often punctuated by transient episodes of enhanced CO_2 release. These CO_2-rich gas pulses have been interpreted as evidence for the ascent of deeply sourced volatile-rich bubbles, which can accumulate in shallow magma reservoirs and contribute to overpressure. Continuous measurements therefore provide a unique opportunity to identify pre-eruptive degassing trends and improve understanding of magma dynamics at depth.

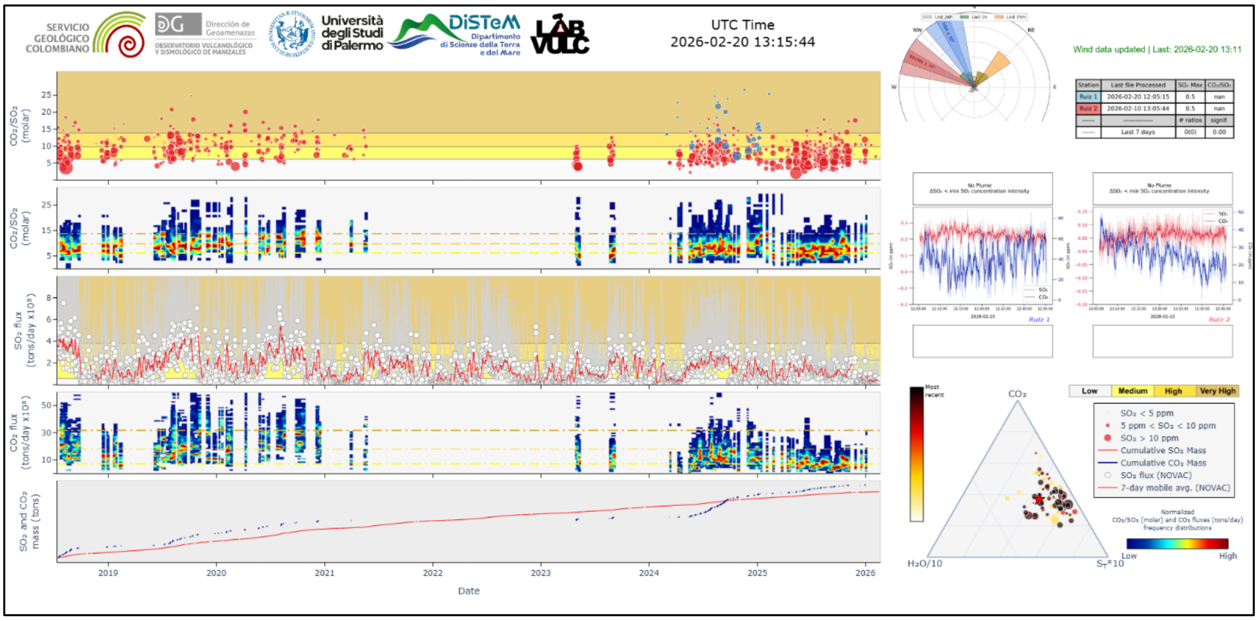
The importance of sustained volcanic gas observations is highlighted by the fact that volcanic gases measured at the surface represent the only direct chemical probe of magma at depth. Variations in gas composition and flux may indicate movement of magma toward the surface, changes in conduit permeability, or pressurization of the magma column. Improving geochemical monitoring infrastructures and enabling real-time analysis protocols are therefore paramount to understanding pre- and syn-eruptive behaviour and mitigating volcanic risk.

The systematic acquisition of compositional time series has demonstrated that precursory changes in the CO_2/SO_2 ratio occur across a wide range of volcanic settings, including both basaltic and andesitic systems. High temporal resolution measurements have revealed that increases in CO_2/SO_2 ratios can precede eruptive transitions by days to months, reflecting enhanced deep volatile input into the shallow plumbing system. Such observations have been reported at several volcanoes, suggesting that degassing of deeply stored magma may play a key role in driving unrest and eruption. These findings demonstrate the value of continuous monitoring networks in capturing the incubation period of eruptive events and identifying subtle changes that may otherwise remain undetected.

In basaltic volcanoes, escalating CO_2 emissions have been linked to the progressive release of CO_2-rich fluids from deep magma reservoirs. Because CO_2 has limited solubility in silicate melts, it exsolves at greater depth than other volatile species and therefore provides early information on magma ascent and reservoir pressurization. Monitoring CO_2 emissions and CO_2/SO_2 ratios is thus particularly relevant for tracking the arrival of deeply sourced magmatic fluids and assessing eruption likelihood. Observations from permanent gas networks have shown that increases in CO_2 flux and CO_2/SO_2 ratios can precede explosive activity, supporting the hypothesis that gas overpressure plays a fundamental role in eruption triggering.

MultiGAS networks also allow integration of gas composition with flux measurements derived from remote sensing techniques such as scanning ultraviolet spectrometers. This combined approach enables the calculation of CO_2 fluxes from SO_2 flux data and gas ratios, providing quantitative constraints on volatile budgets and magma supply rates (Fig. 4.2.1). The integration of plume composition, gas flux and satellite thermal observations allows improved modelling of degassing processes and identification of long-term unrest. Such approaches have demonstrated that large volumes of magma may degas without eruption, highlighting the importance of excess degassing as a driver of prolonged volcanic unrest.

The development of autonomous and telemetered gas monitoring networks has therefore transformed the role of volcanic gas geochemistry from episodic research measurements into an operational component of volcano surveillance. These systems enable detection of both long-term trends and short-term anomalies in degassing behaviour, offering improved capacity for eruption forecasting and hazard mitigation. Continuous records allow discrimination between shallow processes, such as hydrothermal interactions or permeability changes, and deeper magmatic processes linked to volatile supply and magma recharge.



Station	Last file Processed	SO₂ Max	CO₂/SO₂
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Ruiz 2	2026-02-10 13:05:44	0.5	nan
-------	---------------	# ratios	signif.
-------	Last 7 days	0(0)	0.00

Figure 4.2.1 – Example of an integrated MultiGAS network – Nevado del Ruiz volcano, Colombia.

The implementation of dense and multi-parameter monitoring networks represents a key step toward fully integrated volcano observatories. Gas monitoring data can be combined with seismicity, deformation, thermal anomalies and petrological information to constrain magma storage, transport and eruption dynamics. The ability to track compositional changes in real time enhances situational awareness during crises and provides decision makers with robust geochemical indicators of evolving volcanic activity.

Future advances are expected to focus on expanding monitoring coverage to under-instrumented regions, improving sensor robustness, and developing advanced data analysis and modelling frameworks. The integration of ground-based MultiGAS networks with UAV-based systems offers new opportunities to extend monitoring capabilities to remote or hazardous volcanoes, enabling both continuous observations and targeted sampling of inaccessible vents. Such hybrid monitoring strategies are expected to improve early warning systems and contribute to a more comprehensive understanding of the links between degassing, magma dynamics and eruptive behaviour.

4.3 Self-calibrated Laser-Induced Breakdown Spectroscopy for volcanic hazards assessment

4.3.1 Introduction

Volcano monitoring and hazard assessment can be significantly improved by the real-time study of fine ash in volcanic plumes, which are composed of magma fragments released from volcano's craters during explosive eruptions. Numerous analytical techniques can be applied to obtain the chemical characterization of the juvenile pyroclastic material generated in volcanic plumes. Among them, the most appropriate and easily applied to advanced applications in extreme environments is Laser-Induced Breakdown Spectroscopy (LIBS) (De Giacomo et al., 2022).

In the initial phase of our study, we presented the elemental composition of suspended volcanic ash in air, obtained by a self-calibrated LIBS. Various sizes of volcanic ash samples collected from different sites were suspended in the air by laser-induced shockwaves in a dedicated chamber to replicate the conditions of dispersed volcanic ash in the atmosphere. The quantitative analysis was then performed via Calibration-Free (CF) LIBS, which is based on the calculation of the spectral radiance of a uniform plasma in local thermodynamic equilibrium. A significant improvement in our analysis method was the inclusion of a CF-LIBS software, which accounts intrinsically for self-absorption (Hermann, 2010). This adjustment is crucial as self-absorption affects the spectral line intensities, leading to an underestimation of the elemental fraction. Another asset to our analytical technique was to deduce the instrument's response from the ash spectrum itself and avoid the necessity for standard calibration lamps. For that, an intensity calibration of the spectra based on the measurements of Fe lines intensities was employed in this work (Taleb et al., 2024; Bousquet et al., 2023). The results we obtained confirmed the feasibility of real-time elemental analysis measurements of volcanic ash, with a good degree of agreement with the literature composition. Then, we carried out the project by developing a portable instrument integrated into a drone for in-flight CF-LIBS measurements. New devices have been used, such as a small laser, spectrometers that cover a large spectral range, a whole optical system as a censor for focusing the laser and collecting plasma emission, and a gimbal with the lowest possible weight to be mounted on the drone.

4.3.2 Results achieved.

In this project, we studied the composition of fine ash in volcanic plumes which represent magma fragments expelled from the crater during explosive eruptions because it is of primary importance for volcano monitoring and hazard assessment. First a laboratory experiment was carried out by building a set-up based on CF-LIBS to analyse volcanic ash samples. This methodology has been chosen because it does not require any standard calibration and the elemental composition is directly obtained from the laser-induced breakdown optical emission. In this first stage intensified spectrometer has been used, as well as an ablation chamber for high precision measurements. During the laboratory experiments, volcanic ash samples of different sizes were suspended in the air by a laser-induced shockwave in a dedicated chamber, as to mimic the conditions of a volcanic plume, and simultaneously the laser-induced plasma (LIP) spectrum is recorded (see Figure 4.3.1).

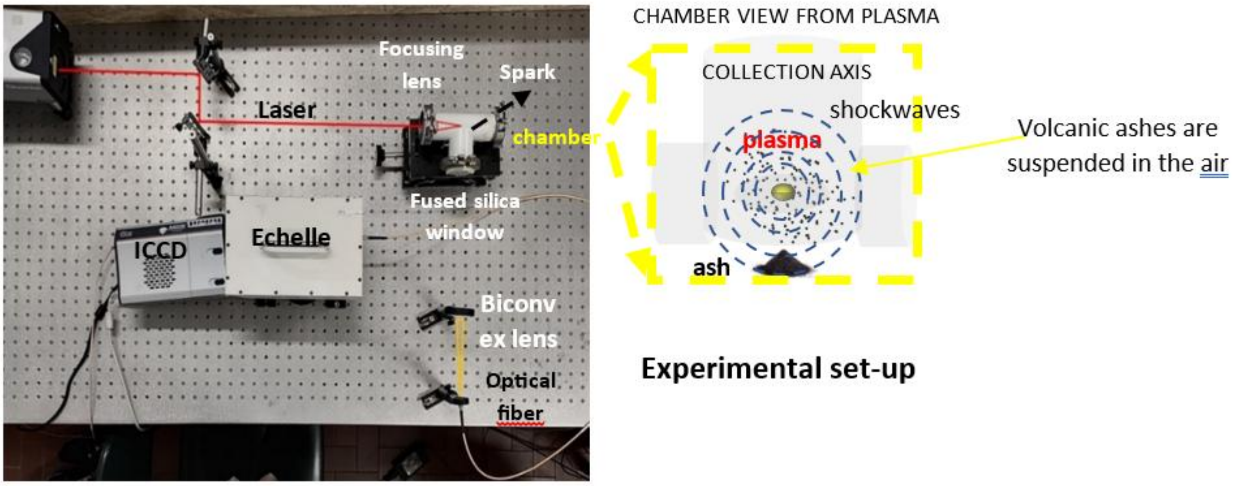


Figure 4.3.1: Experimental set-up

For the analysis, a Calibration-Free analytical model that considers self-absorption called "LTE Spectra" has been used for the estimation of the elemental composition from the plasma emission spectrum lines, due to its rapidity clear advantages for in-situ measurements (see Figure 4.3.2 left). It is based on the comparison between the measured and a calculated spectrum, it doesn't need any preliminary measurement, and all the chemical data are collected by a single acquisition.

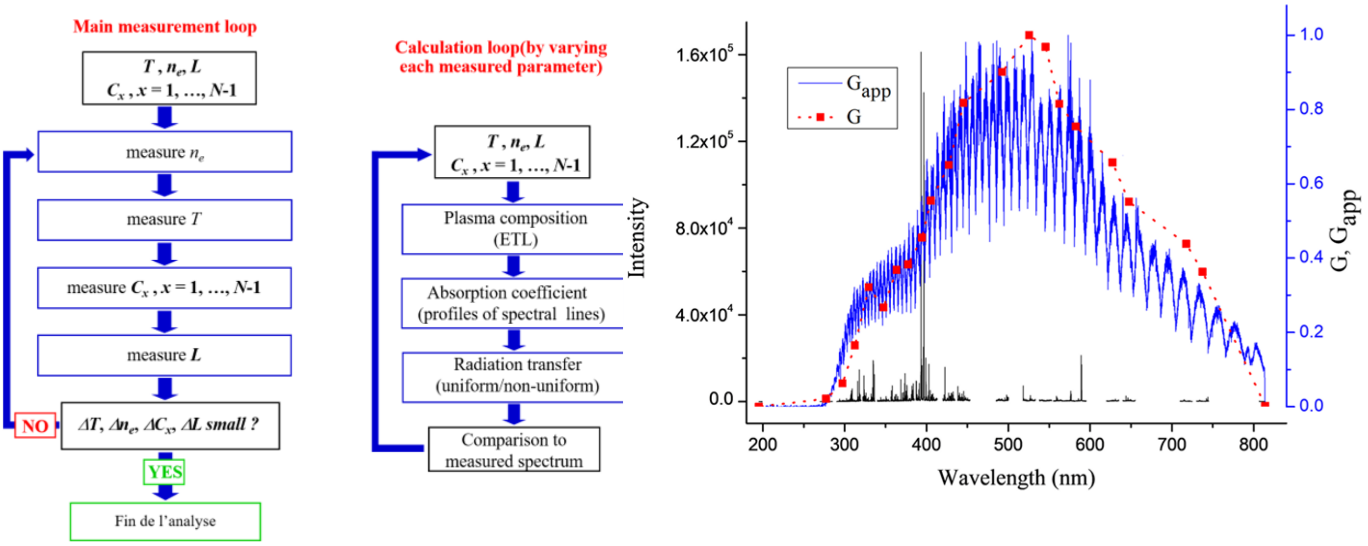


Figure 4.3.2 – Calibration-Free LIBS algorithm "LTE Spectra", (right) Ash plasma emission spectra of 20 acquired spectral ranges (black) and their calibration factors G obtained by intensity ratios calibration procedure (red dotted line, full squares). The G factor curve is compared to the experimental response Gapp (blue) that corresponds to the spectrometer response.

To avoid any kind of instrumental calibration of the volcanic ash spectra, we needed to carry out a way to correct the apparatus response with avoiding the use of radiometric sources. A calibration procedure that exploits the emission spectrum of the ash plasma itself instead of calibration lamps, and based on the measurements of Fe lines intensities was used to deduce the apparatus response. Iron was chosen because of its high number of emission lines ash sample spectra. The intensities of a high number of Fe emission line were calculated, and the intensities of these same Fe lines were measured from the recorded ash spectra. By calculating the ratio between measured intensities and calculated intensities of Fe I lines, we deduced a calibration factor G for each spectral window of the spectrum (see Figure 4.3.2 right). Our results showed that the two calibration factors “G obtained from the ratio between measured and calculated intensities of Fe lines and Gapp obtained from the instrumental response of the Echelle spectrometer (measured with the standard lamps) ”, have a similar trend with wavelength, thus confirming that the intensity ratio procedure can efficiently replace the use of radiometric sources to account for the response of all experimental components. The elemental compositions of Grímsvötn volcano ash obtained by total self-calibrated LIBS are shown in Figure 4.3.3. Results confirmed the feasibility of real-time elemental analysis of volcanic ash, with a good agreement with the literature composition, in both cases: when the apparatus response is deduced from calibration lamps, and when the total self-calibrated methodology is used.

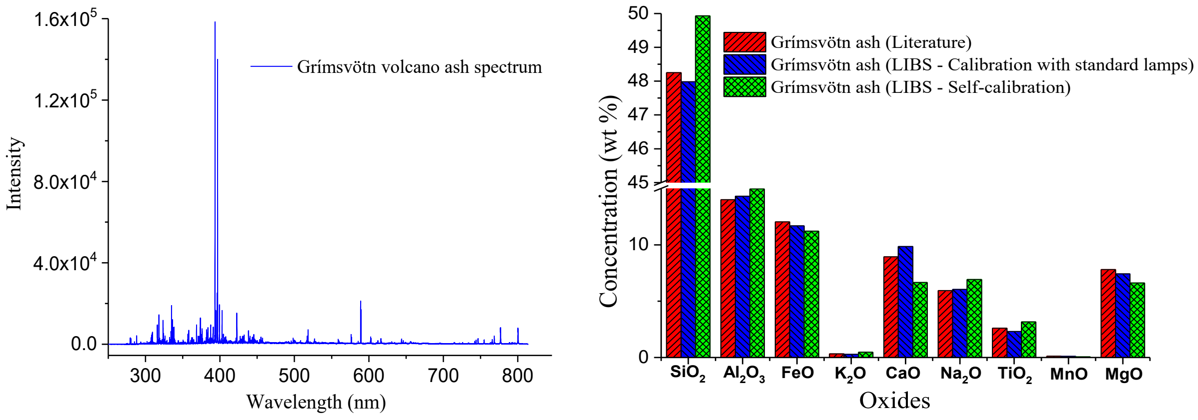


Figure 4.3.3 (left) Plasma emissions spectrum of the finest ash of Grimsvötn. The inset shows a microscope image of this ash, (right) Concentrations in terms of oxides of GS1 ash obtained using CF-LIBS.

	Literature	GSV 3-1 (S1)	GSV 3-1 (S2)	GSV 3-1 (S3)
Oxide	Wt%			
SiO_2	48.25	47.98	49.37	49.96
Al_2O_3	14.00	14.32	13.25	15.47
FeO–Fe_2O_3	12.04	11.69	11.67	10.32
K_2O	0.32	0.28	0.37	0.28
CaO	8.94	9.85	10.22	8.65
Na_2O	5.94	6.04	5.93	5.01
TiO_2	2.60	2.31	2.73	5.50
MnO	0.12	0.11	0.30	0.09
MgO	7.80	7.42	6.16	4.72

Table 4.3.1 Oxides composition of GSV3-1(S1) sample (grain size < 125µm), GSV3-1(S2) sample (grain size > 125µm) and GSV3-1 (S3) sample (grain size > 250µm).

Table 4.3.1 shows oxides composition of 3 different sizes of Grimsvötn ash samples suspended in the air. We could observe different elemental compositions due to the ash size differences. Again, results confirmed the feasibility of real-time elemental analysis of volcanic ash of different sizes using CF-LIBS. Therefore, we proved that our CF-LIBS methodology is a technique that can perform the quantitative analysis of ash suspended in the air without any preliminary measurement or calibration. Just the recording of plasma emission spectra is enough to identify and quantify all elements composing volcanic ash. Thus, we continued the project by building a compact set-up assembled on a drone for in-situ Calibration-Free laser induced breakdown spectroscopy analysis to obtain the elemental composition of ash at an active volcano without using any kind of calibration.

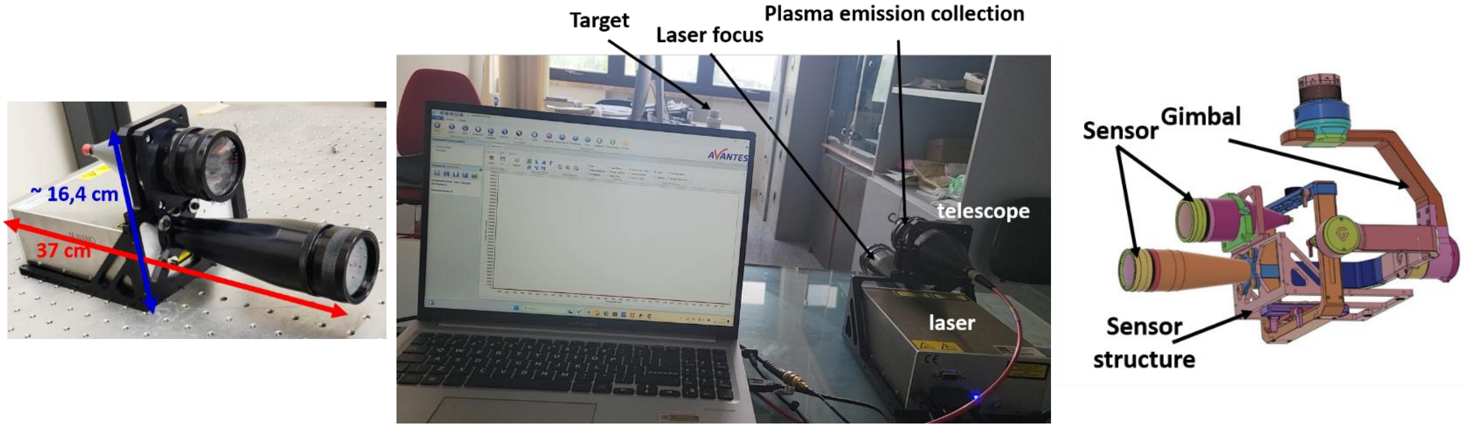
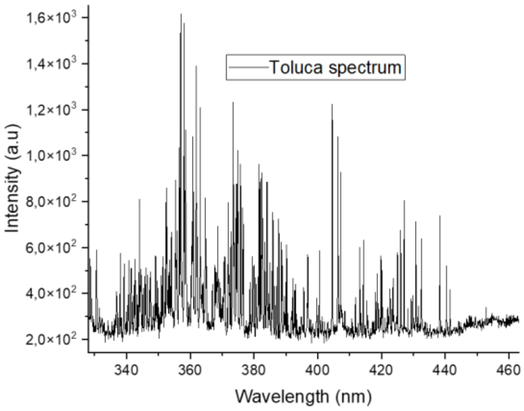
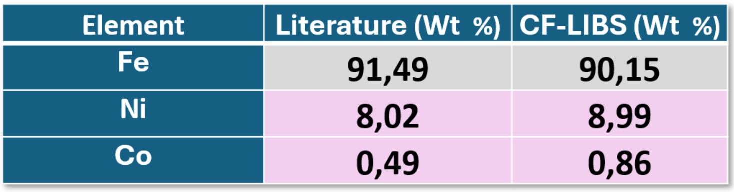


Figure 4.3.4 (a) LIBS sensor, (b) Sensor experiments before mounting on the drone, (c) Sensor attached to the Gimbal.

The build LIBS sensor was composed of a catadioptric optical system and a compact laser (Monfort Laser, M-NANO-Nd: YAG-120mJ-8ns) attached with a metallic structure as shown in Figure 4.3.4a and b. The sensor could focus the laser pulse and collect the plasma emission plasma at a distance between 3,5 and 5 m. After, many tests, trials and experiments with the CF-LIBS sensor were carried out in the lab and confirmed the robustness of the set-up by obtaining precise elemental analysis of different samples. Figure 4.3.5 presents an example of CF-LIBS analysis results on Toluca meteorite sample and its spectrum obtained with the sensor.





Element	Literature (Wt %)	CF-LIBS (Wt %)
Fe	91,49	90,15
Ni	8,02	8,99
Co	0,49	0,86

Figure 4.3.5 (left) Toluca spectrum obtained by the compact sensor, (right) its elemental composition obtained using CF-LIBS

Then the integration of the CF-LIBS system (sensor) on a drone for in situ elemental analysis and on-flight monitoring of volcanic ash was carried out. The system was composed of the LIBS sensor, 4 NEXOS Compact Spectrometers from AVANTES (spectral ranges: 190-358 nm, 320-472 nm, 440-672 nm, 640-844 nm) and a gimbal (see Figure 4 c) that aims the sensor at the object of interest with a Joistick and equipped:

- ✓ Brushless motors: Move the LIBS sensor to counteract drone motion.
- ✓ Sensors (IMU – Inertial Measurement Unit): Detect acceleration, rotation, and vibrations.
- ✓ Electronic controller: Receives sensor data; Moves motors opposite to unwanted movement. in real time

The angular oscillation without the Gimbal was 5° and with Gimbal 0,03°. The laser spot position error without Gimbal was 260 mm at 3 m and 480 mm at 5 m, and the laser spot position error with Gimbal was 1,6 mm at 3 m and 2,6 mm at 5 m. This shows the huge necessity to use the Gimbal to carry out elemental CF-LIBS analysis on suspended volcanic ash LOQ of 1-0,1w%. The project finality was successful, obtaining a CF-LIBS in-situ analysis with an unlimited robustness since all sample information are taken from the measured spectrum only. Figure 4.3.6 shows the optical sensor attached to the gimbal mounted on the drone.

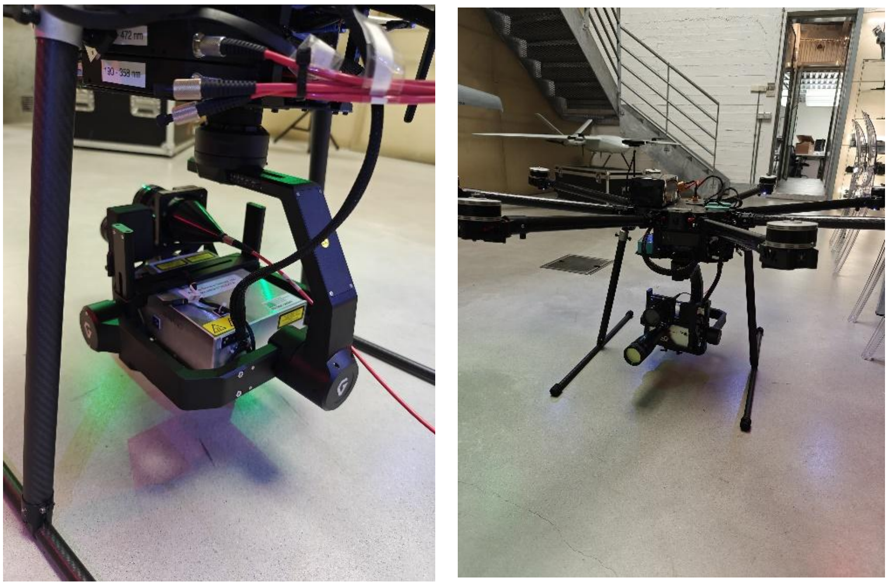


Figure 4.3.6 Pictures of the final CF-LIBS device mounted on the drone.

4.4 Features of ash erupted during different styles of activity

4.4.1 Introduction

Real-time multiparametric monitoring is crucial in order to reduce hazards related to volcanic activity since it allows to forecast eventual system unrests and to improve the knowledge of the dynamics characterizing the monitored volcanic activity. A permanent, real-time monitoring service is active at Stromboli volcano (Eolian Islands, Italy) since early 2003, and its instrument network includes arrays of broadbands seismometers, infrasonic detectors and tilt-meters. Geophysical monitoring is coupled with continuous camera imaging in the visible and IR spectra, and with continuous measurements of the principal gas species dissolved in the plume and diffused from soil degassing (SO_2, CO_2, H_2, H_2O, He, CH4). Importantly, this monitoring system lacks continuous analysis of volcanic ash, which can give important insights on the conduit processes controlling magma characteristics during the different phases of activity.

4.4.1 Results achieved

The original aim of this research task was to integrate the permanent multiparametric system for volcano surveillance with continuous sampling and analysis of volcanic ash through the implementation of an automatic ash sampler. One of the main problems in authomatic sampling of ash during low-level ativity with production and dispersal of small amounts of ash is the identification of resuspended ash. For this reason, in order to start up the volcanic ash monitoring at Stromboli, a preliminary test has been done for estimating the impact of resuspended ash on the sampling of primary ash in creteric area. A statistical wind analysis was done aimed to identify the best spot suitable for the installation of the ash sampler/s. A prototypal, very simple ash sampler (Fig. 4.4.1) was deployed close to the crater rim for a total of two days (2-4 August 2023). The ash sampler was designed with two overlapped collector trays. This tower-like structure was designed to minimize primary sedimentation within the lower tray, nearly completely sheltered by the upper one. The support was built to resist the acid gases attach, and the strong wind blowing at the top of Stromboli vulcano. The upper tray was installed at a height of around 1.60m, while the secondary was setup just below the first, at around 1m.

The ash sampler was deployed about 200 m from the summit of the vent (Pizzo), during a period of intense puffing and small-scale explosive activity from NE and SE craters. During installation phases we noted that the area was affected by low-to-modest ash fallout and by moderate ash resuspention.

The results indicate a strong impact of ash resuspension since both the trays collected in two days a comparable amount of deposit, with the lower one collecting even more ash (1.80g) than the upper one (1.38 g for the upper (Tab. 4.4.1), so immediately posing important doubts about the real efficiency of automatic ash samplers in the summit area. The ash was then observed using a stereo microscope and both granulometric (Fig. 4.4.2) and morphometric (Fig. 4.4.3) analyses, showing strong similarities which confirmed the problematic distinction between primary and resuspended ash. Basing on these preliminary results, we decided to dismiss the project of an automatic ash sampling apparatus to be installed on the crateric area of Stromboli.

Activity of ash monitoring at Stromboli continued by collecting ash samples from specific activity of Stromboli. In particular, thanks to a collaboration with researchers of the INGV-OV, a first set of bulk ash samples was collected on July 5th 2024 and derive from the paroxysmal activity occurred between the 3rd to 5th July 2024. A second set of bulk ash samples was collected directly from the fallout of the paroxysm occurred on July 11th 2024. Samples were then investigated by grain-seize, morphology and stereo and electronic microscopy (SEM) to investigate the textural features of the ash fragments and of the ash aggregates (Fig. 4.4.4). Part of the analyses are still in progress and are aimed to better understand the conduit processes and the activity dynamics which actively controlled these paroxysmal events which had major implication on associated risks.

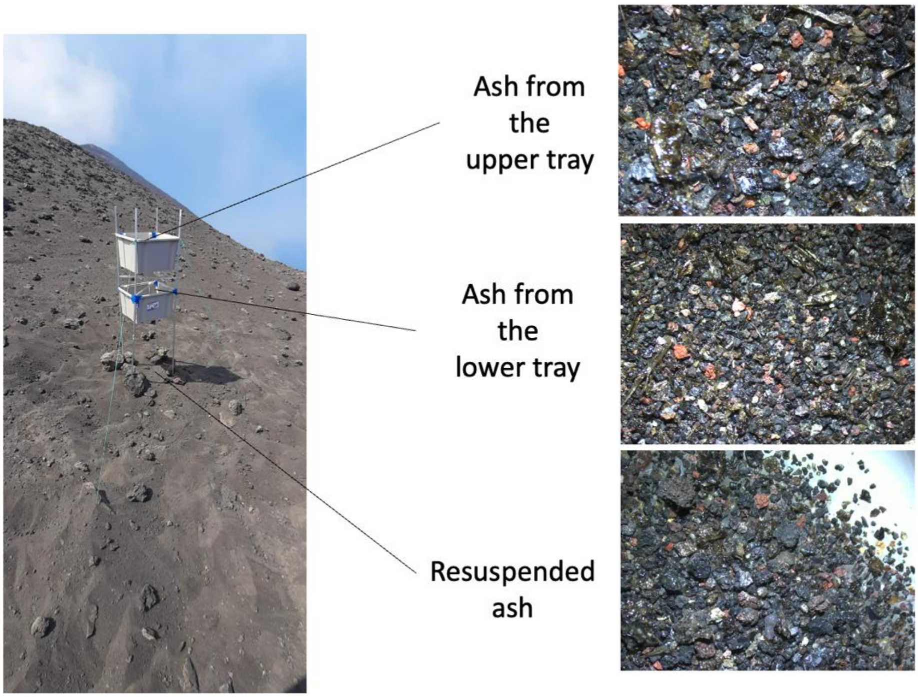


Figure 4.4.1 Apparatus temporarily deploited in the vicinity of Pizzo, aimed at evaluating the impact of resuspended ash.

Trays	weight (g)	sed rate (g/m2*h)
lower tray	1.802	0.291021
upper tray	1.381	0.22303

Tab. 4.4.1 Weight and sedimentation rate of samples collected within upper and lower tray.

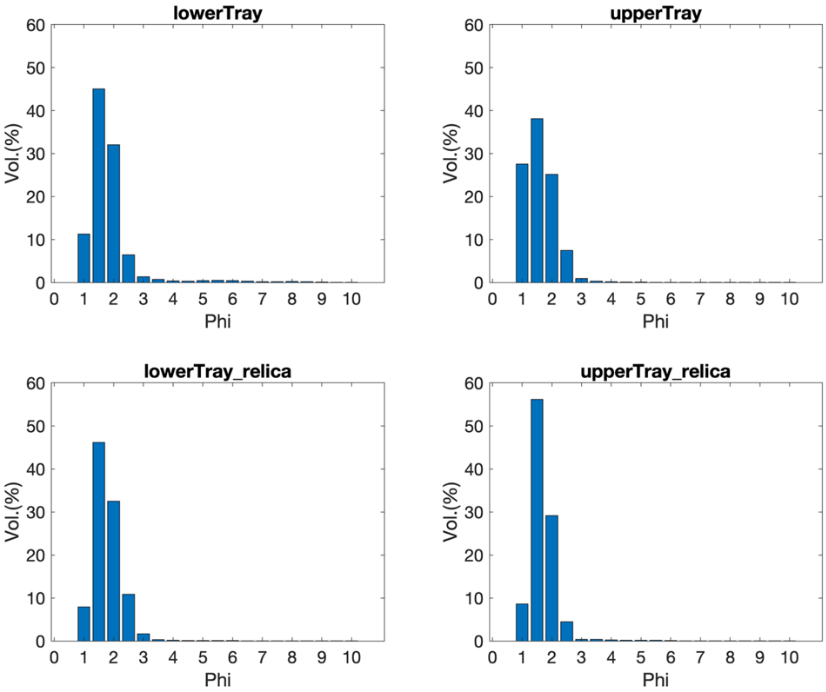


Figure 4.4.2 Grain size distribution analysis of ash from upper and lower trays.

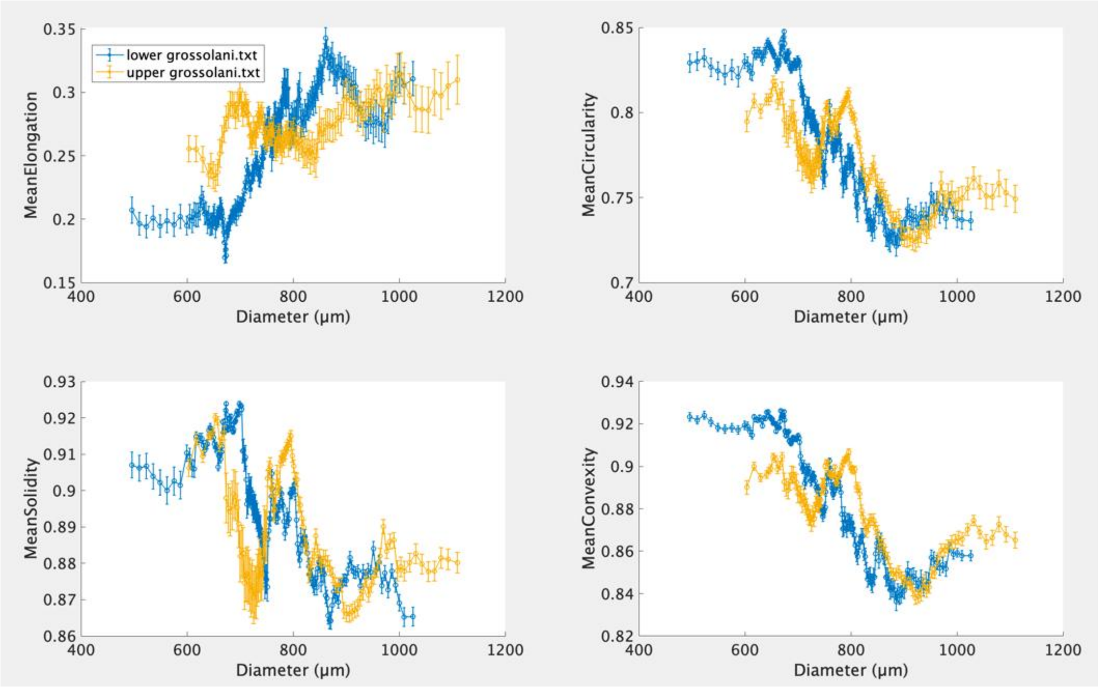


Figure 4.4.3 Shape analysis of ash from upper and lower trays.

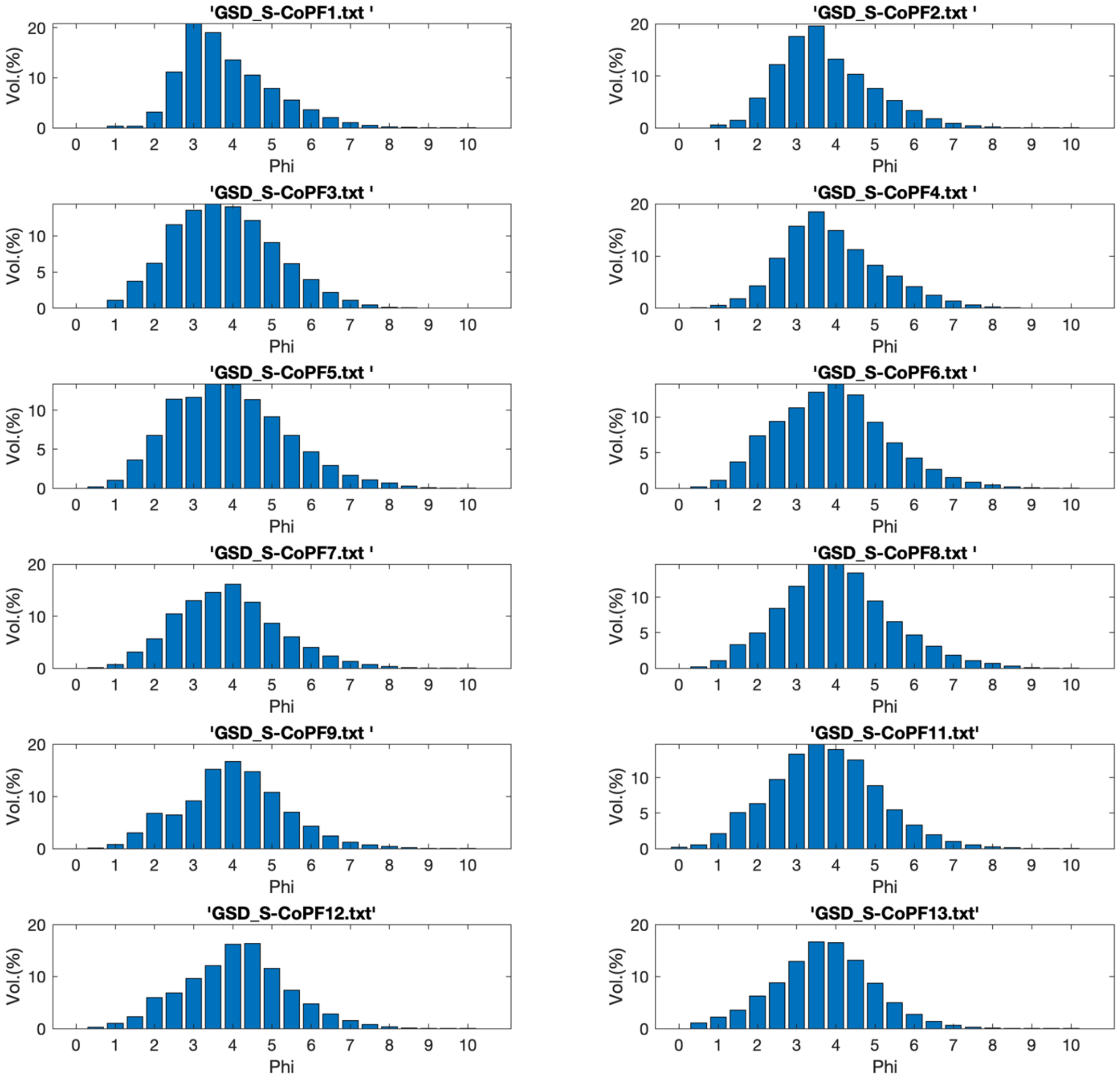


Figure 4.4.4 Grain size distribution of samples collected on July 5th 2024.

5. Conclusions

Research Activities in TK3.2.1 have been finalised as expected with the development of novel technologies and methodologies for the monitoring of volcanoes. Installation and testing and, in some cases, experimental field campaigns have been carried on. A new generation of drone-based volcanic gas real-time sensing units has been designed, assembled and tested in the lab. These instruments allow for real-time airborne (e.g., while mounted on drones) measurement and sampling of volcanic gases, and will therefore revolutionize our ability to monitor volcanic gases during eruptions, or at remote, hardly accessible volcanoes. Their use will pave the way to improved eruption response, in Italy and elsewhere. The construction of a compact portable self-calibrated LIBS instrumentation with low weight and low power consumption (for elemental analysis of fine volcanic ashes for volcano monitoring and hazard assessment) has been realised as expected. A novel automatic ash sampling system was designed and tested on Stromboli.

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