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Tracking Unrest from Chemical Mapping of fumarolic fields

Index

ABSTRACT.....	6
1: INTRODUCTION	8
Studying restless giants.....	8
References.....	12
2: THE PHYSICAL AND CHEMICAL STRUCTURE OF VOLCANO- HYDROTHERMAL SYSTEMS, AND THEIR UNREST.....	13
2.1 General overview on hydrothermal systems: definitions and composition	13
2.2: Structure and chemistry	18
2.2.1: Classification, structure, hydrothermal circulation, chemistry, alteration	18
2.2.2: Circulation and heat transport	20
2.2.3 Fluid chemistry, zonation and maturity	23
2.3.1: At the origin of hydrothermal gases: the chemistry of magmatic gases	25
2.3.2: Redox buffer of the system: H_2/H_2O , $FeO/FeO_{1.5}$, H_2S/SO_2 and Giggenbach's 'buffers war'	29
2.3.3: Behind the mask of the scrubbing.....	38
2.4: Unrest.....	47
2.4.1: Breaching the system	47
2.4.2: Unrest: definitions and uncertainties	48
2.4.3: Degassing and unrest	50
2.4.4: Hydrothermal activity and unrest.....	55
2.4.5: Temperatures and unrest.....	56
2.4.6: Seismicity and unrest	56
REFERENCES.....	58
3: METHODS.....	65
3.1: The Multi-GAS.....	65
3.2: UV-camera.....	73
References.....	77
4: SPATIO-TEMPORAL EVOLUTION OF THE FUMAROLIC FIELD OF LA FOSSA CONE (VULCANO ISLAND, ITALY) IN 2021-2024.....	79
4.1: Introduction.....	79
4.2: Geological background.....	82
4.2.1: The Aeolian archipelago and Vulcano island	82

4.2.2: <i>The La Fossa tuff cone</i>	86
4.2.3: <i>The La Fossa Fumarolic Field</i>	87
4.2.4: <i>The 1987-93 and 2021-present unrest</i>	89
4.3: Methodology	91
4.4: Results	98
4.4.1: <i>Chemical structure of the fumarolic field</i>	98
4.4.2: <i>Temporal evolution of the fumarolic field</i>	101
4.4.3: <i>Evolution of the crater rim fumarolic zone</i>	104
4.4.4: <i>MultiGas and Direct Sampling comparison</i>	105
4.5: Discussion	107
4.6: Conclusions	115
4.7: Acknowledgement	116
REFERENCES	122
5: MULTI-GAS BASED MAPPING OF HYDROTHERMAL FUMARoles AT NISYROS, GREECE	131
5.1: Introduction	132
5.2: Study area	133
5.2.1: <i>Magmatism in the Hellenic Subduction Zone</i>	133
.....	137
5.2.2: <i>Active volcanic centers in Southern Aegean Volcanic Arc</i>	137
5.2.3: <i>The Kos-Nisyros volcanic complex: the islands of Nisyros and the Kos Plateau Tuff</i>	141
5.2.4: <i>The Kos Plateau Tuff Eruption</i>	143
5.2.5: <i>Volcano-stratigraphic units of Nisyros</i>	145
5.2.6: <i>Petrology of Nisyros products and dome chronology</i>	151
5.2.7: <i>Hydrothermal activity at Nisyros</i>	155
5.2.8: <i>Geochemistry of hydrothermal fluids</i>	160
5.3: Methods	163
5.4: Results	164
5.4.1: <i>Gas concentration ranges</i>	164
5.4.2: <i>Gas ratios</i>	169
5.5: Discussion	169

5.5.1: <i>A spatially resolved record of hydrothermal gas composition</i>	169
5.5.2: <i>Temporal evolution of gas composition</i>	173
5.5.3: <i>Implications for gas hazard and human health impact</i>	177
5.6: Conclusions.....	180
5.7: Acknowledgements.....	181
REFERENCES	182
6: CONCLUDING REMARKS	190

ABSTRACT

Hydrothermal degassing is one of the most evident expressions of the still-ongoing activity of quiescent volcanoes. At hydrothermal volcanoes, degassing takes place in a variety of forms, including fumaroles, steaming grounds, mud pools and degassing soils. These hydrothermal surface manifestations have long been targeted by research because their chemistry contains crucial information for understanding the structure and P-T-X properties of the underlying hydrothermal system that feeds them. Even more importantly, these manifestations exhibit large changes in their chemistry and flux when hydrothermal volcanoes become restless during unrest. In particular, tracking the temporal evolution of the chemistry of hydrothermal fumaroles is key to assessing the dynamics, triggers and evolution of volcanic unrest, some of which can eventually escalate into eruption.

Unrest at hydrothermal volcanoes is typically scrutinized by periodic campaigns of direct fumarole sampling. A valuable complement to direct sampling is the use of chemical mapping techniques that, using portable gas sensing units, allow in near-real time to explore and image the chemical diversity of a fumarolic field. These mapping techniques, in contrast to direct sampling that is typically applied to a relatively small number of fumaroles, contribute key information on the spatial heterogeneity of fumarole composition, and on how this heterogeneity varies in time as unrest progresses.

In this PhD dissertation, I report on the application of the chemical mapping technique to two quiescent volcanic systems that have recently been in unrest: La Fossa crater of Vulcano island (Sicily, Italy) and Nisyros island (Greece).

At Vulcano, periodic gas surveys were conducted at La Fossa between 2021 and 2024, in which a portable Multi-component Gas Analyzer System (Multi-GAS) was used to map the spatial variations in gas composition across the fumarolic field in a period encompassing a major degassing unrest started in fall 2021. Results indicate a significant compositional contrast between rim and inner crater fumaroles. The rim fumaroles exhibited more stable magmatic gas signatures (highest CO₂, SO₂, H₂S, and H₂ concentrations) and stable, relatively low CO₂/SO₂ ratios (of ~ 20-30), indicative of minor hydrothermal processing. In contrast, large temporal fluctuations (a wide range of CO₂/SO₂ ratios) in gas compositions were observed in the inner crater fumaroles, which are interpreted as been caused by oscillating phases of expansion and contraction of the gas chimney, centered underneath the 1888-1890 eruption outer crater rim, feeding the unrest. The intermediate, below-background CO₂/SO₂ ratios observed in crater rim area throughout 2021-2024, in conjunction with the higher-than-background SO₂ fluxes, suggest that, despite the

progressive vanishing of degassing activity since the acme of the unrest in fall 2021, hydrothermal activity conditions have not returned to background levels, yet.

The mapping technique was also applied at Nisyros, a quiescent volcanic system in the Aegean Sea (Greece) that was stuck by a seismic/degassing unrest in 1996-2001, that raised concerns of a possible renewal of volcanic (phreatic) activity. At Nisyros, a similar portable Multi-GAS instrument was used to walking traversing the fumarolic fields of Stefanos and Lofos, two of the Nisyros' most active hydrothermal sites, in the attempt to characterize the compositional heterogeneity of fumaroles at high spatial (meters) and temporal (1 Hz) resolution. The obtained spatially resolved gas concentration results allow identifying a cluster of gas-rich spots ($\text{CO}_2 > 1000 \text{ ppmv}$ and $\text{H}_2\text{S} > 80 \text{ ppmv}$) aligned along a ring-shaped degassing structure, corresponding to the Stefanos inner crater rim (or outer caldera floor margin). We additionally provide a spatially resolved record of gas ratios in a larger number of fumaroles than typically investigable with direct sampling techniques, demonstrating an overall compositional homogeneity across the fumarolic fields ($\text{CO}_2/\text{H}_2\text{S}$ ratios of 6.4 to 13.1 and CO_2/H_2 ratios of 166 to 171). The results obtained, interpreted in the context of the multi-decadal record of gas composition at Nisyros, demonstrate more H_2S -depleted compositions in 2025 (this study) than during the 1996-2001 seismic/degassing unrest, indicating a gradual return to background quiescent activity. The potential impact on human health (tourists, visitors and operators) of the atmospheric concentration levels of potentially hazardous gases (CO_2 and H_2S) at Stefanos is also discussed.

Results presented confirm the utility of expedited Multi-GAS surveys to reconstruct the chemical diversity of fumarolic fields (by rapidly analyzing a far larger number of fumaroles than accessible with direct sampling), and hence to contribute understanding drivers and evolution of volcanic unrest.

1: INTRODUCTION

Studying restless giants

Dormant (or quiescent) volcanoes exhibit secondary activity, such as fumaroles, thermal springs, and background seismicity (Rouwet et al., 2014 & 2017; Pritchard et al., 2019). Hydrothermal systems, typical of closed-conduit volcanoes, are common in large silicic calderas, domes, and andesitic edifices (Fournier 2007; Rouwet et al., 2014 & 2017).

A hydrothermal system requires fluids (groundwater, meteoric water or seawater) and a heat source (Todesco, 2008). Magmatic gases (CO_2 , SO_2 , halogens) interact with fluids and surrounding rocks through a process called scrubbing, which selectively allows the escape of less soluble gases like CO_2 , produces new mineral phases, and loads fluids with acidic species such as HCl , HF , and H_2S (Symonds et al., 1994, 2001 & 2003).

The hydrothermal system thus acts as a filter: as long as the liquid phase persists, main fumarolic emissions at the surface consist of H_2O , CO_2 , and H_2S , also influencing springs, crater lakes, and waterbodies connected to the volcano (Pritchard et al., 2019). The separation between magmatic and hydrothermal domains occurs at the brittle-ductile transition (~ 3 km), where reduced permeability and precipitation of minerals form a seal. Its breaching, e.g. due to increased magmatic gases pressure below the seal, opens new pathways to the surface, generating seismicity, fluid migration, ground deformations and changes in fumarole composition (Fournier, 1999 & 2007; Rouwet et al., 2014 & 2017; Tassi et al., 2023). This phenomenon is called unrest (Fournier, 2007; Rouwet et al., 2014 & 2017; Gottsmann et al., 2017; Sandri et al., 2017; Pritchard et al., 2019). Recent examples include Vulcano (2021-2023) and Nisyros (1996-2001), where increases in fumarolic flux and diffuse CO_2 degassing were observed without eruptive manifestations (Paillot-Bonn  tat et al., 2023; Chiodini et al., 2002). Changes in fumarolic gas

composition, particularly in the transition from a “wet” to a “dry” system, represent sensitive indicators of unrest, which can be monitored through ratios of poorly soluble gases (CO_2 , H_2S) versus highly soluble ones (SO_2 , HCl), as well as isotopic markers ($\delta^{13}\text{C}\text{-CO}_2$, $^3\text{He}/^4\text{He}$) (Symonds et al., 1994, 2001 & 2003; Pritchard et al., 2019).

Monitoring fumarolic gases is therefore essential for understanding the evolution of a system during unrest. Unrest at hydrothermal volcanoes is typically studied by periodic campaigns in which fumarolic gases are directly sampled in special glass flasks, and hence transported back to laboratory for analytical determinations. A disadvantage with direct sampling is that no real-time data can be available and, during the hazardous (for operators) and time-consuming sampling operations, a relatively small number of fumaroles can be studied.

A valuable complement to direct sampling is the use of chemical mapping techniques that, using portable gas sensing units, can be used for real-time surveying and imaging the chemical diversity of a fumarolic field. These mapping techniques contribute key information on the spatial heterogeneity of fumarole composition, and on how this heterogeneity varies in time as unrest progresses.

This doctoral work focusses on the application of the compositional mapping technique to two fumarolic fields hosted by two quiescent hydrothermal volcanoes: Vulcano in Italy and Nisyros in Greece. The aim is to demonstrate the utility of fumarole chemical mapping for understanding the dynamics and drivers of unrest at dormant volcanoes in solfatara stage of activity, especially focusing on what the spatio-temporal evolution of a fumarolic fields can tell us on the modes, rates and spatial extent of magmatic gas supply to, and processing within, active hydrothermal systems. The implications of the results for the assessment of gas hazard resulting from the exposure of tourists, visitors and operators to high levels of potentially toxic volcanogenic gases are also discussed.

Focus on Vulcano is motivated by the recent degassing unrest that took place at La Fossa cone between 2021 and 2024. Results are presented for periodic campaigns conducted at the summit fumarolic field of the Gran Cono, in which

geochemical data were collected using Multi-GAS and SO₂ flux observations with a UV camera. In particular, the variations in gas composition during unrest (2021-2024) are compared with previous compositional data (2014-2021). Monitoring the spatiotemporal evolution of fumarolic activity is crucial to understanding unrest processes, at Vulcano island and at other dormant volcanoes. The results of periodic campaigns allow mapping the CO₂/SO₂ ratio compositional diversity of the fumarolic field, and the extent to which this diversity varied during the unrest. Results highlight significant spatiotemporal changes and enable the identification of areas influenced predominantly by magmatic or hydrothermal sources. Integration of these data with infrared thermal imagery and SO₂ flux measurements provides insights into the volcano's state before and after 2021, up to 2024, allowing evaluation of compositional evolution over time. The study highlights spatiotemporal variations in gas composition, maps compositional heterogeneity, and identifies areas predominantly influenced by magmatic or hydrothermal sources. Integration with infrared thermal imagery provides additional insights into the volcano's evolution before and after the 2021 unrest.

Nisyros is taken as an example of a volcanic system that is progressively recovering from seismic and degassing unrest occurred in the 1990s. In addition to being a comparative site to Vulcano, owing to different stages of unrest the two volcanoes are currently experiencing, Nisyros is selected because of its wide accessibility, making it (especially the Stefanos crater) a popular tourist destination. The combination of high visitor exposure and accessible fumarolic sites at Nisyros requires the potential human health risks are accurately assessed. The island in the Aegean was visited in April 2024, when a Multi-GAS data acquisition campaign was realized. The campaign targeted key sites of the hydrothermal system: the explosion crater of Stefanos and the small explosion craters characterizing the nearby Lofos dome, allowing characterization of their composition in terms of the most abundant gas species (CO₂, H₂S, H₂). Results are graphically presented as concentration/ratio maps that allow imaging the compositional heterogeneity of the fumarole fields. The use of Multi-GAS enabled investigation of fumarolic molar ratios,

contributing to the multi-decadal gas composition record at Nisyros, showing how compositions have varied over time, starting from 1996-2001, when the island was considered in unrest (Chiodini et al., 2002). Our results hence enable the characterization of fumarolic compositions and assessment of multi-decadal changes in CO₂, H₂S, and H₂ emissions, and contribute to understanding gas composition evolution over time and the consistency of monitoring techniques across different volcanic settings. Given Nisyros touristic nature, the results are also discussed in terms of potential human health impacts (tourists, visitors, and operators) associated with atmospheric concentrations of potentially hazardous gases, such as CO₂ and H₂S.

Chapter 2 sets the state of the art and puts hydrothermal systems in volcanic contexts. I describe the evolution of magmatic gases towards hydrothermal compositions, the sequence of magmatic-hydrothermal reactions that occur in the hydrothermal envelop, and the set of spy parameters that can geochemically be used to monitor volcanic unrest. **Chapter 3** describes the methods used in this study, while **chapter 4 and 5** report on the results obtained at Vulcano and Nisyros respectively. The main conclusions obtained are summarized in **Chapter 6**.

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2: THE PHYSICAL AND CHEMICAL STRUCTURE OF VOLCANO-HYDROTHERMAL SYSTEMS, AND THEIR UNREST

2.1 General overview on hydrothermal systems: definitions and composition

Hochstein & Browne (2000) and Fischer & Chiodini (2015) provide a definition of a hydrothermal system, starting from the more general definition of geothermal activity, which refers to the transfer of heat transported from a thermal source at depth to the surface. A hydrothermal system is a type of geothermal system in which heat is transferred from a heat source (often a cooling pluton) to the surface via the convective circulation of aqueous fluids, typically of meteoric/marine origin. A hydrothermal system (**Figure 2.1**) consists of (1) a heat source; (2) a reservoir with thermal fluids; (3) a surrounding “recharge region”, and (4) a surface fluids discharge (and heat) area, often counting countless hydrothermal manifestations such as fumaroles, springs, mud pools, steaming grounds and degassing soils.

A volcano-hydrothermal or magmatic-hydrothermal system is a hydrothermal system in a volcanic context, in which ascending (primary) magmatic fluids commonly mix with meteoric/seawater (secondary) fluids (**Figure 2.2**). This definition highlights the importance of mixing between magmatic fluids and meteoric and/or marine fluids, a process that feeds and sustains surface hydrothermal manifestations in volcanic systems. According to Norton (1984), the processes that develop in a hydrothermal system can be described as a continuous redistribution of energy and mass, triggered by fluid circulation. This circulation is activated when a magmatic system comes into contact with a portion of the crust rich in fluids, giving rise to a transfer of thermal, chemical and mechanical energy. This occurs through the

mechanisms of convection, conduction and molecular diffusion, which in turn pro-

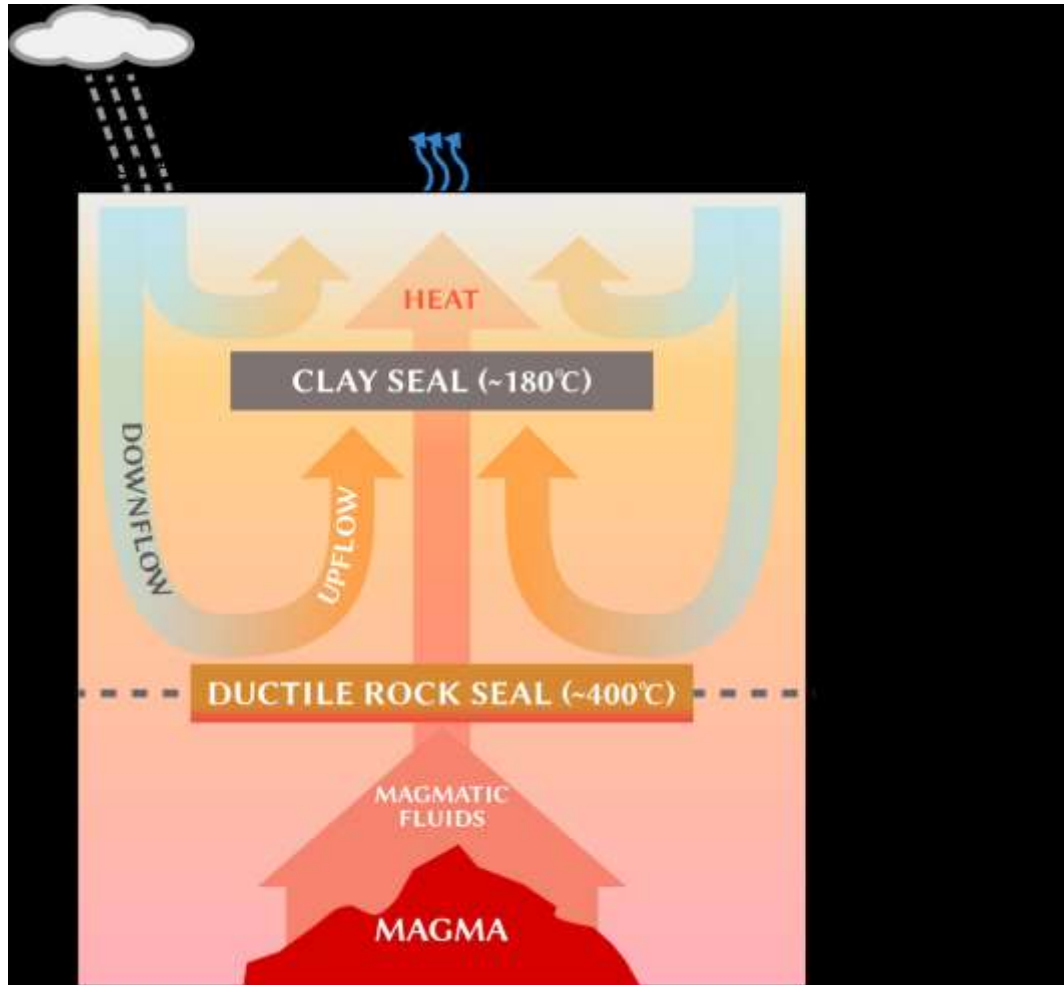


Figure 2.1 A simple model of a hydrothermal system. Adapted from Stimac et al., 2015. For further details see text.

mote chemical reactions between the fluids and the host rock.

The driving force of these processes is the thermal anomaly, which controls heat distribution and influences the stress and strain state of the rock, modulating fracture opening or closure and, consequently, reaction rates and fluid ascent. Hydrothermal systems can therefore be regarded as complex regulators of energy and matter distribution within a volcano. It follows that the entire system responds to

variations occurring in the deep magmatic system (Jessop et al., 2021; de Bremond d'Ars & Gibert, 2022; Marini et al., 2025).

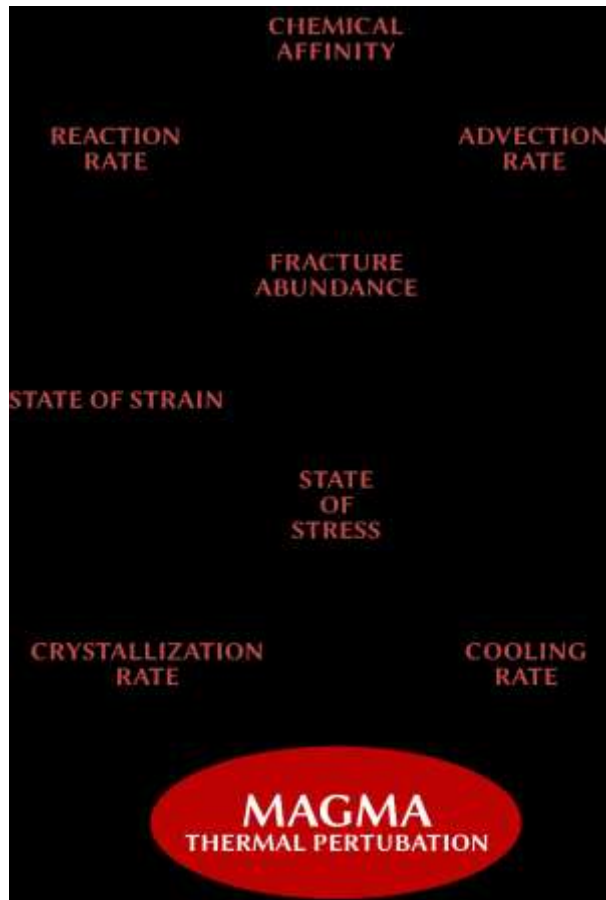


Figure 2.2: Physical processes within hydrothermal systems, adapted from Norton et al., (1984).

The products of hydrothermal systems include mineral products derived from the intense alteration, leaching and mineralogical/chemical transformation of host rock, which often gives rise to mineralization of economic interest (Fournier 1999 & 2007.). Fluids also undergo complex compositional change. The main magmatic gases are essentially H_2O and CO_2 , with additional components such as S_t ($\text{SO}_2 + \text{H}_2\text{S}$), HCl , HF , H_2 , and CO . Upon leaving the source magma, these magmatic gases interact with meteoric/marine fluids and host rocks in the hydrothermal envelope, deeply modifying their composition. These reactions determine a stark compositional contrast between magmatic gases, such as those emitted by a plume in an

open-conduit volcano, and those released by fumaroles in a hydrothermal system within closed-conduit volcano (Oppenheimer et al., 2014; Fischer and Chiodini, 2015) (**Figure 2.3**). For example, hydrothermal gases (the ultimate product of magmatic-hydrothermal interactions) are typically more hydrous, S-Cl-depleted, and more reduced (e.g., enriched in H_2S relative to SO_2) relative to magmatic gases (Giggenbach, 1987, 1996).



Figure 2.3 The fumarolic field at the summit of La Fossa Cone, Vulcano Island, Italy (photo by Simone Lentini).

Several examples reported by Fischer & Chiodini (2015) illustrate compositional differences between magmatic and hydrothermal gases from different volcanoes. For instance, Momotombo, Iwojima, Kudryavy, and Merapi display $\text{SO}_2/\text{S}_\text{t}$ ratios of 1, 0.833, 0.84, and 0.88, respectively, indicating that H_2S is completely absent among the primary gases at Momotombo and present in minor amounts at the other three volcanoes. In contrast, at many/most hydrothermal volcanoes, H_2S is the only detectable S species. Where both coexist, H_2S typically prevails: at Pichincha, the $\text{SO}_2/\text{S}_\text{T}$ ratio is ~ 0.5 , while at White Island the ratio is 0.035, and at El Chichon 0.010, showing that H_2S is by far the dominant sulfur species.

Among halogens, using the same Fischer & Chiodini (2015) dataset, HCl decreases by three orders of magnitude from magmatic gases at Momotombo (0.5 mol %) to hydrothermal gases at Aogashima (0.0007 mol %), corresponding to a 99.87% decrease; a similar behavior is observed for HF (0.384 versus 0.0002, a

decrease of about two orders of magnitude, or 99.5%). H_2 and CO show a comparable decrease, whereas CH_4 and NH_3 increase. Thus, while magmatic gases are dominated by H_2O , CO_2 , SO_2 , HCl , HF , H_2 , and CO , hydrothermal gases, apart from the ubiquitous H_2O and CO_2 , are dominated by H_2S , followed by variable but minor amounts of SO_2 , H_2 and CH_4 . The general trend is that, unlike magmatic volcanic gases, hydrothermal gases typically contain more CO_2 , less total sulfur, almost invariably in reduced form (H_2S), and higher concentrations of CH_4 , NH_3 , and N_2 , and only rarely contain acidic halogen species (Stimac et al., 2015).

2.2: Structure and chemistry

2.2.1: Classification, structure, hydrothermal circulation, chemistry, alteration

In order to classify hydrothermal systems, it is necessary to select a parameter on which the classification is based. Hydrothermal systems were classified by Bogie et al. (2005) according to the marine or continental setting in which the thermal anomaly develops. On continents, two main categories are recognized: systems associated with stratovolcanoes and rifts on the one hand, and systems associated with spreading centers (oceanic or back-arc) on the other. Additional types, not discussed here, complete the overall framework (**Figure 2.4**).

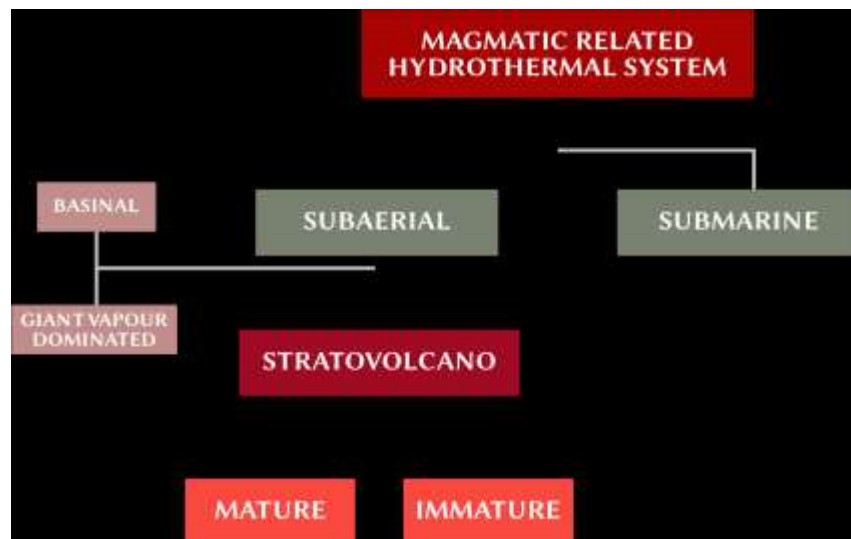


Figure 2.4 Classification of hydrothermal systems after Bogie et al., (2005). The reader is referred to the original publication for further details.

Focusing on systems associated with volcanic settings, it is important to emphasize that Bogie's classification refers exclusively to andesitic volcanoes, overlooking the wide variety of volcanic environments in which hydrothermal systems can develop. Stimac et al. (2015) also include domes and calderas among volcanic systems associated with hydrothermal activity. The Piton de la Fournaise, a basaltic shield volcano, likewise hosts a hydrothermal system with summit fumarolic

manifestations (Mauri et al., 2018). In the Mediterranean region, different volcanic contexts are represented: Vulcano and Nisyros are examples of hydrothermal systems associated with stratovolcanoes, whereas Sousaki, in Corinthia, represents a hydrothermal system developed within a field of Pliocene dacitic-rhyolitic domes and coulée flow-dome, characterized by low-temperature fumaroles (30-45 °C) and hydrothermal alteration (D'Alessandro et al., 2006a & 2006b; Vougioukalakis, Sattow, & Druitt, 2019). The Solfatara crater in the Campi Flegrei is a classic example of a manifestation related to a hydrothermal system within a caldera (Chiodini et al., 2021). Within hydrothermal systems hosted in volcanic settings, Bogie distinguishes between immature and mature systems based on the extent of hydrothermal circulation, which progressively affects increasingly distal portions of the volcanic system. Under these conditions, the permeability of the host rocks, already a fundamental parameter for the initiation of hydrothermal circulation, becomes crucial as the system expands. The structure of a hydrothermal system, generally speaking, has already been introduced above, but warrants further discussion. A magmatic intrusion or magma reservoir (in volcanic settings) provides the heat necessary to sustain fluid circulation. In the vicinity of such bodies, the brittle-ductile transition inhibits fracture propagation and, consequently, downward fluid flow. This zone acts as a lower seal, separating the strictly magmatic domain from the hydrothermal one. Near the surface, fluid-rock interaction alters the host rocks, reducing permeability and forming clay caps, that constitute a second seal. The hydrothermal domain is thus separated from both the surface and the magma chamber by two low-permeability layers. Downward circulation (downflow) of meteoric waters occurs at the margins of the upper seal, while hot fluids rise upward as an upflow (Norton, 1984; Goff & Janik, 2000; Stimac et al., 2015) (See **Figure 2.1**).

2.2.2: Circulation and heat transport

Convection is far more effective than conduction as a mechanism of heat transport (Stimac et al., 2015; Glazner, 2020); most heat is transported by fluid up-flow, whereas the downflow remains relatively cooler. The rate of convective heat removal strongly depends on circulation depth, reservoir temperature, and the mass flux of water within the system. Convective heat transport by hydrothermal circulation has been discussed by Stimac et al. (2015), who estimate that the minimum permeability required to sustain fluid transport under convective conditions is on the order of $5 \times 10^{-15} \text{ m}^2$ (5 mD; darcy being the unit of permeability).

Hydrothermal circulation occurs in rocks with sufficient permeability due to buoyancy effects caused by heating and the consequent thermal expansion of fluids. Cold fluids penetrate interconnected fracture networks and progressively heat up as they pass through increasingly hotter rocks (Stimac et al., 2015). Here, they may mix with magmatic fluids and rise as hot fluid plumes. This description fits well with the model proposed by Fournier (1999, 2007), in which a hydrothermal system consists of (**Figure 2.5**):

- a “deep reservoir” ($h \geq 2 \text{ km}$; $T > 400 \text{ }^\circ\text{C}$) under plastic deformation conditions and lithostatic pressure, hosting magmatic intrusions that store magmatic fluids composed of hypersaline brines and gases. The plastic regime, together with mineral deposition by fluids, seals this domain into what is referred to as a self-sealed zone, corresponding to the lower seal described above;
- a shallow zone under brittle conditions, subject to hydrothermal circulation and hydrostatic pressure.

Episodic rupture of the lower seal allows rapid “expulsion” of magmatic fluids upward and the associated deposition of minerals. The injection of hot fluids into the upper domain leads to pressurization and the opening of new ascent pathways, drawing in additional fluids until the lower seal is re-established.

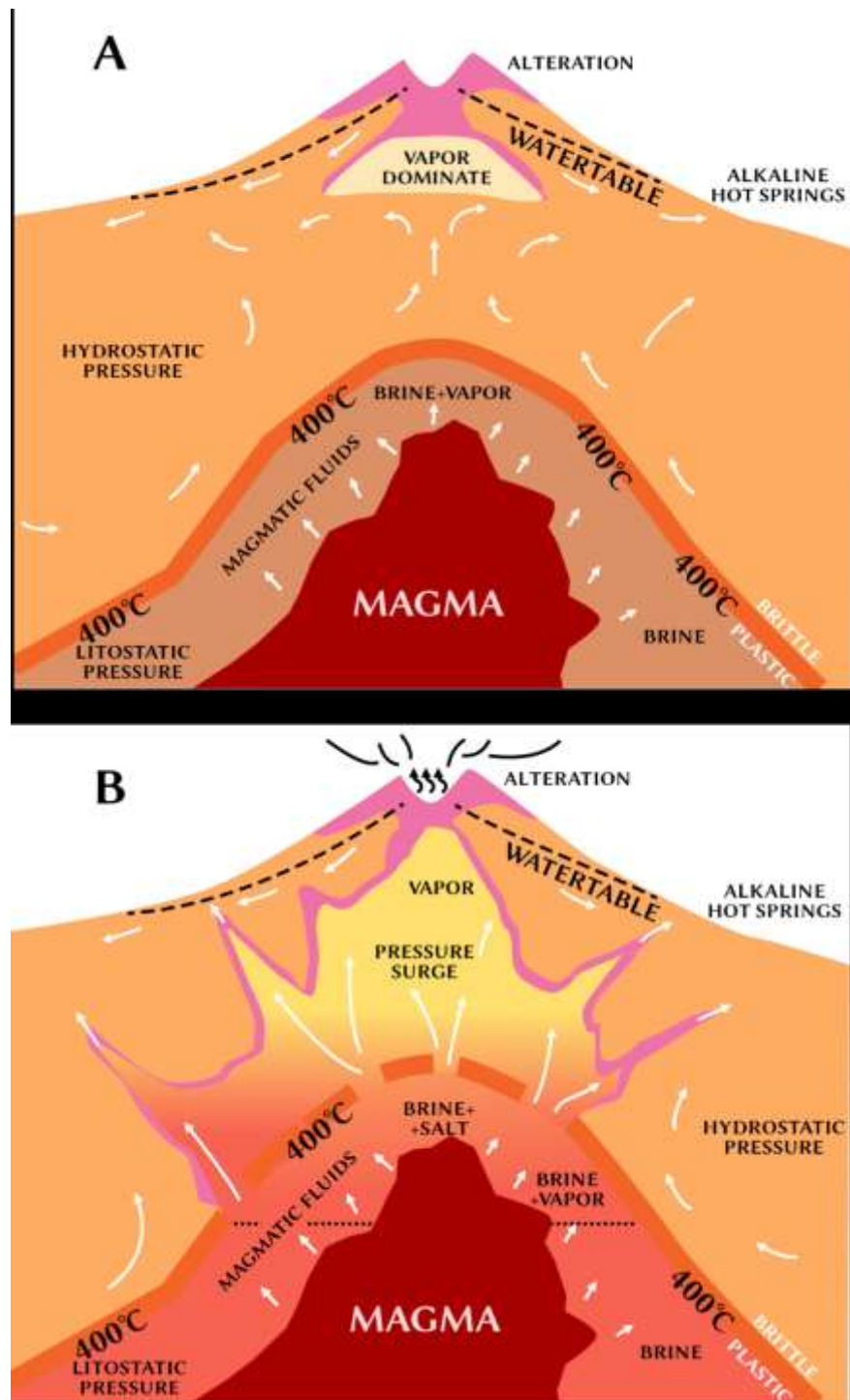


Figure 2.5 Two-domain model of a volcano-hydrothermal system. Episodic breaching of self-sealed zone allows magmatic fluids to flow upward into the hydrothermal system. See text for further details. Adapted from Fournier (2007).

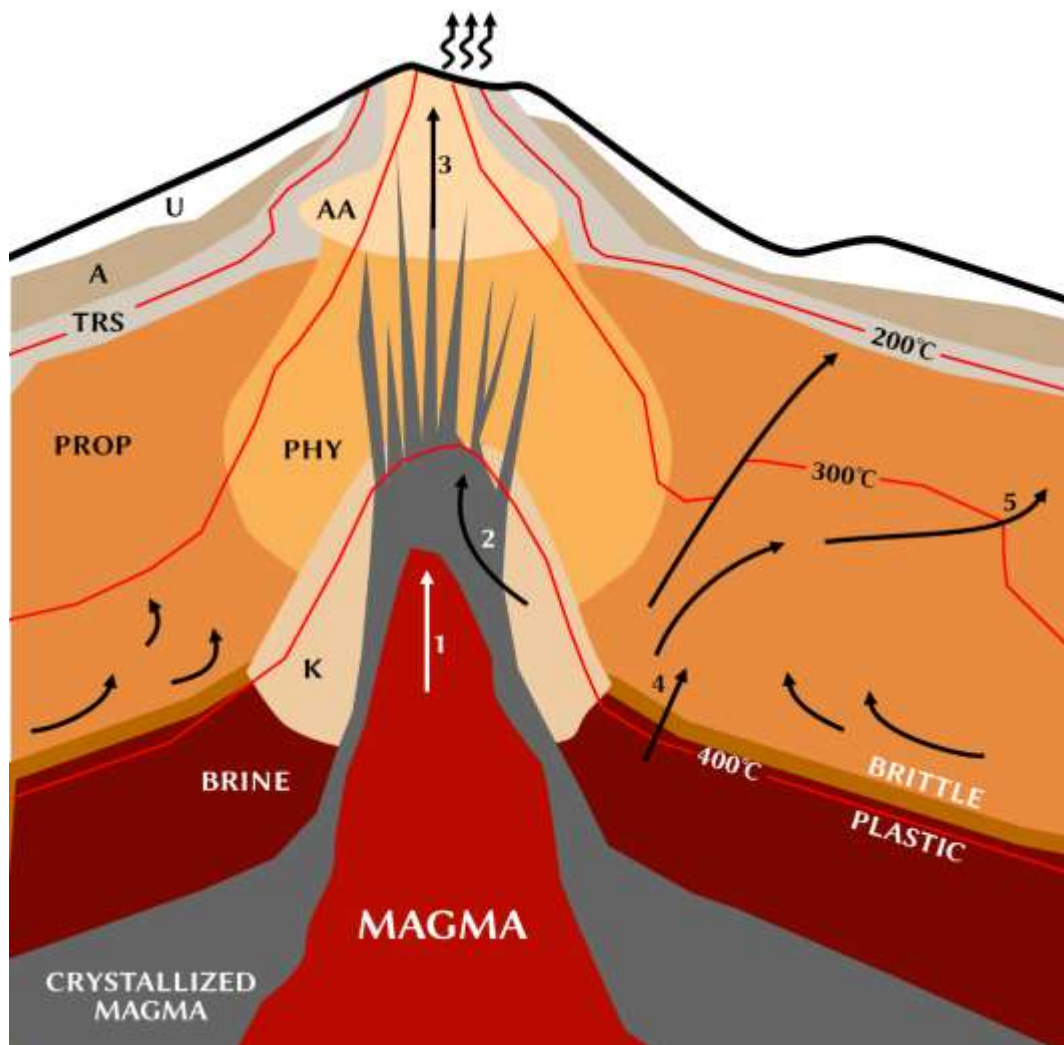


Figure 2.6 Section of a stratovolcano with hydrothermal alterations facies, isotherms and fluid migration paths. K: potassic alteration; PHY, phyllitic alteration; AA: advanced argillitic; PROP: propylitic; TRS: transitional; A: argillitic; U: unaltered. 1: supercritical moderate salinity fluid; 2: brine + low salinity vapor; 3: low acidic vapor; 4: magmatic fluids expelled during a breaching of self-sealed zone; 5: flows of increasing meteoric composition. Adapted from Fischer & Chiodini (2015).

The formation of both lower and upper seals occurs in the context of hydrothermal alteration, expressed through different alteration facies affecting various parts of the volcanic system. Richards (2011) identified 3 main alteration facies in a volcanic edifice affected by a hydrothermal system. The persistent flow of heated meteoric waters affects all rocks above the brittle-ductile transition, particularly near the pluton or magma reservoir. Transitional facies (forming the clay cap and

thus characterized by low permeability), argillitic facies (smectite, dolomite, calcite, cristobalite, pyrite, kaolinite, even less permeable), and a more permeable propylitic facies (albite, chlorite, epidote, pyrite) have been recognized (**Figure 2.6**).

Hydrothermal alteration zones form shell-like envelopes around volcanic conduit systems and are correlated with magmatic volatile fluxes and hydrothermal fluid circulation. Alteration types identified within these shells include potassic (K-feldspar such as adularia and orthoclase, biotite, muscovite, $\pm$ magnetite), phyllitic (quartz, sericite-white mica, illite $\pm$ pyrite), and advanced argillitic (kaolinite, pyrophyllite, illite/sericite).

2.2.3 Fluid chemistry, zonation and maturity

A conceptual model of a geothermal system hosted in a stratovolcano involves meteoric waters percolating to depth, where they are heated by andesitic intrusions (850–1050 °C) and by magmatic volatiles (H₂O, CO₂, sulfur species, HCl, HF, Hg, As). As fluids circulate, they react with host rocks, enriching in Cl, F, Br, B, SO₄²⁻, HCO₃⁻, silica, major cations, and soluble metals. Metamorphic fluids may also contribute, and fluid mixing produces a range of hydrothermal compositions.

Fluids generally ascend buoyantly, forming fumaroles, steam, and non-condensable gases at the surface. Near-surface interaction with meteoric water may oxidize H₂S to sulfuric acid, producing acid-sulfate springs, while neutral-chloride waters originate from deeper reservoirs. Mixing of these types can generate hybrid acid-sulfate-chloride waters. Lateral flow away from the volcanic center produces hydrothermal outflow zones; neutral-chloride springs reflect deep reservoirs, whereas acid-sulfate waters reflect shallow interactions.

Giggenbach (1984, 1988) distinguishes shallow (rapid circulation, far from equilibrium, producing Ca-Mg-SO₄, Ca-Mg-SO₄-Cl, Mg-HCO₃) and deep hydrothermal systems (long residence times, mature Na-Cl brines). Immature systems

show fumaroles, solfataras, acid lakes, limited Cl, and partial magmatic degassing. Mature systems display widespread thermal manifestations with altitudinal zoning: high-elevation CO₂-rich gases, intermediate acid-SO₄ springs, and lower neutral-Cl springs, with progressive water-rock neutralization downslope.

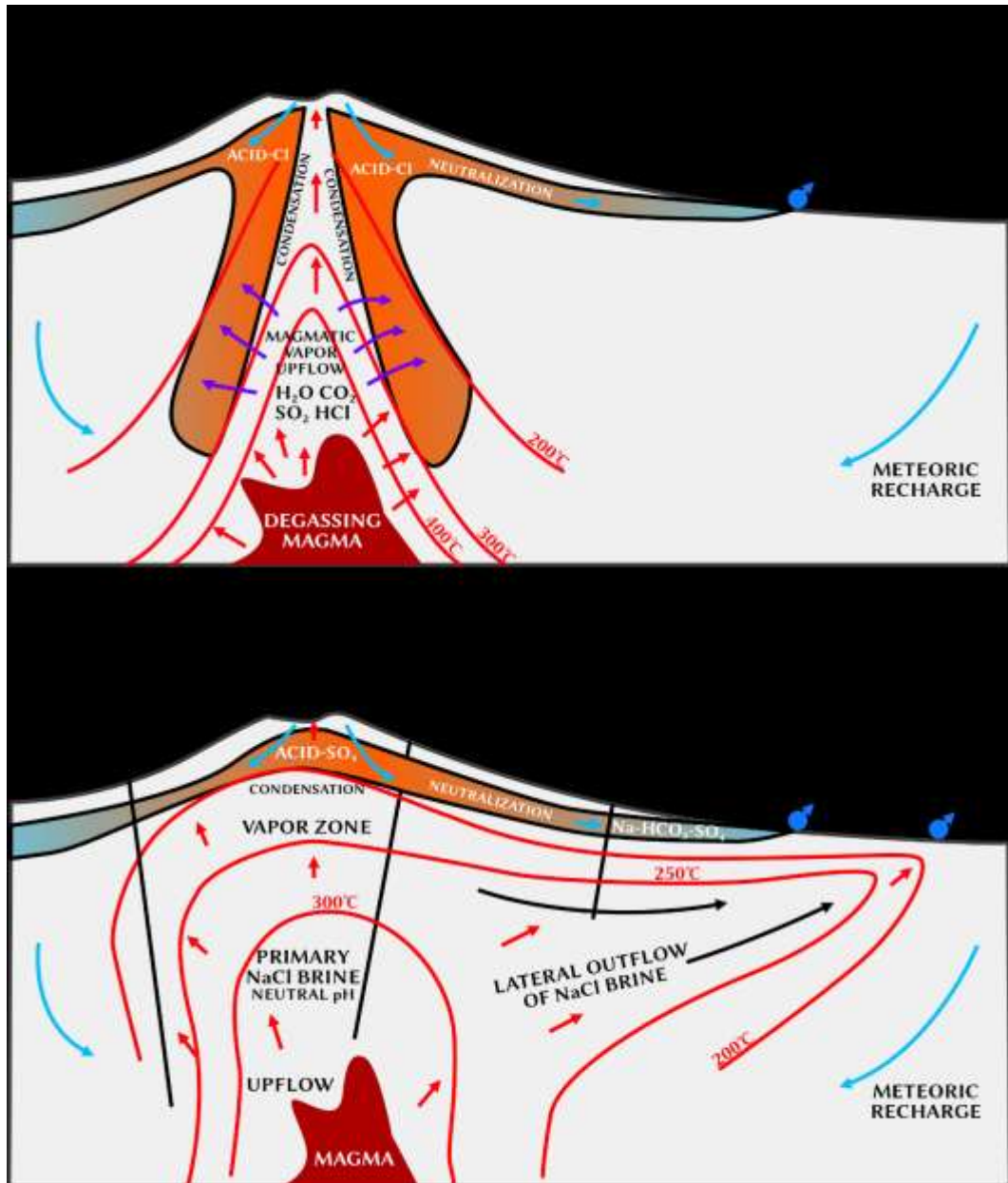


Figure 2.7 Immature systems (A) and mature system (B), and zonation of waters. Adapted from Bogie et al., (2005). For further details see text.

2.3: Geochemistry of hydrothermal processes: redox and scrubbing

2.3.1: At the origin of hydrothermal gases: the chemistry of magmatic gases

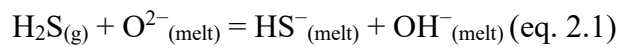
Hydrothermal gases are the product of the interactions between magmatic gases, rocks, and fluids, both magmatic and meteoric origin, with which they come into contact. A brief list of the main magmatic gases has already been provided; here, however, they are discussed in greater detail. In particular, the following gas species can be listed, each characterized by specific features that depend on the geodynamic setting and on the pressure-temperature- f O₂ conditions prevailing in the magma chamber (Symonds et al., 1994): H₂O, CO₂, SO₂, H₂, H₂S, HCl, HF, CO, S₂, COS, plus trace metals.

The dominant magmatic gases are undoubtedly H₂O and CO₂. Owing to the contribution of water from subduction, magmas at convergent margins are more enriched in H₂O than those at divergent margins or hot spots. This so-called arc-type magmatic water; solubility of water in magmas increases with increasing silica content (Dotsika et al., 2009; Fischer & Chiodini, 2015), and thus characterizes silicic magmas (andesitic and rhyolitic). Wallace et al. (2015) report water contents ranging from 3% (Colima, Popocatépetl) to 5.5% (Cascades) and up to 6% (Soufrière Hills), hosted in various glass inclusions from andesitic edifices. Magmas from other geodynamic contexts (back-arc, hot spots, etc.) generally display lower values.

CO₂ may derive from the mantle, from the subduction of carbonate-rich materials, or from crustal assimilation of carbonates (Oppenheimer et al. 2014). This gas tends to become dominant in undersaturated magmas and in carbonatitic magmas, where it is dissolved as CO₃²⁻, whereas in rhyolitic magmas it occurs as molecular CO₂; in andesitic magmas, both forms coexist (Wallace et al., 2015). Wallace et al. (2015) report CO₂ contents <500 ppm in glass inclusions from andesitic magmas, while noting that volcanic gas measurements may show CO₂ fluxes exceeding those of SO₂. The same authors report sulfur contents <1000 ppm in

andesitic magmas and <200 ppm in rhyolitic magmas, emphasizing that sulfur solubility strongly depends on magma redox state.

Sulfur is dissolved in magmas as sulfide and sulfate, depending on magma redox, temperature and chemistry. Wallace et al. (2015) place the sulfide-sulfate speciation transition at $f\text{O}_2$ (NNO) = +2. In the magmatic gas phase, H_2S prevails at high pressure and low redox (at $f\text{O}_2$ (QFM) ≤ -1) (Carroll & Webster, 1994; Symonds et al., 1994), according to the reactions:



SO_2 prevails instead during low pressure degassing of hot, oxidized magmas. Aiuppa & Moussallam (2024) further specify that in high-temperature magmatic gases (> 900 °C), the $\text{H}_2/\text{H}_2\text{O}$ and $\text{H}_2\text{S}/\text{SO}_2$ ratios reflect near-thermodynamic equilibrium conditions, predominantly controlled by redox interactions between the gas phase and the silicate melt. Differences observed between arc and non-arc settings reflect systematic variations in the redox conditions of the source magma, with arc magmas being more oxidized due to subduction-related inputs.

Regarding halogens, HCl and HF are more enriched in convergent-margin magmas, deriving directly from subduction processes (Carroll & Webster, 1994; Symonds et al., 1994; Fischer & Chiodini, 2015; Wallace et al., 2015). In summary, the principal magmatic gases are H_2O , CO_2 , and SO_2 , although in some convergent-margin volcanoes H_2S may replace SO_2 , and HCl may even exceed sulfur species (Carroll & Webster, 1994; Symonds et al., 1994). Convergent-margin gases contain more H_2O than those from divergent margins or hot spots, which are relatively richer in CO_2 and SO_2 . Magmatic gases from convergent margins are also relatively enriched in HCl due to contributions from subduction (**Fig 2.8**).

In volcanic gases, H_2 and H_2S are generally minor components, but their abundances vary widely as a function of emission temperature and geodynamic context. Molecular hydrogen (H_2) tends to be more abundant in very hot

magmatic gases ($>1000\text{ }^{\circ}\text{C}$), particularly in intraplate and continental rift volcanoes, whereas in arc volcanoes it decreases as gases cool down to $T \sim 600\text{ }^{\circ}\text{C}$.

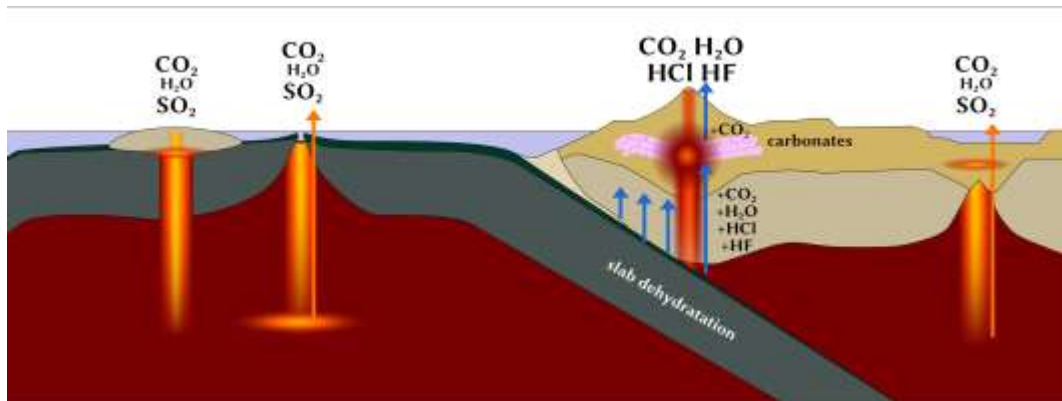


Figure 2.8 Magmatic gas composition in different geodynamic settings. See text for further details.

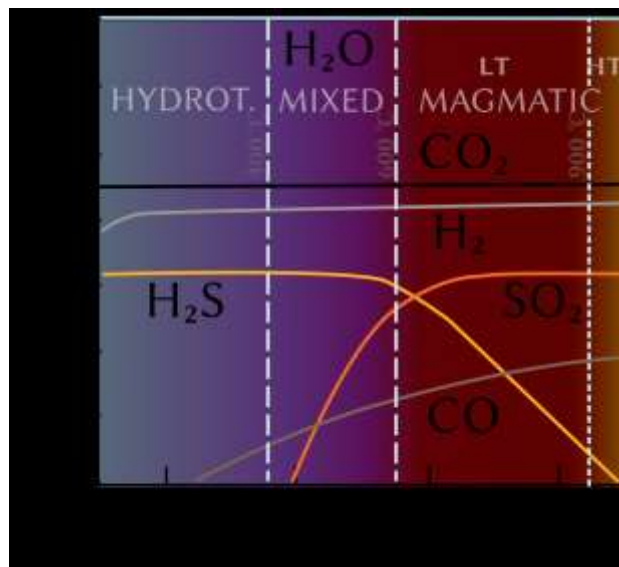


Figure 2.9 Variations in H_2O , CO_2 , CO , H_2S , SO_2 and H_2 with temperature. Thermal ranges are taken from Aiuppa & Moussallam (2024). Adapted from Symonds et al, 1994.

Both magmatic and hydrothermal gases are dominated by CO_2 and H_2O and thus display similar $\text{CO}_2/\text{H}_2\text{O}$ ratios; however, this is not the case for total sulfur contents (Fischer & Chiodini, 2015). As anticipated, H_2S and SO_2 are the species that discriminate primary magmatic gases from secondary hydrothermal gases. H_2S

is the dominant sulfur species in lower-temperature gases, typically hydrothermal ($T < 300\text{ }^{\circ}\text{C}$) or magmatic-hydrothermal ($300\text{ }^{\circ}\text{C} < T < 600\text{ }^{\circ}\text{C}$), where it may reach several tens of percent as a result of reduction and scrubbing reactions affecting SO_2 (Giggenbach, 1987; Williams et al., 1990; Symonds et al., 2001, 2003; Di Napoli et al., 2016; Aiuppa et al., 2005a; Aiuppa & Moussallam, 2024). At intermediate temperatures ($T \leq 600\text{ }^{\circ}\text{C}$), H_2 and H_2S show extreme variability, reflecting complex gas-rock-water interactions in the subsurface. These behaviors confirm the diagnostic role of H_2S . Similarly, the $\text{H}_2/\text{H}_2\text{O}$ ratio provides information on redox conditions and the magmatic nature of emitted gases (Giggenbach, 1987, 1996; Powell, 2000; Aiuppa & Moussallam, 2024) (**Fig 2.9**).

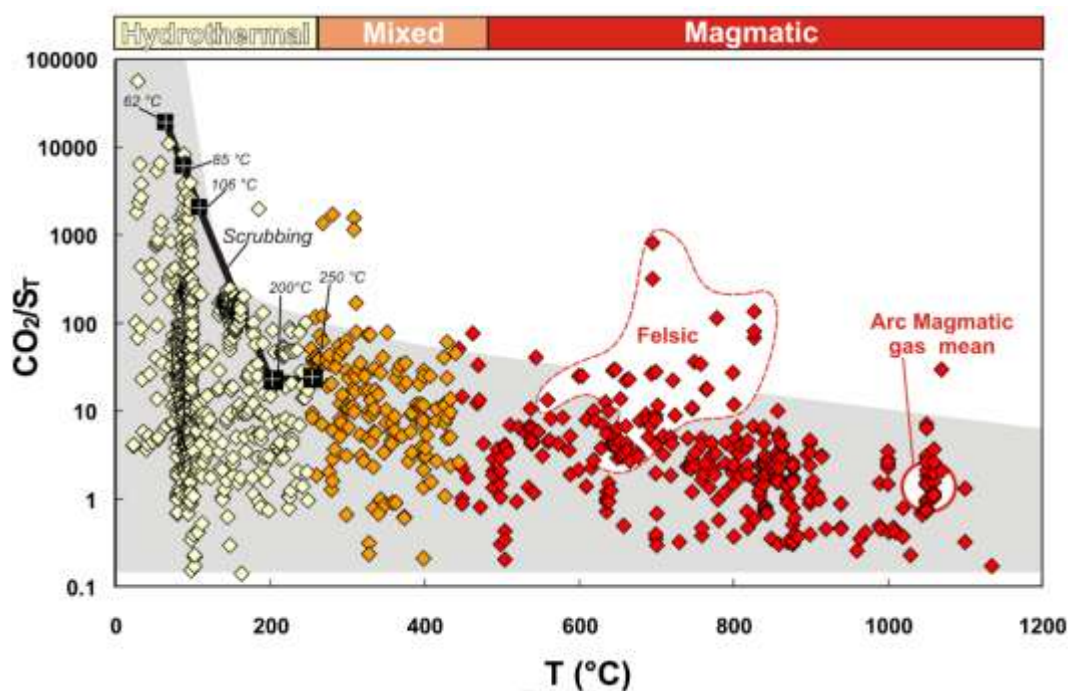


Figure 2.10 Temperature dependence of CO_2/S_T in analyses of volcanic arc gases; diamonds are measured values, black squared are modelled ratios resulting from gas scrubbing at different temperatures. The ratio decreases with temperature. “Felsic” are volcanoes with high ratios. Reproduced from Aiuppa et al., (2017).

Regarding SO_2 , except under the redox conditions discussed above, is the dominant sulfur species in high-temperature magmatic gases ($T > 400\text{ }^{\circ}\text{C}$). Consequently, the $\text{CO}_2/(\text{SO}_2 + \text{H}_2\text{S})$ ratio (CO_2/S_T) becomes a discriminator between magmatic and hydrothermal contributions, with $\text{CO}_2/\text{S}_T > 10$ in hydrothermal gases

(CO₂/H₂S) and CO₂/S_T < 10 in magmatic gases (CO₂/SO₂) (**Fig. 2.10**). The appearance and increase of SO₂ in hydrothermal outputs are interpreted as evidence of increasing magmatic input and are regarded as potential indicators of pre-eruptive conditions (Giggenbach, 1987; Symonds et al., 1994; Aiuppa et al., 2007, 2009).

2.3.2: Redox buffer of the system: H₂/H₂O, FeO/FeO_{1.5}, H₂S/SO₂ and Giggenbach's 'buffers war'

In high-temperature magmatic gases, ratios between redox species are often compatible with a state of near-thermodynamic equilibrium, controlled by the following reactions (Aiuppa & Moussallam, 2024):



However, Giggenbach (1987, 1996, and related literature) showed that the considerations outlined above do not hold for low-temperature gases, where multiple redox couples become important, together with interactions with deep and shallow fluids of meteoric origin, as well as with the host rock (Giggenbach, 1987, 1996; Chiodini and Marini, 1993; Symonds et al., 1994, 2001, 2003; Marini & Gambardella, 2005; Di Napoli et al., 2016; Aiuppa & Moussallam, 2024). When magmatic gases enter a hydrothermal domain, these interactions lead to the establishment of new equilibrium conditions and to the removal of specific species from the gas phase, a process referred to as scrubbing. The contrasting equilibrium behavior of high-temperature (> 900 °C) and low-temperature (< 300 °C) gases is captured by the correspondence temperature (CT), defined as the temperature at which the concentration of a given gaseous species matches its equilibrium value. For high-temperature gas species, the corresponding CT values are broadly similar, supporting the assumption of equilibrium at high temperatures. This assumption,

however, does not apply to the conditions prevailing within hydrothermal systems, as demonstrated by Giggenbach (1987, 1996).

What is currently known about hydrothermal systems and their equilibria has its roots in the late 1980s, with the paper by Giggenbach (1987). In his study of the fumaroles of White Island, the author identifies a magmatic component and another of purely hydrothermal origin. The former, rich in SO₂, rises directly from the underlying magma. The latter ascends more slowly from a region surrounding the magmatic body and consists of hypersaline brines and vapor enveloping the magmatic system. During ascent, the different species react at different rates and under different redox conditions, giving rise to what Giggenbach metaphorically termed a “war between buffers”.

Giggenbach constructs a model based on a series of reactions involving redox couples in order to describe them, parameterizing their thermodynamic behavior under different conditions of T , $f\text{H}_2\text{O} = \log f\text{H}_2\text{O}$, and R_H , and thus linking them to pressure and temperature ranges through the logarithm of their equilibrium constants, $\log K$, such that a general expression of the following form can be written:

$$\log (x_{\text{ox}}/x_{\text{rid}}) = \sum n_i A/T \pm \sum n_i B \quad (\text{eq. 2.5})$$

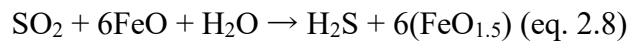
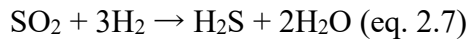
where n_i is stoichiometric coefficient of i -th component, A and B are tabulated coefficients for each reaction, where x_{ox} and x_{rid} are the molar fractions of the oxidized and reduced species. This formula can be written for each reaction that takes part during magmatic-hydrothermal interactions (Giggenbach 1987 & 1996). Here, the R_H parameter is a function of the redox conditions of the environment and is equal to (Giggenbach 1996, Powell, 2000; Fischer & Chiodini, 2015; Aiuppa & Moussallam, 2024):

$$R_H = \log (f\text{H}_2/f\text{H}_2\text{O}) \approx \log (x\text{H}_2/x\text{H}_2\text{O}) \quad (\text{eq. 2.6})$$

for fixed P-T. For $P \approx P_{\text{atm}}$, R_H can be approximated to $\log (x_{\text{H}_2}/x_{\text{H}_2\text{O}})$. An R_H value of -2.82 ± 0.02 is considered discriminant between oxidizing conditions ($R_H < -2.82 \pm 0.02$) and reducing conditions ($R_H > -2.82 \pm 0.02$) (Giggenbach, 1987).

The parameter R_H is related to the concept of f_{O_2} , as it effectively acts as a proxy for oxygen fugacity; since O_2 is virtually absent in hydrothermal gases at $T < 500^\circ\text{C}$ (Giggenbach, 1987), redox conditions can best be approximated by H_2 and H_2O , species that are present in fumarolic gases. R_H is hence considered as a probe of redox conditions operating in a hydrothermal system when fluid buffers (magmatic and hydrothermal) and the silicate system (rock/magma) interact. Not coincidentally, the $\text{H}_2/\text{H}_2\text{O}$ pair has been considered by Giggenbach (1987 & 1996; Aiuppa & Moussallam, 2024) to be a couple capable of responding rapidly to changes in redox conditions. Away from the high-temperature equilibria of magmas, this pair is influenced by the $\text{H}_2\text{S}/\text{SO}_2$ couple (Giggenbach, 1987; Aiuppa & Moussallam, 2024).

The $\text{H}_2\text{S}/\text{SO}_2$ ratio buffers redox state of magmatic gases, which rise rapidly from the degassing magma. At high temperatures ($T > 400^\circ\text{C}$), the dominant species is SO_2 ; however, in order to maintain fluid-rock equilibrium, this species must be converted into H_2S , thereby oxidizing the rock (Giggenbach, 1987 & 1996; Symonds et al., 2001):



When magmatic gases rise rapidly, the $\text{H}_2\text{S}/\text{SO}_2$ buffer dominates the gas system. The greater the interaction with the rock, that is, the longer the contact time, the lower the ascent velocity and the lower the effectiveness of the reaction. For this reason, the presence of SO_2 at fumaroles indicates a rapid ascent of magmatic gases.

Aiuppa and Moussallam (2024) have demonstrated that, in a global volcanic gas dataset, $\text{SO}_2/\text{H}_2\text{S}$ ratios are independent on temperature at $T > 600^\circ\text{C}$. According to Henley and Fischer (2021), however, the two pairs $\text{H}_2/\text{H}_2\text{O}$ and $\text{H}_2\text{S}/\text{SO}_2$ do re-equilibrate upon interaction with the rocks at hydrothermal temperatures, generating both H_2S and sulphates, together with other minerals. Both gas pairs indeed decrease for $T < 600^\circ\text{C}$, indicating sulphur dioxide is progressively removed from the gas (Aiuppa & Moussallam, 2024) (**Fig. 2.11**).

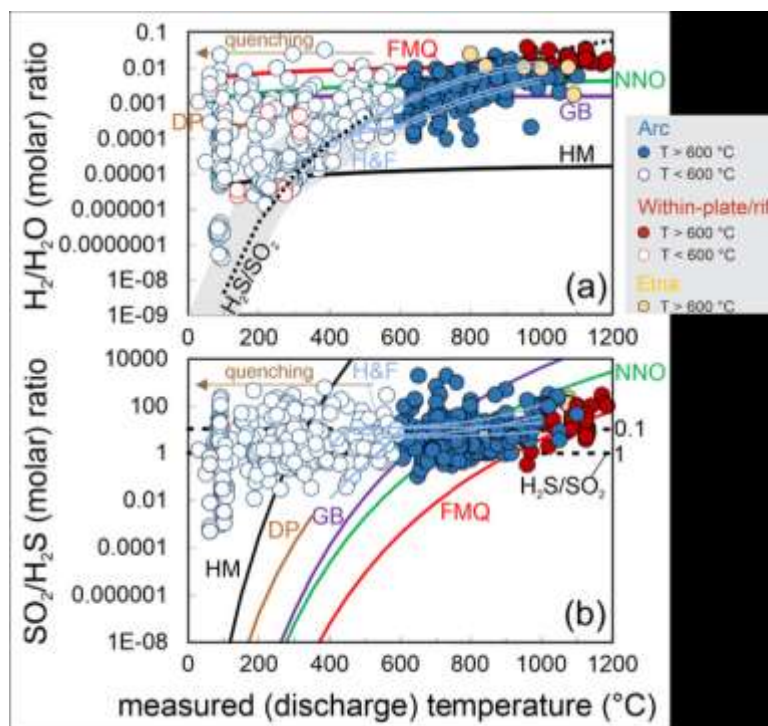


Figure 2.11 $\text{H}_2/\text{H}_2\text{O}$ and $\text{SO}_2/\text{H}_2\text{S}$ versus temperature reproduced from Aiuppa & Moussallam (2024). Aiuppa and Moussallam (2024) investigated global volcanic gas datasets and showed that $\text{SO}_2/\text{H}_2\text{S}$ ratios remain largely independent of temperature at $T > 600^\circ\text{C}$, reflecting gas compositions dominated by magmatic inputs. In contrast, at hydrothermal temperatures ($T < 600^\circ\text{C}$), both $\text{H}_2/\text{H}_2\text{O}$ and $\text{SO}_2/\text{H}_2\text{S}$ ratios decrease due to progressive interaction with rocks and fluids, indicating SO_2 removal and the development of more H_2S -rich, hydrothermally influenced gases. Quenching refers to gases preserving high-temperature signatures.

This makes the $\text{H}_2\text{S}/\text{SO}_2$ ratio a valuable tool for volcano monitoring: H_2S is in fact a key component of hydrothermal gases emitted by quiescent or conduit-closed volcanoes, and its ratio with SO_2 in fumaroles can signal magmatic ascent or potential episodes of volcanic unrest. The combined use of the $\text{H}_2/\text{H}_2\text{O}$ and

H₂S/SO₂ ratios has recently been proposed as a method to estimate temperature and redox conditions of magmatic gases (see review in Aiuppa & Moussallam, 2024).

The use of this pair as a geothermometer assumes that full equilibrium in reaction 2.7. Once the concentrations of the species involved are known, for example as measured at a fumarole, *T* can be derived from the equilibrium constant of this reaction; this Apparent Equilibrium Temperature (AET) (Moussallam et al., 2022) can then be compared with measured (fumarole) temperature. If the two temperatures coincide, the system has effectively reached equilibrium; otherwise, the gas preserves a frozen magmatic signature due to rapid ascent.

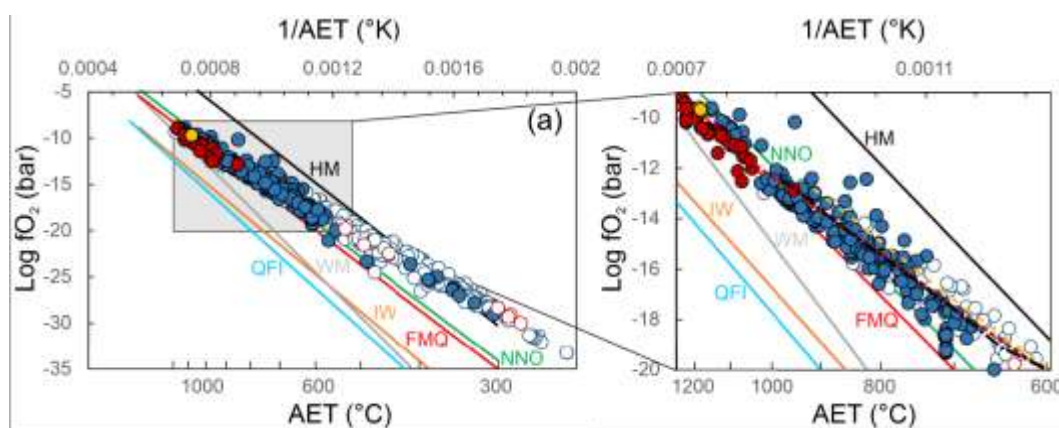
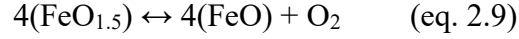


Figure 2.12. Fugacities versus temperature reproduced from Aiuppa & Moussallam (2024). Symbols are same of figure 2.11. For further details, see text.

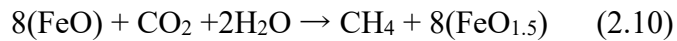
Using the relationship $\log (H_2/H_2O) = f(T, fO_2)$ (under equilibrium conditions, fO_2 is linked to the H₂/H₂O ratio), it is possible to derive the oxygen fugacity of the gases. By plotting an fO_2 versus T diagram together with the main mineralogical buffers (FMQ, NNO, HM, etc.), the measurements will fall along the buffer representing the equilibrium state of the gas; deviations from these lines indicate non-equilibrated systems or “quenched” magmatic signatures (**Fig. 2.12**).

Another buffer is that associated with the silicate system (rock/magma) (Giggenbach, 1987), which can be expressed as a reaction between Fe(II) and Fe(III), incorporated in a generic Al-silicate or oxide:



fayalite (Fe(II)) and hematite (Fe(III)) are potential thermodynamic proxies for the two iron minerals. Giggenbach observes that the traditional redox buffers of the rock/magma system, such as fayalite-magnetite (QFM) and magnetite-hematite (HM), provide a reference for low reduction potentials (low R_H); however, in hydrothermal systems the exact nature of ferrous minerals is often unknown or uncertain. The Ni-NiO (NNO) couple, on the other hand, is suitable for high-temperature basaltic magmas. To overcome the uncertainty related to mineral phases, Giggenbach proposes the FeO-FeO_{1.5} buffer as a generalized representation of reduced and oxidized ferrous phases, allowing redox conditions of magma and hydrothermal fluids to be linked to gas chemistry without having to assume the presence of specific minerals. The three buffers can be arranged along a scale from the most reducing to the most oxidizing, yielding: FeO-FeO_{1.5} (more reducing, $R_H > -2.82$) < QFM $\approx$ HM < NNO (more oxidizing, $R_H < -2.82$).

This buffer acts by regulating the redox conditions of systems at equilibrium at low temperatures ($T < 300^\circ\text{C}$) on a gas rich in CO₂ and with long interaction times with the rock.



The final effect will be the oxidation of the rock matrix. The presence of CH₄ is therefore indicative of a mature system, characterized by long-lasting interactions between fluids and rock at depth and by low temperatures (Giggenbach, 1987). An increase in the CO₂/CH₄ ratio is interpreted as a departure from system equilibrium, driven by a massive ascent of CO₂ and indicative of a potential system instability (Symonds et al., 1994).

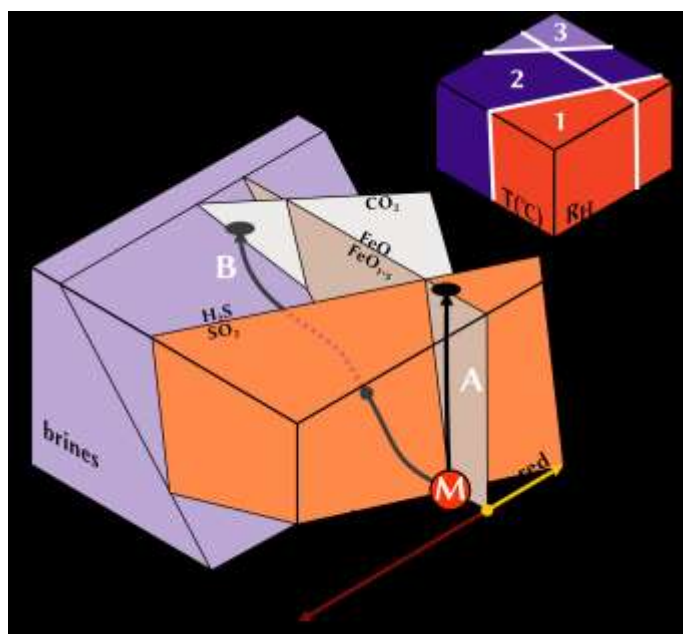
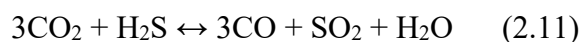


Figure 2.13. System H₂O-H₂-C-S-Fe. Different buffers identify three volumes: 1: magmatic; 2: hydrothermal; 3: low grade metamorphism. Fluids released from a degassing magmatic body follow different evolutionary paths. A: quenched gases preserving a magmatic chemical signature; B: gases that experienced prolonged interaction with hydrothermal fluids and mineral phases. Paths A and B are examples of many possible paths. Adapted from Giggenbach (1987).

The last buffer is that of CO₂/CO, which responds more slowly to changes in conditions and reflects equilibrium at depths corresponding to temperatures of approximately 300-400°C. Such equilibria can be represented by a single reaction:



In his modelling, Giggenbach places the magmatic body at $P = 600$ bar and $T = 1000^\circ\text{C}$, under redox conditions that represent a compromise between the FeO_{1.5}-FeO buffer and the H₂S-SO₂ buffer, corresponding to $R_H = -2.82 \pm 0.02$. From this starting point, he then traces different gas pathways under different conditions, controlled by the kinetics of reactions among gases, water, and rock in an attempt to reach equilibrium, as guided by the different buffers of the individual components (rock, water, gas) (**Fig. 2.13**).

- 1) Pathways describing magmatic degassing, which are regulated by the $\text{H}_2\text{S}/\text{SO}_2$ buffer:
 - a) An out-of-equilibrium pathway, consisting of the direct ascent of magmatic gases, and characterized by equal amounts of H_2S and SO_2 ;
 - b) A pathway in which gases equilibrate at low pressures: gases rise together with magma and the dominant gas phase is SO_2 . Giggenbach associates this pathway with the context of effusive eruptions;
 - c) A pathway in which gases rise with the magma (for example, associated with lava lakes) and in which redox conditions become more reducing, maintaining high H_2S ; again, this is indicative of a lack of equilibrium attained by the gases. This is especially true when the gas derives directly from a magmatic body located at depth, i.e., at high pressures, where the gas has equilibrated with the molten rock under strongly reducing conditions that favor the H_2S stability. The rapid ascent of such gas explains the occurrence of high-temperature emissions enriched in H_2S (Giggenbach, 1987; Symonds et al., 1994).
- 2) Pathways describing interaction with rock and fluids (gas and water). Magmatic fluids move away from the magmatic source toward lower-temperature zones, triggering the conversion of SO_2 into H_2S through the reactions previously described for sulfur species. Through persistent interaction with the rock, they remain in equilibrium with the $\text{FeO}-\text{FeO}_{1.5}$ buffer, and this signature is preserved up to the fumaroles. Any deviations toward more oxidizing values suggest interference with other processes. Under these conditions, H_2S and CO_2 dominate. A decrease in temperature ($T < 200^\circ\text{C}$) may drive the fluids toward a new equilibrium in which CO_2 evolves into methane and further oxidizes the rock (reaction 4). Once the fluids have exhausted their oxidizing capacity, the $\text{FeO}-\text{FeO}_{1.5}$ buffer prevails, imprinting its signature on the fluids.

Summarizing, the composition of fumarolic emissions can be described as the result of a continuous interaction among three buffers: the $\text{FeO}/\text{FeO}_{1.5}$ buffer of the

rock system (molten/solid), which tends to keep R_H fixed (around -2.8), and the buffers of magmatic gases, namely H_2S/SO_2 (dominant for $T > 400^\circ C$), and of hydrothermal fluids, CO_2/CO and CO_2/CH_4 (for $T < 300^\circ C$), which by their nature tend toward even more negative R_H values. Giggenbach acknowledges that fluids may locally “win,” but ultimately it is the rock that prevails, transforming high-temperature magmatic components (CO_2 and SO_2) into their low-temperature reduced counterparts (CH_4 and H_2S). High-temperature magmatic gases CO_2 and SO_2 are converted into their reduced counterparts (Tassi et al., 2016a) (with CO_2 converted to methane for $T < 300^\circ C$ when the $FeO-FeO_{1.5}$ buffer dominates redox conditions and kinetics allow). The resulting oxidation of minerals promotes their dissolution into the fluids. If some SO_2 survives, it is disproportionated into additional H_2S and H_2SO_4 , the stable S^{6+} form in liquid water (Giggenbach, 1987):



With regard to HF and HCl , these species complete their ascent in the liquid phase, forming acidic fluids that may lead to mineralization processes (Giggenbach, 1996). The highly acidic and oxidizing conditions, influenced by HCl , HF , and H_2SO_4 , present in hydrothermal zones give rise to intense fluid-rock interaction, dissolution of the cationic components of rocks, and the formation of highly mineralized brines, which represent potential source fluids for precious metal deposits associated with volcanic edifices. Experimental studies and thermochemical models (Gerlach et al., 1996) show that, in two-phase hydrothermal systems at moderate temperatures ($100-350^\circ C$), the separation of volatiles between vapor and liquid makes H_2S by far the most abundant sulfur-bearing gas after CO_2 , rendering other sulfur species negligible. It is interesting to note that, according to these models, even rapid and complete boiling of sulfate-rich fluids within a temperature range of $400-800^\circ C$ would not be capable of releasing significant amounts of SO_2 ; on the contrary, sulfur would tend to precipitate as sulfates (Symonds et al., 2001 & 2003).

The complex interplay of redox buffers described by Giggenbach finds quantitative application in the concept of gas scrubbing. While Giggenbach modelled the thermodynamic equilibrium framework of gas-fluid-rock interactions, Symonds et al. (2001) explored how the interaction between magmatic gases and hydrothermal systems acts as a true chemical “filter”. According to Symonds and co-workers, scrubbing is not merely a redox conversion, but a process of selective removal, involving the sequestration of more soluble and reactive gases, such as HCl, HF, and SO₂ itself, which are “washed out” and retained by the liquid phase, thereby drastically altering the ratios of species that ultimately reach the surface.

2.3.3: Behind the mask of the scrubbing

The concept of scrubbing, a process modelled through numerical simulations by Symonds et al. (2001), arises from the observation that volcanic eruptions are not always anticipated by increasing SO₂ release; according to the authors, this is due to the fact that many volcanic edifices possess aquifers that “wash out” magmatic gases, masking their effect at the surface (Symonds et al., 1994, 2001 & 2003), at least until the onset of dry pathways through which magmatic fluids can travel to the surface: only in the absence of water does the magmatic signature become evident.

To demonstrate the action of scrubbing on magmatic gases, the authors performed various thermochemical simulations, starting from a baseline case of a mixture of magmatic gases at 915°C with air-saturated water at 25°C, in which the gas:water ratio was varied from 0.0002 to 100 while keeping the pressure constant at 0.1 MPa. From this baseline model, further simulations were conducted by varying some parameters in each case.

More specifically, the simulation involves two components, combined in different proportions:

- Water (1 kg) at 25°C and 0.1 MPa;

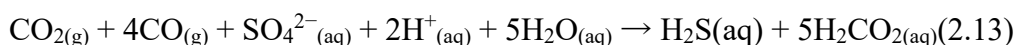
- A mixture of ‘magmatic’ gases (100 kg) at 915°C, consisting of:
 - Major components (> 1%): H₂O (88.87%), CO₂ (7.07%); H₂ (1.54%); SO₂ (1.15%); H₂S (1.12%);
 - Minor components (1-0.1%): HCl (0.59%), CO (0.16%);
 - Trace components (< 1%): S₂ (0.08%), HF (0.04%).

The gases are gradually added to the water in increasing amounts, starting from 0.0002 kg. The overall effect of injecting ‘magmatic’ gases into the water is a gradual increase in the solution’s temperature, causing an originally liquid phase to evolve into a two-phase liquid + gas system, and eventually into a gas-dominated single phase. As the temperature rises, the pH decreases. At the end of the simulation, temperature exceeds 800°C, reaching 900°C, while the pH reaches –0.5.

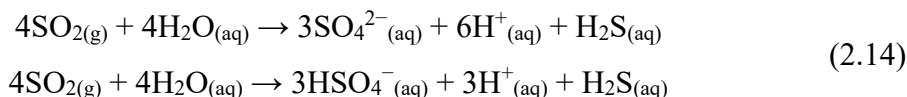
Different scenarios can be identified in liquid-dominated, liquid + gas, and gas-dominated environments.

Liquid-dominated phase. With the gradual increase of the gas:water ratio, as already mentioned, there is a gradual rise in temperature and a drop in pH. All gaseous species are dissolved in the water, while sulfur species precipitate as elemental sulfur starting from a gas:water ratio of 0.008. Under these conditions, sulfur precipitation is more effective than hydrolysis in removing SO_{2(g)}/H₂S_(g) from the gas mixture. The major scrubbing reactions are:

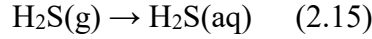
CO(g)/CO₂(g) Scrubbing



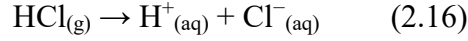
SO_{2(g)} Scrubbing



H₂S_(g) Scrubbing



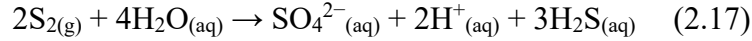
HCl_(g) Scrubbing (pH > 1)



HF_(g) Scrubbing (a: < 0.003 gas:water; b: > 0.003 gas:water)



HF_(g) Scrubbing



This simulation replicates the injection of magmatic gases into a volcanic aquifer, which will dissolve into the water, including poorly soluble gases such as CO₂. An example of this phenomenon is the drop-in soil degassing of CO₂ observed at the Mammoth Mountains during the thaw period (McGee and Gerlach, 1998). The simulation in question also applies to observations in volcanic lakes, where the injection of magmatic gases deposits sulfur, facilitated by the pH drop and temperature increase (Brantley et al., 1987; Reyes, 1991; Rowe et al., 1992; Rowe, 1994; Campita et al., 1996; Symonds et al., 2001).

Liquid + gas phase. When the gas:water ratio increases from 0.008 to 1.7 and the temperature reaches 106°C, the system evolves into the liquid + gas coexistence field. Variations in pH and temperature become more drastic, causing the less soluble gases (CO_{2(g)}, H₂O_(g), H₂S_(g), N_{2(g)}) to separate from the liquid phase. The gas composition evolves to H₂O_(g)-CO_{2(g)}-H₂S_(g), to which 10-4% of HF_(g) and HCl_(g) are added, and these continue to increase, approaching magmatic values.

When pH < 1 and gas:water > 0.4, the low solubility of HCl in acidic fluids causes it to exsolve more rapidly, and its scrubbing reaction shifts to the left. Both gases thus reach almost magmatic levels when the system returns to a single gas-dominated phase. For gas:water < 0.07, the composition is CO_{2(g)}-H₂O_(g)-H₂S_(g)-

$\text{N}_{2(g)}$, while when gas:water > 0.07, the composition becomes $\text{CO}_{2(g)}$ - $\text{H}_2\text{S}_{(g)}$ with minor $\text{HF}_{(g)}$ >> $\text{HCl}_{(g)}$ and trace $\text{SO}_{2(g)}$; however, HCl significantly exsolves from the residual acidic fluid. Throughout this process, the reaction with the rock is neglected.

According to Symonds et al. (1994, 2001, 2003), the first composition is typical of cold emissions, such as those at the Mammoth Mountains, while the latter are more consistent with the hydrothermal emissions of Cascades and Aleutian Arc volcanoes, which show the effect of a magmatic component affected by scrubbing by deep (150-300°C) and shallow waters.

Gas-dominated phase. When the gas:water ratio > 1.7, the system enters a univariant domain dominated by gas. $\text{SO}_{2(g)}$ increases, and further gas addition causes the temperature to rise, making the magmatic signature evident in the gas component, so the emissions become a mix of steam and magmatic gases.

The effect, according to Symonds, replicates the composition of high-temperature fumaroles (600-830°C) observed at St. Helens between 1980 and 1982. The terminal phase of the simulation demonstrates that in a volcanic system, magmatic gases can reach the surface only through dry pathways. The absence of the liquid phase suppresses scrubbing, which therefore acts as a filter, or a mask.

Among the various simulations conducted by Symonds et al. (2001), the most interesting is the one that involves not only water and gas, but also the rock itself, represented in the simulation by andesite.

The initial mixture is 1 kg of water + 0.1 kg of gas, to which 0.001-100 g of andesite is gradually added, representing the chemistry typical of convergent-margin magmas. The overall effect is an increase in temperature to approximately 90°C, a decrease in $\text{HF}_{(g)}$ and $\text{H}_2\text{S}_{(g)}$, and, if the reaction with the rock is pervasive and prolonged, also a decrease in $\text{CO}_{2(g)}$, while $\text{H}_{2(g)}$ increases.

Among the first effects observed is that the increase in pH resulting from the reaction with the rock causes native sulfur to generate $\text{H}_2\text{S}_{(g)}$; this event leads to an increase in H_2 . However, with the further addition of rock, H_2S reverses its growth trend and reacts to form pyrite (Py) (Warr, 2021). Hematite (Hem) is

generated when rock interaction with rock increase, (Warr, 2021). Consequently, the addition of rock to the gases causes the removal of HF(g), triggering the deposition of Al-fluorides, then, fluorite (Flr) and then fluorapatite (F-Ap, adapted from Warr, (2021)). The increasing of rock interaction removes CO₂, yielding calcite (Cal) (Warr, 2021), while SO₂ is also removed by adding alunite (Alu) and anhydrite (Anh) (Warr, 2021). This precipitation causes all reactions that consume SO₂ (g) to produce sulphate, consuming further SO₂ (g). Ultimately, the fluid consists solely of H₂O(g) and minor quantities of N₂ (g). Interaction with the rock causes HCl to be consumed as well. Overall, the interaction between SO₄-Cl-acid fluids and andesite results in a sequence of mineral phases associated with alteration facies argillitic, sericite and propylite aforementioned. (Symonds et al., 2001).

After what we have seen, it is natural to ask the inevitable question: which gas reaches the surface?

An initial response provided by the simulations of Symonds et al. (2001) simulations may be as follows: CO₂ and H₂S are likely to reach the surface. HF is scavenged by the rocks. If gas ascent is slow and allows greater interaction with the rock, H₂S may also be affected, forming sulfides and disappearing from the gases recorded at the surface. CO₂ is normally conservative, but if the interaction with the rocks becomes more prolonged it can be lost too, due to the formation of calcite. Symonds et al. (2001) suggest H₂ depends on the redox reactions that influence the sulphur species, the temperature, the redox state of the magma and the pH of the system. However, according to Akaku et al. (1991), the speed of the reactions between H₂, SO₄²⁻ and H₂S could be slow enough for H₂ to escape. SO₂ and HCl can also be eliminated in low-temperature wet systems. These gases survive only when they rise rapidly or when there is no water, i.e. in conditions of high temperature and high acidity, such as acidic residual fluids in the liquid + gas phase. In this regard, the appearance of sulphur volcanoes at Poás, immediately after the drying up of a crater lake (Oppenheimer, 1992), could be linked to this dynamic.

Increasing pressure has the effect of extending the liquid phase towards higher temperatures, lowering the pH, making SO₂ and HCl less soluble (Symonds et al., 2001). The result is that these gases are easier to detect in the case of SO₄-acidic, hot and high-pressure fluids. Another way to produce such conditions, without requiring high pressure, is to inject more gas than the reactions can consume. However, the same authors suggest that these fluids have a strong altering effect on the rock (in the pH range 3-7), so they would have a short life. The reaction with the rock limits the development of SO₂ and HCl, as the former precipitates as sulphates and the latter affects the pH. It is therefore assumed that hydrothermal fluids that have interacted with the rock for a long time produce little or no SO₂ and HCl.

The results of Symonds et al., (2001) were confirmed by Marini & Gambardella (2005), who used the EQ3/6 package to simulate the injection of magmatic gas into water at 0.1 MPa. Their models show that as long as the environment remains hydrated, the emission of acidic gas species is strongly suppressed.

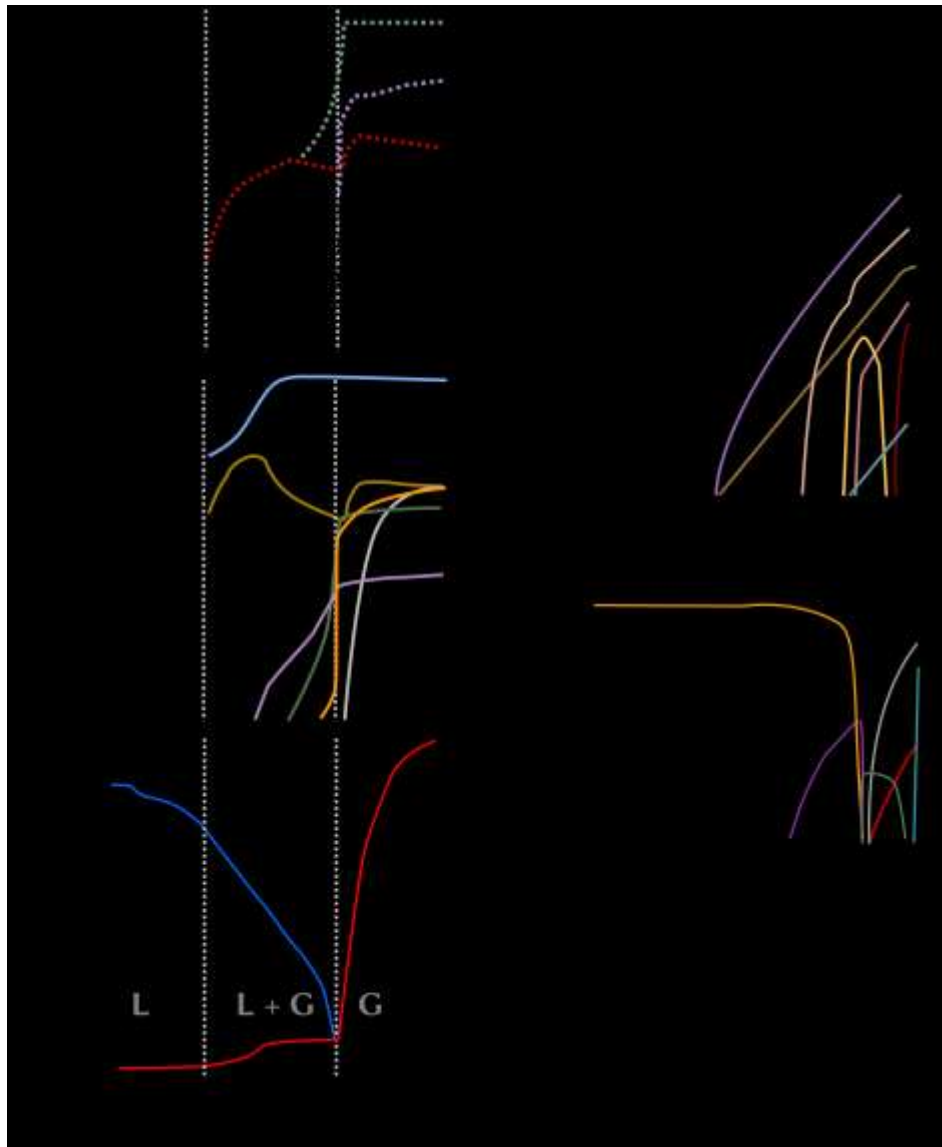


Figure 2.14. Gas species evolved from liquid in simulations carried out by Symonds et al., (2001). Left: water ($T = 25^{\circ}\text{C}$) + magmatic gases ($T = 915^{\circ}\text{C}$); Right: simulation with andesite. For further details and mineral symbols see text. Modified from Symonds et al., 2001.

Di Napoli et al. (2016) also included gas-water-rock interaction, finding good agreement with actual data on hydrothermal fluids and surface gases (obtained in Iceland). The model shows how the modelled gas varies with temperature and the degree of interaction with the hydrothermal system: at low temperatures ($\leq 80^{\circ}\text{C}$) and under conditions of strong scrubbing, the gas is dominated by CO_2 , while at higher temperatures it becomes richer in H_2O and H_2S . They also highlight how the

aqueous composition evolves along the “maturation” path: from young, acidic, Mg-rich waters to mature, salt-rich Na-Cl brines, consistent with many natural occurrences. They also integrate the effect of interaction with rock (dissolution, alteration), making the simulations more realistic.

According to Symonds et al. (2001) Tassi et al., (2013; 2016b and 2018), scrubbing prevents significant SO₂ and HCl until anhydrous pathways open up; therefore, the absence of SO₂ does not rule out degassing. Its reappearance indicates the presence of anhydrous pathways or reduced scrubbing efficiency (Symonds et al., 2001).

Symonds et al. (2003) identify two levels at which scrubbing occurs: deep and shallow. Hydrothermal water (150-350 °C) acts as the first filter, whilst shallow meteoric water acts as the second, significantly altering the gases. This double filtering process may explain the absence of acidic gases in some volcanoes. This scenario is documented at Domyo volcanic complex (Andes), where the lack of acidic species (SO₂ and halogens) points to efficient gas scrubbing processes by a shallow and a deep aquifer system (Tassi et al., 2016b).

If the hydrothermal system filters the gases, allowing mainly CO₂, H₂S (and H₂O) to pass through (Symonds et al., 1994, 2001 & 2003; Tassi et al., 2013), can we deduce from surface emissions if there is a change at depth, if the heat source (magmatic intrusion, magma chamber) is degassing?

To investigate these processes and look beyond the mask of scrubbing, gas ratios such as H₂O_(g)/CO_{2(g)}, SO_{2(g)}/CO_{2(g)}, CO_{2(g)}/HCl_(g), SO_{2(g)}/H₂S_(g), H₂S_(g)/CO_{2(g)}, and HCl_(g)/HF_(g) are used. These can help to frame the drying-out process that a hydrothermal system undergoes when it receives a new magmatic contribution, triggering gas-water and gas-water-rock reactions, depending on the rates of ascent. Similarly, the HCl/SO_{2(g)} ratio can monitor surface systems characterised by low pH (Symonds et al., 1994, 2001 & 2003).

Scrubbing can cause mineral alteration affecting the stability of the volcanic edifice and the likelihood of collapses or hydrothermal eruptions (Symonds et al., 2003). Geochemical modelling (EQ3/6, reaction path) and field data (fumaroles,

waters, isotopes) show how scrubbing masks actual magmatic degassing and how integrated monitoring is needed, considering CO₂, H₂S, other less affected gases and chemical parameters of the waters.

In situ observations, modelling and geophysical interpretation will enable us to better predict the evolution of volcanic systems and the associated risks (Marini & Gambardella, 2005).

The effect of scrubbing is well evident in volcanic gas datasets collected at many volcanoes worldwide. Aiuppa et al., (2005 & 2006), in a study on H₂S fluxes from Sicilian volcanoes (Etna, Stromboli, Vulcano), found a wide range of SO₂/H₂S ratios that they explained as due to variable extents of magmatic gas scrubbing a processing, especially at Vulcano island (Chiodini et al., 1993; Di Liberto et al., 2002; Aiuppa 2005 and 2006).

A study on Redoubt Volcano (Alaska) prior to the 2009 eruption showed high CO₂ emission values (up to $\approx$ 9,018 tonnes/day) and a very high C/S ratio ($\geq$ 30) (Werner et al., 2012). This was interpreted by the authors as SO₂ scrubbing by surface aquifers, resulting in the expected absence of SO₂ from surface emissions.

Hurwitz & Anderson (2019) studied temporal variations in the concentration of sulphates and chlorides in groundwater from Kīlauea (Hawaii) between 2003 and 2011, finding that these variations were correlated with changes in magmatic and volcanic activity. They estimated that, in 2006, up to approximately 40% of the sulphur (SO₂) and chlorine (HCl) degassed from the magma may have been removed from the aquifers by scrubbing, thus loading the groundwater with sulphates and chlorides.

Another example is provided by Tamburello et al. (2019), who studied the La Soufrière system (Guadeloupe), subject to hydrothermal unrest up to two decades prior to the study. Emissions from the central vents, directly connected to the volcanic conduit, showed higher CO₂/SO₂ and H₂S/SO₂ ratios than peripheral emissions, suggesting SO₂ scrubbing within the hydrothermal system at a depth of 80-100 m. In contrast, peripheral emissions appeared to be low in both SO₂ and H₂S, a phenomenon attributed to the deposition of sulfides in the system.

2.4: Unrest

Hydrothermal systems can occasionally depart from their mild, background activity to enter phases of heightened seismicity, deformation and degassing, referred to as unrest. Unrest is a complex process that can be initiated by a variety of processes.

2.4.1: Breaching the system

In the two-domain model of hydrothermal systems (Fournier, 1999; 2007), the deep magmatic body is confined within the plastic zone, whose rheological behavior seals fractures; the deposition of mineral phases further strengthens this seal. As long as the seal remains intact, magmatic fluids are trapped at depth; its rupture, conversely, allows rapid transfer of mass and energy toward the volcano surface. Unrest at hydrothermal volcanoes have frequently been associated with failure of the seal. Seal breaching may occur through two main types of processes (Fournier, 2007):

- Pressurization of the plastic zone, caused by
 - accumulation of magmatic fluids beneath the seal, resulting in increased stresses acting on the carapace;
 - deformation induced by the arrival of new magmatic batches, capable of temporarily changing the mechanical behavior of the rock from plastic to brittle, thereby shifting the brittle-plastic transition to greater depths (Fournier, 1999; 2007).
- Depressurization of the brittle zone, due to
 - collapse of part of the volcanic edifice or seismic events, which reduce the overburden load and may trigger degassing of the magmatic body;

- cooling of the brittle domain which, if extending down to the self-sealed zone, may promote thermal contraction and fracturing.

Once a breach is formed, magmatic fluids can migrate upward, interacting with cooler fluids and the surrounding host rocks through the reactions described above. Seal breaching is accompanied by a pressure drop, causing fluid expansion and additional overpressure that drives upward-propagating fracturing (Fournier et al., 1999 & 2007). The seal follows cycles of sealing and breaching; some of these episodes are classified as *major* by Fournier (2007). These events can propagate their effects to the surface, with significant consequences (Fournier, 1999; 2007), beginning with seismic activity associated with fracturing processes.

Surface manifestations span a wide range of phenomena, from various forms of volcanic/non-volcanic unrest to the initiation of eruptive activity (Fournier, 1999; 2007; Rouwet et al., 2014; Gottsmann et al., 2017; Jasim et al., 2018; Pritchard et al., 2019).

2.4.2: *Unrest: definitions and uncertainties*

Unrest can be defined as a measurable deviation from the background state of a volcanic system (Philipson et al., 2013; Rouwet et al., 2014), recognizable through anomalies in geophysical, geochemical, or geodetic signals, and associated with an increase in volcanic hazard and risk. Unrest is therefore not only a geological phenomenon, but also a *social*, *economic*, and *regulatory* one, involving exposed populations, the scientific community, and civil protection authorities in volcanic risk management (Gottsmann et al., 2017; Bretton et al., 2018).

Rouwet et al. (2014) and Pritchard et al. (2019) distinguish between magmatic and non-magmatic unrest, considering them as different phases of a single event that, at different times, affects distinct components of the volcanic system. This results in a variety of manifestations, each characterized by different processes and sources of hazard.

The distinction between these two types of unrest is not always clear-cut (Rouwet et al., 2014; Moretti et al., 2020). A key challenge lies in identifying signals of magma migration (“magma on the move” sensu Rouwet et al., 2014), which represent a prerequisite for a potential eruptive event and are crucial for discriminating between magmatic and non-magmatic unrest. However, this distinction is intrinsically uncertain. In this context, probabilistic tools such as bayesian event trees are essential, as they allow the integration of multiple datasets, the evaluation of alternative scenarios, and the estimation of risk under uncertainty (Rouwet et al., 2014; Sandri et al., 2017). These tools represent the possible evolutionary paths of a volcanic event from the current system state, assigning conditional probabilities to each scenario and enabling quantitative risk assessment in the presence of uncertainty (**Fig. 2.15**).

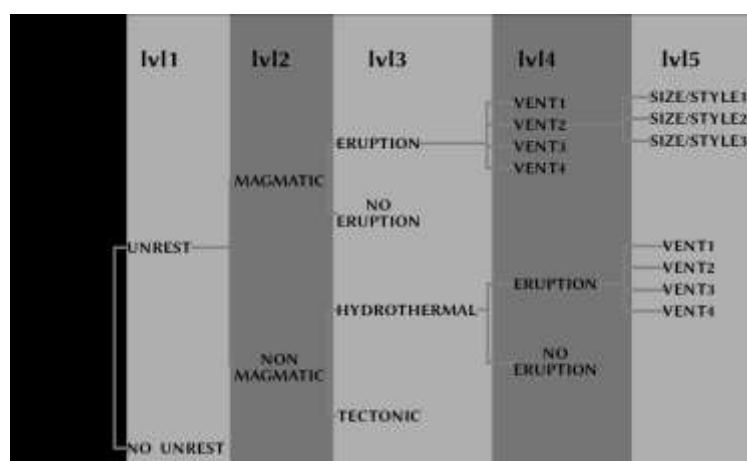


Figure 2.15 Bayesian event tree modified from Sandri et al., (2017). For further details, see text.

It should be emphasized that unrest does not necessarily lead to eruptive activity (Gottsmann et al., 2017; Jasim et al., 2018; Pritchard et al., 2019). For example, Turrialba entered a phase of unrest in 2001 and erupted only in 2016, after fourteen years of progressively intensifying phenomena (Rouwet et al., 2017). Conversely, a pre-eruptive state may develop with clear signals of an imminent eruption only a few hours in advance, as observed at Kelud in 2014 and Calbuco in 2015 (Romero et al., 2016; Cassidy et al., 2019). Such volcanoes are classified by Stix et al. (2018) as fast volcanoes.

As noted by Gottsmann et al. (2017), citing Stirling (2010): “*The scientific interpretation of volcanic unrest is surrounded by substantial uncertainty, ambiguity and ignorance regarding causes and eventual outcome. Since the contributing subsurface processes cannot be directly observed, volcanic unrest is likely among the least understood phenomena in volcanology [...] Ambiguity, uncertainty and ignorance have impact on probabilistic forecasting of duration, spatio-temporal evolution, causal relationships between sequential events and outcomes of unrest episodes [...]*”.

Consequently, there is no universal or unambiguous threshold for defining unrest, particularly with regard to distinguishing between magmatic and non-magmatic unrest. The relevance and interpretation of signals depend on the volcanic system, the monitoring networks in place, and the interpretative frameworks adopted by observers (Rouwet et al., 2014; Gottsmann et al., 2017; Sandri et al., 2017). Unrest signals are often ambiguous and non-unique, as subsurface processes cannot be directly observed. Their evaluation depends on expert judgment, available data, and local context, introducing an unavoidable degree of subjectivity. This may lead to divergent interpretations and potential false alerts, in the absence of a single global standard.

2.4.3: Degassing and unrest

Symonds et al. (2001) and subsequent studies have shown that increasing injections of magmatic gases is a recurrent driver of unrest. Degassing leads to a drying-out process driven by rising temperatures (Chiodini et al., 2016). As a result, an initially liquid-dominated phase evolves into a liquid + vapor system, marking the onset of drying out. If this process continues, the liquid phase is progressively exhausted, leaving a gas-dominated system. These three stages can be associated with three fluid ascent regimes, occurring along wet paths (liquid-dominated), dry paths

(gas-dominated), and a transitional regime characterized by drying out (liquid + gas), during which the first gas exsolution from the liquid phase takes place.

The ascent of fresh magma from greater depths to shallower levels inevitably results in increased gas release, with CO₂ representing the most sensitive and earliest gaseous signal of this process (Symonds et al., 2001, 2003; Aiuppa et al., 2004, 2007, 2008). The associated transition from a “wet” to a progressively “dry” hydrothermal system, driven by magma intrusion and related degassing, can be monitored through variations in gas ratios involving species with contrasting solubilities in water, specifically poorly soluble species such as CO₂ and H₂S versus highly soluble species such as SO₂ and HCl. These ratios reflect the evolution of fluid pathways and the progressive loss of water from the system. It should be noted that H₂S can also be removed through reactions with the host rock.

Once dry paths are established, SO₂ and halogens (Tassi et al., 2016b and 2023)) detection at the surface becomes more pronounced, indicating a more direct connection between the magma and the atmosphere. SO₂ therefore represents a key marker of systems evolving toward pre-eruptive conditions. Symonds et al. (2001, 2003) suggested that ratios such as H₂O/CO₂, SO₂/CO₂, CO₂/HCl, SO₂/H₂S, H₂S/CO₂, and potentially HCl/HF can be used to monitor the drying-out process. The HCl/SO₂ ratio has also proven useful in probing drying hydrothermal systems characterized by acidic fluids (Symonds et al., 2001). Several of these ratios have been widely applied in the literature and are now considered pre-eruptive markers, particularly CO₂/SO₂, H₂S/SO₂, and CO₂/H₂S (Aiuppa et al., 2007, 2008, 2021).

Isotopic ratios can also serve as pre-eruptive markers, particularly when long-term background values are available. The $\delta^{13}\text{C}$ -CO₂ may vary in response to magmatic degassing; however, its interpretation must consider contributions from mantle-derived CO₂, subducted carbonates or crustal magma assimilation by magma (Tassi et al., 2018), and organic matter, making the geodynamic setting crucial (Fischer & Chiodini, 2015). Similarly, magmatic intrusions and seismic activity are often associated with increases in the ³He/⁴He ratio. Because ³He is of primordial origin and resides exclusively in the mantle, and because it is highly incompatible

relative to solids, each melting event in the mantle leads to a permanent loss of ^3He . An increase of ^3He relative to ^4He , produced in the crust by radioactive decay of U, Th, and Pb, can therefore indicate magma ascent under appropriate conditions. This ratio is commonly expressed as R/R_a , where $R = ^3\text{He}/^4\text{He}$ and R_a represents the atmospheric value. Symonds et al. (2003) pointed out that although R/R_a can be an effective marker, some volcanoes in the Cascades and Aleutians already exhibit near-magmatic R/R_a values, limiting the magnitude of further increases associated with new magma input. Examples include the increase in R/R_a observed at Augustine Volcano between 1976 and 1986, and the suggestion that similar increases could occur at Mount Shasta, Mount Rainier, and Makushin, where R/R_a values range from 2.76 to 5.78, compared to values of 7-8 at other volcanoes studied. Additional examples of the use of this ratio include its role as a precursor to the 2011-2012 submarine eruption at El Hierro (Canary Islands; Padrón et al., 2013), as an indicator of volcanic activity at Etna (Paonita et al., 2016), and as a pre-eruptive marker prior to the 2021 eruption of Cumbre Vieja (Padrón et al., 2022). Changes in R/R_a were also recorded at Nea Kameni fumaroles in 2011-2012 unrest and at Planchón-Peteroa-Azufre Volcanic Complex (Chile-Argentina) in 2010-2015 (Tassi et al., 2013 and 2016a).

Among gas ratios, CO_2/SO_2 is one of the most widely used markers. Aiuppa et al. (2007) demonstrated its effectiveness during Etna's activity between 2005 and 2006. Continuous observations showed that the CO_2/SO_2 ratio in gases emitted from the main crater could discriminate between degassing of magma already present in the conduit and the ascent of new magma.

Aiuppa et al. (2007) analyzed real-time CO_2/SO_2 ratios in the plume of Stromboli during the pre-eruptive phase and the 2007 eruption, showing that significant variations preceded the onset of effusive activity, as previously observed at Etna. During mid-2006 quiescence, CO_2/SO_2 ratios were relatively low and stable, whereas in early 2007 rapid and pronounced increases occurred, reaching values up to 26 compared to background values of ~ 0.9 -5. These peaks were interpreted as evidence for ascent of CO_2 -rich gases exsolved from deep magma at intermediate

depths (~1-3 km) and transferred toward the surface. Similar variations in CO_2/SO_2 and $\text{H}_2\text{S}/\text{SO}_2$ ratios prior to the 2010 Merapi eruption were interpreted as signals of deep degassing associated with fresh, likely mafic magma input (Pritchard et al., 2019).

Chiodini (2009) demonstrated that the CO_2/CH_4 ratio is a particularly sensitive tracer of magmatic contributions to hydrothermal systems, as magmatic gases exhibit CO_2/CH_4 ratios orders of magnitude higher than hydrothermal fluids. Long-term time series from Campi Flegrei, Mammoth Mountain, Panarea, and Nisyros show that rapid increases in this ratio coincide with unrest phases. At Campi Flegrei, CO_2/CH_4 variations closely correlate with vertical ground movements, suggesting that both reflect changes in hydrothermal fluid pressure driven by deep magmatic degassing. These processes can induce deformation and seismicity even without magma reaching the surface, indicating that unrest during apparent quiescence is often dominated by fluid transfer rather than imminent eruption.

What should therefore be expected during unrest? Gas emissions may manifest in different ways. In basaltic volcanoes such as Etna and Villarrica, degassing may occur directly at a magma-atmosphere interface (open-conduit volcanoes), whereas in closed-conduit systems emissions are dominated by fumaroles, thermal springs, crater lakes, or diffuse soil degassing. This diversity strongly influences the interpretation of geochemical signals (Pritchard et al., 2019). In this context, long-term geochemical monitoring and the generation of geochemical and flux maps can provide a key tool for distinguishing transient unrest signals from baseline degassing behavior (Viveiros, et al., 2010; 2015; 2017 and 2024).

As previously noted, CO_2 , which exsolves at higher pressures than SO_2 (Wallace et al., 2015), often represents the earliest signal of magma ascent or injection, typically reflected by high CO_2/SO_2 ratios. In contrast, SO_2 is favored under low-pressure and high-temperature conditions, and its appearance at the surface often requires the development of dry paths through the hydrothermal system. Consequently, increases in SO_2 flux are commonly interpreted as indicative of shallow

magma or advanced unrest, as exemplified by the 1991 Pinatubo eruption (Pritchard et al., 2019).

Gas ratios, particularly CO_2/SO_2 , have therefore been proposed as valuable tools for monitoring volcanic systems both in contexts dominated by strong hydrothermal scrubbing (e.g., Poás) and in open-conduit volcanoes. Because many volcanoes experience prolonged unrest with magmatic involvement, these ratios are especially effective for detecting hazardous changes within an already active system.

Pritchard et al. (2019) emphasize that the presence of typically magmatic gases such as SO_2 and HCl does not necessarily imply magma ascent. These species may also be released through convection within the plumbing system or by crystallization and late-stage degassing of stagnant magma. Kawah Ijen represents a key example of this ambiguity: despite long-standing unrest and intense magmatic gas input, its activity remains predominantly phreatic rather than magmatic, producing sulfur deposition, an acidic crater lake, and flows of molten sulfur. Similar conditions were found in El Chichón during 1992 (Oppenheimer 1992).

According to Pritchard et al. (2019), in caldera systems or volcanoes reawakening after long periods of quiescence, early surface degassing may be dominated by diffuse CO_2 emissions. In such contexts, molar ratios and isotopic variations, such as $\delta^{13}\text{C}\text{-CO}_2$ and $^3\text{He}/^4\text{He}$, become particularly important. $\delta^{13}\text{C}$ values between -4 and -8‰ and $^3\text{He}/^4\text{He}$ ratios >3 Ra are generally indicative of a deep magmatic source (Symonds et al., 2003). Additionally, variations in redox-sensitive species (CO , H_2 , CH_4) may reflect temperature changes in the system, potentially linked to magmatic intrusions.

Overall, the study of volcanic gases provides crucial insights into the evolution of magmatic and hydrothermal systems but requires integrated interpretation with geophysical and structural data. Gas signals are inherently non-unique and must be evaluated within the specific context of each volcano to be effectively used in forecasting unrest and eruptions (Pritchard et al., 2019).

2.4.4: Hydrothermal activity and unrest

Fumaroles of a hydrothermal system begin to show changes in the composition of their emissions and in heat fluxes, deviating from the established baseline (where applicable) (Rouwet et al., 2014 & 2017; Pritchard et al., 2019). This condition is an unrest. However, the key question arises: is this a non-magmatic unrest or a magmatic unrest? This is where the ambiguity of hydrothermal activity lies, and the considerations discussed earlier for Kawah Ijen apply once again. This ambiguity is precisely what makes volcanic unrest difficult to define.

While it is true that some large hydrothermal systems, particularly those of large silicic calderas (e.g., Campi Flegrei, Long Valley, Yellowstone), are inevitably linked to an underlying magmatic heat source, it is also true that other systems appear to lack such coexistence between an extensive hydrothermal system and a shallow magma, as is the case, for example, at Hekla (Pritchard et al., 2019).

It might therefore seem intuitive to assume that, if a volcanic system lacking evident hydrothermal activity, enters a phase of unrest, such unrest must necessarily be of magmatic origin. However, Pritchard et al. (2019) clearly demonstrate that this assumption is not always valid. These are what the authors refer to as “blind systems”, namely hydrothermal systems that do not develop due to prohibitive permeability conditions, forcing magmatic fluids to deviate and migrate over long distances. Under such circumstances, hydrothermal activity, typically considered a proxy for unrest, may be entirely absent.

The case of Kawah Ijen highlights how surface waters (in this case crater lakes, but the same applies to thermal springs and rivers) constitute important indirect indicators of deep-seated processes, as their chemical composition reflects the interaction between volcanic fluid inputs, meteoric waters, and the host rocks of the volcanic edifice. Significant variations in the chemistry of crater lakes and thermal waters are often associated with changes in the composition or flux of magmatic

fluids and therefore represent valuable tools for volcanic monitoring (Rouwet et al., 2014, 2017; Pritchard et al., 2019).

Finally, variations in crater lake water levels and in surface water fluxes may accompany phases of unrest, as documented in historical cases such as El Chichón and Poás. These changes can also be monitored using indirect geophysical methods, including self-potential, microgravity, and electrical resistivity measurements (Rouwet et al., 2014, 2017; Pritchard et al., 2019).

2.4.5: Temperatures and unrest

The magmatic unrest requires *magma on movement* (to quote Rouwet et al., 2014). When there is no magma, the unrest is non-magmatic. There are volcanic systems that show high-temperature fumaroles but, paradoxically, seem to show no magma movement. Pritchard et al., (2019) point out that some of these systems have been showing such values for decades, usually accompanied by ground deformation and seismicity (Long Valley and Yellowstone, to name two); these systems are associated with stagnant magmatic bodies that are cooling or subject to convection, so they could be defined as dormant. However, temperature is the most ambiguous of the parameters that can distinguish magmatic unrest from non-magmatic unrest. If a fumarolic field begins to increase in temperature, above what thermal threshold can we start to talk about magmatic unrest, especially if the changes are transient? For this reason, Pritchard et al. (2019) consider the thermal signals from fumaroles to be a source of doubt, while Sandri et al. (2017) set a sort of watershed at 300°C, whereby higher temperatures are indicative of magmatic unrest, while temperatures up to 200°C may be associated with non-magmatic unrest.

2.4.6: Seismicity and unrest

Seismicity, and in particular swarms of volcano-tectonic earthquakes (VT), are one of the first signs of unrest, especially in dormant volcanoes; above all, these earthquakes appear before the signs of migrating magma and do not always imply an eruption (Pritchard et al., 2019). Therefore, VT alone are not an unequivocal indicator of magmatic unrest, so, as with other parameters, other phenomena must be considered. McNutt (1996) developed the Generic Volcanic Earthquake Swarm Model (GVESM), which structures a well-defined sequence of seismic events consisting of an increase in VT, followed by quiescence and a renewed increase in seismicity with long-period (LP) events, and tremors. These represent transient and sustained fluids movements (magma, gas, water) at shallow depths (Pritchard et al., 2019). If the entire GVESM sequence were to be observed, then the probability of magmatic unrest would increase, but Pritchard and colleagues point out that the sequence is never complete. In summary, individual VT swarms provide only weak clues, while the combination of event sequences (VT > LP > tremor), variations in the number of small or large events (b-value) and reduced displacement (the cumulative amplitude of ground motion generated by volcanic tremor, normalized to make it comparable) and the appearance of deep LP/ VLP provides a more reliable view of magmatic activity and eruption risk.

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3: METHODS

Results presented in this PhD dissertation stand upon the use of two gas sensing methodologies, which principles and functionalities are described in the following sections.

3.1: The Multi-GAS

The study of volcanic gases relies on a variety of methods, each with its advantages and limitations. Traditional approaches, such as the direct collection of fumarolic gases using Giggenbach bottles, provide highly accurate analysis of gas chemical compositions, and allow the analysis of many different species (Giggenbach, 1975; Shinohara, 2005; Aiuppa et al., 2005), including isotopes (Oppenheimer et al., 2014). However, these methods are time-consuming, require laboratory processing, and can only sample a few fumaroles at a time, making them insufficient for capturing the chemical variability across an entire fumarolic field. Remote sensing techniques, including COSPEC, FTIR, and DOAS (Oppenheimer et al., 2014; Campion et al. 2025), offer real-time monitoring and the ability to observe “bulk” gas emissions over larger areas, yet they generally fail to quantify important components such as CO₂ and H₂S. As a result, key aspects of volcanic degassing, particularly the emission of major greenhouse and toxic gases, often remain poorly constrained.

The Multi-component Gas Analyzer System (Multi-GAS) technique has been developed to overcome some of these challenges (Shinohara, 2005; Aiuppa et al., 2005b). The Multi-GAS has been designed to allow near-real-time measurements of CO₂, SO₂, H₂, and H₂S directly in the field. A variety of prototypes have been assembled by different groups. The unit used in this work (**Fig 3.1**), assembled at the LabVulc laboratory of DiSTeM (Università di Palermo), is commanded by a Campbell Scientific CR6 WiFi data logger, is powered by a LiFe 4S battery, and integrates GPS for positioning. The sensor kit in the Multi-GAS

includes a non-dispersive infrared (NDIR) NG Gascard spectrometer (calibration range, 0-10,000 ppm and a typical accuracy of $\pm 2\%$ of full scale, reported by the manufacturer) from Edinburgh Sensors for CO₂, and three CiTiceL electrochemical sensors for SO₂ (model T3STF), H₂S (model T3H) and H₂ (model T3HYT) (all having 0-200 ppm calibration range and a reported repeatability of $\pm 1\%$ (SO₂-H₂S) and $\pm 2\%$ (H₂) of the signal). Tests made in the laboratory demonstrate that the electrochemical sensors used can quantitatively measure gas concentrations down to ~ 0.5 ppm, while still offering qualitative detection in the 0.1-0.5 ppm range. Tests made with gas mixtures show that all sensors are gas specific except the H₂S sensor, which exhibits ~ 10 -14% cross-sensitivity to SO₂ (this can be compensated for during data post-processing). All sensors are calibrated in the laboratory prior to and after field work using certified standard gases. The system also includes a KVM3/5 Galltec-Mela sensor for measuring temperature and relative humidity and to indirectly estimate H₂O concentrations using the Arden-Buck equation (Buck 1981). Real-time data visualization on both Tablet or Smartphone (iOS, Android) is possible, and data post-processing can be accomplished using the Ratiocalc software (Tamburello, 2015). The unit is managed by an editable setting file, deposited in a MicroSD.

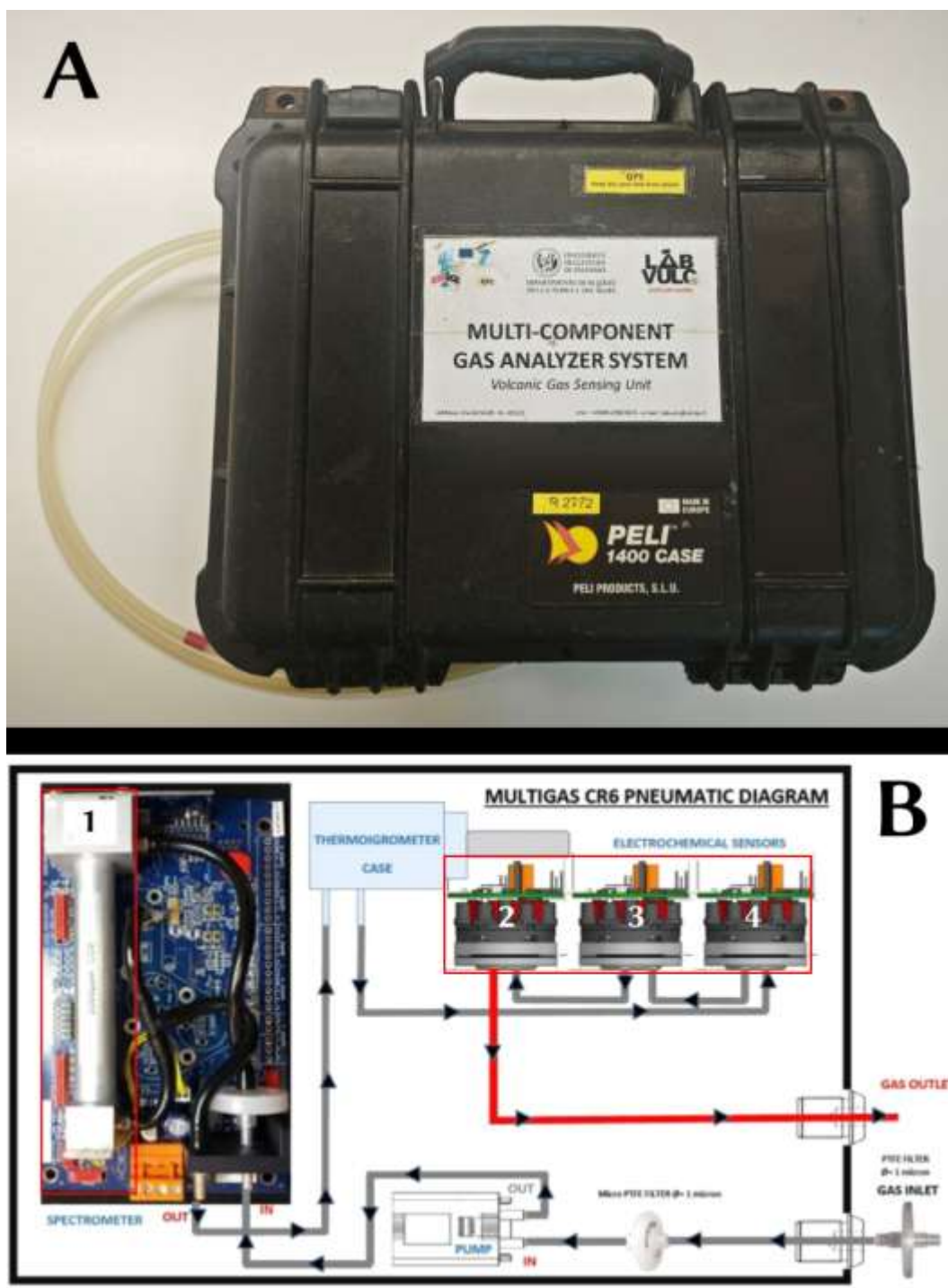


Figure 3.1 A: Multi-GAS portable unit housed in a peli case. B: Multi-GAS Pneumatic diagram. 1: spectrometer (CO₂ 0-10000 ppmv) and electrochemical sensors (H₂S, SO₂, and H₂, 0-200 ppmv).

Each time it is switched on, the Multi-GAS performs a series of basic operations: connection to the GPS network, followed by a warm-up of the sensors. When the data acquisition process begins, a single CSV file is generated in SD card; the file is named YYYYMMDDHHMM.csv, where HHMM indicates the start time of the acquisition. The file stores acquisition date and time, CO₂, SO₂, H₂, H₂S concentrations (ppmv), Rh (%), Patm (mbar), case temperature (°C), battery voltage (V), coordinates and altitude. These data are acquired and stored at a frequency of 1 Hz. The gases start to be flushed through the system, entering the inlet tube at a constant flow-rate of 1.2 l/min, passing through the sensors, and exiting from the output.

The Multi-GAS works in two ways:

- **Permanent mode (Fig 3.2A):** In the permanent mode, the instrument behaves as a fully automated, stand-alone (no operator needed) volcano monitoring device. The permanent mode is ideal for use in continuous (real time) mode, in instrumental volcano networks, or for long-period (days, weeks) field experiments. In the permanent mode, operations are commanded by the data logger using the configuration parameters set in the “settings.txt” in the MicroSD memory card. The acquired data can be transferred using a radio device at the local volcano observatory (3G, 5 GHz WiFi, TCP-IP protocol). The Multi-GAS can operate as either FTP client or FTP server. In the former case, data are sent automatically by the Multi-GAS to a dedicated FTP server. In the latter case, data have to be downloaded manually accessing the Multi-GAS via connection with an FTP client at the FTP server address. Internal time of the Multi-GAS is synchronized automatically via connection with an NTP server. In the field, the instrument has to be installed with external batteries, solar panel, and telemetry system. The unit must be housed inside a waterproof case;
- **Portable mode (Fig 3.2B):** this is specifically designed for campaign mode volcano surveys. The Multi-GAS system is a light (4 kg) compact, field-deployable instrument housed in a compact peli case to provide near

real-time measurements of key volcanic gas species, allowing measurements to be made directly within the volcanic plume or fumarolic emissions, often in proximity to the vent. The inlet is positioned near the fumarole vent at a distance sufficient to avoid sensor saturation. Exposure times of several tens of seconds were typically sufficient to capture compositional variations, although optimal duration depended on the fumarole, as some vents saturated sensors rapidly while others did not. Saturated signals are filtered out and excluded from further processing. Its portability enables rapid deployment across complex or hazardous fumarolic fields, providing high spatial and temporal resolution data that capture the chemical heterogeneity of the system.

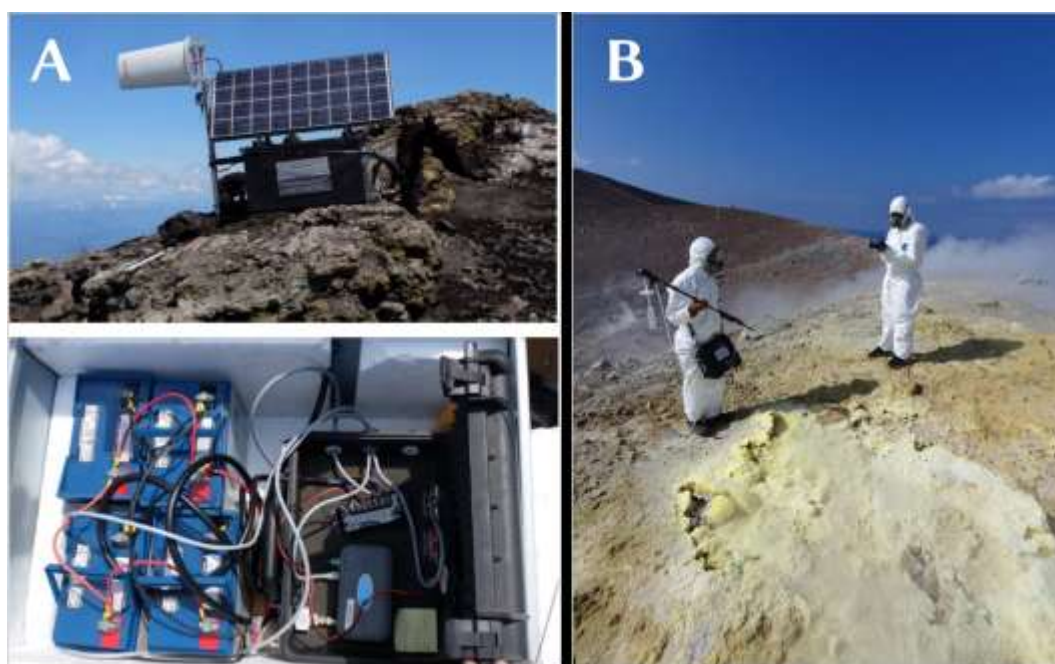


Figure 3.2 **A**: Multi-GAS in permanent mode at the top of Villarica volcano. **B**: Multi-GAS portable unit during a survey at the fumarolic field of Vulcano Island.

The portability of the Multi-GAS allows rapid, high spatial/temporal resolution analysis of a fumarolic field. It also reduces the exposure time to each vent during the acquisition of compositions. Real-time readings allow re-searchers to

identify areas with distinct degassing characteristics, track the distribution of oxidizing versus hydrothermally influenced zones, and detect temporal changes that may indicate evolving volcanic activity.

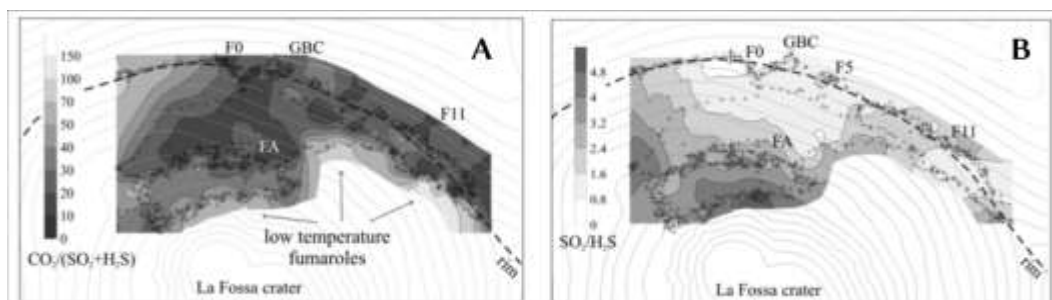
Unlike traditional laboratory-based analyses, the portable system integrates multiple sensors in a single device. This approach makes it possible to rapidly elaborate maps showing the chemical structure of fumarolic systems, identify regions of differing degassing behavior, and detect temporal variations that may signal changes in volcanic activity.

It should however be noted that the Multi-GAS technique, in addition to some advantages, also brings caveats and limitations. Firstly, only a few chemical species are detectable, implying that direct sampling remains the only available method for a more complete, multi-species characterization of fumarole composition. Secondly, the Multi-GAS targets the fumarole atmospheric plume rather than the fumarole itself. Hence, Multi-GAS results can only be representative of source (fumarole) conditions provided atmospheric processes (condensation, oxidation) and reactions have not altered the composition of the gas. While this is generally the case for SO_2 and H_2S , whose abundance ratio is typically preserved for plume ages of seconds to a few minutes, near-vent condensation typically hampers detection of volcanic H_2O . The Multi-GAS also cannot quantitatively resolve gas concentrations below 0.5 ppm, and it is therefore not adequate to the characterization of distal (dilute) volcanic plumes. Cross-sensitivity issue (for H_2S) also exist, see above. It is therefore advisable that the Multi-GAS technique is effectively integrated with direct sampling to match the advantage of real-time monitoring with the need of precise laboratory-based determinations. Table 3.1 provides a comparison of the two methodologies.

Table 3.1 main advantages and limitations of Multigas and Traditional Sampling		
	<i>Multigas</i>	<i>Traditional Sampling</i>
Data acquisition	Near real-time	Delayed (laboratory analysis required)
Temporal resolution	High (continuous measurement)	Low (discrete samples)
Space resolution	High	Low (discrete samples)

Data processing	Nearly immediate	Requires laboratory analysis
Portability	High	Low
Detect rapid changes	High	Low
Chemical characterization	Limited to a few species	Full composition, traces included
Maintenance	Frequent calibration needed	Less frequent
Crossing sensitivity	Yes (eliminated in post-processing)	No
Saturation	Yes (eliminated in post-processing)	No

The first Multi-GAS-based mapping exercise was accomplished at La Fossa Crater on Vulcano Island by Aiuppa et al., (2005). The authors demonstrated for the first time the ability of the Multi-GAS to rapidly explore the chemical diversity of a fumarolic field. They conducted more than 3000 individual readings, revealing a clear spatial pattern: a central zone dominated by high $\text{SO}_2/\text{H}_2\text{S}$ ratio fumaroles, indicative of more oxidizing conditions, and a northern margin where hydrothermal contributions were stronger, as reflected by lower $\text{SO}_2/\text{H}_2\text{S}$ ratios (**Fig. 3.3A and B**). The same authors also analyzed the spatial variability of CO_2/SO_2 ratios in the fumarolic field. Such high-resolution data enabled more reliable estimates of gas fluxes (~ 420 t/d of CO_2 and ~ 4 t/d of H_2S) than previously possible with traditional sampling, while also highlighting areas of the field most sensitive to changes in degassing.



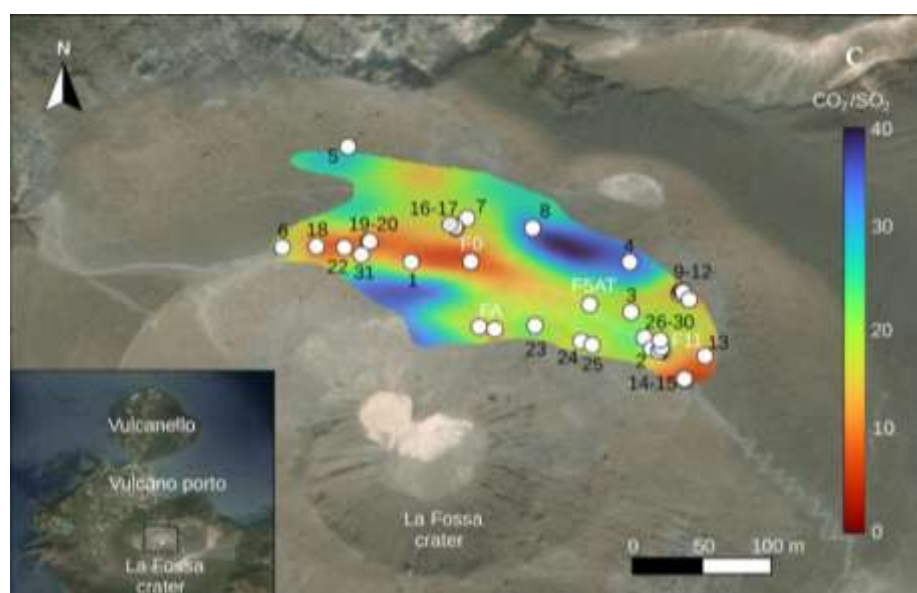


Figure 3.3 Results of the first chemical mapping campaign of CO₂/Sr (A) and SO₂/H₂S (B) ratios carried out at the La Fossa cone fumarolic field, Vulcano Island. C: CO₂/SO₂ ratio variations at the same site in 2021. Figures reproduced from Aiuppa et al., (2005) and Aiuppa et al., (2022).

Aiuppa et al., (2022) used the same mapping technique to characterize the temporal evolution of the La Fossa crater unrest started in 2021. They elaborated novel mapping of the CO₂/SO₂ ratio distribution across the La Fossa Crater fumarolic field, derived from high-resolution, in-situ Multi-GAS measurements. Data revealed a marked chemical heterogeneity, showing that fumaroles emit gases with significantly varying compositions even over short distances (**Fig. 3.3 C**).

The same mapping technique has, over the years, been used elsewhere, such as at Campi Flegrei (Aiuppa et al., 2013; Tamburello et al., 2019) and at Fogo vulcano at Sao Miguel island in the Azores (Aiuppa et al., 2025). Overall, the use of Multi-GAS instruments complements classical and re-mote sensing techniques, providing a versatile tool not only to study volcanic degassing processes and assess emission budgets, but also to generate high-resolution spatial maps of gas compositions, thereby supporting detailed characterization of fumarolic fields and improving the capacity for early-warning and hazard assessment in active volcanic systems. The chemical mapping approach used here is reminiscent of that commonly used (Viveiros et al. 2010; 2017 and 2024) to map diffuse soil CO₂ emissions.

3.2: UV-camera

Ultraviolet (UV) cameras (Bluth et al., 2007; Mori and Burton, 2006) have emerged as one of the most effective remote sensing tools for monitoring volcanic gas emissions in real time (**Fig 3.4**). These instruments operate by exploiting the strong absorption of solar ultraviolet radiation by SO₂ molecules, particularly in the 300-320 nm range.

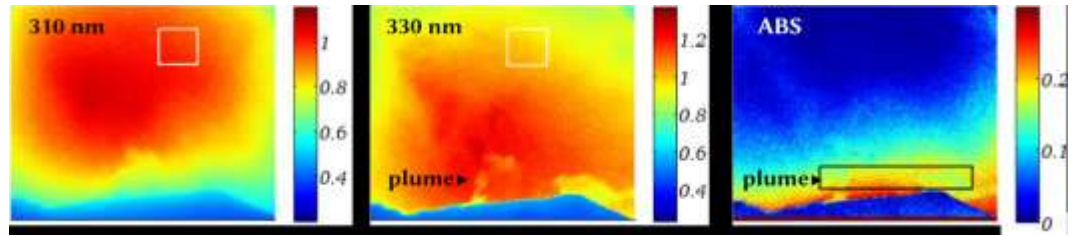


Figure 3.4 Processing of images related to the fumarolic field of Vulcano Island, as captured by a fixed UV camera.

The attenuation of the incident solar radiation as it propagates through a volcanic gas plume can be described by the Lambert-Beer law, which relates the transmitted spectral irradiance E_λ , to the incident spectral irradiance $E_{0,\lambda}$ as:

$$E_\lambda = E_{0,\lambda} \exp[-\sigma(\lambda) N L] \quad (3.1)$$

where $\sigma(\lambda)$ is the absorption cross section of SO₂ at wavelength λ , N is the molecular number density along the optical path, and L is the effective path length through the plume. This exponential dependence forms the physical basis for retrieving SO₂ column densities from measured UV radiation. By capturing images at two distinct wavelengths, typically around 310 nm, where SO₂ absorbs strongly, and 330 nm, where absorption is minimal, UV cameras are able to distinguish gas

absorption from other effects such as scattering by aerosols, ash, or the atmosphere. Taking the ratio of the measured irradiances at these two wavelengths and expressing it in logarithmic form yields a differential absorbance:

$$A = -\log_{10} (E_{310}/E_{330}) - A_0 \quad (3.2)$$

where the constant term A_0 accounts for wavelength-independent contributions arising from instrumental response and broadband atmospheric effects and A represents the differential absorbance associated with SO_2 , an adimensional quantity proportional to the SO_2 slant column density along the line of sight. This dual-band approach can be implemented using either a single camera with a filter wheel or, more commonly, two co-aligned cameras, which acquire both wavelengths simultaneously to minimize motion-related errors and improve measurement reliability (**Fig. 3.5**).

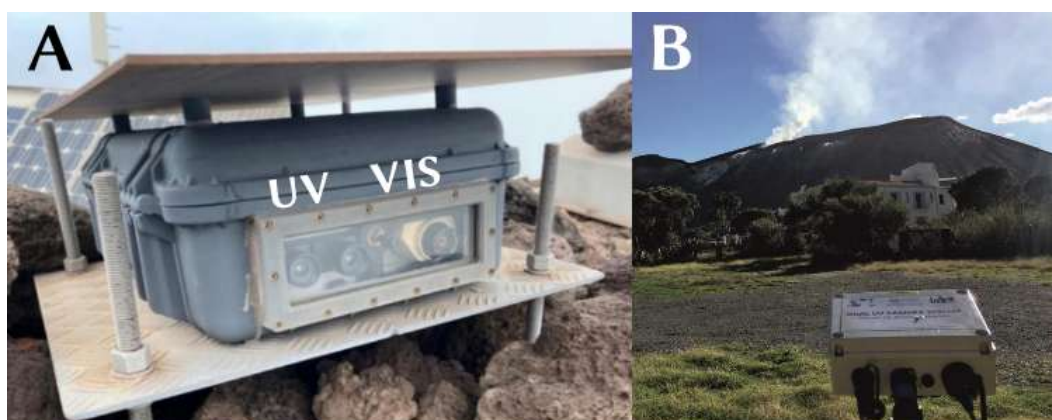


Figure 3.5 **A**: UV camera equipped with two objectives at 310 and 330 nm; the visual camera is shown on the right.. **B**: UV cam at Vulcano Island on december 15th 2021. From Aiuppa et al., (2022).

The raw pixel intensities recorded by the cameras are converted into absorbance values, which are then calibrated to obtain SO_2 column densities. Calibration is achieved either through reference gas cells of known concentration or, more flexibly, using co-aligned UV spectrometers that provide real-time spectroscopic

measurements. This in-situ calibration captures the actual environmental and instrumental conditions, making the derived SO₂ concentrations more accurate than those based on static gas cells. By integrating column densities along a line crossing the gas plume and combining these values with estimates of plume velocity, it is possible to compute SO₂ fluxes with high temporal resolution, often at sub-second scales.

Plume speed, a key parameter to calculate the flux, is typically derived through optical flow or cross-correlation techniques applied to sequential images (**Fig 3.6**). These methods allow not the estimation of horizontal and vertical transport speed near the vent, where wind effects are minimal. This capacity to measure plume dynamics directly from images significantly reduces uncertainties in flux calculations, enabling a more detailed and dynamic understanding of volcanic degassing processes.

Permanent UV Camera systems (**Fig. 3.5A**), such as those installed at Mount Etna, Stromboli and Vulcano by LabVulc, DiSTeM, Università di Palermo, provide continuous monitoring of SO₂ emissions over long periods. Strategic placement of the cameras, usually close to active vents, is critical to ensure that the instruments

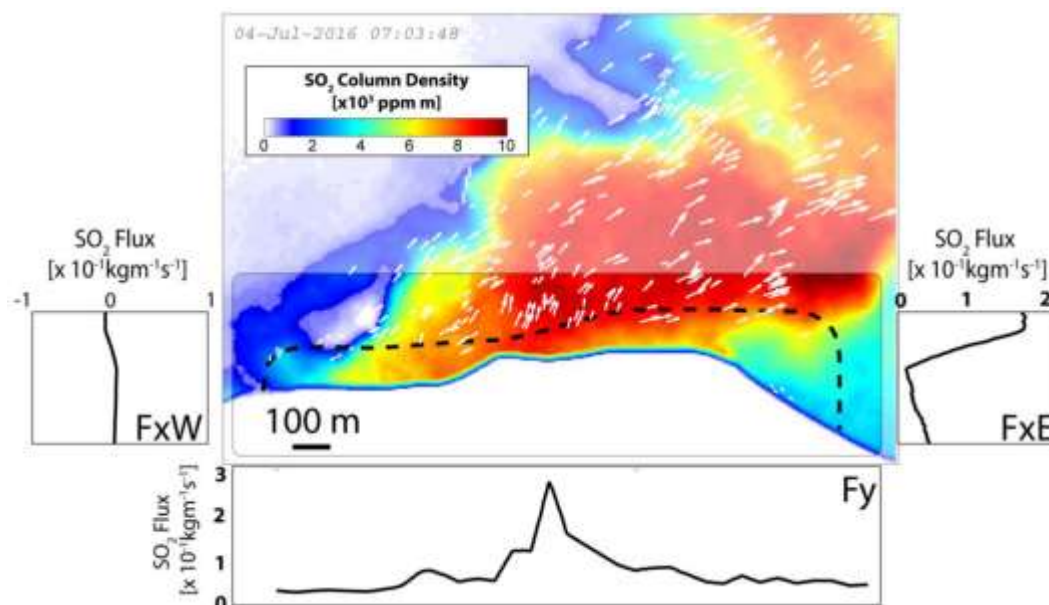


Figure 3.6 SO₂ density flux calculated over the sub-area encompassing the Etna summit craters. White arrows indicate gas velocity vectors of plume. Reproduced from Delle Donne et al., (2019).

capture a representative cross-section of the plume. At Stromboli, for instance, cameras

are positioned only a few hundred meters from the active vents, providing clear and detailed images of the plume (Lo Bue Trisciuzzi et al., 2025), while at Etna (Delle Donne et al., 2019) and Vulcano (this study, chapter 4) the larger distance and complex summit morphology require careful selection of the observation area and manual image processing to account for wind-driven plume deflection or partial obscuration by the terrain.

Data processing involves several steps, including synchronization of dual-band images, computation of absorbance, integration of column densities across the plume, and derivation of velocity profiles. Automated algorithms facilitate these tasks. Through this approach, continuous time series of SO₂ fluxes can be produced, enabling the detection of rapid changes in degassing activity, short-lived pulses, and longer-term trends.

Despite their capabilities, UV Camera systems face practical and technical limitations. Harsh volcanic environments pose challenges such as power supply instability, network interruptions, lens fouling from ash or condensation, and filter degradation in acidic conditions. Furthermore, complex crater morphology and adverse weather, including strong winds and cloud cover, can prevent the camera from fully capturing the gas plume. Careful siting and routine maintenance are therefore essential to ensure accurate and reliable measurements.

When properly implemented, permanent UV Camera networks provide a unique combination of high temporal and spatial resolution, continuous operation, and near-real-time data acquisition. These characteristics make them invaluable for studying the dynamics of volcanic degassing, quantifying gas budgets, and assessing potential hazards. By revealing both fast, short-lived events and long-term changes in plume composition and flux, UV Camera systems contribute directly to volcanic monitoring and early-warning efforts, offering insights that are complementary to those obtained from classical sampling or remote-sensing techniques

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4: SPATIO-TEMPORAL EVOLUTION OF THE FUMAROLIC FIELD OF LA FOSSA CONE (VULCANO ISLAND, ITALY) IN 2021-2024.

Published in *Volcanica*, 8(2), 543-561

<https://doi.org/10.30909/vol/tayr9210>

(Lentini et al., 2025)

Abstract - Monitoring the spatiotemporal evolution of fumarolic activity is key to understanding volcanic unrest at dormant volcanoes. Here, we present the results of periodic gas surveys conducted at La Fossa (Vulcano Island, Italy) between 2021 and 2024, in which a portable Multi-GAS instrument is used to map the spatial variations in gas composition across the fumarolic field. We identify substantial spatiotemporal changes in gas composition. The crater rim fumaroles exhibit the highest CO₂, SO₂, H₂S, H₂ concentrations and stable, relatively low CO₂/SO₂ ratios (around 20-30), all indicative of a larger magmatic contribution. In contrast, the inner crater fumaroles display more variable and generally higher CO₂/SO₂ ratios, indicating a larger hydrothermal influence. These data, combined with infrared thermal imaging and SO₂ flux results, are indicative of a volcanic unrest that, after having reached its climax in late 2021, has gradually vanished since, although not fully returning to pre-unrest conditions.

4.1: Introduction

The behavior of active volcanoes on Earth is primarily controlled by the rates and mechanisms of magma and gas transport throughout their transcrustal magmatic plumbing system (Cashmann et al., 2017; Wallace and Edmonds, 2017). At open-vent volcanoes, mafic magma is efficiently transferred from deeper storage regions to the shallow feeding conduit system to sustain persistent activity,

characterized by intense passive degassing and interspersed relatively mild eruptive activity (Vergnolle and Métrich, 2022; Edmonds et al., 2022). Closed-vent volcanoes, in contrast, undergo long-lasting periods of dormancy during which mild fumarolic activity is sustained by degassing of deeply stored, stationary magma. During this background activity, the ascent of magmatic fluids from the magmatic source to surface is limited by the relatively low permeability of rocks/minerals composing the overlying hydrothermal carapace, and is ultimately modulated by spatio-temporal changes in permeability due to variations in the local and regional stress regime (Norton, 1984; Chiodini et al., 2022; Marini et al., 2022). Ultimately, hydrothermal alteration of rocks, and the fluids they host, act as chemical filters (Symonds et al., 2001; Stix and de Moor, 2018; Kern et al., 2022) for reactive, water soluble magmatic volatiles (primarily SO_2 , H_2S , HCl). Complex gas-water-rock interactions (Giggenbach, 1987, 1997; Henley and Fischer, 2021) control the chemistry and redox state (Chiodini and Marini, 1998; Fischer and Chiodini, 2015) of volcanic gases at surface and the physical properties of rocks and associated hazards (Darmawan et al., 2021; Kereszturi et al., 2023).

As previously discussed, because of these intense hydrothermal interactions, closed-conduit volcanoes, during their long inter-eruptive quiescence periods, typically exhibit low temperature fumarolic fields with hydrothermal gas signatures (Giggenbach, 1987; Chiodini and Marini, 1998). Typical characteristics include high $\text{H}_2\text{O}/\text{CO}_2$ ratios (because of dilution of magmatic volatiles by hydrothermal steam; Chiodini et al., 1993) and high $\text{CO}_2/\text{S}_\text{T}$ ratios (because of preferential sulfur scrubbing by hydrothermal reactions; S_T , as already mentioned, here stands for total sulphur and corresponds to the sum of SO_2 and H_2S ; Aiuppa et al., 2017). The same fluids also typically have low $\text{SO}_2/\text{H}_2\text{S}$ and CO/CO_2 ratios, and CO_2/CH_4 ratios lower than magmatic gases, because hydrothermal conditions are colder and more reducing than hot, oxidized magma (e.g. Giggenbach, 1997; Chiodini and Marini, 1998; Chiodini, 2009; Oppenheimer et al., 2014; Fischer and Chiodini, 2015; Aiuppa and Moussallam, 2023). However, as a volcano becomes restless during unrest, gas composition progressively evolves toward more magmatic compositions

(e.g., Turrialba, Vaselli et al., 2010; Kern et al., 2022), as typically indicated by decreasing $\text{H}_2\text{O}/\text{CO}_2$ ratios (e.g. Campi Flegrei, Chiodini et al., 2016; Vulcano, Paonita et al., 2013), decreasing $\text{CO}_2/\text{S}_\text{T}$ ratios (e.g. Turrialba, Vaselli et al., 2010), and increasing $\text{SO}_2/\text{H}_2\text{S}$ (e.g. Poás and Turrialba; de Moor et al., 2016, 2017), CO/CO_2 (e.g. Campi Flegrei, Chiodini et al., 2013) and CO_2/CH_4 (Chiodini, 2009) ratios. Capturing and interpreting such hydrothermal-to-magmatic transition during volcanic unrest is crucial for volcanic risk mitigation, as it contributes to recognizing when/if the volcanic system is becoming increasingly unstable, and potentially more prone to erupt (Phillipson et al., 2013; Rosi et al., 2022).

To monitor such variations, volcanologists traditionally rely on direct fumarole sampling. However, in large fumarolic fields this approach can be time-consuming and spatially limited. For this reason, complementary techniques such as portable Multi-GAS instruments are increasingly used to rapidly assess gas composition over wide areas. The present study builds on previous work by Aiuppa et al. (2005, 2006, 2022) by reporting on the spatio-temporal variations of the fumarolic CO_2/SO_2 ratio across the Vulcano fumarolic field during 2014 to 2024. We focus on CO_2/SO_2 because, as it has been shown previously at Vulcano (Inguaggiato et al., 2018; Aiuppa et al., 2022) and elsewhere (Aiuppa et al., 2017), this ratio is typically high during periods of reduced hydrothermal activity, when any magmatic sulphur is sequestered by hydrothermal minerals/solutions in the subsurface (Chiodini et al., 1993; Di Liberto et al., 2022). In contrast, the ratio decreases during phases of unrest when SO_2 escalates faster than CO_2 (Inguaggiato et al., 2022), either because of degassing of mafic magma at depth (Aiuppa et al., 2022) or because of sulphur remobilization from hydrothermal minerals (Chiodini et al., 1993) (or a combination of both). The fumarolic field CO_2/SO_2 ratio serves as a useful tracer to track the alternation of calm and unrest periods that has characterized the activity of La Fossa since the late 1970s (Selva et al., 2020). Our aim is to reconstruct how the chemistry of the fumarolic field varied in space and time during a period encompassing the autumn 2021 Vulcano degassing unrest (Aiuppa et al., 2022; Di Martino et al., 2022; Inguaggiato et al., 2022, 2023; Di Traglia et al., 2023; Paillot-

Bonn  tat et al., 2023; M  ller et al., 2024). We hence extend previous results by describing how the chemical heterogeneity of the fumarolic field evolved after the peak of the unrest was reached in September-December 2021, but has not fully declined yet by time of writing (June 2025).

4.2: Geological background

4.2.1: The Aeolian archipelago and Vulcano island

Vulcano is the southernmost island (Fig. 4.1A) of the Aeolian archipelago, an active volcanic arc in the southern Tyrrhenian Sea north of the Sicilian coast, consisting of seven emerged volcanic islands (Stromboli, Panarea, Vulcano, Lipari, Salina, Alicudi and Filicudi) and several submerged seamounts. The Aeolian Islands represent a classic example of volcanic island arc associated with subduction, in this case of the Ionian oceanic crust underneath the accretionary complex south of the Calabrian coast (Fig. 4.1A). The existence of a slab below the arc is confirmed by the distribution of hypocenters along a northwestward subducting plane. The regional tectonics is controlled by the interaction between the spreading Tyrrhenian basins to the north, the subduction of the Ionian slab to the south, and the movements of the Calabro-Peloritan block, mobilized by right lateral strike-slip faults: the Taormina Line (WNW-ESE) until the Middle Pleistocene and then by the Tindari-Letojanni (NNW-SSE) (Mantovani et al. 2023) (Fig. 4.1A). While subaerial volcanic activity started at 1.3 Ma, subaerial volcanism recently concentrated along two axes, Lipari-Salina-Filicudi (270 -250 ka) and Stromboli-Panarea-Vulcano-Alicudi (204-106 ka). Erupted magmas range from mafic to silicic, and are calc-alkaline to high-K calc-alkaline series to shoshonitic affinity. Alkaline rocks containing leucite also outcrop at Vulcano (particularly in the Vulcanello area) and Stromboli (Peccerillo, 2017).

The geological history of Vulcano alternated phases of (i) construction of volcanic edifices of different size and eruption style, and (ii) caldera collapse events and quiescent phases, characterized by erosion (Keller, 1980; Di Traglia et al., 2013; Peccerillo, 2017; De Astis et al., 2023). De Astis (2013, 2023) summarizes the evolution of the island in eight eruptive phases beginning by ~130 ka (Soligo et al., 2000; De Astis et al., 2013) (Fig. 4.1B). Between 127 ka and 100 ka, the construction of a shoshonite lava shield (Capo Secco) (Peccerillo, 2017) took place, soon covered by a high-K basaltic andesite stratovolcano, known as Vulcano Primordiale that occupied the southern portion of the present island. After an initial caldera collapse (Piano 1) and the emplacement of the Scoglio Conigliara lava flows (99.5 ka), renewed caldera collapse (La Fossa 1) cut the northern section of the previous collapse (78 ka). This event led to the opening of fissures at Timpa del Corvo and Monte Aria, associated lava flows, and the formation of scoria cone at Casa Petrulla (De Astis et al., 2013).

Between 70 ka and 42 ka, after a third caldera collapse cutting through the central portion of the first collapse (Piano 2), new eruptive products were emplaced, mainly from the eruptive fissure at Monte Luccia, as well as from the two scoria cones at Monte Rosso and La Sommata, and from Il Cardo tuff cone (Paleo-La

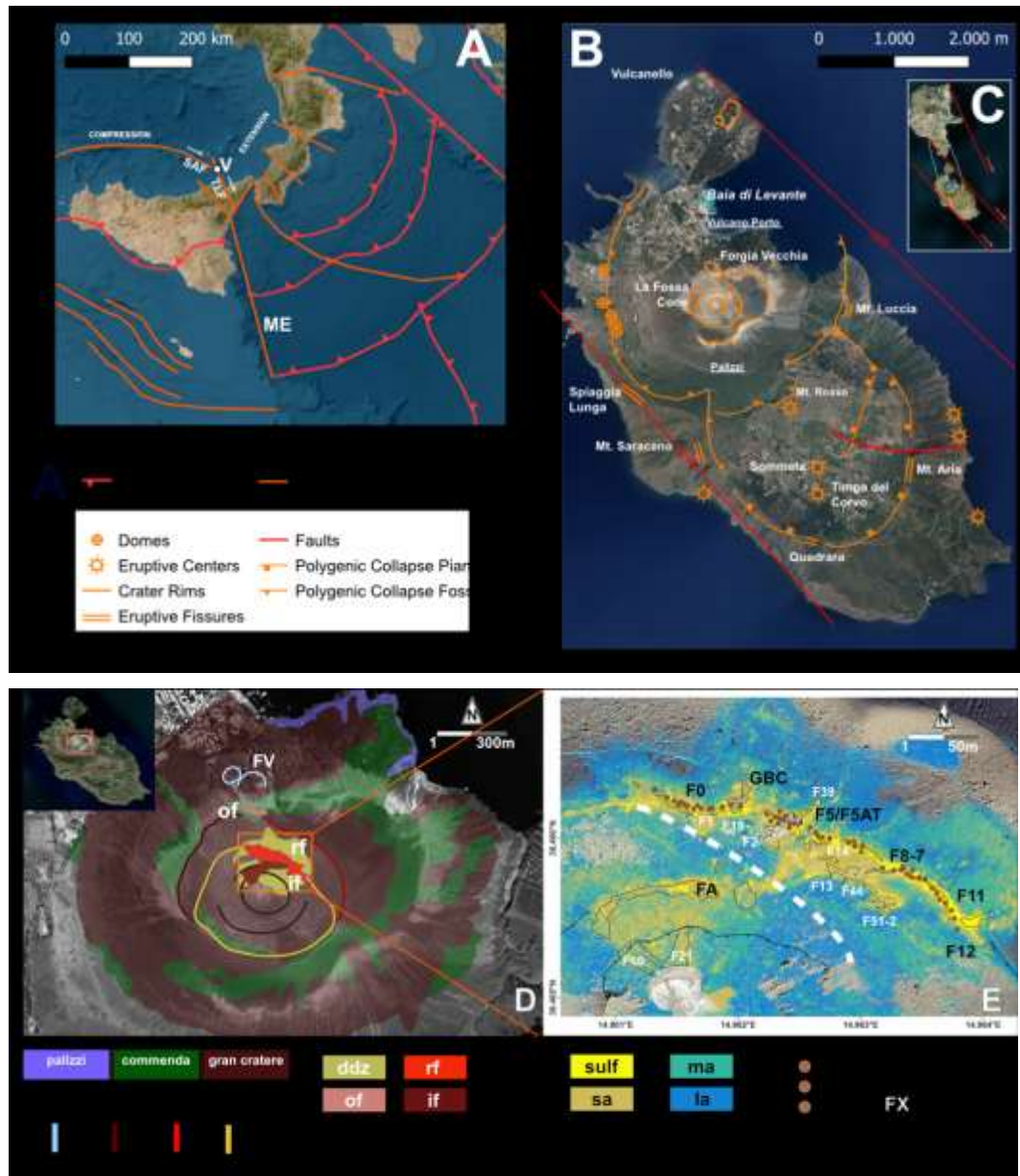


Figure. 4.1 **A:** Tectonic sketch of Sicily and nearby areas illustrating the major faults and different orogenic fronts; the strike-slip faults Sisifo–Alicudi (SAF) and Tindari–Letoianni (TLF), along with their junction at Vulcano-Lipari (V), are highlighted. SAF and the TLF forms a transfer zone that channels tectonic stresses from the compressional area west of the Aeolian Islands toward the Ionian subduction zone in the south. The interaction of SAF-TLF junction with an extensional belt to the east (Vulcano Gioia Basin-Paola Basin) produces N-S-trending structures on Lipari and Vulcano that favour the ascent of deep fluids (panels B and C). Reworked from Ruch et al. (2016) and Mantovani et al. (2023). **B:** volcano-tectonic sketch of Vulcano island with major eruptive centers, fissures, polygenic collapses defined by volcano-tectonic circular faults (il Piano 1-2 and La Fossa 1-2-3-4). Reworked by De Astis et al. (2013). **C:** volcano-tectonic sketch of Vulcano of the islands of Lipari and Vulcano. Reworked by Holohan et al. (2008). **D:** The main units of the La Fossa cone, as inferred by Di Traglia et al. (2024). The La Fossa cone consists of the superposition of multiple units (cones in the geomorphological sense, lithosomes in the stratigraphic sense), separated by craters of different ages that overlap to create a nested crater. Age of the craters inferred from Di Traglia et al., (2013). The La Fossa cone summit hosts three main fumarolic zones: a marginal one on the rim of FV (outer fumaroles, of); the (rim

fumaroles, rf) on the 1731-1888 crater rim; and the inner crater fumaroles (if). The rim and inner crater fumaroles are surrounded by an alteration zone in which diffuse degassing occurs (ddz). A detail of the rf and if fumaroles showing the boundary between the hotter, more magmatic (lower CO₂/SO₂ ratio) rf and the colder, more hydrothermal if. Dots indicate the crater rim traverse (results displayed in Fig. 4.7). In figure E is a map of inner and rim fumaroles with nomenclature and outlines of fumaroles; in this area are presents sulfur deposits (sulf) surrounded by areas of strong (sa) to moderate (ma) to slight (la) alteration. Figure E is adapted from Müller et al., (2024).

Fossa cone according to De Astis, 2013), which occupied the current location of the La Fossa cone. These deposits covered the previous collapses.

Between 28 ka and 21 ka, a fourth caldera collapse (La Fossa 2) partially affected the northeastern margin of La Fossa, forming the present-day La Fossa caldera. Along its western margins, the Monte Lentia latite to trachy-rhyolite lava domes, flows and pyroclastics were emplaced (Peccerillo, 2017), while at the southwestern margins of Piano, the Spiaggia Lunga fissure opened emitting shoshonitic basalt and shoshonite lavas. Additionally, along the southwestern margins of the Piano caldera, the shoshonite to trachyte scoria and pumices of Quadrara fissure formed, accompanied by the Punta Bandiera lava flows to the southeast.

The construction of the La Fossa tuff cone took place between 8 ka to the present (Peccerillo, 2017), while the Vulcanello peninsula possibly emerged at circa 2 ka (Di Traglia et al., 2013; Fusillo et al., 2015; Peccerillo, 2017; De Astis et al., 2023), or in the Middle Age (Malaguti et al., 2021). The most recent estimate of the age of early Vulcanello products is 900-1040 AD (Di Traglia et al., 2024). Vulcanello is a shoshonite (leucite bearing) to latite lava composite cone with three partially overlapping scoria cones arranged along a NE-SW alignment (De Astis et al., 2013; Di Traglia et al., 2013; Fusillo et al., 2015). Eventually, by the year 1000, the island of Vulcano became connected to Vulcanello due to activity from La Fossa cone. Compositionally, the La Fossa volcanic successions contain some of the most evolved (trachytic to rhyolitic) rocks on the island, due to a combination of magmatic differentiation and (low extents of) assimilation of upper crust materials of the Calabro-Peloritan Block (Peccerillo, 2017). In contrast, the products of Vulcanello, while sharing some geochemical and isotopic affinity with more evolved La

Fossa magmas, represent the most mafic magmas erupted on the island over the last 6000 years. (De Astis et al., 2013; Peccerillo, 2017).

4.2.2: The La Fossa tuff cone

The La Fossa tuff cone (Fig. 4.1D) emerges 391 m above sea level on the northern sector of the island. This composite edifice is dominated by a main structure (a tuff cone) rising to an elevation of 251 m, where a sharp slope change separates the crater associated with the Pietre Cotte phase (1731-1775) to the west (De Astis et al., 2013; Di Traglia et al., 2013 & 2024) from the post 1775 craters to the east. Several subcircular craters, dating and predating the 1888-1890 eruption (Mercalli and Silvestri, 1891), can now be found on the volcano summit (Fig. 4.1D), demonstrating the dynamic and diverse eruptive behavior over the last millennium.

The eruptive activity at La Fossa cone and associated volcanic sequences have been reconstructed and dated by different authors. De Astis et al. (2013) recognize three main sequences: i) a lower sequence that includes the Punte Nere and Grotta di Palizzi 1 formations, erupted between ~3550 and 950 BCE (Frazzetta et al., 1984); ii) an intermediate portion (Grotta di Palizzi 2 and 3, Carruggi formations and Forgia Vecchia formations), emplaced between ~250 BCE and 776 AD (Keller, 1980; Frazzetta et al., 1984); and an upper sequence, characterized by the Pietre Cotte and Gran Cratere formations, erupted between 1739 and last eruptive activity occurred in the 1888-1890 eruption (Mercalli and Silvestri, 1891).

A different chronology, indicating more frequent eruptive activity in mediaeval time, has been elaborated by Di Traglia et al. (2013), Malaguti et al., (2021) and Di Traglia et al. (2024). According to Di Traglia et al. (2024) intense vulcanian activity (eventually accompanied by the emplacement of lava flows) between 900 AD and 1250 AD deposited the thick Palizzi sequence. This was followed by deposition of the Breccie di Commenda products (1250-1300 AD) (Rosi et al., 2018; Di Traglia et al., 2024), ascribed to a violent phreatic eruption occurring

simultaneously with the Rocche Rosse eruption in Lipari (Di Traglia et al., 2024). From circa 1400 AD to the early XVIII century, volcanic activity concentrated both at La Fossa and at the eccentric La Forgia craters, generating a sequence of phreatic and vulcanian eruptions (Malaguti et al., 2021; Di Traglia et al., 2024). The last three centuries of activity comprise two long-lived eruption episodes in 1727-1739 (Pietre Cotte sequence) and 1888-1890 (Gran Cratere sequence) (Di Traglia et al., 2024), and some shorter or even discrete episodes, interspersed within rest periods of background hydrothermal activity lasting for decades (Table 4.1).

Table 4.1: The last three centuries of volcanic activity at Vulcano (data from Selva et al., 2020 and Di Traglia et al., 2024)	
Long-lived eruptive periods	1771, 1783, 1786, 1823-24, 1873, 1876, 1878-79, 1886
Shorter/discrete eruptive episodes	1771, 1783, 1786, 1823-24, 1873, 1876, 1878-79, 1886
Quiescence and fumarolic activity periods	1740-1770, 1772-1782, 1783-1786, 1787-1832 1873-1876, 1879-1885, 1886-1887

4.2.3: The La Fossa Fumarolic Field

Fumarolic activity today concentrates from vents and fractures on the volcano summit (Paonita et al., 2013). This summit fumarolic field consists of two main adjacent zones: i) a linear network of fractures and satellite vents that develop along the crater rim (rim fumaroles), including from west to east, the F0, GBC, F5AT, F7-8, F11, and F12 fumaroles; ii) the inner fumaroles, located on the inner slope of the crater. This area consists of discrete vents or vents aligned along sealed fractures, embedded in an extended field of hydrothermal alteration, deposition and mineralization (Mueller et al., 2021). The FA fumarole, situated near the inner crater of the 1888-1890 eruption and extending toward the inner crater wall, has traditionally been the main degassing spot in the inner fumarolic field. The central-eastern section of the rim fumaroles is surrounded by a dark grey impermeable crust, and

bleached surface at a distance representing areas of increased diffuse surface gas flux (Mueller et al., 2021, 2024). In addition, a small degassing area (the outer fumaroles; Fig. 4.1E) is also located within and along the outer rims of the eccentric La Forgia craters. Degassing occurs not only through fractures and vents but also via diffuse soil degassing, affecting the areas near the rim fumaroles, both inside and outside the crater (Paillot-Bonn  tat et al., 2023 and references cited therein). This diffusive output (Chiodini et al., 2005; Inguaggiato et al., 2012, 2018; Harris et al., 2009; Mannini et al., 2019; Paillot-Bonn  tat et al., 2023) contributes 5 to 13 MW, or circa 93% of the total volcano heat budget. The latter is thought to be sustained by convection of magmatic-hydrothermal fluids through a heat chimney composed of fractured feeding conduit rocks (Harris and Maciejewski, 2000; Paillot-Bonn  tat et al., 2022; Mueller et al., 2021), while conduction prevails in the last few meters. Such inner structure of the La Fossa cone, and especially the ascent pathways of magmatic-hydrothermal fluids, has been reconstructed and modelled using electrical resistivity tomography, self-potential, temperature, and diffuse degassing measurements (Revil et al., 2008, 2010; Barde-Cabusson et al., 2009). Variations in temperature and number of fumaroles, although less influential on the overall energy balance, provide fundamental indication of the state of the system, signaling heating or cooling phases (Chiodini et al., 2005; Harris et al., 2009; Diliberto, 2013; Madonia et al., 2016; Mannini et al., 2019; Paillot-Bonn  tat et al., 2023; Diliberto et al., 2024).

Magmatic gases released by the fumarolic system are thought to be source by magma stored in a complex, transcrustal plumbing system. Consensus exists for the presence of deep magma storage zone of basaltic to shoshonitic magma at 12-20 km depth b.s.l. (below sea level), overlain by an intermediate latitic magma reservoir at 3-5 km b.s.l. depth, and by a shallow K-trachyte/rhyolite reservoir at 1-2 km depth b.s.l. (De Astis et al., 2013, Peccerillo, 2017; Selva et al., 2020; Aiuppa et al., 2022). Upon ascent, these magmatic fluids get admixed with steam boiled off from seawater-derived hydrothermal brines (Nuccio et al., 1999; Nuccio and Paonita, 2001).

4.2.4: The 1987-93 and 2021-present unrest

After the 1888-1890 eruption, La Fossa entered a state of quiescence. However, degassing activity has intensified multiple times since then, with hydrothermal unrest being recorded in 1916-24, 1977-1980, 1987-1993, 2004-5, and 2009 (Selva et al., 2020; De Astis et al., 2023). A major unrest, associated with macroscopic changes in the fumarolic field, was observed between 1987 and 1993 (Barberi et al., 1991). At that time, new fractures (F0, GBC, F11, F12, satellite fractures) formed and existing fractures (FA, F5AT, F7-8) expanded and reorganized, in parallel with substantial changes in fumarole composition and flux, and seismicity (Italiano et al., 1998; Harris et al., 2012; Alparone et al., 2010; Diliberto et al., 2017). Fumarole temperature increased from 435°C in 1988 to 692°C in 1992, before dropping again to 428°C in 1999. During this period, the fumarolic field expanded towards the bottom of the crater as the FA area grew (Harris & Maciejewski, 2000; Diliberto et al., 2017). Fumarolic gas composition also varied substantially, indicating an increased contribution of magmatic volatiles and (potentially) a change in hydrothermal fluid conditions from biphasic to dry gas conditions (Nuccio et al., 1999; Chiodini et al., 1993, 1995; Paonita et al., 2002).

The most recent hydrothermal unrest at Vulcano started in September 2021 (Federico et al., 2023), when an abrupt increase in thermal (Coppola et al., 2022; Inguaggiato et al., 2022; Campus et al., 2024; Pailot-Bonn  tat et al., 2023; Diliberto et al., 2024) and gas (Aiuppa et al., 2022; Di Martino et al., 2022; Inguaggiato et al., 2022, 2023; Federico et al., 2023; Giuffrida et al., 2025) output was observed. According to Pailot-Bonn  tat et al. (2023) and Diliberto et al. (2024), the main hydrothermal unrest may have been preceded by a sluggish phase of soil/fumarole increase starting as early as February 2021. Inguaggiato et al. (2022) also found a precursory phase of soil CO₂ emission increase beginning in early 2021. During the main (post-September 2021) phase of the unrest, fumarole composition manifestly became more CO₂- and S-rich (more magmatic), as also indicated by He isotope compositions in the fumaroles (Federico et al., 2023). Among the lowest ever

measured $\text{CO}_2/\text{S}_\text{T}$ ratios (10-15) at Vulcano were observed during fall 2021, confirming a more magmatic signature and a reduced hydrothermal processing (Aiuppa et al., 2022). Later in winter-spring 2022, the unrest manifested also at the base of La Fossa and in the nearby Baia di Levante hydrothermal area, where a general increase in gas output resulted into significant environmental and health impact when CO_2 and H_2S concentrations in soil and air rose to potentially hazardous levels for the population (Di Martino et al., 2022; Inguaggiato et al., 2022, 2024). In some wells in the Vulcano Porto village, water temperatures close to 70°C were recorded (Inguaggiato et al., 2024) and, between September 2021 and May 2022, the CO_2 flux increased 32-fold in the Crater, and 15-fold in the Baia di Levante area compared to local background values. The anomaly delay between the crater and peripheral areas has been interpreted as due to the interaction with local shallow hydrothermal aquifers, which may have buffered the ascent of fluids until saturation was reached, at which point gas would have been able to migrate toward the surface (Di Martino et al., 2022; Inguaggiato et al., 2022). One notable effect was the appearance of a milky-white seawater coloration in the Baia di Levante bay offshore (Coppola et al., 2022), which was caused by the presence of suspended fine mineral particles (sulfides and sulfates) that precipitated in the water column in response to increased hydrothermal fluid inflow (Diliberto et al., 2022). Geophysical data indicate that the La Fossa unrest was associated with mild ground uplift (Di Traglia et al., 2023; Federico et al., 2023) and in shallow VPL (Very Long Period) seismicity (Federico et al., 2023). These were interpreted as due to pressurization of the shallow (< 1 km) hydrothermal system by rising magmatic fluids. Di Traglia et al., (2023), using GNSS and InSAR time-series data, modelled the inflation source as a dipping prolate spheroid model located at a depth of 600 m, pressurized by magmatic fluids. Fluid migration along N-S-trending fractures may have favoured extension of the area affected by the unrest in the following months. Volcano tectonic (VT) seismicity was moderate in fall 2021 (Federico et al., 2023).

Paillot-Bonn  tat et al. (2023) interpreted the unrest as caused by the following sequence of events. A mild increase in magmatic fluid input into the shallow

hydrothermal system may have started as early as January-June 2021, as evidenced by soil temperature records. The increase in magmatic fluids led to gradual formation of a gas chimney and to a slow rise in heat flux, which was initially confined to within the partially sealed fracture network that had developed beneath the Fossa fumarolic field during and after the 1988-96 unrest. However, starting in spring 2021, the emission area gradually expanded toward the peripheral zones of the fumarolic field and, at the beginning of September 2021, the impermeable seal surrounding the chimney failed due to fracturing, triggering VLP swarms and causing a sudden and significant expansion of the thermal and gas output. In addition to Di Traglia et al. (2023), Stumpp et al. (2024) also imaged a sub-vertical conduit with very low S-wave velocities (0.8 km/s), extending to a depth of at least 2.5 km, which would have acted as the transport feeding conduit for the ascent and pressurization of magmatic gases during the unrest. The unrest gradually vanished in 2023-to-present, as evidenced by decreasing gas fluxes (Inguaggiato et al., 2024; Giuffrida et al., 2025) and composition/temperature records (INGV monitoring reports).

4.3: Methodology

The results we report on this study are obtained from periodic field surveys using a portable Multi-GAS (Aiuppa et al., 2005, 2007), complemented with thermal infrared results obtained from drone surveys. The Multi-GAS unit used has the same configuration as that employed by Aiuppa et al (2022), and includes a non-dispersive infrared (NDIR) NG Gascard spectrometer (calibration range, 0-10,000 ppm) from Edinburgh Sensors for CO₂, and three CiTiceL electrochemical sensors for SO₂ (model T3STF), H₂S (model T3H) and H₂ (model T3HYT) (all having 0-200 ppm calibration range). All sensors were calibrated in the laboratory prior to and after field work using certified standard gases, finding a typical uncertainty/precision of $\sim \pm 5\%$ at the concentration levels encountered at Vulcano. The system also includes a KVM3/5 Galltec-Mela sensor for measuring temperature and relative humidity and to indirectly estimate H₂O concentrations in the plume using the

Arden-Buck equation (Buck, 1981), which calculates the saturation vapor pressure of water as a function of temperature. A Campbell CR6 datalogger acquires signals from the various sensors at 1 Hz rate and stores them on an SD card (data are also Wi-Fi transferred and visualized in real-time in external palm). Equipment is housed in a water-proof case.

In the field, the portable Multi-GAS unit (<3 kg) is carried by an operator across the field, continuously acquiring data at 1 Hz, and with position recorded by a GPS synchronized at the start of the instrumentation. Acquired gas concentration data is displayed in real-time on an external palm-sized device. The fumarolic field is then traversed by walk with the held-hand Multi-GAS, while keeping the instrument's inlet exposed to the gases at 50 cm distance from the vent to avoid sensor saturation. Each fumarolic vent is monitored for a few minutes, and the different fumaroles are analysed sequentially to cover the entire field in about an hour. The range and diversity of gas concentrations over the fumarolic field is then determined and mapped (Figures 4.2, 4.3).

The gas concentration time-series acquired within each campaign are processed using a processing routine (Aiuppa et al., 2021, 2022), written in the R-code (<https://www.r-project.org/>). This routine automatically scans the gas concentrations time series, searching for periods of high temporal coherence ($R^2 \geq 0.7$) between couples of gas species in 60 s long moving windows. Specifically, within each of such sequentially scanned time windows, the routine calculates a ratio (for example, the CO₂/SO₂ ratio) if two criteria are met: i) the Pearson correlation coefficient is ≥ 0.7 and ii) the SO₂ concentration threshold of 20 ppm is reached (Aiuppa et al. 2022). The obtained georeferenced ratios are finally illustrated in the form of either contour (Figure 4.4) or dotted (Figure 4.5) maps.

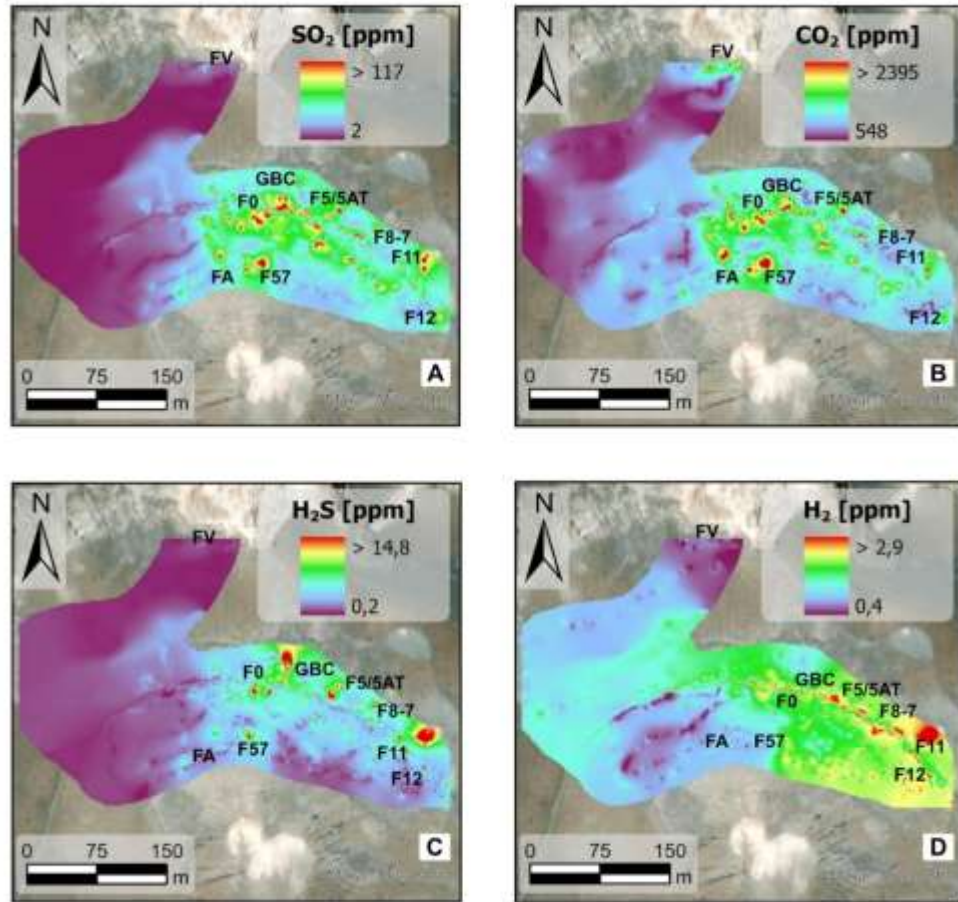


Figure 4.2 SO₂, CO₂, H₂S and H₂ concentration maps (June 2024 campaign). The most actively degassing fumaroles are identified as peak gas concentration spots.

Eleven field campaigns were realized during 2021 to 2024, and the results are illustrated in Supplementary Figure 1. To illustrate the temporal evolution of the fumarolic field, four exemplificative maps are shown in Figure 4 where, for comparison, we also present the (unpublished) results of two campaigns taken in April 2014 and June 2018 that correspond to periods of background (reduced) degassing activity (as indicated by INGV monitoring reports, available at <http://www2.ct.ingv.it/it/rapporti/multidisciplinari.html?view=docman>, and SO₂ flux results; Giuffrida et al., 2025). Because of accessibility and time constraints,

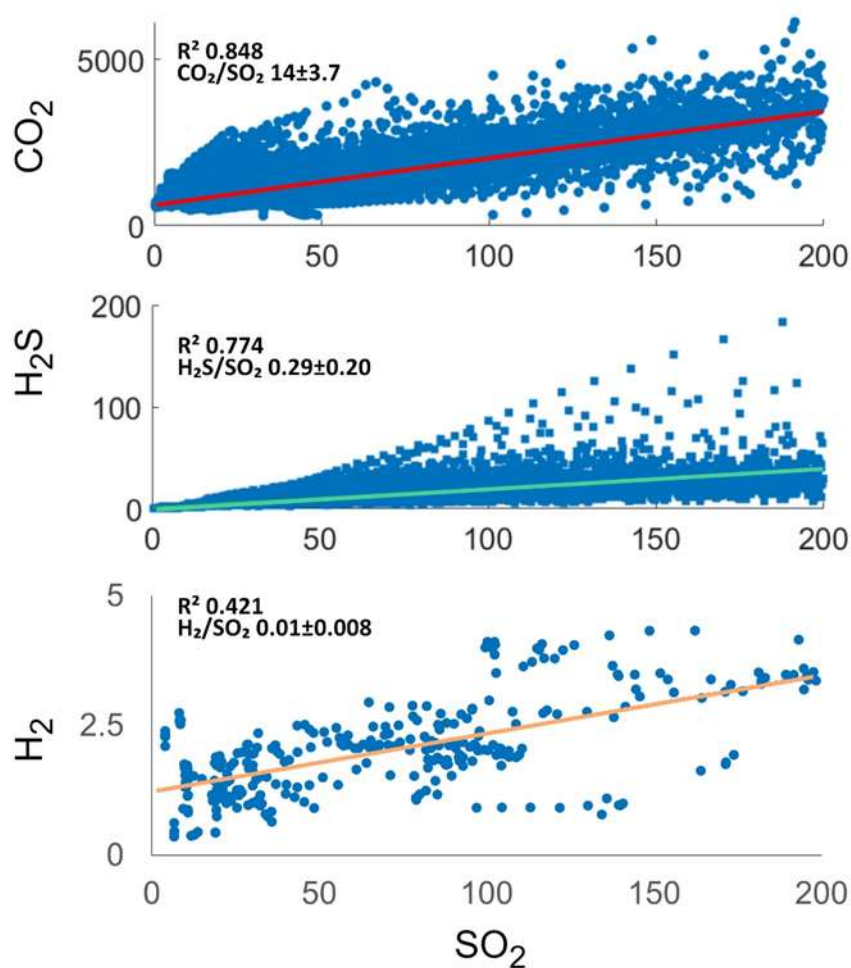


Figure 4.3 Scatter plot of SO_2 vs. (a) CO_2 , (b) H_2S and (c) H_2 concentrations

the area covered by observations varies from one survey to another (Fig. 4.4 and Supplementary Figure 4). However, all surveys cover the crater rim area where the hottest and most actively degassing fumaroles have been active in the last decade(s), e.g., since when fumarolic activity in the inner FA fumarole declined after the 1987-93 unrest.

As a complement to Multi-GAS records, thermal infrared data were acquired using a FLIR Tau 2 radiometric thermal infrared camera system mounted on a DJI Phantom 4 Pro. The FLIR Tau 2 is a fully radiometric sensor system with a sensor

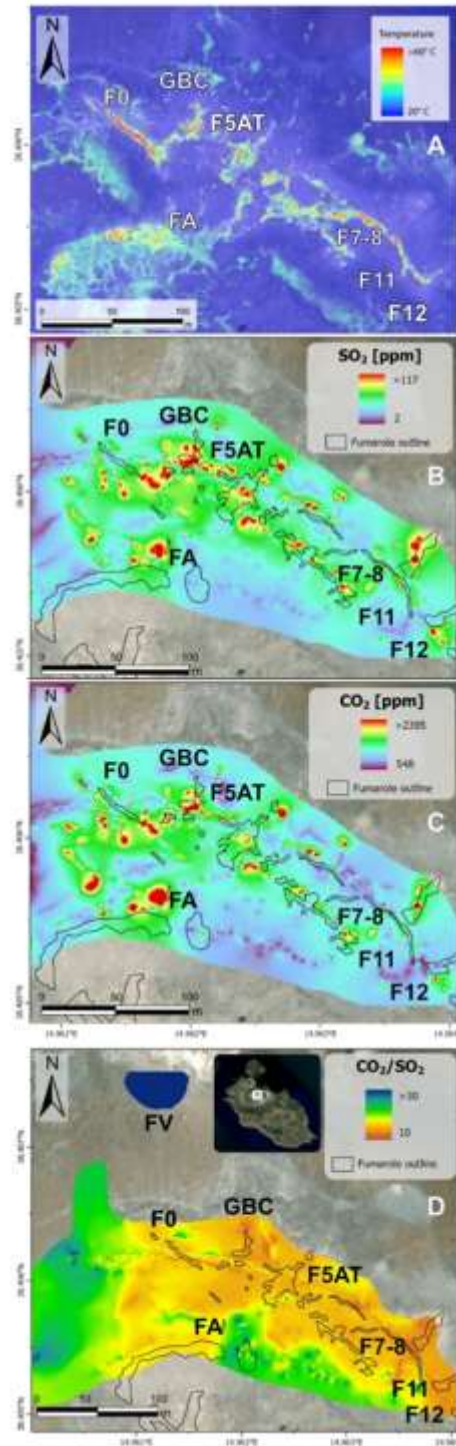


Figure 4.4 **A**: Drone thermography of the fumarolic field, taken on October 20th 2021. The locations of the main degassing fissures and vents, as indicated by peak apparent temperatures, broadly correspond to the peak SO_2 . **B** and CO_2 **C** concentration spots, as revealed by the Multi-GAS measurements. The CO_2/SO_2 ratio map **D** shows the contrast between the rim fumaroles (lower ratios) and the peripheries of the fumarolic field (higher ratios). FV identifies the Forgia Vecchia fumaroles.

resolution of 640×512 pixels. It measures in the thermal infrared spectral range between 7.5 and 13 μm . The data is recorded by a TEAX Thermal Capture 2 data logger at 8 Hz and geotagged using an external GPS antenna. Infrared data acquisition is performed by flying in loops at a constant altitude over the target area, ensuring a minimum overlap of 65% for each image. This is necessary for subsequent photogrammetric processing. The data were then inspected and quality checked in ThermoViewer (version 3.0.0), and images of poor quality or out of focus were excluded. Quality check also included selection of images taken at constant flight attitude. The selected images were exported in 16-bit greyscale tiff format and processed in Agisoft metashape to produce a thermal mosaic covering the central crater region of La Fossa cone.

We also report on a SO_2 flux time-series from La Fossa crater (Fig. 4.6) obtained by a fixed UV Camera system located at Orsa Maggiore Hotel, ~ 1.49 km NW from the summit. Functionalities of this fully autonomous UV camera system are described in Aiuppa et al. (2022). In brief, the unit assembles two JAI CM-140GE-UV cameras sensible to UV-radiation, fitted with two distinct band-pass optical filters (both of 10 nm Full Width at Half Maximum) with central wavelengths of 310 (SO_2 absorption) and 330 nm (no SO_2 absorption) (Delle Donne et al., 2016, 2019; Lo Bue Trisciuzzi et al., 2024). Images are simultaneously acquired by the two cameras at 0.5 Hz. During post-processing, sets of co-acquired images are combined into absorbance images that are later converted into calibrated slant column amount (SCA) images. From this, Integrated Column Amounts (ICA) time-series are obtained by integration along a cross-section perpendicular to plume transport. The SO_2 flux time is finally derived by multiplying ICA by plume speed, as derived by tracking the motion of plume gas fronts in image sequences, using an optical flow algorithm (Delle Donne et al., 2016, 2019; Lo Bue Trisciuzzi et al.,

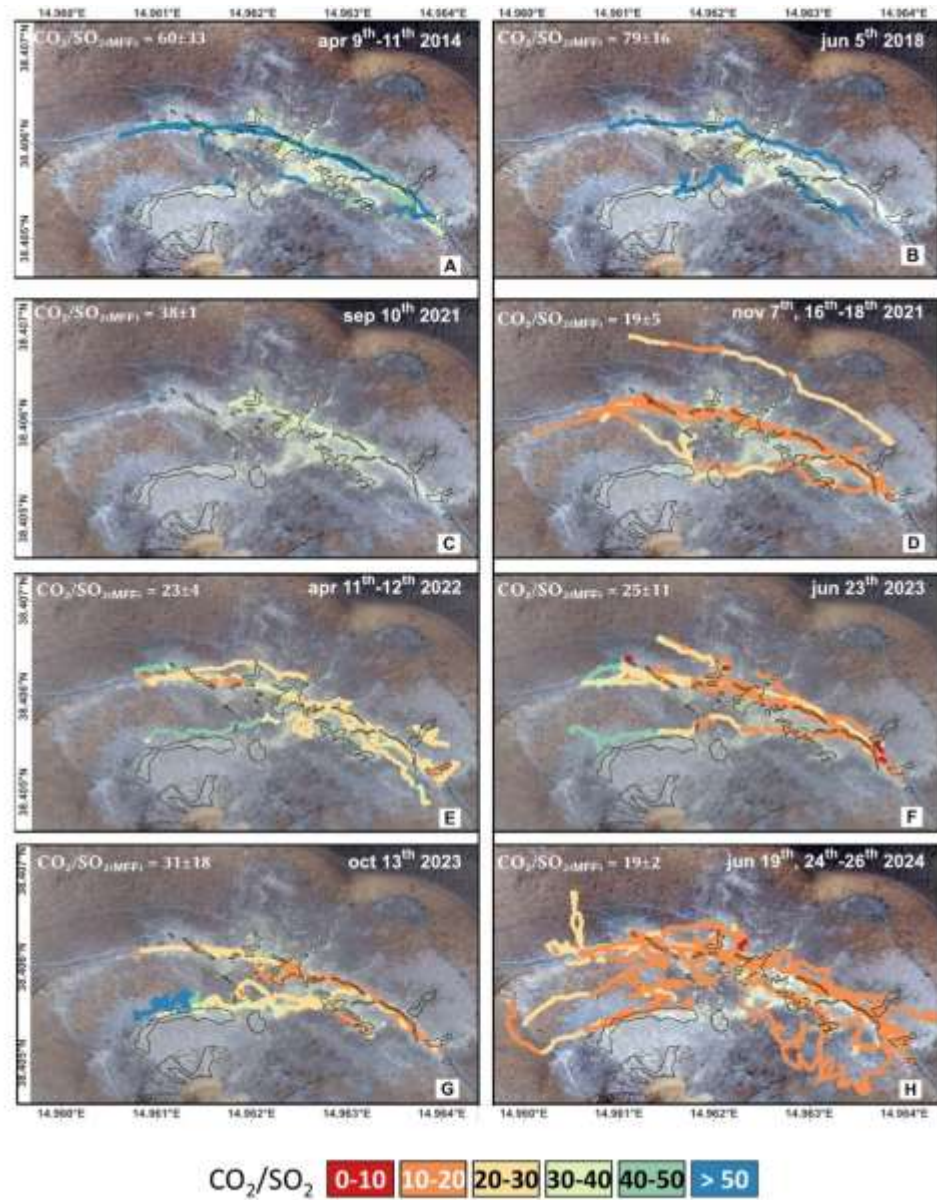


Figure 4.5 Selected dotted maps of the CO_2/SO_2 ratio in the La Fossa fumarolic field, obtained in 8 distinct campaigns September 2021 to June 2024. For reference, the upper two panels illustrate results for the April 2014 and June 2018 surveys, here taken as representative of phases of background hydrothermal activity (e.g., with limited transport of sulphur-rich magmatic gases). The 8 maps shown are extracted from the whole dataset shown in Supplementary Figure 1. The CO_2/SO_2 values in the maps are plotted using a color scale in which red tones are representative of magmatic compositions ($\text{CO}_2/\text{SO}_2 < 10$; Aiuppa et al., 2022) while deep blue tones correspond to hydrothermal gas compositions ($\text{CO}_2/\text{SO}_2 \gg 30$). Intermediate color tones indicate intermediate CO_2/SO_2 ratio compositions, as typical of mixed magmatic-hydrothermal compositions. All maps realized in QGIS (<https://qgis.org/>).

2024). Uncertainty is evaluated at $\sim \pm 30\%$, and is mainly determined by radiative transfer issues (e.g., light dilution effects and in-plume scattering effects; Kern et al., 2010). Results shown in Figure 6 are daily averages calculated over temporal windows with optimal viewing conditions (clear sky, high plume visibility, un-condensed plume).

4.4: Results

4.4.1: Chemical structure of the fumarolic field

In a dedicated campaign in June 2024, the entire La Fossa fumarolic field was covered by a series of Multi-GAS walking traverses released during four measurement days (19, 24, 25 and 26 June). This detailed survey allows the chemical structure of the fumarolic field to be fully reconstructed and visualized. Results are shown in the gas concentration maps of Figure 2, which are based on the interpolation of 16779 individual Multi-GAS measurements of each of the species determined (SO_2 , CO_2 , H_2S and H_2). Data interpolation is realized using the Inverse Distance Weighted (IDW) interpolation method, which assumes that the relative weight of each measurement on its surroundings diminishes with distance (d) according to a power law of the type $1/d^p$, where $p = 2$ in our case. To limit spatial interpolation to areas reasonably close to the measurement path, a barrier polygon function is used. We yet caution that since IDW assumes isotropic spatial influence, while gas outflow is controlled by the anisotropic distribution of fractures, topographic lineaments and wind pattern, physical processes such as gas challenging (by fractures) and atmospheric dispersion are not considered, which means the maps do not capture geological realities in full. Still, our maps clearly locate the positions of the most actively degassing fumaroles as visible spots of high gas concentrations (Figure 2).

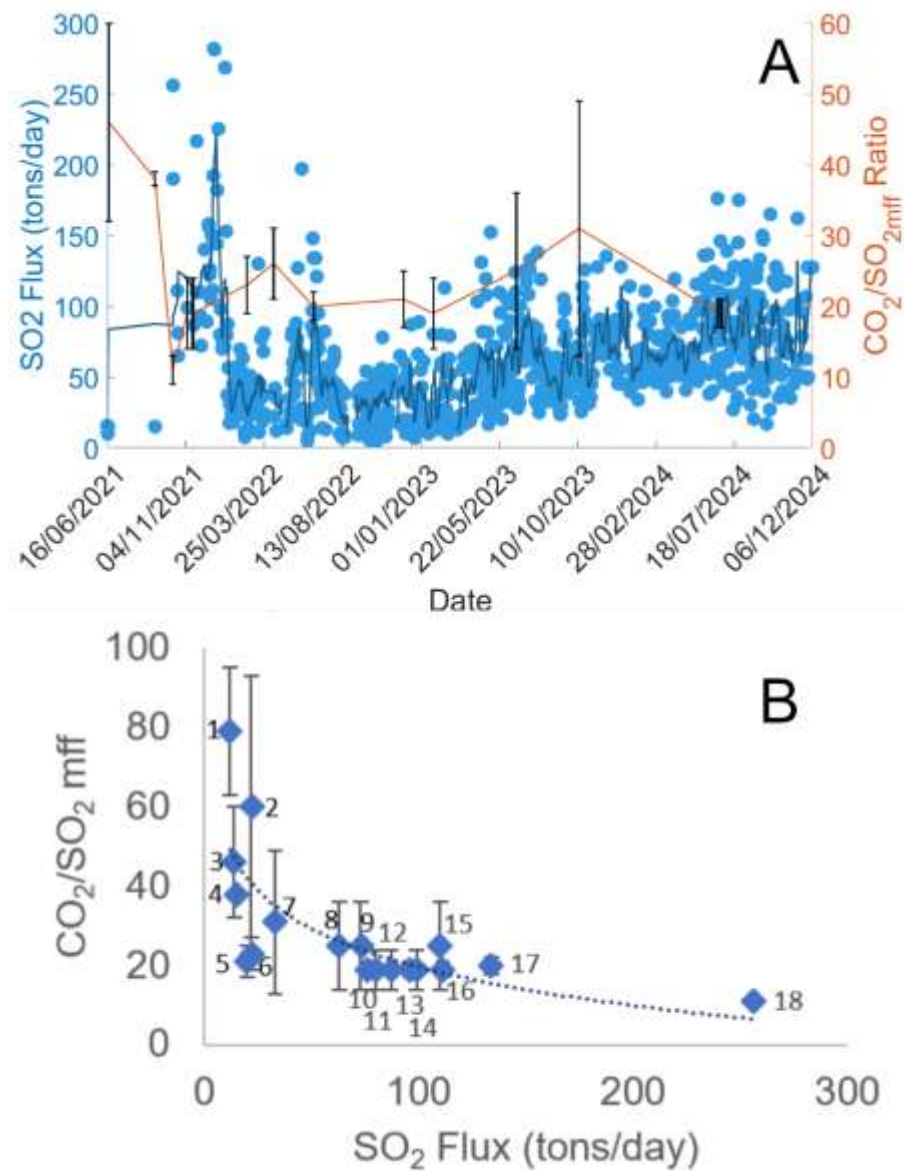


Figure 4.6 **A**: Temporal record of the SO₂ flux (in tons/day) and of the CO₂/SO₂_(MFF) ratio (from the maps of Figure 5 and Supplementary Figure 1). The blue line is a moving average of the SO₂ flux. A scatter plot comparing the two parameters is shown in **B**. 1: June 5th 2018; 2: April 12th 2014; 3: June 19th 2021; 4: 10 September 2021; 5: December 1st 2022; 6: February 23th 2022; 7: October 13th 2023; 8: June 22th 2023; 9: June 23th 2023; 10: June 24th 2024; 11: January 24th 2023; 12: November 18th 2021; 13: June 25th 2024; 14: November 7th 2021; 15: June 21th 2023; 16: June 19th 2024; 17: June 22th 2022; 18: October 12th 2021.

We find the main degassing areas in the eastern portion of the investigated area, along the post-1731, 1888-90 crater rim (see Figure 1d) and in the inner crater area connecting the F0 and FA fumarolic areas. The peak concentrations observed

are respectively 193 ppmv (SO₂), 4521 ppmv (CO₂), 117 ppmv (H₂S) and 4.1 ppmv (H₂). Hydrogen and (to a lesser extent) H₂S show no evident peaks in the FA area and hence are mostly degassed by the rim fumaroles. In contrast, lower, closer-to-background gas concentrations are observed in the western-most segment of the surveyed area, where strongly altered, mineralized rocks with minimal (if any) fumarolic activity prevail. A secondary CO₂ concentration peak is observed in the northern-most part of the surveyed area, in correspondence with the southern area of the Forgia Vecchia explosion vents (FV in Figure 1d).

The scatter plots of Figure 3 highlight correlation between the four gases species but also show large scatter indicative of chemical diversity in the fumarolic field. The CO₂/SO₂ ratios (Fig. 4.3A) in June 2024 ranges between 7 and 29 (the slope of the best fit regression line is 14.1 ± 3.7). SO₂ prevails over H₂S over the entire fumarolic system (the average H₂S/SO₂ ratio for the fumarolic system, 0.29 ± 0.20 ; Fig. 4.3B) except in the proximity of the Forgia Vecchia area. The average H₂/SO₂ ratio is $9 \times 10^{-3} \pm 6 \times 10^{-3}$ (Fig. 4.3C).

Figure 4 illustrates a zoomed view of the apparent temperature of the fumarolic field (Fig. 4.4A), in comparison to the main SO₂ and CO₂ concentration peaks are identified in a narrow NW-SE-oriented area stretching between the F0, GBC and F5/F5AT fumaroles. High SO₂ and CO₂ concentrations are also observed in the atmospheric plumes of F11, F12 and FA fumaroles (Fig. 4.4B and 4.4C). Overall, there is good correspondence between the most actively degassing areas (the gas concentration peaks) and the area of most intense thermal anomaly, as identified by the drone-based thermal map of Figure 4a. The contour map of Figure 4d shows a broad range of relatively homogeneous and prevailing low (mean, 19 ± 2) CO₂/SO₂ ratios over the entire crater rim area. In contrast, higher CO₂/SO₂ ratios (range, 20-26), indicative of more hydrothermally processed compositions, are observed in at westernmost margin of the fumarolic field, and in the intra-crater sector comprised between the FA, F13 and F12 fumaroles.

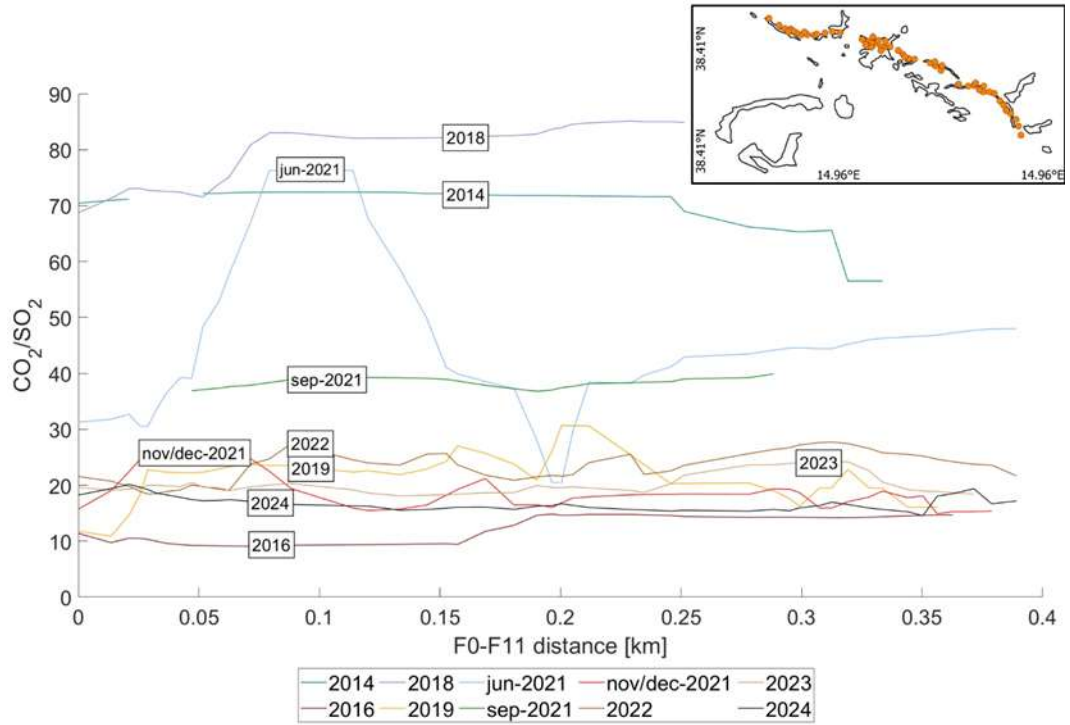


Figure 4.7 Moving-averaged CO_2/SO_2 ratios along a crater rim transects stretching from F0 to F11. Except for 2021, data obtained in different campaigns in the same year are averaged to obtain averaged yearly trend. 1: June 5th 2018; 2: April 12th 2014; 3: June 19th 2021; 4: 10 September 2021; 5: December 1st 2022; 6: February 23th 2022; 7: October 13th 2023; 8: June 22th 2023; 9: June 23th 2023; 10: June 24th 2024; 11: January 24th 2023; 12: November 18th 2021; 13: June 25th 2024; 14: November 7th 2021; 15: June 21th 2023; 16 June 19th 2024; 17: June 22th 2022; 18: October 12th 2021.

4.4.2: Temporal evolution of the fumarolic field

The maps of Figure 5 offer a graphical representation of the evolution of the fumarolic field during the study period. In the maps, color tones are adapted to convey information on the temporal alternation between phase of high (green to blue tones) and low (orange to red) CO_2/SO_2 ratios. In each of the maps, the spatial variations of color tones provide clues on the spatial variations of the CO_2/SO_2 ratio over the fumarolic field, and hence on its spatial homogeneity/heterogeneity. For each map, the average ratio (± 1 standard deviation), calculated as the arithmetic mean of all the ratios across the entire field (referred as $\text{CO}_2/\text{SO}_2(\text{MFF})$), is also reported.

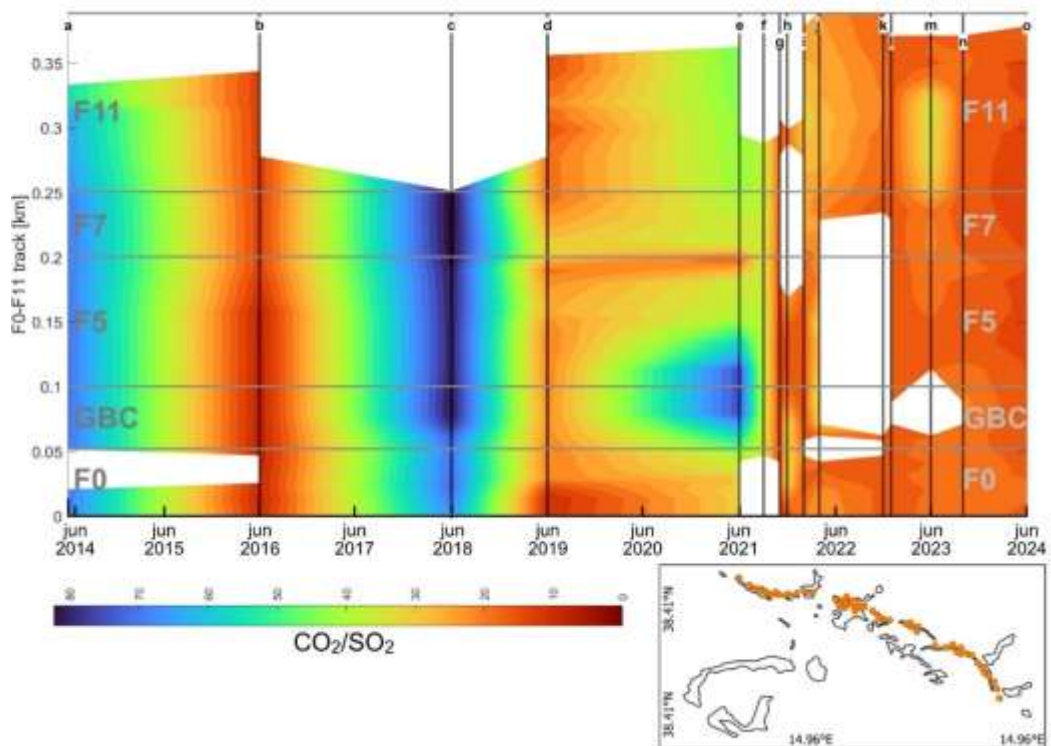


Figure 4.8 Mesh diagram showing the spatio-temporal evolution of the CO_2/SO_2 ratio across the crater rim fumaroles during 2014 to 2024. Time is the x-axis, distance along the F0-F11 transect on the y-scale. Color tones are proportional to the CO_2/SO_2 ratio (see legend). A remarkable compositional homogeneity of the fumarolic field is observed since the onset of the unrest in fall 2021. Letters identify the different campaigns.

Figures 4.5A and 4.5B are examples of CO_2/SO_2 ratio maps taken in periods of reduced (background) hydrothermal activity at La Fossa, e.g., April 2014 and June 2018. In both periods, the fumarolic field exhibits uniform and high (> 50) CO_2/SO_2 ratios, both in crater rim and inner crater fumaroles (same as for the May 2017 survey; see Supplementary Figure 1c). This chemical homogeneity of the fumarolic field is graphically illustrated by the dominance of blues color tones. In quantitative terms, the mean fumarolic field (MFF) ratio is ≈ 80 .

In contrast, Figure 5d is a map of the CO_2/SO_2 ratio taken in November 2021, near the acme of the La Fossa 2021 unrest (Federico et al., 2023). Here, low ($10 < \text{CO}_2/\text{SO}_2 < 20$) to locally very low ($\text{CO}_2/\text{SO}_2 < 10$) ratios are observed over the entire crater rim area. In contrast, the inner and outer crater fumaroles are associated

with intermediate (20 to 30) CO_2/SO_2 ratios. The CO_2/SO_2 (MFF) in November 2021 is ≈ 19 . Importantly, results for the June 2021 (Supplementary Figure 1f) and September 2021 (Fig. 4.5C) surveys, made only a few months/days prior to the unrest onset (nominally fixed at in the second half of September; Coppola et al., 2022; Federico et al., 2023; Di Traglia et al., 2023), still exhibit the prevalence of high-very high (June: $\text{CO}_2/\text{SO}_2(\text{MFF}) \approx 46$) to intermediate (September: CO_2/SO_2 (MFF) ≈ 38) CO_2/SO_2 ratios, confirming the abrupt onset of the unrest.

Surveys taken after November 2021 (Fig. 4.5 E-H and Supplementary Figures 3 and 4) demonstrate persistence of the unrest, yet at alternating levels. Broadly speaking, the dominance of orange color tones in the February 2022 to June 2024 maps supports the persistence of intermediate (20 to 30) CO_2/SO_2 ratio compositions in the fumarolic field. However, our results also reveal the alternation of periods of declining unrest, e.g., from November 2021 to February 2022 and in April 2022 during which a progression toward higher CO_2/SO_2 ratios are observed, with periods of accelerating unrest, when CO_2/SO_2 decrease again (e.g., June to December 2022 and June 2024). We also find that while the crater rim fumaroles exhibit relatively invariant CO_2/SO_2 ratios throughout February 2022 to June 2024 (except perhaps in April 2022), the inner crater fumaroles show larger temporal variability, especially those in the western sector of the fumarolic field (Supplementary Figures 3 and 4). An especially large compositional diversity in the fumarolic field, with a west to east progression from high/very high ratios to low ratios, is observed in the June 2023 and October 2023 maps (Supplementary Figures 3 and 4).

Figure 4.6 explores the relationship between the $\text{CO}_2/\text{SO}_2(\text{MFF})$ and the daily-averaged SO_2 flux. Figure 6a shows that the SO_2 flux increased from 14 ± 3 tons/day in June-early September 2021 to 135 ± 60 tons/day in October-November 2021. The SO_2 flux then decreased to < 50 tons/day in early 2022, paralleled by a $\text{CO}_2/\text{SO}_2(\text{MFF})$ increase to ~ 23 in April 2022 (Supplementary Figure 1). A new pulse of SO_2 flux increase (to > 100 tons/day) was then observed in fall-summer 2022, contemporaneous with onset of the degassing unrest at the peripheral Baia di Levante hydrothermal site (Coppola et al., 2022; Federico et al., 2023; Inguaggiato et

al., 2024). After a relatively low SO₂ flux phase in late 2022 to early 2023, the SO₂ flux progressively and moderately increased from May 2023, and stabilized to levels of 50-100 tons/day from the onward. The CO₂/SO_{2(MFF)} fluctuated at intermediate levels of 20 to 30 in the same temporal interval (Figure 6a). Overall, the SO₂ flux vs. CO₂/SO_{2(MFF)} dependency (Fig. 4.6B) identifies a background state for the fumarolic field associated with low (< 30 tons/day) SO₂ fluxes and high (hydrothermal) CO₂/SO_{2(MFF)} ratios (>50) that is clearly distinct from a “degassing unrest” population, with high (> 50 tons/day) SO₂ fluxes and low (< 30) CO₂/SO_{2(MFF)} ratios. The most-magmatic compositional pole (SO₂ fluxes of > 250 tons/day and CO₂/SO_{2(MFF)} ratios of circa 10) is exemplified by the October 2021 composition.

4.4.3: Evolution of the crater rim fumarolic zone

While the fumarolic field was irregularly covered in the different field campaigns, the crater rim area was more systematically investigated, allowing more careful analysis. Therefore, we present the results (Fig. 4.7) for compositional variations along a 370 m long “rim crater path”, traversing 54 individual measurement points (shown in Fig. 4.1E) across the crater-rim in a roughly west-to-east direction. The path starts at F0 and crosses GBC fumaroles, the central part of F5AT, F8 fumaroles and ends at the fumaroles F11. For simplicity and for improving readability of the figure, results of surveys taken in the same year are averaged except for 2021 (to more finely resolve gas composition variation at the unrest onset), and a smoothing (3 points mobile average) is applied.

Results (Fig. 4.7) demonstrate relatively uniform (spatially invariant) CO₂/SO₂ ratios along the crater rim during background activity (see 2014 and 2018 lines). In June 2021, ~3 months before initiation of the unrest, the crater rim fumaroles exhibited wider compositional diversity, with a progression toward intermediate ratios in the western (F0 area; < 0.05 km distance) and central (F5-F7 area; 0.15-0.25 km distance range) segments of the transect (see also Figure 4.8). By

early September 2021, just a few days/weeks prior to the unrest onset, the crater rim fumaroles had homogenized to intermediate ratios of circa ~ 38 (Fig. 4.7; see also Fig. 4.5). From November 2021 to June 2024, we observe a remarkable chemical homogeneity of the crater rim fumarolic field at lower (more magmatic) ratios of 15 to 30 (Fig. 4.7), with important implications discussed below.

4.4.4: MultiGas and Direct Sampling comparison

The La Fossa cone degassing unrest has been carefully analysed using the results of regular direct sampling techniques (Federico et al., 2023, 2026; Capecchiacci et al., 2025), and it is therefore convenient to put our Multi-GAS results in context by comparing them with fumarole composition results.

This comparison is attempted in Figure 4.9, which illustrates the temporal record of $\text{CO}_2/\text{S}_\text{T}$ ratios obtained in this study using the Multi-GAS (expressed by the $\text{CO}_2/\text{S}_\text{T}(\text{MFF})$ ratio defined above; green line with diamonds) plotted against the corresponding direct sampling results of (a) INGV-Palermo (results presented in Federico et al., 2026; dataset of Paonita et al., 2025) and (b) University of Florence (results presented in Capecchiacci et al., 2025).

This comparison demonstrates that the Multi-GAS derived $\text{CO}_2/\text{S}_\text{T}$ ratios match well the evolution of the fumarole $\text{CO}_2/\text{S}_\text{T}$ ratio, as inferred by INGV-Pa from periodic direct sampling surveys (Fig. 4.9a). Nicely, the two independent datasets nicely record the simultaneous drop of the fumarolic $\text{CO}_2/\text{S}_\text{T}$ ratio at the onset of the 2021 unrest, and the persistence of relatively low ratios (<20) throughout 2021 to 2023. A similar agreement between Multi-GAS-derived and direct sampling-derived $\text{CO}_2/\text{S}_\text{T}$ ratios is observed using the University of Florence dataset (Fig. 4.9b).

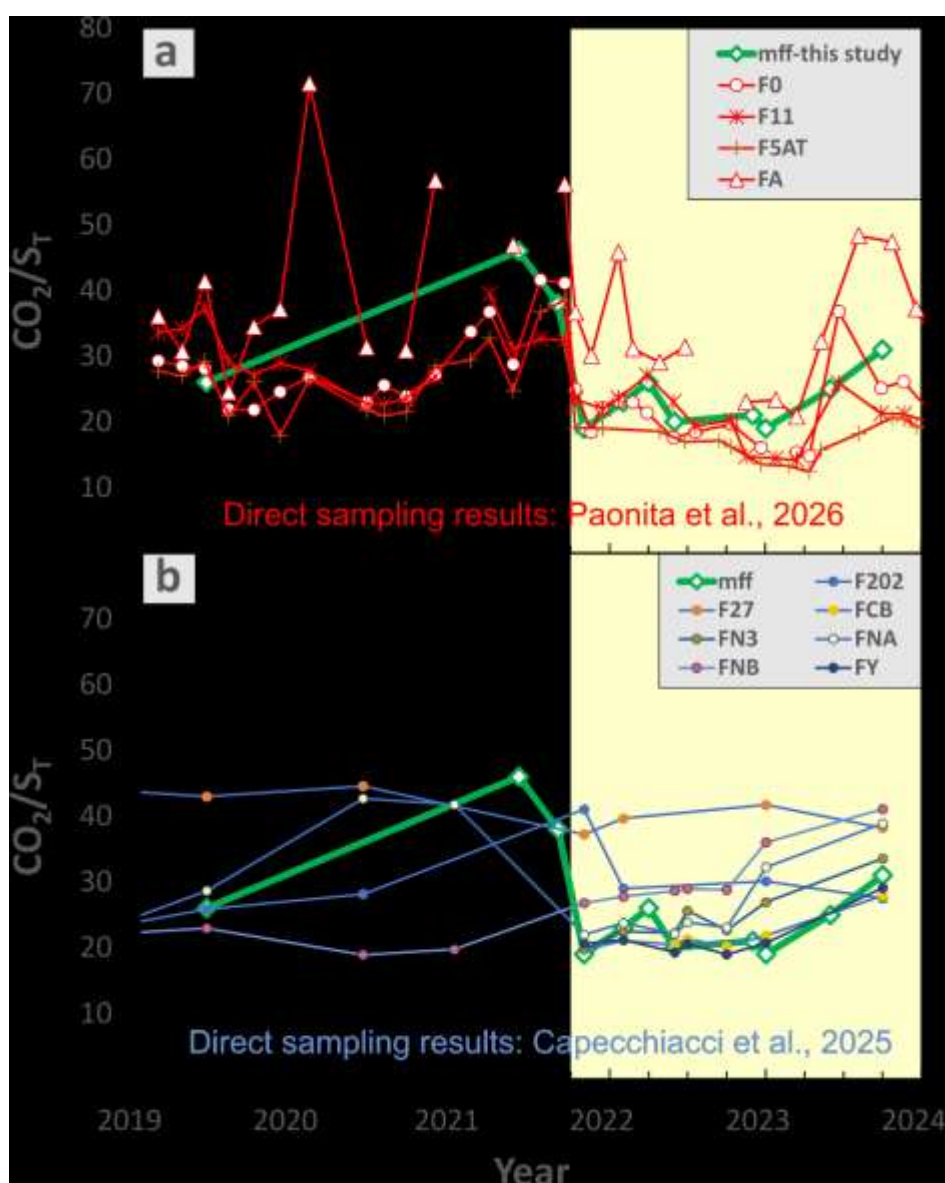


Figure 4.9 A comparison between Multi-GAS derived average $\text{CO}_2/\text{S}_\text{T}$ ratio across the fumarole field (mff; green line with diamonds) and those derived via direct sampling by (a) INGV-PA (Paonita et al., 2025) and the University of Florence (Capecchiacci et al., 2025) (mff-DS). The La Fossa unrest is indicated by yellow shading.

Overall, this comparison provides validation for the use of the Multi-GAS to monitor degassing unrest at hydrothermal volcanoes. The overlapping compositions of fumaroles (direct sampling) and plumes (Multi-GAS) additionally suggest that the atmospheric processing of sulphur species in near-vent plumes is marginal, so that $\text{CO}_2/\text{S}_\text{T}$ proportions are conserved, at least for short plume travelling times

(seconds) and distances (meters). These observations provide confidence on the use of plume observations for monitoring volcanoes in fumarolic stage of activity.

4.5: Discussion

Chemically profiling a fumarolic field with a real-time sensing Multi-GAS unit provides intrinsically less precise results than reachable with traditional direct sampling, and especially poses severe limitations to the number of chemicals that can be analysed. During unrest, however, expedite Multi-GAS surveys can be beneficial in reducing exposure of operators to toxic gases, and can help reconstructing the chemical diversity of the fumarolic field by rapidly analysing a far larger number of fumaroles than accessible with direct sampling.

In the extremely well monitored 2021-present La Fossa unrest (Federico et al., 2023), Multi-GAS surveys can complement available gas information by imaging (Figs. 2, 4-8) the spatio-temporal evolution of the fumarolic field, hence contributing to interpreting dynamics and evolution of the unrest.

Our results show that, within the context of the large spatio-temporal variability of the fumarolic field (Figs. 2, 4-5), the crater rim fumaroles have maintained a relatively uniform (space- and time-invariant) CO_2/SO_2 ratio signature throughout 2021 to 2024 (Figs. 5, 7-8). This contrasts with the southwestern portion of the fumarolic field that has experienced instead wider spatio-temporal fluctuations in composition, alternating (in both space and time) high and low CO_2/SO_2 ratio compositions (Fig. 4.5 and Supplementary Fig. 1-4). These two distinct regions are broadly separated by a NW-SE trending boundary zone (Fig. 4.1E), to the north-east of which more magmatic, relatively uniform CO_2/SO_2 ratios (in the 19 to 31 range) have been observed. Our results thus help confining the boundaries of the most actively degassing zone at La Fossa (Fig. 4.3), and point to the crater rim sector as the surface expression of the magmatic gas transport conduit (the heat chimney of Paillot-Bonn  tat et al., 2023) feeding the 2021-2024 unrest. The crater rim fumarolic area corresponds to the norther edge of the cr6 crater identified by Di

Traglia et al. (2013), interpreted as the outer rim of the crater that fed the post-1739 open-vent activity of La Fossa (Selva et al., 2020), including its last eruption in 1888-90 (Fig. 4.1D). This geological discontinuity may thus have served as a preferential gas ascent pathway for deeply rising magmatic volatiles (Federico et al., 2023), consistent with the peak fumarolic temperatures recorded there (Diliberto et al., 2024). The 2021-present unrest hence differs from the 1988-93 unrest, during which the peak temperatures and most magmatic gas compositions were observed in the inner crater fumarolic zone, especially in the FA fumarole area (Selva et al., 2020 and references cited therein). In contrast, during 2021-2024, the space-time compositional variability observed in the FA region, and more broadly on the southwestern portion of the fumarolic field (Supplementary Fig. 4.1), may be interpreted to reflect the alternation of phases of expansion (e.g., see June 2024 map) and contraction (e.g., see October 2023 map) of the gas/heat feeding conduit, in response to changes in magmatic gas supply from below, and/or permeability changes in the shallow hydrothermal system (Paillot-Bonn  tat et al., 2023). As previously noted (Paillot-Bonn  tat et al., 2023), the very dynamic (spatially and temporally changing) nature of the south-western margin of the fumarolic field makes it very useful target to deciphering evolution of the unrest. A compositional shift of the southwestern fumaroles, from hydrothermal to magmatic, and hence a tendency toward a general compositional homogenization of the entire fumarolic field, should be viewed as potential signs of heightened future unrest at Vulcano.

Our results also contribute to interpreting the temporal evolution of the unrest. At La Fossa cone, there is a well-documented record of periodic increases in degassing activity since the late 1970s (Selva et al., 2020 and references therein). Some of these degassing pulses have manifested in evident, macroscopic changes such as the emission of large plumes from the volcano summit, increases in toxic gases in soil and air at the volcano periphery, and/or changes in temperature, acidity and salinity of water bodies onshore and offshore (Barberi et al., 1991; Federico et al., 2023); while some others have produced more subtle changes that could only be captured thanks to careful monitoring (Paonita et al., 2013; Inguaggiato et al., 2018).

One common aspect of these events has been their abrupt initiation, a fact that has led to models (Paonita et al., 2013) explaining unrest as caused by sudden outburst of magmatic gases previously accumulated (during quiescence) at some structural/permeability discontinuity in the shallow hydrothermal system. The implication of these models would be that unrest is essentially hydrothermal in nature, and that hence there is no upward migrating magma involved.

The more recent unrest of La Fossa also started in mid-September 2021 (Coppola et al., 2022; Di Martino et al., 2022; Inguaggiato et al., 2022, 2023; Di Traglia et al., 2023; Federico et al., 2023; Paillot-Bonn  tat et al., 2023; Campus et al., 2024; Diliberto et al., 2024; Mueller et al., 2024; Giuffrida et al., 2025), and reached its climax in October-November 2021, when a peak in degassing, seismo-volcanic activity and fumarole temperatures was reached. The lowest (< 10), most magmatic CO_2/SO_2 ratios in our dataset (Aiuppa et al., 2022) were consistently observed in this phase, associated with the largest SO_2 fluxes (Fig. 4.6A). From late 2021 onward, degassing and seismicity at the summit slowly but progressively declined, accompanied by a progressive expansion and shift of the degassing unrest towards more peripheral areas (the Vulcano Porto plain and Baia di Levante area) in early/mid 2022 (Coppola et al., 2022; Federico et al., 2023; Inguaggiato et al., 2023). Our results track well this declining unrest at La Fossa summit, as indicated by CO_2/SO_2 (MFF) ratios increasing again to intermediate values of 19 to 31 (Supplementary Figures 1-4) and SO_2 fluxes decreasing to < 100 tons/day (except for a phase of SO_2 flux increase in fall-summer 2022 concomitant with onset of the degassing unrest at the peripheral Baia di Levante). Therefore, following a steep activity increase and peak in late 2021, a 3-year long coda was observed.

In this context of vanishing unrest, we yet notice that the CO_2/SO_2 ratio levels observed at the crater rim in 2021-2024 (Figs. 6-8) are still well below those observed during phases of reduced (background) hydrothermal activity at La Fossa (see for example the April 2014, May 2027 and Jun 2018 maps of Supplementary Fig. 1-4 and Fig. 4.6B), during which gases with CO_2/SO_2 ratios $\gg 30$ (Figure 6b), and eventually > 100 (see Paonita et al., 2013), are emitted. This, combined with the

intermediate SO₂ fluxes observed especially since May 2023 (the May 2023 to June 2024 SO₂ flux average is 68 ± 26 tons/day), indicates that the sulphur output regime at La Fossa may have not completely recovered to background levels yet (see also Inguaggiato et al., 2023; Vita et al., 2023; Giuffrida et al., 2025). It is important to keep in mind that volcanic systems often exhibit complex, non-linear behavior, and hence can stabilize at new baselines/states of monitored parameters without necessarily returning to prior conditions, e.g., at more evaluated sulfur degassing regime in the Vulcano case. The drivers for this higher-than-normal sulphur release (Inguaggiato et al., 2023) are still debated, but can potentially include a combination of (i) sulphur remobilization from hydrothermal minerals (Chiodini et al., 1993; Di Liberto et al., 2002), and (or) (ii) an increased supply of magmatic sulphur from mafic magma at depth b.s.l. (~ 5 km) (Aiuppa et al., 2022; Giuffrida et al., 2025), perhaps combined with a reduced scrubbing of magmatic sulphur in the hydrothermal system, due to more rapid gas transit in the ascent conduit. Petrological evidence has found that multiple episodes of mafic magma resupply to the shallow magmatic system have taken places in the ~ 140 year temporal interval preceding the 1888-90 La Fossa eruption (Giuffrida et al., 2025) and, although ground uplift (~ 7 cm) has been interpreted (Di Traglia et al., 2023) as caused by pressurization of a conduit-like gas feeding system within the shallow hydrothermal system (Chiarabba et al., 2004; Di Giuseppe et al., 2023), the fact this deformation is permanent (in spite of vanishing degassing activity at surface) leaves the possibility open that some (minor) reconfiguration of the plumbing system (e.g., the addition of small volume of magma at depth; Aiuppa et al., 2022; Giuffrida et al., 2025) may have taken place. As a complement to ongoing multi-parametric monitoring (Federico et al., 2023), periodic mapping of the fumarolic system may allow interpreting any further evolution of the unrest.

Our results are also relevant to understanding the potential gas hazard associated with the exhaling activity at La Fossa. Volcanic and hydrothermal gases can exert a wide range of impacts on human health, ranging from mild (fatigue, shortness of breath, irritation of nose, throat, eyes, or skin, headache, nausea) to serious

(cardiovascular effects, aggravation of asthma, unconsciousness, pulmonary edema), or even lethal in the most extreme cases (Baxter et al., 1982; Baxter, 1990, 2000; Hansell and Oppenheimer, 2004; Stewart et al., 2022; Horwell et al. 2023). Effects depend on gas concentration level, length of exposure, and personal sensitivity (IVHHN, 2025).

The effects of H₂S at relatively small concentration levels (20-150 ppm) include loss of smell, irritation, nausea and headache, enterogastric and pulmonary problems, while long exposures to 50 ppm cause pharyngitis and bronchitis and edemas. Very high exposures (to more than 200-500 ppm) can cause rapid unconsciousness or death within minutes (Legator 2001; Bates 2002; Balagizi et al. 2018; IVHHN, 2025).

SO₂ is an irritant gas that primarily affects the eyes and respiratory tract. Even brief exposure can cause coughing, burning eyes, breathing difficulties and a tightness in the chest. People with asthma are much more sensitive and may react even at very low concentrations (0.2-0.5 ppm) (see NIOSH 1981; Wellburn, 1994; Baxter, 2000; Nemery, 2001). Those with heart or lung conditions are also more vulnerable to prolonged exposure at low concentrations (1-5 ppm). As the concentration increases, the effects worsen rapidly: from simple irritation (around 6 ppm) to severe respiratory damage, possible toxicity with prolonged exposure (10-15 ppm), and serious or fatal risks at very high concentrations (over 20 ppm for prolonged periods). At extreme levels (around 150 ppm), even a few minutes can be tolerated only by healthy individuals. (Wellburn, 1994; Baxter, 2000; Nemery, 2001; IVHHN, 2025).

Some of the most extreme human health effects of volcanic gases have historically been related to exposure to high CO₂ levels (Baxter, 2000; Faivre-Pierret & Le Guern, 1983; IVHHN, 2025). CO₂ is a colorless, odorless, and non-flammable gas with a density 1.5 times greater than air, allowing it to accumulate in depressions and poorly ventilated zones (Sax & Lewis 1989). Such gas layering can lead to oxygen depletion, and hence determine very severe consequences, especially where high outdoor/indoor concentrations are reached (Viveiros et al. 2024).

To evaluate the possible human health impacts of hydrothermal/volcanic gases at Vulcano island, we use CO₂, SO₂ and H₂S concentration results obtained in a dedicated campaign conducted on Vulcano in 2025, in which measurements were conducted in 3 distinct zone: (i) along the upper flank of the cone (along the tourist ascent path), (ii) across the outer crater rim (an area frequently visited by tourists), and (iii) the fumarolic field (only infrequently traversed by tourists and only for short temporal intervals).

The frequency distribution diagrams of gas concentrations in the three areas (flank, outer rim and fumarolic field) are illustrated in Figure 4.10. The potential human health impacts to exposure to these gas concentration levels are inferred from comparison with maximum exposure limit (MEL) concentrations - thresholds above exposure to gas can develop harmful effect to human health. These are derived using characteristic exposure times of 1-5 minutes (fumarole field) and 30-60 minutes (flank and outer crater rim). For SO₂ and H₂S, MEL values are inferred from the maximum permitted limit of 5/10 ppm over a 15-minute exposure time (from now on, simply MEL₁₅), a reference for short exposures suggested by the UK Health and Safety Executive in 2020 (HSE, 2020). From these, the 1-5 minutes (fumarole field) and 30-60 minutes (flank and outer crater rim) thresholds are derived using Haber's law (Gaylor, 2000), which expresses the relationship between the toxic effect k of any chemical agent, its concentration C and exposure time t (e.g., $C \cdot t = k$ is a equivalent dose). These thresholds do not apply to people with heart or respiratory conditions or children and the elderly (IVHHN, 2025).

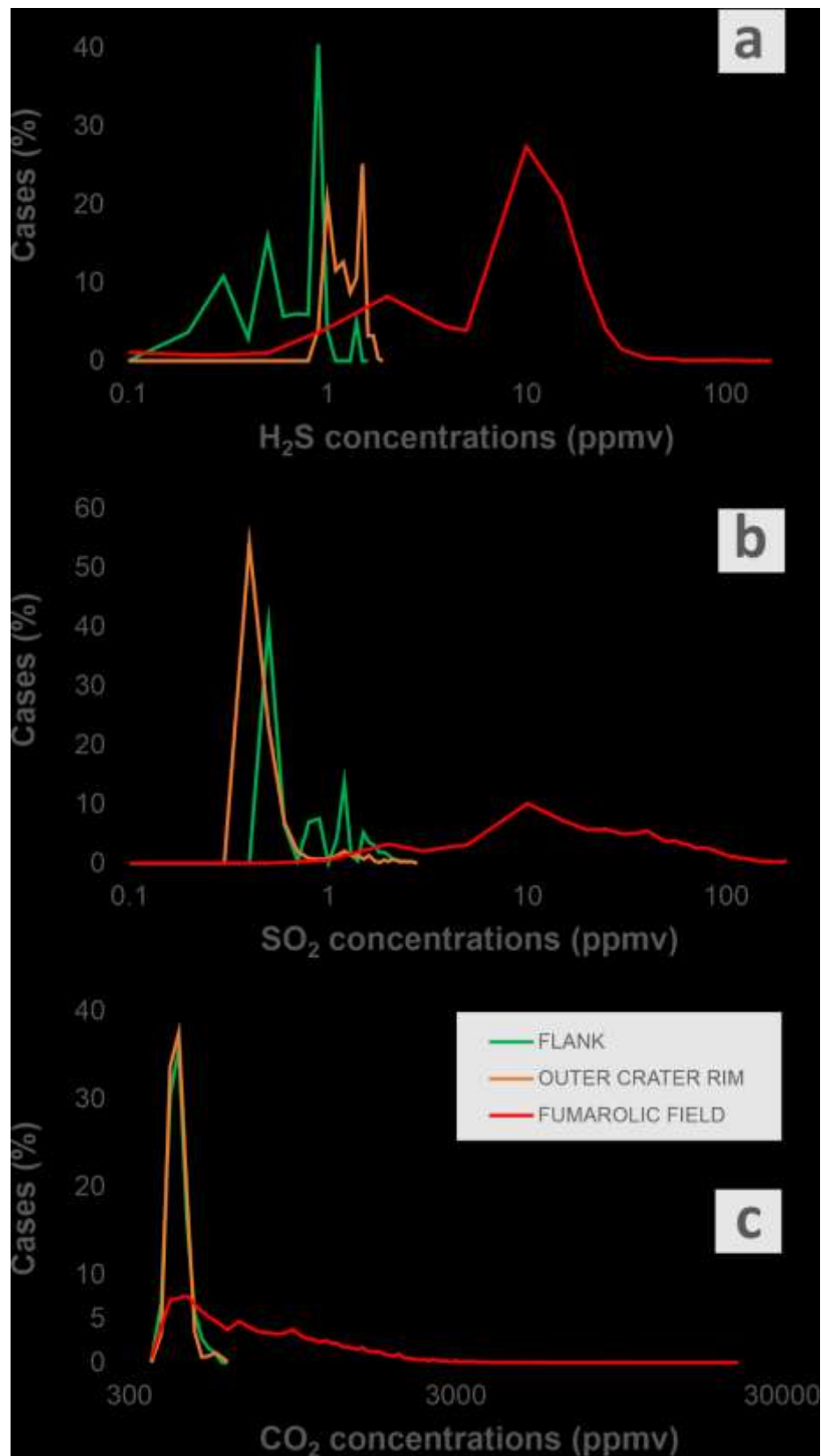
The frequency distribution diagram of Figure 4.10A exhibits an H₂S distribution in the fumarolic field with a mode at ~10 ppm (27% frequency). Considering the aforementioned MEL₁₅ = 10 ppm and using Haber's law, we obtain the corresponding MEL₁ of 150 ppm [(10 ppm 15 min)/1 min] and MEL₅ of 30 ppm [(10 ppm 15 min)/5 min]. In Figure 4.10A, concentrations > 150 ppm are associated with negligible frequencies, whilst concentrations > 30 ppm occur in less than 1.5% of cases. The same exercise, carried out at the flank and along the path around the crater rim, yields MEL₃₀ and MEL₆₀ values of 5 ppm and 2.5 ppm respectively for

exposure times of 30 minutes and 60 minutes. The distribution of H₂S concentrations at the crater rim and along the path around the crater shows that these concentrations are never reached. It should be noted, however, that an exposure time of 15 minutes or more at the fumarole field results in concentrations exceeding 10 ppm in our H₂S frequency distribution graph. Tourists, however, do not tend to linger for very long at the fumarole field.

The SO₂ frequency distribution in the fumarolic field has a mode at ~10 ppm (10% frequency; Fig. 4.10b). The MEL₁₅ for SO₂ is of 5 ppm (HSE, 2020; IVHHN, 2025) and the corresponding MEL₁ and MEL₅ are then 75 ppm and 15 ppm. In Figure 4.10B, concentrations 75 ppm occur in ~2.6% of cases, whilst concentrations 15 ppm are associated with 7.5% frequencies. Therefore, one in thirteen people may experience an adverse effect, particularly if the individual in question has asthma (as aforementioned). The same exercise, carried out at the flank and along the path around the outer crater rim, yields MEL₃₀ and MEL₆₀ values of 2.5 ppm and 1.3 ppm respectively. Along the flank and outer crater rim, concentrations of 1.3 ppm show almost identical frequencies of 1.3%, whilst those of 2.5 ppm show negligible frequencies. It should be noted that such concentrations nevertheless have mild effects on healthy individuals; for asthmatics, as mentioned above, the effects may be more pronounced.

Regarding CO₂ concentrations, this gas becomes toxic at levels exceeding 1%. Figure 4.10 C never reaches such levels, so this gas poses no cause for concern for tourists.

Whilst volcanologists work in the fumarole field wearing appropriate personal protective equipment (suits and masks) to cope with the environmental conditions, these conditions pose a greater risk to tourists, who, often unaware of the hazards, venture into the fumaroles without specific protections. Our exercise here shows, however, that at the current level of degassing activity of La Fossa, adverse effects are only likely to develop in a marginal set of circumstances, and potentially only for individuals with pre-existing respiratory issues.



4.6: Conclusions

We have presented results of periodic gas surveys made at La Fossa cone on Vulcano Island, in which the spatial diversity of the summit fumarolic field was mapped and reconstructed over 2021 to 2024 using a portable Multi-GAS unit operated in walking traverse mode. Our results demonstrate a significant spatio-temporal evolution of the fumarolic field during the 2021-present degassing unrest. We have shown that the fumarolic field is broadly separated in two regions, separated by a NW-SE trending boundary zone: (i) the crater rim area to the NE that has exhibited relatively uniform, intermediate CO_2/SO_2 ratio compositions (range, 19-31), and (ii) the inner crater fumaroles to the SW, that have exhibited wider temporal fluctuations, and overall dominance of more hydrothermal (CO_2/SO_2 ratios) gas signatures. The zonation pattern observed in this study, identified from mapping of the fumarolic field, is perfectly consistent with that identified by Capacchiacci et al. (2025) based on independent diureact sampling evidence. This is interpreted as caused by oscillating phases of expansion and contraction of the gas chimney, centered underneath the 1888-90 eruption outer crater rim (the cr6 crater rim of Di Traglia et al., 2013), acting as the main transport structure of magmatic volatiles toward the surface. The intermediate, below-background CO_2/SO_2 ratios observed in crater rim area throughout 2021-2024, in conjunction with the higher-than-background SO_2 fluxes recorded, suggest that, despite the progressive vanishing of degassing activity since the acme of the unrest reached in fall 2021, hydrothermal activity conditions may stabilised at higher sulphur degassing levels than before the unrest.

This is reflected in the SO_2 concentration of 10 ppm recorded at the fumarole field in 2025, which is twice the 15-minute maximum exposure limit of 5 ppm. Given that adverse effects in vulnerable individuals occur at even lower concentrations, these findings emphasize that the fumarolic field requires stricter monitoring to prevent prolonged exposure and mitigate respiratory risks.

4.7: Acknowledgement

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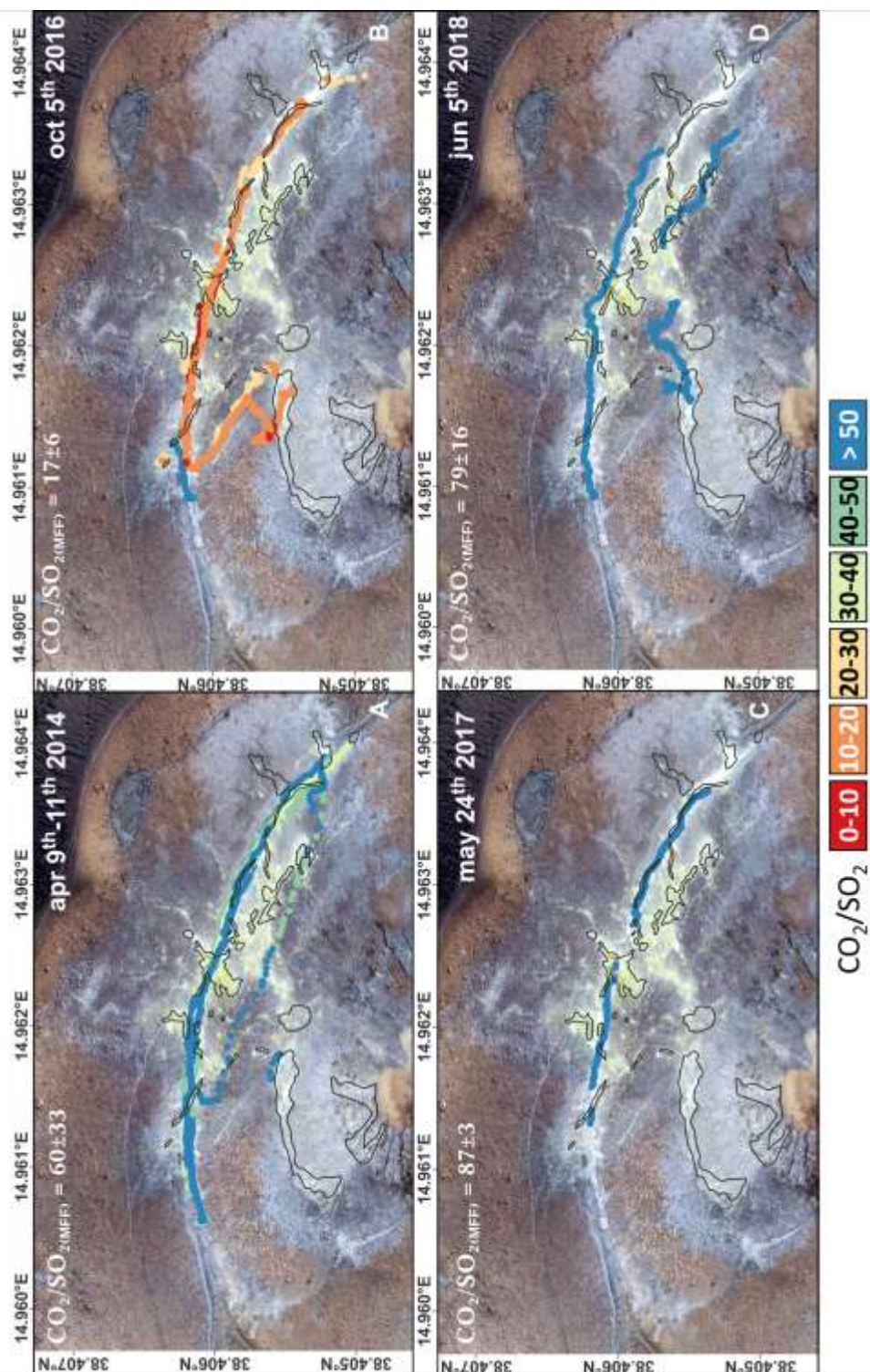
Author contributions

Simone Lentini: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. Marcello Bitetto: Methodology, Investigation, Data curation. Luciano Curcio: Writing – review & editing, Methodology, Investigation, Data curation. Malte Seefeld: Visualization, Methodology, Investigation, Formal analysis. Angelo Vitale: Methodology, Investigation, Data curation. Piero Dellino: Supervision, Project administration, Funding acquisition. Roberto Sulpizio: Supervision, Project administration, Funding acquisition. Daniel Muller: Writing – review & editing, Methodology, Investigation, Data curation. Thomas R. Walter: Writing – review & editing, Methodology, Investigation. Alessandro Aiuppa: Writing – original draft, Investigation, Formal analysis, Data curation, Supervision, Project administration, Funding acquisition.

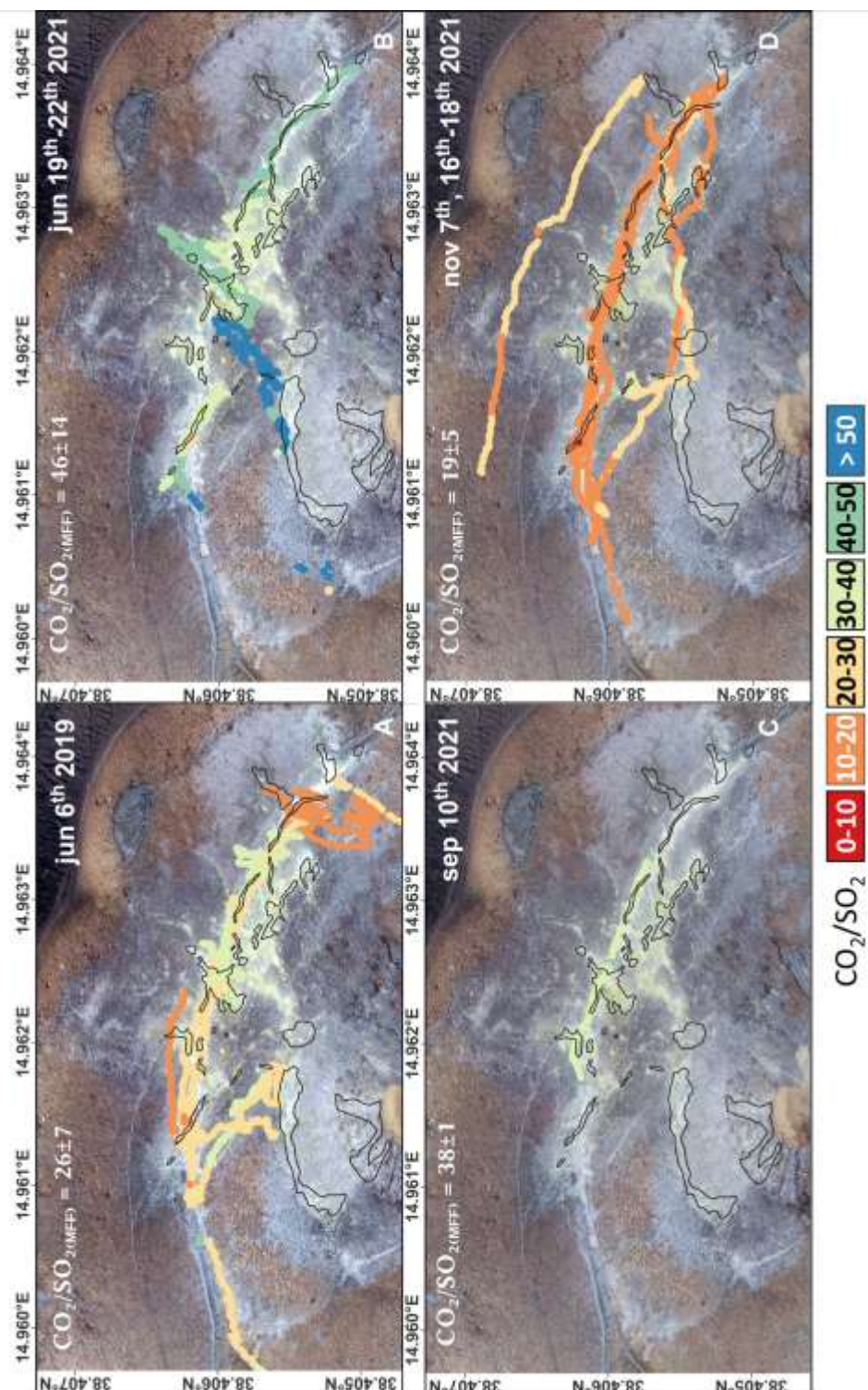
Data availability

The data in csv format supporting the conclusions reached in this article (Relative DOI. 10.5281/zenodo.15298147.) are available in a 7zip file at <https://zenodo.org/records/15298147>

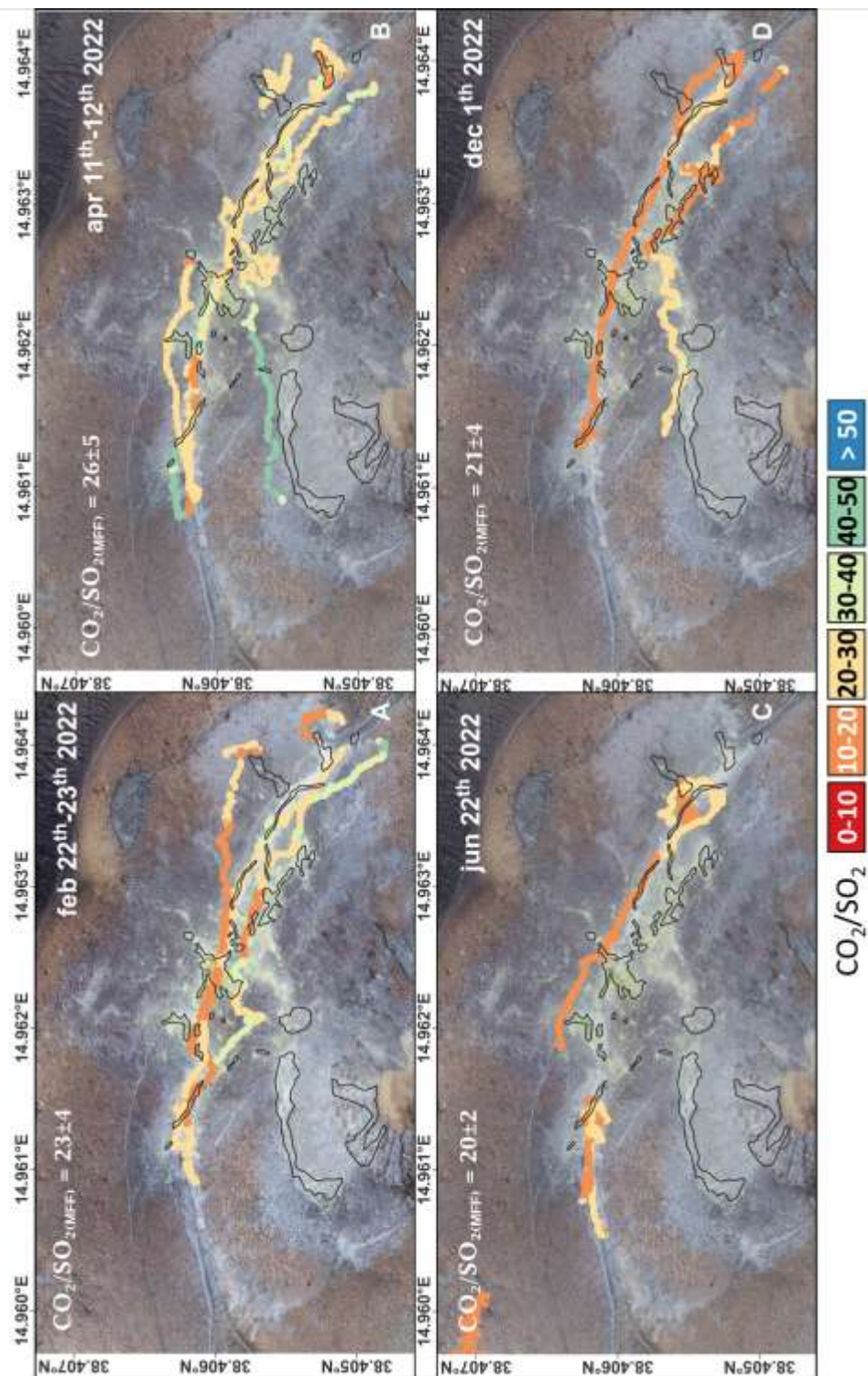
Supplementary figure 1



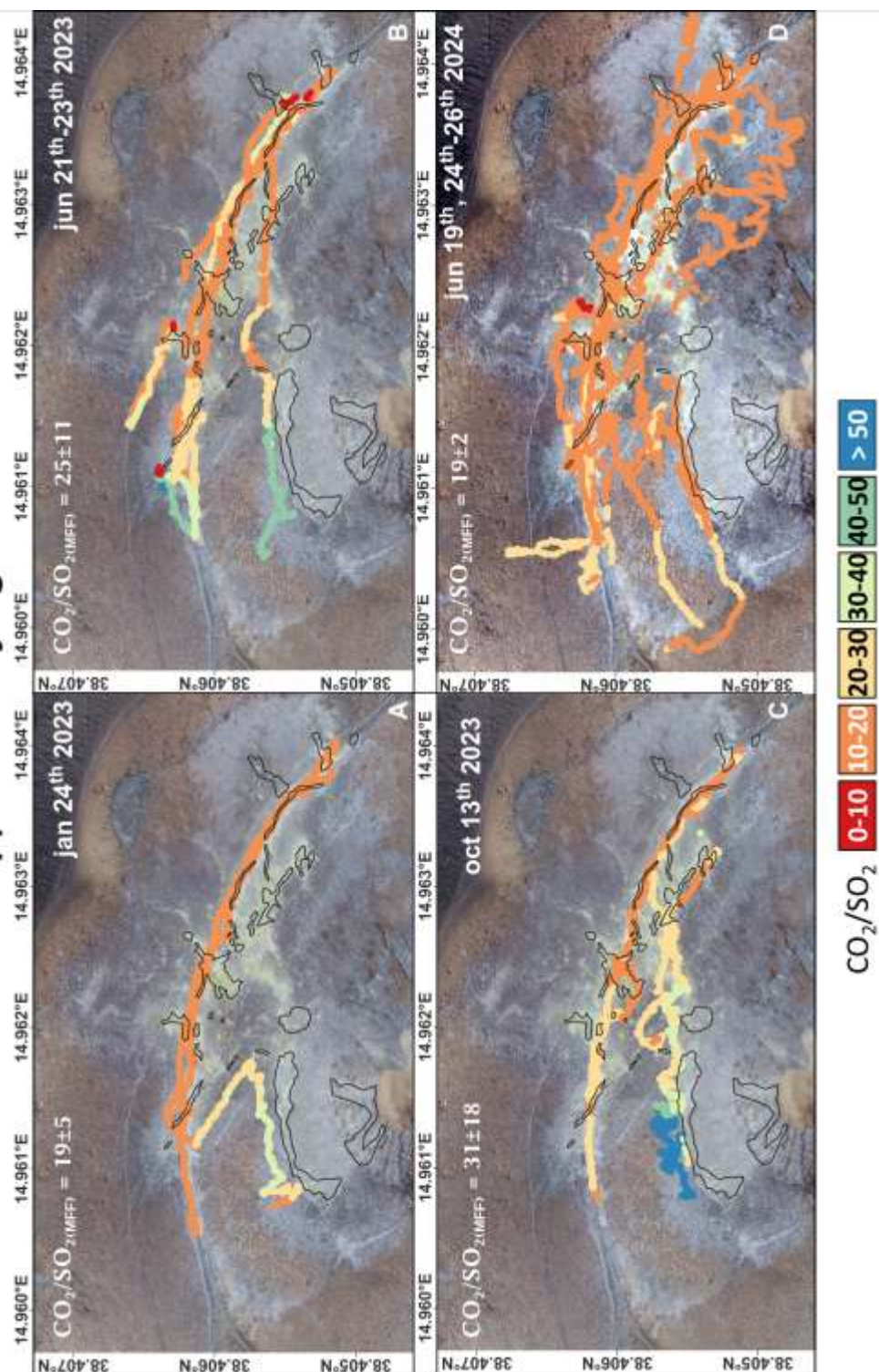
Supplementary figure 2



Supplementary figure 3



Supplementary figure 4



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5: MULTI-GAS BASED MAPPING OF HYDROTHERMAL FUMARoles AT NISYROS, GREECE

Abstract - This study reports the results of a volcanic gas survey conducted at Nisyros, a volcanic island in the Aegean Sea (Greece) hosting a polygenetic volcanic system recurrently active in the holocene, and today home of intense hydrothermal circulation. We used a portable Multi-component Gas Analyzer System (Multi-GAS) to traverse (by walk) the fumarolic fields of Stefanos and Lofos, two of the Nisyros' most active hydrothermal sites, with the aim of characterizing the compositional signatures (CO_2 , H_2S , H_2 and SO_2) of their proximal fumarolic atmospheric plumes at high spatial ($\sim$ meters) and temporal (1 Hz) resolution. Our spatially resolved gas concentration results allow mapping the most actively degassing vents at Stefanos. In our maps, these take the form of clusters of gas-rich spots ($\text{CO}_2 > 1000$ ppmv and $\text{H}_2\text{S} > 80$ ppmv) that overall define a ring-shaped structure, corresponding to the inner crater rim (or outer caldera floor margin). Even higher atmospheric gas concentrations (up to 2250 ppmv CO_2 , 200 ppmv H_2S , 10.6 ppmv H_2 and 0.4 ppmv SO_2) are detected in the atmospheric plumes of the fumaroles located on top the Lofos dome. We additionally provide a spatially resolved record of gas ratios in a larger number of fumaroles than typically investigable with direct sampling techniques, finding an overall compositional homogeneity ($\text{CO}_2/\text{H}_2\text{S}$ ratios of 6.4 to 13.1 and CO_2/H_2 ratios of 166 to 171). Our results contribute to completing the multi-decadal record of gas composition at Nisyros, demonstrating H_2S -poorer compositions in 2025 (this study) than observed during the 1996-2001 seismic/degassing unrest. Finally, considering that the Nisyros hydrothermal manifestations are frequently visited touristic destinations, we conclude by discussing the implications of our results for an assessment of the potential impact on human health (tourists, visitors and operators) of the atmospheric concentration levels of potentially hazardous gases (CO_2 and H_2S).

5.1: Introduction

Closed-conduit stratovolcanoes and calderas undergo long-lived repose periods, frequently lasting centuries to millennia, during which surface hydrothermal manifestations, such as fumaroles, steaming grounds, mud pools and degassing soils, are the main expression of still active volcanism (Delmelle and Stix, 2000; Stix et al., 2025). Because hydrothermal volcanoes in repose are often seismically silent and geodetically stable, studying the geochemistry of such hydrothermal manifestations has long been demonstrated as a powerful tool to study the behavior and pressure-temperature-compositional conditions of the underneath hydrothermal system(s) sourcing them (Giggenbach, 1980, 1997; Chiodini and Marini, 1998, Fischer and Chiodini, 2015). This is especially so when escalating degassing of magmatic volatiles at these manifestations (Chiodini, 2009; Chiodini et al., 2012, 2016) allows capturing early signs of hydrothermal volcanoes becoming restless during unrest (see Aiuppa et al., 2025a for a recent review).

Because volcano reawakening during unrest generally lasts decades to years (Philipson et al., 2013; Rosi et al., 2022), intensifying hydrothermal degassing can suitably be tracked by periodic campaigns involving direct sampling of fumaroles and post-sampling analysis laboratory (e.g., Vaselli et al., 2010). During peak of unrest (Paonita et al., 2013; Federico et al., 2023), however, direct sampling becomes increasingly impractical (e.g., risky for operators), requiring instruments are put in place that can autonomously record gas composition (de Moor et al., 2016a, Kern et al., 2022; Aiuppa et al., 2025a, b). The Multi-component Gas Analyzer System (Multi-GAS) technique (Aiuppa et al., 2005; Shinohara, 2005), in particular, has revealed especially useful to track changes in gas compositions, e.g., changes in CO₂ to total sulphur (S_T) proportions (the CO₂/S_T ratio) and/or in sulphur speciation (the SO₂/H₂S ratio), during intensification of the unrest in the eruption run-up (e.g., Shinohara et al., 2011, 2018; de Moor et al., 2016b, 2019). At volcanoes hosting large fumarolic systems with multiple emission sources, the Multi-GAS technique has also released useful in mapping the spatial heterogeneity of chemical

composition, which can be accomplished by traversing a fumarolic field with a GPS-synchronized portable unit recording (at 1 second steps) the concentrations of key (major) gas compounds (Aiuppa et al., 2005, 2006, 2022; Lentini et al., 2025).

Here, we employ this Multi-GAS walking traverse approach for measuring the spatial diversity of gas (CO_2 , H_2S , H_2 , SO_2) concentrations in the atmospheric plumes of the fumaroles on Stefanos and Lofos craters, the two largest hydrothermal fumarole manifestations at Nisyros, a dormant volcanic system in the Aegean Sea (Greece). This hydrothermal volcano has experienced significant seismic (Papadopoulos et al., 1998) and degassing unrest (Chiodini et al., 2002; Marini et al., 2002, 2005; Brombach et al., 2003) in the late 1990s that raised concerns for a possible renewal of volcanic activity, with the most likely scenario being a hydrothermal explosion (Marini et al., 1993). Although no eruption finally took place, our results contribute to our understanding of the temporal evolution of the unrest. Our gas concentration results also bring implications for the potential gas hazard exerted by fumarolic emissions on human health (Hansell and Oppenheimer, 2004), considering that these popular hydrothermal sites are visited by thousands of visitors (tourists and operators) every year.

5.2: Study area

5.2.1: Magmatism in the Hellenic Subduction Zone

The Hellenic Subduction Zone (HSZ) is one of the most geodynamically active and complex areas in the Mediterranean, where the African plate subducts beneath the Aegean microplate. The interaction between the two plates is responsible for intense seismic activity, volcanism, and crustal deformation. The HSZ extends along an arc from the eastern Ionian Sea to the Dodecanese, with a complex three-dimensional geometry. Seismic tomography studies have shown that the slab

penetrates the upper mantle to depths of at least 600 km (Spakman et al., 1988) (**Fig 5.1**).

Subduction in the HSZ began approximately 15 million years ago, consuming oceanic crust belonging to the Neotethys Ocean or an even older oceanic domain (Le Pichon & Angelies 1979; Angelier et al., 1982; Taymaz et al., 1990; Shaw & Jackson 2010; Granot 2016; Vougioukalakis et al., 2019; Boehm et al., 2023; Triantafyllou et al., 2024). Subduction resulted in the formation of the southern Aegean volcanic arc. The region is characterized by back-arc extension, slab rollback, and slab detachment (Spakman et al., 1988).

The HSZ is the most seismically active deformation zone in the Mediterranean. Seismicity is distributed along the entire arc, with significant events recorded in the period 2009-2023, including earthquakes with magnitudes greater than 6.0. Some of these events generated tsunamis, highlighting the tsunamigenic potential of the region (Spakman et al. 1988; Bocchini et al., 2020). Geodetic analyses indicate a low ratio between deformation rates and seismicity (seismic coupling) (Vernant et al. 2014; Sparacino et al., 2022) suggesting that most of the deformation is released aseismically. This is particularly true in the central Aegean area, which has experienced predominantly aseismic deformation and low seismic energy release over the past millennium. The absence of large-magnitude earthquakes ($M \geq 8$) along the HSZ (a seismic gap) suggests that such events may still occur in the future (Sparacino et al., 2022).

The western region of Crete has shown vertical deformation oscillating between subsidence and uplift over a period from 42 ka to the present, with subsidence of 2.6-3.2 mm/a (42-23 ka) then uplift of 7.7 mm/a (23-5 ka) followed by a slow-down to 3.3 mm/a in the last 5 ky (Tiberti et al., 2014).

Ongoing subduction in the HSZ is strongly influenced by geodynamic events in the area, including (Catlos & Çemen, 2023) (**Fig. 5.2A**):

- Paleogene - Lower Miocene (65 - 23 Ma): Subduction of the African plate beneath Eurasia towards the north (formation of the Alps). Possible precursor subduction further north in the Aegean region;

- Upper Miocene (ca. 12 Ma): Onset of slab rollback;
- Upper Miocene-Present (12 Ma-today): Extension in the Aegean Sea intensifies due to slab rollback and westward extrusion of the Anatolian plate (accommodated by the North Anatolian and East Anatolian Faults), triggered by the northward push of the Arabian plate against Eurasia. This caused a southward migration of the current Hellenic arc and then westward thrust of the Anatolian plate (accommodated by the North Anatolian Fault and East Anatolian Fault), triggered by the northward thrust of the Arabian plate against Eurasia, leading to the formation of the current Hellenic arc and its southward migration (Taymaz, Yilmaz, and Dilek, 2007).

These processes have significant implications for magmatism, particularly:

- Slab Rollback: As the African plate subducts and the trench moves southward, the melting zone in the overlying mantle also shifts, causing volcanic activity to migrate;
- Regional Extension: The extension of the Aegean crust, driven by slab rollback and extrusion of the Anatolian plate extrusion, affects magma ascent pathways and eruption sites;
- Evolution of subducting plate geometry: changes in the angle and depth of the subducting African plate influence the location of magma generation;
- Mantle Flow: Subduction-induced mantle flow also contribute to the migration of magmatism.

However, the volcanic arc of the southern Aegean is the last step in an evolution that took place throughout the Cenozoic era, and which saw the following phases starting from a band of calc-alkaline magmatism 70 Ma ago in Bulgaria-Thrace (Jolivet & Brun., 2010; Ring et al., 2010):

(a) Eocene-Lower Oligocene (c.a. 45-30 Ma). Post-Collisional Magmatism of the North Aegean. This phase follows the main collision phase and is associated with post-orogenic magmatism due to extension and possibly slab break-off further

north. Magmatism is typically calc-alkaline, high-potassium (High-K), and shoshonitic;

(b) Upper Oligocene-Middle Miocene (c.a. 30-15 Ma). Magmatic activity concentrates in northern Aegean regions such as Macedonia and Thrace (e.g., Rhodope volcanism), with extensional magmatism in the Cyclades and western Anatolia. This phase is linked to early subduction and post-collisional extension, driven by the onset of slab rollback. Magmatism remains predominantly calc-alkaline but shows increasing chemical variability, including more alkaline trends in some areas.

(c) Upper Miocene-Pliocene (c.a. 12-5 Ma). Transition to the current volcanic arc. Volcanic activity gradually shifts southward, affecting the Cyclades (e.g., Serifos, Sifnos) and Euboea. This period is marked by intense extension due to slab rollback. The subduction front becomes more defined, and the volcanic arc begins to migrate south. Magmatism transitions to a typical arc signature, with intermediate calc-alkaline rocks (andesites, dacites), but also includes basalts and rhyolites. Intraplate alkaline rocks appear in some areas. Isotopic data indicate increasing contributions from subducted sediments and altered oceanic crust.

(d) Pliocene-Quaternary (c.a. 5 Ma-Present). The South Aegean volcanic arc becomes the most active magmatic zone, including volcanoes such as Methana, Aegina, Poros, Milos, Santorini, Kos, and Nisyros.

This arc is directly linked to the current subduction of the Hellenic arc and its southward retreat. It is a well-developed and active volcanic arc, dominated by calc-alkaline rocks ranging from basalts to rhyolites. Chemical zoning is observed along the arc, with variations in potassium (K) and other incompatible elements potentially related to the depth of the Benioff zone and the degree of partial melting. For example, Santorini exhibits slightly different geochemistry compared to Nisyros or Milos. Magmatic differentiation processes such as fractional crystallization, crustal assimilation, and magma mixing play key role in the evolution of individual magma chambers.

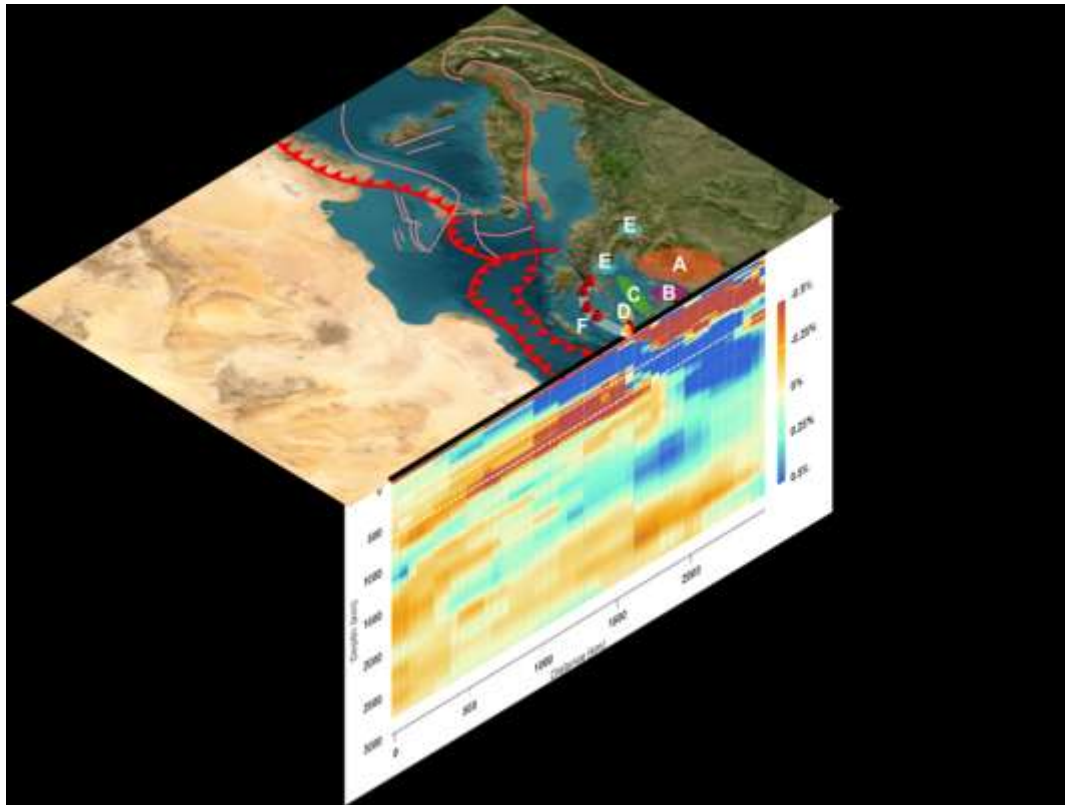


Figure 5.1 Seismic tomography of the Aegean area as discussed in *Atlas of Underworld* (van der Meere et al., 2018). Associated with this is the progression of magmatism from Thrace towards the southern Aegean over the last 40 million years. A: 40 million years ago – Northeastern Greece; B approx. 20 million years ago – Northern Aegean; C: 15 Ma – Central Aegean; D 10 Ma – Eastern Aegean, also including centers in the Cyclades north of the current arc; E approx. 5 Ma – widespread volcanic centers in Macedonia-Gulf of Volos-Euboea; F current volcanic arc. Nisyros is the cone in orange. Modified from Royden et al. (2011).

5.2.2: Active volcanic centers in Southern Aegean Volcanic Arc

At present, Aegean volcanism occurs in several centers located along the Southern Aegean Volcanic Arc, an approximately 450 km long arc whose southernmost point is Santorini, located approximately 400 km north of the subduction trench. Volcanism in the arc is well described in the review by Vougioukalakis et al. (2019) (**Fig. 5.2B**). The westernmost centers are located at the Isthmus of Corinth and consist of the volcanic centers of the Sousaki Volcanic Field (4.1-2.3 Ma), consisting of dacitic domes, lava flows, and tephra scattered over an area

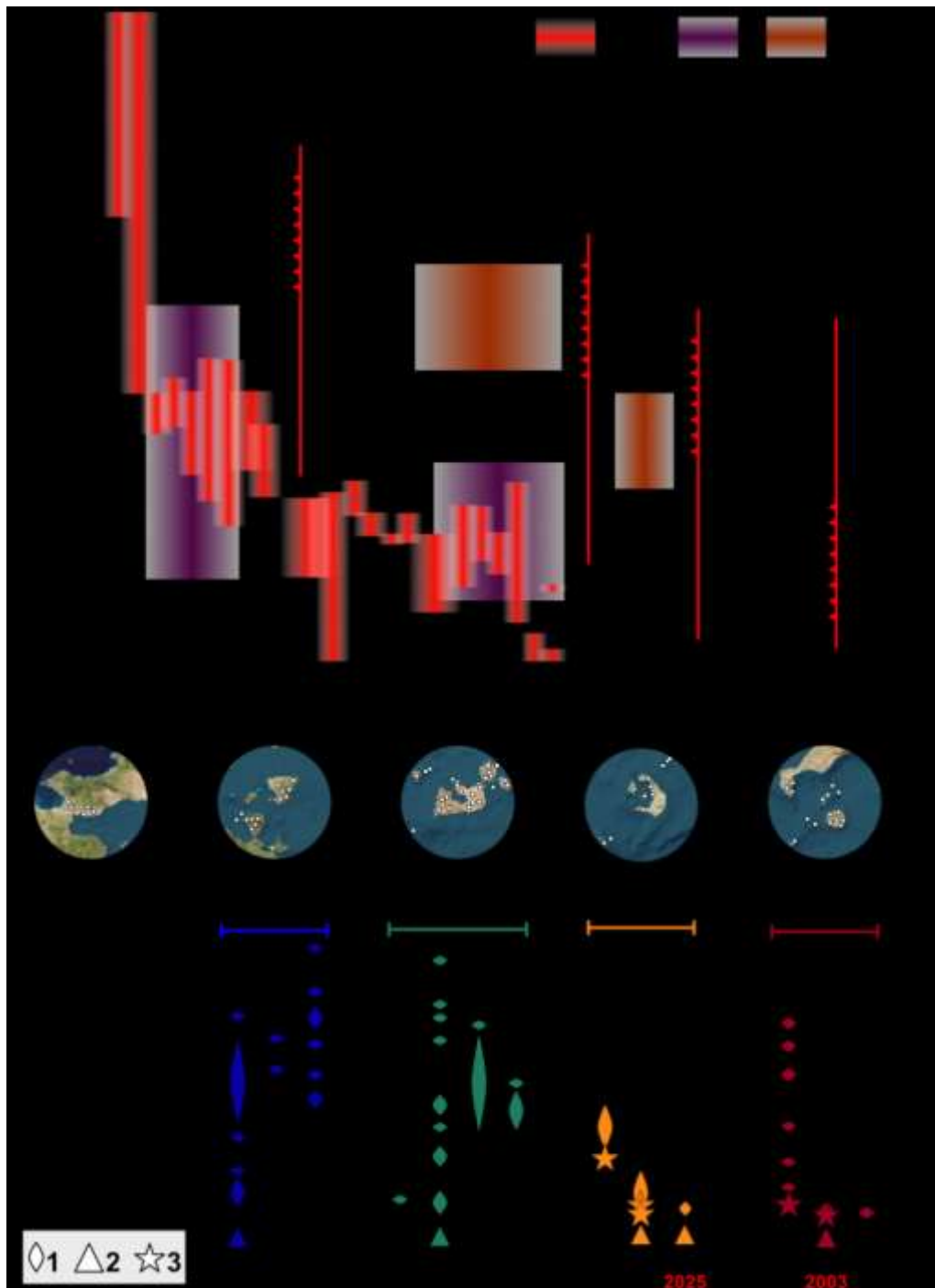


Figure 5.2 **A**: Chronology of Cenozoic volcanism in the Aegean Sea (developing in latitude) as derived from Jolivet et al. (2010). **B** Volcanism in the South Aegean volcanic arc from west to east as derived from field observations and correlations, radiometric dating and biostratigraphic/magnetostratigraphic data as derived from Vougioukalakis et al. (2019); 1: activity period; 2: historical eruptions; 3: caldera forming eruptions. Last magmatic activity is reported for any holocene volcanic field and is derived from Global Volcanism Program, 2025. [Database] Volcanoes of the World (v. 5.3.2; 30 Sep 2025); the red dates are last non-magmatic activity (seismic activity/unrest), as derived from Global Volcanism Program data for Kolumbo and Nisyros.

between Corinth and Megara, which is still subject to hydrothermal activity. Beyond the isthmus, in the Saronic Gulf, lie the Aegina-Methana-Poros centers, whose activity, (4.7 Ma-Present), in the context of the Saronic Gulf Graben, continued until historical times (230 BCE), seeing the transition from submarine activity (pillow lavas and tuffs) to subaerial activity and the formation of andesitic-dacitic domes, basalt-andesitic flows, and block-and-ash flows (D'Alessandro et al., 2008; Vougioukalakis et al., 2019; Global Volcanism Program, (Methana) 2025).

Cycladic volcanism consists of several centers.

The Milos Volcanic Field comprises widespread centers and vents, with initial activity dated to approximately 4.5-3.7 Ma on Milos, characterized by lava domes emplaced over marine and subaerial volcanoclastic deposits. Between 3.5-1.5 Ma, volcanism became both explosive and extrusive in Milos, Ananes, Kimolos, and Polyegos. Activity then continued until approximately 19 ka in Antimilos and Milos, mainly through explosive activity (tuff ring), extrusive activity (domes), and rhyolitic flows. Hydrothermal eruptions were also reported during historical times, particularly in the 1st-2nd centuries CE (Fytikas et al., 1986; Stewart, A. L., & McPhie, 2006; Vougioukalakis et al., 2019; Global Volcanism Program, 2025).

The Christiana-Santorini-Kolumbo volcanic field is perhaps the most renowned, primarily due to the Minoan eruption of Thera (Santorini) in 1630 BCE, which had a profound impact on Minoan and Mycenaean civilizations. It consists of a SW-NE alignment formed by Christiana-Santorini and Kolumbo together with other submerged edifices. The andesitic-dacitic domes and associated lava flows forming the tuff rings of Christiana (i.e., Christiani-Askania-Eschati, which represent the eroded remnants) have not yet been dated. Thera, Therasia, and Aspronisi form the caldera resulting from the Minoan eruption, at the center of which lie Palea and Nea Kameni. Volcanic activity, which began at 650 ka, became more explosive around 250 ka, with at least 100 explosive eruptions, including twelve Plinian events and four caldera-forming eruptions. Santorini's most recent activity



Figure 5.3 K: Kos Island, D: Datça Peninsula; S: Stronggyli Island; G: Giali Island; Pg: Pergousa Island; Ph: Pachia Island; Kd: Kandeloussa Island; N: Nisyros Island; T: Tilos Island.

concentrated at Palea and Nea Kameni during historical times, with a shift toward dacitic magmas since 197 BCE, after which nine eruptions occurred, the most recent in 1950. Santorini's eruptive history ranks it among the most explosive volcanoes in the world. Kolumbo is the easternmost edifice of the volcanic field and remained active until 1650 CE (Parks et al., 2012; Vougioukalakis et al., 2019; Global Volcanism Program, 2025).

5.2.3: The Kos-Nisyros volcanic complex: the islands of Nisyros and the Kos Plateau Tuff

Activity the Kos-Nisyros-Gyali-Pacheia-Pergoussa-Strongyli complex (**Fig. 5.3 and 5.4**) began in the southern part of Kos around 3.4-1.6 Ma with the emplacement of dacitic-rhyolitic domes, continued with explosive activity at 0.5 Ma, and culminated in the eruption of the Kos Plateau Tuff (KTP) 161 ka ago, the most violent in the entire current volcanic arc. Gyali is the youngest center of the arc, dated to > 33 ka.

The magmatic source is located at a depth of approximately 150-200 km, along a slab dipping at 38° (Makropoulos et al., 1984; Allen 2001). According to Nomikou et al. (2018), this is due to adiabatic upwelling induced by the thinning of the Aegean continental block, resulting from differential movements of the central Aegean (35 mm/yr southward) and the Anatolian block (20 mm/yr westward), implying variable subduction rates along the Hellenic trench. The volcanic field is characterized by intense neotectonics and volcanism. While volcanic activity in the region began 15 Ma (Jackson 1994; Smith et al., 1996), the earliest products in the Kos-Nisyros area date back 3.5 Ma. The most important eruption associated with the Nisyros area is the Ultra-Plinian Kos Plateau Tuff that occurred 161 ka and was characterized by a Dense Rock Equivalent (DRE) volume of 60 km³, devastating an area of 3,000 km² (Allen 2001; Nomikou et al., 2018).

The Nisyros volcanic field, which also includes the small islands of Gyali, Strongyli to the north of Nisyros, and Pergoussa and Pacheia to the west, occupies a pre-Miocene uplifted block with an ENE-WSW trend that extends from the Datça Peninsula (Turkey) to the islet of Kandeliossa, west of Nisyros. To the NE and E of Kandeliossa, lava domes have been identified on the sea floor, though without hydrothermal alteration; columnar basalts are found to the SE of the island. The volcanic group is separated from Kos and Tilos by two grabens, each subdivided into basins, one of which is Avyssos, located immediately NE of Strongyli, a caldera lying at a depth of 680 m (Nomikou et al., 2018).

Gyali, north of Nisyros, is the youngest of the volcanic centers, and includes remnants of a caldera later dissected by N-S trending faults. It consists of two parts: a western sector made up of pumice deposits and an eastern sector, separated by an isthmus, formed by dacitic-rhyolitic domes dated to 31 ka in the Volcano Global

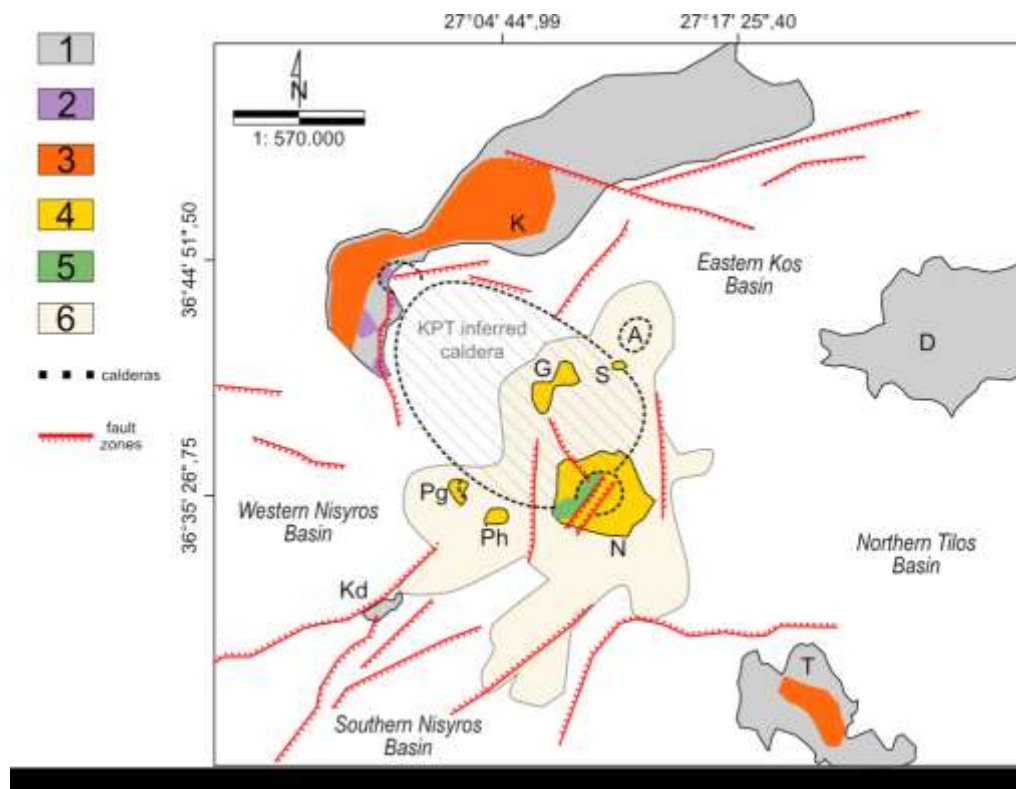


Figure 5.4. Geological sketch of Nisyros area. 1: other units; 2: Pre-KPT volcanics; 3: KPT tuff deposits; 4: Post-KPT volcanics; 5: Nisyros Domes post-caldera; 6: Submarine extension of Nisyros volcano. Letters are same of preceding figure. A: Abyssos caldera. Modified by Nomikou et al. (2017) and Papadimitriou et al. (2017).

Risk Identification and Analysis Project (VOGRIPA) database. The island of Strongyli is located east of Gyali and north of Nisyros. The edifice rises above sea-floor along the buried rim of the Abyssos underwater crater, at 680 m depth. Strongyli is older than Gyali, though it has not yet been dated. Abyssos itself, 3 × 4 km wide, may be the vent responsible for the Kos Plateau Tuff eruption, according to Nomikou et al. (2018). Pergoussa and Pacheia, west of Nisyros, contain deposits of the KPT. The absence of such deposits on Nisyros and Gyali suggests that these islands emerged later, exposing the KPT deposits. Pyroclastic rocks on Pergoussa

indicate the collapse of a previous volcanic edifice. Lavas on both islands range from andesitic-dacitic to dacitic in composition.

5.2.4: The Kos Plateau Tuff Eruption

The eruption of the Kos Plateau Tuff (**Fig. 5.4**) is discussed in terms of its phases and related deposits by Allen (2001). The event was of extraordinary proportions, divided into several distinct phases, reflecting the progressive evolution of an eruption that culminated in the caldera collapse of the western portion of Kos.

According to Allen, the eruption began with a Plinian phase, characterized by a highly explosive and sustained eruption. During this initial phase, an eruptive column probably rose over 30 km, releasing large quantities of pumice and fine ash that dispersed over a wide area, forming a thick layer of pyroclastic fall. This material, predominantly rhyolitic in composition, is evidence of violent degassing of silicic magma stored in a shallow chamber. This first Plinian phase likely lasted several hours or a few days.

The eruption then entered a transitional phase, during which the eruptive column became unstable. The partial collapse of the column gave rise to the first pyroclastic flows, alternating with residual fall phases, indicating growing instability in the system. This phase, although less spectacular than the next, was crucial in transition from a sustained eruptive column style to collapsing column, forming the vast ignimbrite deposits typical of the KPT. This phase is also estimated to have lasted several hours to a few days.

The central and most destructive phase of the eruption occurred when the column collapsed completely, and the eruption became dominated by large-scale pyroclastic flows. These flows, extremely dense, hot, and fast-moving, covered the entire region with thick ignimbrite deposits, in some cases partially welded due to high temperatures. It was during this phase that the magma chamber collapsed, forming the Kos caldera. The energy released and the volume of erupted material

were such that the eruption was classified as a VEI 7 event, one of the most powerful ever recorded in the Mediterranean.

The eruption ended with a less energetic final phase, characterized by the emission of weaker pyroclastic flows, likely representing the last products of the waning magmatic system. The deposits from this phase are finer-grained and more limited in distribution, indicating a rapidly declining system. The eruption left behind a radically transformed landscape and a caldera that today represents one of the most significant volcanic structures in the eastern Aegean. The main phase was accompanied and followed by interaction with seawater, which triggered phreato-magmatic explosions, evidenced in the deposits by fine laminated layers (indicative of pulsating explosions) and high fragmentation, with abundant fine ash. These last two phases are estimated to have lasted several hours.

The complete sequence is found on Kos, where it reaches its maximum thickness (up to 100 m). Fall pumices, non-welded and welded ignimbrites are found within ~10-15 km of the Kos caldera. In a range of 15-40 km, covering the islands of Kalymnos, Pserimos and northern Nisyros, thinner but clearly recognizable deposits are found. In some cases, only Plinian fall units, or non-welded ignimbrites are found. The ignimbrites often appear as massive, fine-grained deposits, but are less welded than those in the central area.

In the seabed between Kos and Kalymnos, high-resolution seismic studies have identified a tens of meters thick unit, interpreted as an underwater pyroclastic flow deposit associated with the KPT eruption. In the area beyond 40 km and up to 80 km, deposits have also been found on the seafloor of the southeastern Aegean. Marine ignimbrites have been identified throughout the Kos area. Based on the study by Allen (2001) and subsequent geophysical and bathymetric research (such as that cited by Nomikou et al., 2021), the center of the volcanic edifice responsible

for the KPT eruption is believed to have been located in the southwestern part of the island of Kos, extending offshore towards the area between Kos, Gyalí, and Nisyros.

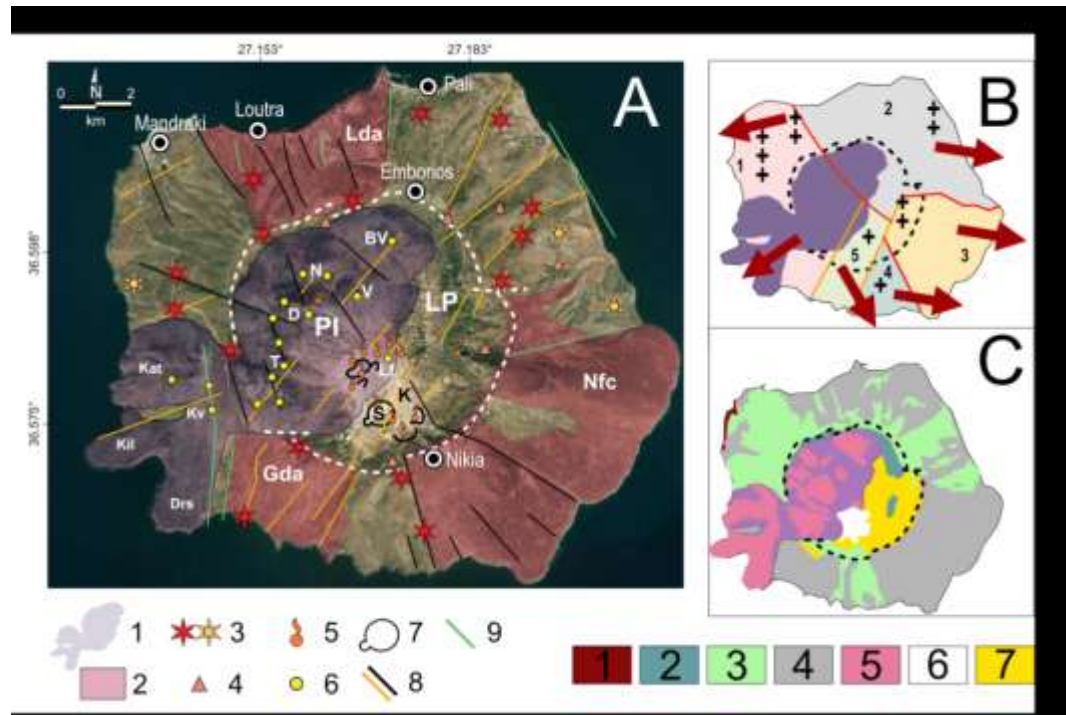


Figure 5.5 **A**: Simplified geological sketch of Nisyros Island showing mean fault system and other minor faults, domes post-caldera and flank instabilities. PI: Profitis Ilias dome; T: Mount Trapezina dome; D: Dhiavatis Mount dome; N: Mount Nymfios dome; V: Mount Visternia dome; BV: Boriatiko Vouno dome; LP: Lakki Plain; S: Stefanos crater; Lda: Loutra debris avalanche; Gda: Ghrani debris avalanche; Nfc: Nikia flank collapse. 1: post-caldera domes; 2: gravitational instabilities (avalanches and flank collapses); 3: scoria (red) and tuff (yellow) cones; 4: necks; 5: degassing areas; 6: inferred dome vents; 7: hydrothermal explosion craters; 8: mean fault system F1-F2 (yellow) and F3-F4 (black); 9: minor fault systems. **B**: in Nisyros fault systems intersect to identify five blocks, subjected to differential uplifting rates. 1: Profitis Ilias block; 2: Emborios block; 3: Nikia block; 4: Avlaki block; 5: Agia Irini block. The 'plus' signs show different uplifting rates. **C**: Volcanic cycles in Nisyros: 1: submarine volcanic base; 2: shield volcanic cycles; 3: composite volcano cycles; 4: caldera and caldera collapses cycles; 5: post-caldera domes (light colour) and debris (dark colour); 6: hydrothermal cycles; 7: recent deposits. Modified by Volentik et al. (2003); Dietrich & Lagios (2017) and Antoniou et al. (2021). Faults are from Nomikou P. (2004).

5.2.5: Volcano-stratigraphic units of Nisyros

Nisyros and its volcanological evolution have been well outlined by Dietrich (2017). The island of Nisyros is characterized by its almost pentagonal shape and the presence of a 3.6 km-wide caldera with walls up to 350 m high. The caldera is

partly obstructed by domes, the highest of which is Profitis Ilias, rising to almost 700 m (**Fig. 5.5 and 5.6**). The caldera floor forms the Lakki plain and ends against the caldera walls and the domes, where explosion craters and small domes can be found, marked by fumarolic activity.

Neotectonics, which shaped the area into horsts and grabens as previously noted, has created on the island a system of main and secondary conjugate faults that divide it into sectors (**Fig 5.5B**). The F1-2 fault system consists of two parallel N30°E-trending faults that match the general trend of the graben in which the volcanic complex of Kos-Nisyros-Gyali-Pacheia-Pergoussa-Strongyli was built. F1 and F2 form an ENE-WSW graben that includes the remnants of the KPT caldera and makes up the Lakki caldera plain. Rhyodacitic lava domes are found along F1, suggesting that this fault facilitated magma ascent from the lower crust. F1 is also subject to horizontal movements, responsible for shallow and intermediate earthquakes with magnitudes > 5.

Conjugated with F1-2 are faults F3-4, which extend from Tilos towards Kos, cutting across Nisyros, the domes and associated explosion craters, and Gyali; their trend is NNW-SSE. Explosion craters are located at the intersections between F1-2 and F4. The main fault system leads to the subdivision of Nisyros into five blocks, each subject to uplift at different rates.

The largest block, Emborio, comprises the northeastern half of the island, followed clockwise by the Nikia sector, the small Avlaki sector to the south, the Agia Irini sector including the Lakki plain and the SW flank, and finally the Ilias block in the northwestern sector. The first three tend to move eastward and show essentially identical uplift rates, while Agia Irini moves southeast with a lower uplift rate, and Ilias moves westward with a marked uplift rate (**Fig 5.5B**).

In general terms, the island is undergoing extension, with the axis of this movement once again corresponding to an ideal NE-SW-trending line passing through the Lakki plain.

Dietrich (2018) identified four phases, each consisting of different cycles (**Fig 5.5C**) based on thirty litho-/tephrostratigraphic units observed in the field. The

entire island is of volcanic origin, although the Mesozoic limestone basement was encountered beneath the Lakki plain at a depth of 650 m. While the Kos Plateau Tuff has well-determined and reliable ages (161 ± 1 and 166 ± 2 ka) (Smith et al. 1996; Guillong et al. 2014), the geochronology of Nisyros is still uncertain: many measurements have proven to be inconsistent, other data show significant errors and old K-Ar dates are not considered reliable (as they are based on low K-amphibole/plagioclase, on scarce occurrences of biotite and sanidine or on rich-K but altered glass) (Bachmann et al. 2010; Dietrich 2018); the first acceptable estimates of maximum eruption ages obtained using the U-Pb method come from zircons from the youngest products (Guillong et al. 2014; Dietrich 2018;). Other younger estimates ages can be found in Popa et al. (2020) and Locher et al. (2025). Youngest products of Phase IV and Phase V occur within a range between 65-55 ka and 30-13 ka, respectively, (Popa et al. 2020; Locher et al. 2025), while Phase I, II and III has estimated range of 160-120 ka (Locher et al. 2025). Phase I possibly is possibly contemporary with or slightly later than the KPT tuff eruption (Dietrich 2018).

The first recognized phase is that of the **Submarine volcanic base (Phase I**, possibly contemporary of KPT eruption), characterized by hyaloclastites deposited in shallow marine to subaerial environments, pillow lavas, and breccias of basaltic-andesitic composition. This sequence alternates with lava lenses and tuffs affected by hydrothermal alteration. Although Dietrich (2018), has combined this phase with the following phase II, we consider them separate in order to distinguish submarine products from subaerial ones.

Dietrich links this level to deposits found on the seafloor of the western and eastern Kos basins (NW and NE of Nisyros), which are related either to the eruptive cycle of the 161 ka Kos Plateau Tuff (KPT) or to equivalent basin deposits from the earliest cycles of Nisyros (and therefore not directly connected to the KPT products). These deposits make up what Dietrich calls the "submarine volcanic basement".

This volcanic submarine base is followed by the **Early Shield Volcano cycles (Phase II**, 160-120 ka), structured into three distinct cycles that occurred in close temporal succession, as indicated by the absence of paleosols between them. The

unit marking the beginning of this cycle (ESV1) is a lava flow, which represents the first subaerial activity of the volcano; its composition has been linked by Papanikolaou et al. (1991) to the submarine products of the preceding cycle.

The next cycle (EVS2) is of subplinian character, producing subsequent pyroclastic density currents, capped by another subplinian phase and then a basaltic-andesitic lava flow. The third cycle (EVS3) is distinctly more explosive, starting with intense water-magma interaction that generated surges and subsequent fallout, followed by two more pyroclastic density currents sealing the end of the cycle. The large amount of lithic material has led Volentik et al. (2002) to suggest the possibility of caldera collapse. It has been hypothesized that the present-day caldera occupies the same location as the crater of the original shield volcano. Dietrich further proposes that during this stage, magma ascent from the mantle was facilitated by tectonics, and by the F1-2 fault system in particular.

This cycle is followed by the deposition of lacustrine sediments, later capped by basaltic-andesitic lava flows. A new, more explosive cycle is recorded in the northern part of the island, beginning with a subplinian eruption that deposited a reddish pumice and fine surge deposits; these are followed by pyroclastic density currents with abundant lithics and pumice at the base, then another surge and subsequent fallout that seals the cycle. The presence of a stratovolcano forming above the previous caldera has been hypothesized. Subsequent sedimentary sequences suggest strong erosion, possibly due to uplift triggered by magma intrusion into the upper crust.

Second phase recognized is that of the **Composite Stratovolcano cycles (Phase III)**. The phase involves the transition from a shield volcano to a composite cone, then the construction of several centers located on the southern and eastern sides of the stratovolcano; this phase ends with a caldera collapse. Magmas during this transition shield-stratovolcano were andesitic-dacitic. Two lava flows were erupted from central vents, with the second showing evidence of magma mixing between dacitic and andesitic magmas, the latter injected into a reservoir already

dominated by dacite. A third andesitic lava flow closed the transition shield-stratovolcano.

Eruptive centers (Monastery Stavros, Avlaki) in the southern part of the island produced a basaltic-andesitic pyroclastic succession, consisting of various pyroclastic density currents, with hydrothermally altered material, clearly the product of a shallow hydrothermal system. The eruption of a voluminous rhyolitic lava flow marked the end of this cycle. The presence of dykes with different orientations suggests an extensional regime that facilitated magma ascent, likely guided once again by the regional tectonic framework.

A cluster of eruptive centers in the eastern island sector (Tuffs Cones of Kyra, Afionas; Kremastos, Lies, Evria), of undetermined age, are associated with pyroclastic density currents and fallout, probably linked to two eruptive events. The lithics within these deposits include andesitic and cumulate rocks, as well as limestone, marble, and skarns, indicating that andesitic magmas recharged a dacitic reservoir, incorporating wall-rock material into the eruption.

The stratovolcano (Kremares, Pali, Mandraki) associated with this phase, consist of several parasitic cones fed by radial dykes around a central conduit; once again, regional tectonics played a role in vent distribution. Dietrich estimates the duration of this cycle in the order of hundreds to thousands of years, based on field relationships among the units. This period is associated with widespread evidence of Strombolian activity from scoria/cinder cones and emission of basaltic andesites. The products of these eccentric activities include basaltic andesite, cumulates, and metamorphic material as described earlier. It is thought that the edifice ultimately underwent summit collapse, producing a hyper-concentrated debris flow on the W and N flanks, associated with generalized uplift followed by tilting toward the W-NW.

On the northern flank, a debris avalanche known as Loutra has been identified, compatible with the collapse of northern rim of a caldera. Late phase III products seem to have occurred after a period of quiescence and differs dramatically from the previous ones, as eruptive products became more silicic in composition and

effusive in eruptive style. Dietrich suggests this drastic change was either controlled by change in the regional tectonic regime or by variations in local magma reservoir. All lava flows are located on the high northern flanks, suggesting the existence of eruptive centers along a caldera rim, again controlled by the intersection of the F1-2 and F3-4 faults. This was associated with the uplift of the central-southern portions of the island and the emplacement of dacitic domes within the caldera. The products include basaltic andesite to andesite lava flows erupted on the old western caldera rim and that reached the sea, contrasting with dacitic flows on the eastern flank near the village of Emborio, associated with a dome. The Loutra debris avalanche marks the end of this cycle, with the aforementioned northern rim collapse and an andesitic lava flow, the last andesitic eruptive product in the island's history.

The **Caldera-forming and Collapses cycles (Phase IV, 80-50 ka)** (Popa et al. 2020, Locher et al. 2025) consist of two sequences of caldera-forming eruptions and relative collapses. Widespread paleosols between Loutra and Emborios, to the east, mark a long period of quiescence between the andesitic-dacitic products of the preceding cycle and those of the following one, characterized by extreme differentiation. This cycle began with a Plinian eruption that produced the so-called Lower Pumice (LP), deposited across the entire island. The LP is divided into several phases: an initial fallout layer rich in breccia and lithics (up to 50%), overlain by a mixed unit of weakly stratified fallout deposits and pyroclastic flow units. Both units seem to be synchronous, related to a single eruptive event. Among the lithics, in addition to the metamorphic and cumulate materials already observed, hydrothermally altered fragments are also present. This again indicates a hydrothermal system associated with a large magma reservoir. On the SW and SE flanks, respectively Ghrana and Nikia Flank Collapse, two debris avalanches have been recognized, potentially triggered at the onset of the eruptive event. Paleosols above the LP again mark a period of inactivity, though its duration is undetermined.

The onset of the second caldera-forming and collapse event it is represented by a rhyolitic pyroclastic sequence known as the Upper Pumice (UP), distributed across the island and consisting of fallout and pyroclastic density current deposits.

This eruption likely originated from a northwestern center, once again where the F1-2 and F3-4 fault systems intersect. Lithics in these deposits show increasing hydrothermal alteration, consistent with thermal gradients rising from 70-150 °C to > 350 °C. Similar temperatures have been measured in geothermal wells at Lakki, at depths of 1000 and 1880 m. A second eruptive event was followed by a second caldera collapse, as indicated by the altered lithics. The ages of the two caldera-forming events of Phase IV have been estimated with conflicting results. Guillong (2014) provides U-Pb ages of 124 ± 35 ka for the LP and 70 ± 35 ka for the UP, while younger estimates using U-Th disequilibrium dating to zircon crystals gives 63.1 ± 4.7 ka and 58.4 ± 2.7 ka (Popa et al. 2020; Locher et al. 2025).

Today, the caldera is occupied by six rhyodacitic domes (**Fig. 5.6A**), emplaced after the formation of the caldera, during the **Post Caldera cycles (Phase V)**. Their emplacement was not accompanied by any explosive precursors, making this final cycle purely effusive. The domes include Profitis Ilias-Diavatis, Nymfios, Visternia, Trapezina, Lofos, and Boriatko Vouno in the NE, as well as Karaviotis with the associated flow lobes of Kateros, Kilia, and Drakospilia in the SE. The ages provided by Locher et al. (2025) for the emplacement of the domes span a range between 26 ± 2.7 ka (Karaviotis) and 13 ± 1.9 ka (Visternia).

5.2.6: Petrology of Nisyros products and dome chronology

Dietrich & Popa (2018) describe the petrology of erupted materials throughout the entire tephro-stratigraphic sequence of Nisyros. It is immediately evident that the most primitive compositions, ranging from basaltic andesites to andesites, are concentrated in the oldest units as well as in the stratovolcano cycle. Between these and the later more differentiated products, a small compositional gap is observed. The terminal products of the stratovolcano cycle and the subsequent caldera-forming and post-caldera stages cluster within the dacite-rhyolite field, following a trend that connects them to the earlier products. Rocks show affinity

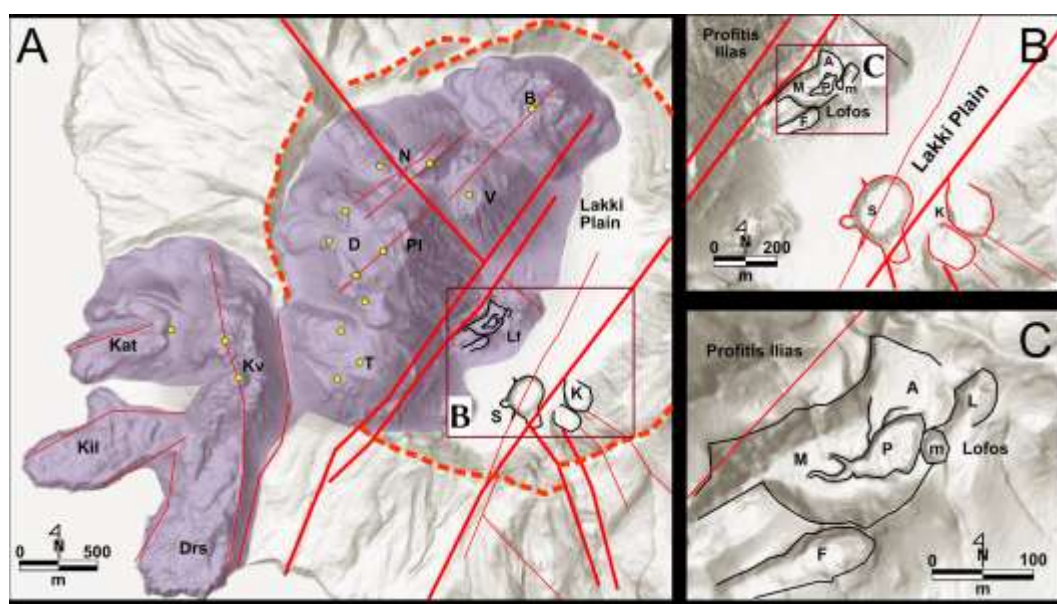


Figure 5.6 Hillshade map to highlight post-caldera domes, their debris layers and the hydrothermal explosion craters. A: the rhyodacitic domes with Profitis Ilias to dominate the island; outside of caldera rim Mout Karaviotis dome with the lava flows (southward) Kateros, Kilia and Drakospilia. B: the area of hydrothermal cycles with Stefanos (S) and Kiminakia craters (K) and the craters of Lofos dome at the foothills of Profitis Ilias. C: the nested explosion craters in Lofos dome. F: Flegheton; the three Polyvotis craters (M: Megalos Polyvotis, P: Polyvotis, m: Mikros Polyvotis); L: Logotethis; A: Ahilleas. Mean faults, taken from Nomikou P. (2004), are highlighted.

for the low- to medium-K calc-alkaline series, typical of the geodynamic setting of the island. The isotopic ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ vs ϵNd also align with those of Santorini (Dietrich & Popa, 2018), indicating crustal contamination at upper levels, derived from a mantle source enriched in fluids.

The difference between effusive and explosive products has been linked to the pre-eruptive conditions of the magmatic storage system: effusive products are thought to have erupted from cooler, water-saturated magmas (700-800 °C, >~5-5.5 wt% H_2O dissolved) stored at ~6-8 km depth, whereas explosive products originated from slightly hotter, less water-rich magmas (800-850 °C, 4-5 wt% H_2O dissolved) at similar depths. Notably, at Nisyros, water-rich magmas are associated with effusive eruptions. This has been explained by the increased compressibility induced by the high-water content in the magma, which allows overpressures from new magmatic intrusions to be absorbed. These intrusions simultaneously heat and reduce the viscosity of the resident magma, rendering it more fluid. Consequently,

long repose periods at Nisyros appear to favor effusive eruptions, as they allow magma to become water-saturated (Popa et al., 2021a; Popa et al., 2021b).

Further work on the chronology of post-caldera domes was carried out by Locher et al. (2025). One of these, the Trapezina dome, has been dated to 19.9 ± 1.5 ka, while the others are presumed to have similar ages. Dome formation is thought to have occurred between 30 ka and 12 ka, with a peak around 19 ka. Locher et al (2025) notes that dome ages increase toward the southwest, whereas earlier studies suggested the opposite trend. This implies that the northeastern portion of the dome complex is the youngest part of the island. These conclusions are based on U-Th dating of ~ 350 zircons from seven post-caldera domes.

By analyzing mafic enclaves and variations in strontium isotopic composition in plagioclase crystals within the post-caldera domes, it was inferred that the domes formed through mixing between pre-caldera rhyolitic magma already residing in the magma chamber and newly injected, less evolved magma (Braschi et al., 2012; Braschi et al., 2014). Zircon crystals revealed age distributions spanning a broad interval, beginning prior to the caldera collapse events but clustering immediately afterward. This suggests crystallization was triggered by recharge following the LP and UP caldera-forming eruptions.

Locher et al. (2025) also conducted whole-rock chemical analyses, showing that the dome complex formed between ~ 26 ka and 13 ka, about 30 ka after the last caldera-forming eruption. As already noted (Dietrich 2017; Dietrich & Popa 2018), the volcanic centers are aligned along neo-tectonic lineaments with an overall NE-SW regional trend. They also observed spatial migration of vents and a slight shift toward more mafic compositions over time, which may reflect the increasing influence of persistent mafic recharge pulses in the upper crustal magma chamber during this eruptive period.

Dating, however, has limitations. Excess argon in older volcanic rocks may reduce the accuracy of age determinations, while the absence of charcoal in younger deposits prevents radiocarbon dating. Moreover, much of the volcanic complex lies underwater, leaving few exposed rocks for study. Considering the broader Kos-

Nisyros-Gyali-Strongyli-Pergoussa-Pacheia system, a recent synthesis of the chronological framework has been provided by Locher et al. (2025) as follows:

- 3 Ma: First activity of the volcanic complex;
- 161 ka: Major caldera-forming eruption, the largest in the area and region, with volumes of $\sim 64 \text{ km}^3$, producing the Kos Plateau Tuff (KPT). The resulting caldera lies between the Kephalos Peninsula (Kos) and Nisyros;
- Post-KPT activity at Nisyros: basaltic andesites formed a submarine volcano on the caldera rim. Subaerial activity alternated between effusive/explosive phases, erupting andesitic and dacitic magmas to build a stratovolcano;
- 120 ka: Shift to more differentiated compositions, with rhyolitic lava flows at Avlaki ($118.7 \pm 10 \text{ ka}$) and Nikia ($73.3 \pm 5.8 \text{ ka}$), and two major explosive eruptions forming calderas (Lower Pumice at $63.1 \pm 4.7 \text{ ka}$ and Upper Pumice at $58.4 \pm 2.7 \text{ ka}$). These two caldera-forming events created the present-day caldera, though their erupted volumes were ten times smaller than the KPT;
- Recent activity: The most recent events are the extrusion of post-caldera lava domes (Keller, 1982). The Trapezina dome is dated at $19.9 \pm 1.5 \text{ ka}$, while others are presumed to be of similar age. Dome formation appears to have begun around 26 ka with Karaviotis, continued with Profitis Ilias, Ayos Vasilios, Bouka, and Trapezina (22-19 ka), followed by Nymfios (16 ka), and ended with Boriatiko Vouno and Visternia ($\sim 12 \text{ ka}$). Locher notes that dome ages increase toward the SW, while previous studies suggested the opposite trend. Thus, the NE dome complex is the youngest part of the island.

In summary, the caldera cycle of Nisyros appears to follow a sequence:

- Magma reservoir formation with eruptions of intermediate compositions;

- Magma evolution with the first rhyolitic eruptions;
- Catastrophic caldera-forming event that partially empties the reservoir;
- Period of quiescence with reconstruction and differentiation of the reservoir;
- Renewed activity with eruptions of evolved (rhyodacitic) magmas and new magma recharge.

Within the caldera cycle framework of de Maisonneuve et al. (2021), Nisyros seems to correspond to the "fermentation" stage, marked by reduced/quiescent volcanic activity and volatile release, consistent with the presence of an active hydrothermal system (Popa et al., 2020; de Maisonneuve et al., 2021; Locher et al., 2025).

5.2.7: Hydrothermal activity at Nisyros

Surface hydrothermal activity of Nisyros is mainly concentrated at the foot of Profitis Ilias, along neo-tectonic lineaments and their intersections, where manifestations range from simple hot springs to fumaroles with associated CO₂ and H₂S emissions at T > 60 °C (Dietrich et al., 2018).

The springs of Nisyros were already known to Strabo, who in his *Geographia* (10, 5,16) writes: “Nisyros lies to the north of Telos, about sixty stadia from both it and from Kos. It is round, high, and rocky, and the rock is of the kind used for millstones [andesite or dacite?]; in any case, the neighboring peoples procure millstones from there in abundance. It also has a city of the same name, a harbor, hot springs, and a temple of Poseidon. Its circumference is eighty stadia. Near it are some islands called the Isles of the Nisyrians [Strongyli, Gyali, Pergoussa, and Pacheia]. They say that Nisyros is a fragment of Kos, and add the myth that Poseidon, when pursuing one of the giants, Polybotes, broke off a piece of Kos with his trident and hurled it at him, and the missile became an island, Nisyros, with the giant lying beneath it. But some say he lies beneath Kos.”

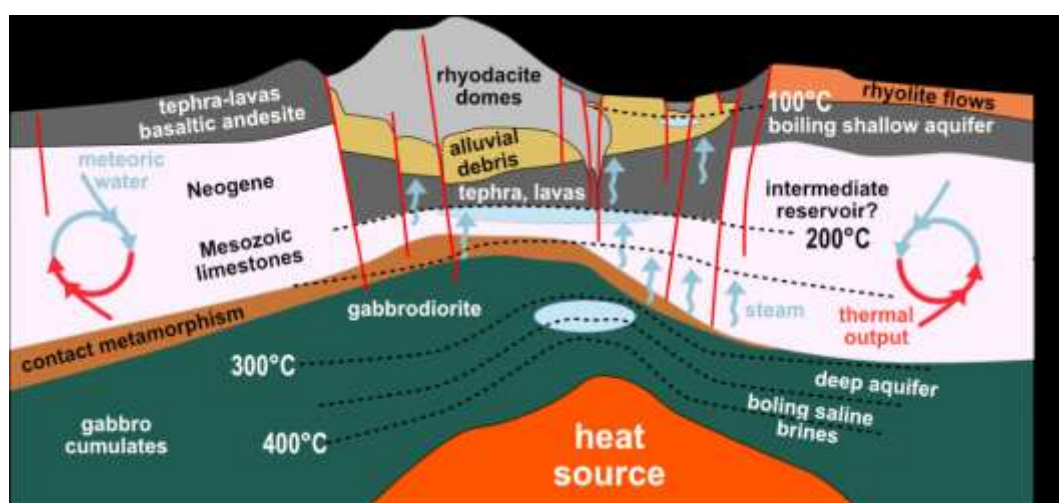


Figure 5.7 Section of a tripartite hydrothermal system, where a shallow, intermediate and deep aquifer are highlighted. Modified by Dietrich et al. (2017).

Cristoforo Buondelmonti (born in Florence around 1385, died ca. 1430), a geographer and Christian monk of Florentine nobility, is known as a pioneer in promoting direct knowledge of Greece and its antiquities in the Western world. He left Florence around 1414 and traveled extensively, especially among the Greek islands of the Aegean. He also visited Constantinople in the 1420s. Interested in rediscovering lost civilizations, he created maps of the islands he visited. Most notably, he wrote the *Liber insularum Archipelagi* (Book of the Islands of the Archipelago) in 1420, dedicated to Cardinal Giordano Orsini. This work describes the islands of the Aegean with maps and historical/geographical information. Buondelmonti describes Nisyros as follows: “In the center of the island there is a very high mountain that emits sulfurous flames from the underground day and night, as happens on the island of Stromboli near Lipari. A stone’s throw from the mountain there is a hot spring whose waters flow into a deep, dark lake in the plain below. The inhabitants of the island collect sulfur in large quantities and sell it to passing merchants. From halfway up the mountain to the top the heat is so intense that no one dares climb without wooden shoes to protect their feet.” The reference to Profitis Ilias is evident, though the mention of flames instead of fumarolic activity is puzzling. This could suggest a phenomenon similar to that observed at Kawah Ijen,

where sulfur gases appear as bluish flames at night, together with glowing flows of molten sulfur (often mistakenly called “blue lava”). The sulfur trade mentioned by Buondelmonti again recalls the activity at Kawah Ijen. According to Dietrich et al. (2017), the dark-water lake he describes corresponds to the Stefanos crater, which therefore must have formed before Buondelmonti’s visit.

The hydrothermal system of Nisyros underwent several hydrothermal explosions between 1871-1873, accompanied by earthquakes and tremors (Dietrich et al., 2017). Another event occurred in 1887, after which the system became quiescent. Between 1997 and 2001, the system experienced compositional changes following a seismic crisis in 1996-1997 (Papadopoulos et al., 1998), accompanied by increased fumarolic activity (Chiodini et al., 2002). According to Dietrich et al. (2018), this was caused by seismic activity opening new pathways for deep fluids to ascend. Once again, tectonic activity plays a fundamental role in controlling the evolution of the system. At present, the Nisyros hydrothermal system comprises several degassing structures, well discussed by Dietrich et al. (2017).

Dietrich et al. (2017) identified the faults that acted as pathways for the ascent of pressurized fluids to trigger hydrothermal explosions in the recent past. Unsurprisingly, these faults align with the regional NE trend (F2 lineament), which essentially defines the southern side of the Lakki graben. F2 may have acted as a hydrothermal explosion fault. The most striking features, however, are the hydrothermal explosion craters scattered across the Lakki plain. One group occurs on the Lofos dome, on the southern slopes of Profitis Ilias, where several explosion craters formed between 1871 and 1887. These explosions sometimes persisted for days (Dietrich et al., 2018), occasionally accompanied by true geyser activity. On the flank of Lofos several craters are present, including Logothetis, Achilleas, Mikros Polyvotis (1887), Polyvotis (1871-1873), Megalos Polyvotis (unknown age), and Flegethon or Alexandros (1871-1873) (**Fig. 6B and 6C**). The Kaminakia craters are considered by Dietrich et al. (2018) to represent the earliest signs of hydrothermal activity on the island; they are located on the opposite side of the domes, still trending NE-SW, and are heavily eroded and open toward the Lakki plain. The most

significant hydrothermal explosion crater is undoubtedly Stefanos, whose age is unknown. Its NE-SW trend once again reflects the island's general tectonic framework. It is 300 m wide and 27 m deep.

The exposed sequence along the walls of Stefanos is as follows:

- Up to 5 m of dark gray, black, and green andesitic lava, heavily altered;
- 1-3 m of clay-rich mafic epiclastics dipping NW, ending with a sharp reddish erosional contact;
- 0.5-1 m of thinly laminated, light pink clay layers thinning to the north;
- 5-8 m of fine-grained, whitish lacustrine strata with varves alternating with clay-rich epiclastics;
- 1-2 m of compact white unit, turning reddish to the south, up to 4 m thick; likely linked to the Kaminakia explosions. Rich in sulfur deposits, releasing sulfurous waters through fractures;
- Up to 5 m of light green stratified unit with large blocks (up to meters), deposits from the Stefanos explosion. Sandy matrix rich in gypsum; anhydrite veins within lava blocks;
- A 1-3 m tripartite sequence of greenish, white, and orange fine-grained clay-silt-sand layers, possibly from the Polyvotis explosions.

Interpretation of the sequence is given by Dietrich et al. (2018):

- Unit (i) (andesitic lava, altered): Indicates a previous andesitic volcanic phase, possibly linked to the early cycles of Nisyros.
- Unit (ii) (epiclastics): Suggests erosion and redeposition of mafic volcanic rocks, transported into a depression NW of Stefanos.
- Unit (iii) (thin laminated clays): Deposition in a low-energy environment, likely a small pond or swamp.
- Unit (iv) (lacustrine varves): A larger, more stable lake system with seasonal deposition.

- Unit (v) (sulfur-rich compact unit): Explosive activity (Kaminakia), with fumarolic deposition of sulfur.
- Unit (vi) (light green, blocky): Hydrothermal explosion deposits of Stefanos itself, with gypsum/anhydrite mineralization.
- Unit (vii) (tripartite clays/sands): Later explosive phases, likely from Polyvotis craters.

Geothermal wells in the Lakki plain (NIS1, south side of the caldera; NIS2, north side) reached temperatures of 340 °C at 1816 m and 320 °C at 1527 m. Together with geochemical data, this suggests a hydrothermal system with at least two aquifers: a deep, very hot, saline reservoir, and a shallower, cooler one. According to Dietrich et al. (2018), the hydrothermal system can be summarized as follows:

- A magmatic reservoir supplying heat and magmatic fluids to the hydrothermal system above. Isotopic compositions of H₂O, S, and He in fumarolic gases provide evidence, with helium possibly derived from deeper sources.
- A deep saline Na-Cl brine aquifer at 300-350 °C, where vapor phase separation likely occurs, fed by both volcanic and marine fluids;
- Intermediate aquifers at 180-260 °C, supplied by vapor from the deeper aquifer. Supported by drilling data from NIS1-2.
- A shallow degassing zone, including diffuse soil degassing structures, fumaroles in the Lakki plain, and coastal hot springs, fed by a shallow thermal aquifer dominated by condensates. This area releases ~68 ton/day of CO₂ (Dietrich et al. 2017) of hydrothermal-volcanic origin, corresponding to ~58 MW of thermal energy (**Fig. 5.7**).

5.2.8: Geochemistry of hydrothermal fluids

The geochemistry of Nisyros fumaroles has thoroughly been analyzed by Chiodini et al. (1993). The authors, based on the observed hydrothermal paragenesis, temperature gradient measurements in wells, and physical-chemical characteristics of the fluids, suggested the existence of two distinct hydrothermal aquifers: (i) a deep aquifer, at more than 900 m depth, with $T > 290^{\circ}\text{C}$ and hosting Cl-rich fluids (50 g/L) and (ii) a shallow aquifer with lower Cl content (21 g/L), located at 500 m below the surface. In the southern part of Lakki, high subsurface temperatures sustain degassing from the Stefanos and Lofos fumaroles (Chiodini et al. 1993). The authors assume that the two systems are not communicating one each other. Deep hydrothermal temperatures were estimated at 180°C to 320°C (with most values concentrating in the $200\text{--}260^{\circ}\text{C}$ range) using hydrothermal gas equilibria in the H_2O , H_2 , CO_2 , CH_4 , and CO system (Chiodini & Marini, 1998), a very powerful for estimating the temperature of deep hydrothermal aquifers. These temperatures estimated by the gas geothermometer are lower than those measured directly in geothermal wells during testing. This is because the gases may have mixed with colder fluids during their ascent, or the system may not be in a state of complete chemical equilibrium. Physicochemical conditions of the deep aquifer are best reflected by the $\text{CH}_4\text{--CO}_2$ ratio, which depends on temperature, pressure, and redox potential of the deep equilibration conditions, considering these gases do not easily re-equilibrate during ascent (Marini & Fiebig 2005). In contrast, the CO--CO_2 system is able to re-equilibrate at lower temperatures and bears physicochemical information on the ascent of the liquids from the deep aquifer to the vapor separation zone. The depth at which vapor separation occurs varies in space and, possibly, in time. According to Ambrosio et al., (2010) the gases equilibrate at redox conditions close to the $\text{FeO--FeO}_{1.5}$ buffer of Giggenbach (1987), suggesting a dominant redox control from the hydrothermal host rocks.

The origin of degassing CO_2 at Nisyros has been attributed by Dietrich et al. (2017) to a mixture of two components of different origins. Data from the Lofos

and Stefanos fumaroles, when plotted on a $\text{CO}_2/{}^3\text{He}$ vs. $\delta^{13}\text{C}$ diagram, can be interpreted as derived from a mixture of mantle fluids and fluids originating from thermal decomposition of limestones, which are present on the Mesozoic basement on which the island of Nisyros rests (Marini & Fiebig. 2005, Dietrich et al. 2017). Regarding sulphur, the $\delta^{34}\text{S}$ of elemental sulfur, fumaroles and sulfate minerals has been interpreted to reflect degassing of rhyodacitic magma with a signature of $+6.3\pm 1.5\text{‰}$ versus CDT. In contrast, the $\delta^{34}\text{S}$ signature of the thermal springs is consistent with a prevalent seawater contribution (Marini & Fiebig. 2005, Dietrich et al. 2017). Marini & Fiebig (2005) found that H_2O in Nisyros fumaroles has $\delta^2\text{H} = -20\text{‰}\pm 10\text{‰}$, as typically found in converging margins. This contribution is associated to Arc-Type Magmatic Water (ATMW) as established by Dotsika et al. (2009), who showed that thermal waters along the Aegean Arc are affected by a direct participation of magmatic fluids rich in volatile components (H_2O , CO_2) and with distinctive isotopic signatures. Marini & Fiebig (2005) suggested that hydrothermal fluids contain a mixture of 75% andesitic-magmatic water with 25% seawater (see also Ambrosio et al., 2010). Seawater contribution increases moving towards peripheral locations, such as Kaminakia and Lofos craters.

Most thermal spring waters at Nisyros are Cl-neutral. This also applies to the waters of the NIS2 well, located in the Lakki plain. Compositionally, thermal springs are interpreted as mixtures of seawater with brines from the NIS2 well (Dotsika et al. 2009). Ambrosio et al. (2010) found that high Cl are also associated with high B and Li concentrations, as typical of deep hydrothermal brines.

Bini et al. (2019) provided key contributions to understanding the dynamics of surface degassing in the caldera. The authors mapped the diffuse emission of CO_2 and the release of convective heat, identifying large anomalies located mainly in the central and southwestern parts of the caldera. This behavior is consistent with permeability controlled by the fracture network. The heat output was estimated at 134-270 MW, as caused by the convective ascent of deep fluids. For comparison, Dietrich et al. (2017) found a total heat output of 42.5 MW for the Stefanos, Lofos,

and Kaminakia area, to which Lofos and Stefanos contribute 20.4 MW and 12.1 MW, respectively.

In a later study, Bini et al. (2020) characterized the hydrothermal system based on a multiparametric approach combining soil CO₂ fluxes, radon (Rn) concentration, carbon isotopes ($\delta^{13}\text{C-CO}_2$), and geophysical and structural parameters. Based on soil degassing mapping, they proposed the hydrothermal system is fed by of a deep (magmatic) gas source characterized by less negative isotopic signatures (-1‰ / -3‰) than the typical MORB mantle, with minor additional contributions from a biogenic component. The radon spatial distribution exhibited a marked dependence on local faults and was therefore taken as an excellent tracer of structurally controlled permeability.

The recent study of Bini et al. (2022) provides decisive evidence for the existence of an active and degassing magmatic system beneath Nisyros. They found very low N₂/He ratios compared to those typical of arc volcanoes (which are in the order of 1,000-10,000), suggesting that the Nisyros magma may have preferentially lost nitrogen (N₂ depletion) during degassing. This behavior is consistent with a magmatic source consisting in silicic (dacitic/rhyodacitic) magma in a highly crystallized reservoir in the upper crust. Through the analysis of ³He/⁴He, N₂/He, and He/Ar, the authors also found that many fumaroles on the island retain a clear magmatic signature, with episodic signals of increased deep degassing. These results support a model in which a shallow magmatic reservoir (a few kilometers deep bsl) degasses periodically, the gases rise through a complex fractured system, and degassing can vary over time depending on the pressure in the conduits and the state of the hydrothermal fluids. The authors proposed that magmatic fluids accumulate in magma storage zones as magma cools and crystallizes. Upon reaching an overpressure threshold, fluids are then released towards the surface in repeated episodes when local pressure causes rock fracturing. Upon injection into the overlying hydrothermal system, these magmatic fluids cause temperature increase (up to ~325 °C) vapor separation, and rock fracturing (seismicity). The estimated time for magmatic fluids to reach the surface is about 2 years, determined by the mobility

of fluids between ductile and brittle zones and the presence of the hydrothermal system.

5.3: Methods

We conducted a Multi-GAS survey at Nisyros between 21 and 26 April 2025 in the attempt to real-time measure the concentrations of CO₂, H₂S, H₂ and SO₂ in the near-source atmospheric plumes of the main hydrothermal fumaroles. As in previous work at hydrothermal systems elsewhere (e.g., Aiuppa et al., 2005, 2022a, b; Lentini et al., 2025), measurements were performed by traversing by walking the fumarolic fields with a hand-held Multi-GAS, operating at 1 Hz and with geo-referenced position given by a co-located GPS. The survey focused on the Stefanos crater, where gas concentrations were measured at 28366 individual points along the inner crater rim and in the center of the caldera floor (Fig. 5.8A). In addition to the Stefanos area, a walking traverse path was also realized along the crater rims of the Lofos dome (Fig. 5.8B). Specifically, Multi-GAS measurements were conducted along the rims of the three nested craters known in the literature as Polyvotis, Megalo Polyvotis and Mikros Polyvotis. A spot was also visited at the of the two Kaminakia craters (Fig. 5.8B).

The portable Multi-GAS unit (<3 kg) used was the same employed by Aiuppa et al (2022a) and Lentini et al., (2025) at Vulcano Island (Italy). The unit included a non-dispersive infrared (NDIR) NG Gascard spectrometer (calibration range, 0-10,000 ppm) from Edinburgh Sensors for CO₂, and three CiTiceL electrochemical sensors for SO₂ (model T3STF), H₂S (model T3H) and H₂ (model T3HYT) (all with 0-200 ppm calibration range). Calibration of the sensors in the laboratory using certified standard gases was conducted prior to and after field work. We also used a KVM3/5 Galltec-Mela sensor for measuring temperature and relative humidity and to indirectly estimate H₂O concentrations in the plume using the Arden-Buck equation. H₂O are not reported here because the plume was strongly condensing at

all field conditions encountered. Signals from all sensors were simultaneously acquired (at 1 Hz rate) by a Campbell CR6 datalogger, and stored on an SD card (data were also Wi-Fi transferred to an external palm for real-time visualization during field operations). All sensors were housed in a water-proof case, in which fumarolic gas was pumped (at 1 liter per minutes) using a KNF, NMP 015M internal pump.

During field operations, an operator transported the Multi-GAS across the fumarolic field. The unit continuously acquired data (at 1 Hz), and with position recorded by a synchronized GPS. During the walking traverse, the operator stopped (for a few minutes) at each of the fumaroles encountered, where the instrument's inlet was exposed to the gases at 50 cm distance from the vent to avoid sensor saturation.

5.4: Results

5.4.1: Gas concentration ranges

Our Multi-GAS observations reveal a wide range of gas concentrations. In the Stefanos fumaroles' atmospheric plumes (sites identified by red points in **Fig. 5.8A**), CO₂, H₂S, H₂ and SO₂ concentrations range 461-1774 ppmv, 0.5-202 ppmv, <0.5-6.9 ppmv and <0.5-0.97 ppmv, respectively (note that concentrations in the 0.1-0.5 ppm range are subject to severe uncertainties, as close to the sensors' detection limits, as should hence be treated as semiquantitative estimates). Considering that no SO₂ is reported in the Stefanos fumaroles (Chiodini et al., 2002), we cannot exclude that the detected SO₂ is an analytical artefact. However, no cross-sensitivity to H₂S was observed on the SO₂ sensor during calibration in the laboratory (when H₂S standards exceeding 100 ppm concentrations were used). We hence consider likely that the very small SO₂ levels encountered reflect some (minor) extent of H₂S oxidation in the inlet/filter tubing system of the Multi-GAS, a process that typically occurs when the plume is condensing (a relatively high humidity (51%) was encountered during the observations). (Sitthikhankaew et al, (2014);

Pompanon et al, (2022)) Along the descent path to the Stefanos crater floor, and at the center of the caldera floor itself (sites identified by grey points in **Fig 5.8A**), CO₂, H₂S, H₂ and SO₂ concentrations are typically lower, and range 473-595 ppmv, 1.8-3.9 ppmv, <0.5-1.1 ppmv and <0.5 ppmv, respectively. The highest gas concentrations are observed across the Lofos dome walking traverse,

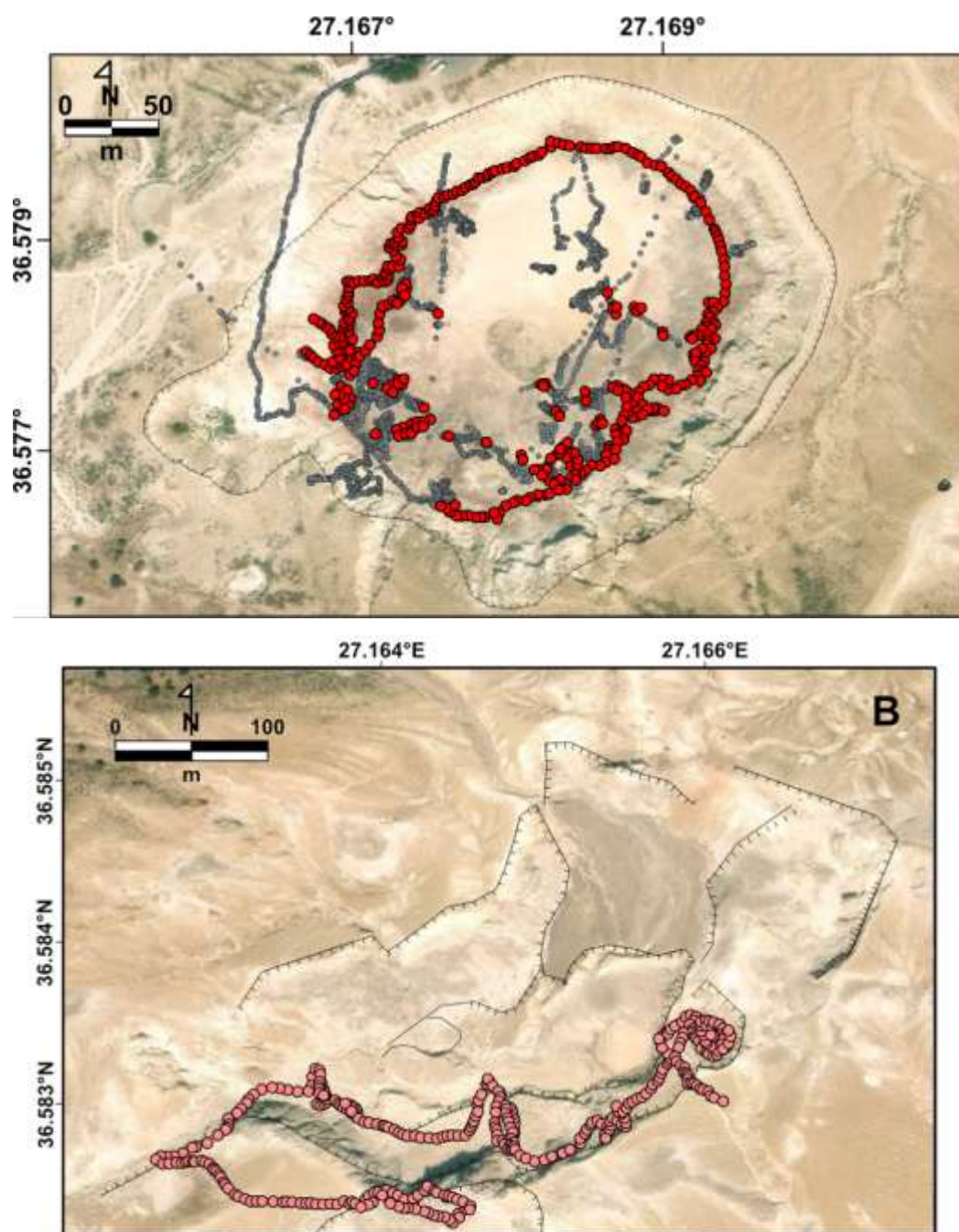


Figure 5.8 (previously page) **A:** Multi-GAS measurement points in the Stefanos crater. Red points correspond to a walking traverse path in which all the main fumaroles (concentrated on the inner crater rim) were analyzed in circa 1 hour on April 26th 2024. Grey points indicated the geo-referenced location of other measurement points (observations taken on April 21-26). **B:** Location of the Multi-GAS walking traverse in the Lofos dome. For further details, see text.

where CO₂, H₂S, concentrations range 478-2247 ppmv, 0.7-202 ppmv, while H₂ and SO₂ are below detection limits.

The Figures 5.9A-D are distribution maps of gas concentrations within the Stefanos crater. The maps are created with QGIS Desktop 3.22.16 (QGIS Development Team, 2025) and using the Inverse Distance Weighting (IDW) interpolation method (Shepard, 1968). The Inverse Distance Weighting (IDW) method is an interpolation technique in which the weight of each measurement point at each node of an interpolation grid is taken inversely proportional to its distance (d) from that specific node, e.g., $1/d^p$, where p is a power coefficient.

The CO₂, H₂S, H₂ concentration maps (**Fig. 5.9A-C**) consistently identify a cluster of concentration peaks distributed along a ring structure that corresponds to the internal rim of the Stefanos crater. These clustered concentration peaks along the inner crater rim correspond to the area where most fumaroles are concentrated, suggesting a structural control on hydrothermal gas ascent and surface discharge. The maps indicate that the peak CO₂ and H₂S concentrations are observed along the north-western and south-eastern portions of the inner crater rim. In these areas, CO₂ and H₂S concentrations in the fumarole's atmospheric plumes exceed 1000 and 80 ppmv, respectively. In contrast, lower CO₂ and H₂S concentrations (of circa 450 ppmv and 0.5 ppmv, respectively) are observed in its north-eastern and south-western margins of the inner crater rim. These are hence interpreted as hydrothermally more silent sectors. The H₂ map exhibits similar ring-shaped degassing structures, but the gas concentration peaks are more randomly distributed (than for CO₂ and H₂S), likely reflecting the lower concentration levels (≤ 5 ppmv) and hence higher uncertainties ($>15\%$; estimated based on tests made in the laboratory with reference gas standards).

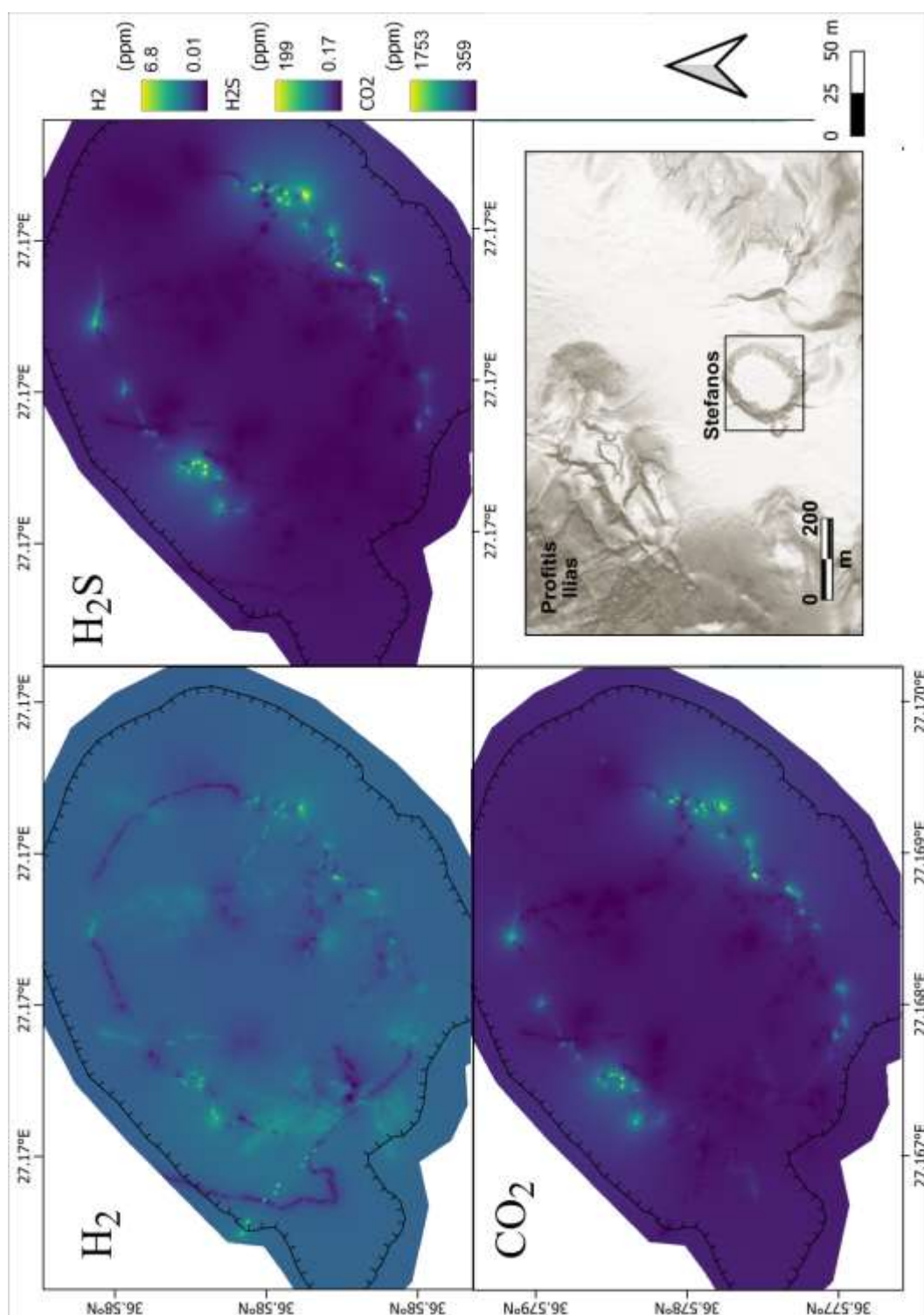


Figure 5.9 Gas concentration maps interpolated with the IDW method. Maps are elaborated in QGIS. See text for details.

5.4.2: Gas ratios

The Figures 5.10 are scatter plots of (A) CO₂ vs H₂S and (B) CO₂ vs H₂ concentrations in the fumarolic atmospheric plumes of Stefanos and Lofos. The positive correlations observed among the three gas species testify to their common hydrothermal origin and suggest a relative homogeneity of gas ratios in the fumarolic fields.

We initially estimate the fumarolic CO₂/H₂S and CO₂/H₂ ratios from the gradients of the best-fit regression lines in the CO₂ vs. H₂S and CO₂ vs. H₂ concentration scatter plots (Fig. 5.10). We find similar CO₂/H₂S and CO₂/H₂ ratios at both sites. The mean CO₂/H₂S and CO₂/H₂ ratios at Stefanos, obtained from linear regression through the entire dataset, are 7.2 ± 0.2 and 159 ± 18 . The same operation, applied to subsets of gas couples that correspond to individual larger fumaroles (see inset in Fig. 5.10a), sets the CO₂/H₂S variability at Stefanos in the 6.4 ± 0.7 to 13.1 ± 2.5 range. For comparison, the Lofos fumaroles have slightly lower CO₂/H₂S ratios, ranging from 5.1 ± 1.0 to 7.8 ± 0.4 range, and the average ratio for entire Lofos fumarolic field is 7.7 ± 0.4 . CO₂/H₂ ratios are lower at Lofos (133 ± 7.7) than at Stefanos (from 146 ± 30 to 170 ± 15) (Fig. 5.10B).

5.5: Discussion

5.5.1: A spatially resolved record of hydrothermal gas composition

Multi-GAS surveys at hydrothermal volcanoes pave the way to rapidly analyzing many fumarolic vents in short temporal intervals, hence contributing to revealing any spatial heterogeneity in gas composition across a fumarolic field.

Our gas concentration maps identify the most vigorous degassing fumaroles at Stefanos as areas associated with large CO₂ and H₂S concentrations (Fig. 5.9). The CO₂- and H₂S-rich signature of the Nysiros gas has already been found in

previous direct sampling studies (e.g., Chiodini et al., 2002). These areas are preferentially concentrated along the outer margins of the crater floor, and specifically form two roughly parallel, NE-trending clusters in the north-western and south-eastern portions of the inner crater rim. NE-trending faults are structurally dominant lineaments at Nisyros (Papadopoulos et al., 1998), and the crater itself has an asymmetric (elliptical) shape with a prevalent NE-SW trending axis. Our results hence suggest that NW-trending faults are controlling the overall geochemistry, and directions of fluid ascent and discharge, at Nisyros (Marini et al., 1993; Chiodini et al., 2002; Bini et al., 2019, 2020).

Our results also allow exploration of the spatial diversity of gas/gas ratios in the Nisyros fumaroles. Gas scatter plots (Fig. 5.10), while pointing to an overall homogeneity in fumarole composition, also support some level of inter-fumarole CO₂/H₂S ratio diversity. In the attempt to more fully examine such spatial variability of CO₂/H₂S ratios throughout the fumarolic fields, we process the CO₂ and H₂S concentration time-series using a routine in the R-code (<https://www.r-project.org/>) (written by Giancarlo Tamburello; same routine used in Aiuppa et al., 2022 and Lentini et al., 2025). This automatic routine sequentially scans the gas concentration time-series, searching for (and identifying) periods of high temporal coherence between CO₂ and H₂S in 60 s long moving windows. Within each of these time windows, the routine calculates a CO₂/H₂S ratio when two selected thresholds for the (i) correlation coefficient (Pearson correlation coefficient ≥ 0.7) and ii) H₂S concentration (≥ 20 ppmv) are reached. The obtained ratios are georeferenced using the co-acquired GPS positions.

The derived ratios are illustrated in the maps of Figures 5.11-5.13. The Stefanos dotted map (Fig. 5.11) shows relatively homogeneous, low (≤ 10) CO₂/H₂S along the ring-shaped degassing structure identified above (in Fig. 5.9). In contrast, higher ratios (>10 , and as high as 118) are identified in the south-western portion of the investigated area, across a segment stretching from W2 to SE1 fumaroles (Fig. 5.11). The same results are illustrated in the contour map of Figure 5.12. Despite the limits of the map, which depend on the limited number of points and their

non-uniform distribution, the map reveals the dominance of low $\text{CO}_2/\text{H}_2\text{S}$ ratio compositions in two sectors (labelled A and B) in the central portions of the eastern

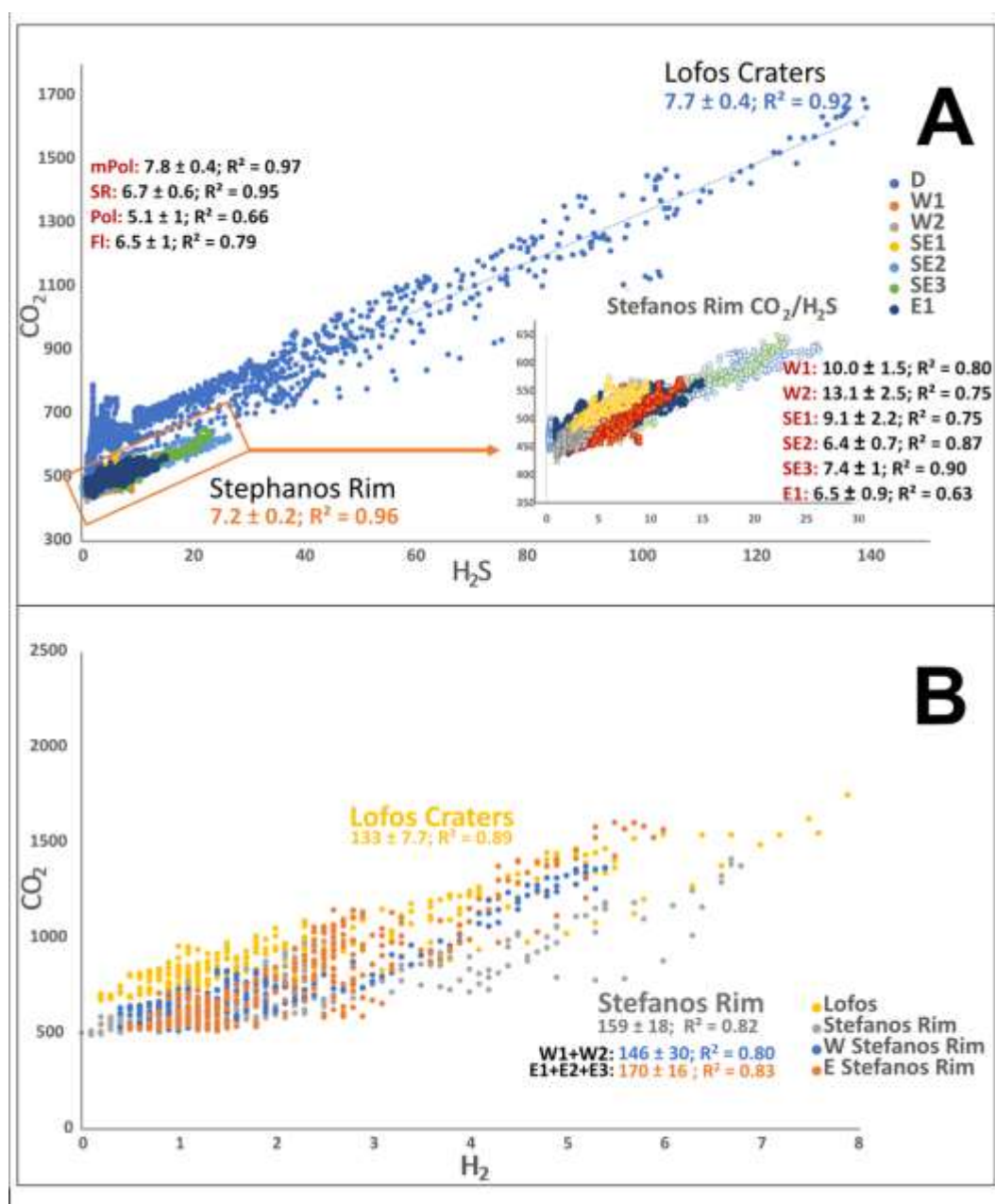


Figure 5.10 Scatter plot of A, CO₂ vs H₂S and B, CO₂ vs. H₂ concentrations in the Stefanos and Lofos fumaroles.

and western branches of the ring-shaped degassing structure. These are encircled by areas of higher $\text{CO}_2/\text{H}_2\text{S}$ ratio ($>> 10$) along the south-western (and north-eastern) segments of the ring structure.

H_2S is more reactive than CO_2 during hydrothermal interactions of magmatic/hydrothermal gases with hydrothermal solutions and rocks (Symonds et al.,

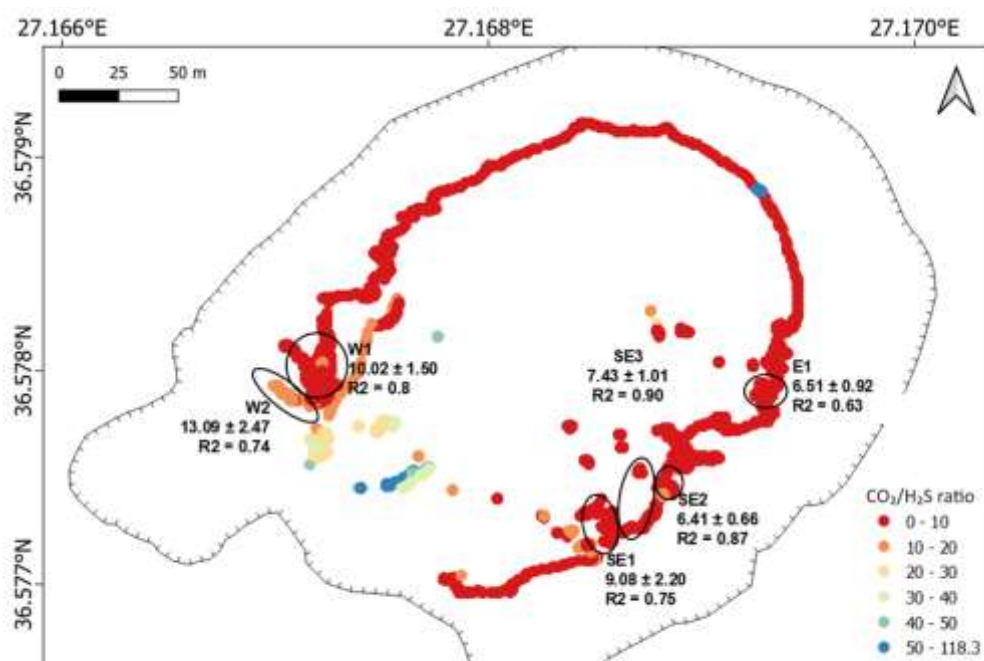


Figure 5.11 Dotted $\text{CO}_2/\text{H}_2\text{S}$ ratio map illustrating the output of the unsupervised (automatic) R routine applied to the Stefanos gas concentration time-series. The derived ratios are contrasted with those obtained using a supervised (operator-based) procedure (numbers; same values reported in Figure 5.10A).

2001). This renders the $\text{CO}_2/\text{H}_2\text{S}$ ratio a tracer of hydrothermal reactions, in which higher ratios are representative of more intense sulphur chemical processing (e.g., scrubbing from gas) upon hydrothermal interactions (Stix and de Moor, 2018). Higher sulphur depletion upon cooling (during hydrothermal interactions) justifies the characteristic negative temperature dependence of $\text{CO}_2/\text{S}_\text{T}$ ratios (where S_T is total sulphur, corresponding to H_2S at hydrothermal conditions; Aiuppa and Mousallam, 2024), seen at hydrothermal volcanoes globally (Aiuppa et al., 2017). We hence conclude that, at Stefanos, the least-processed fumaroles (by shallow hydrothermal interactions) are emitted in sectors A and B (Fig. 5.12), that consistently

host the most vigorously degassing fumaroles (see the concentration maps of Fig. 5.9).

A similar dotted map for the Lofos transect (Fig. 5.13) finds low (<10), relatively uniform $\text{CO}_2/\text{H}_2\text{S}$ ratios. Such prevailing low ratios, similar to those observed in zones A and B at Stefanos, suggest that the Lofos dome is affected by a sustained

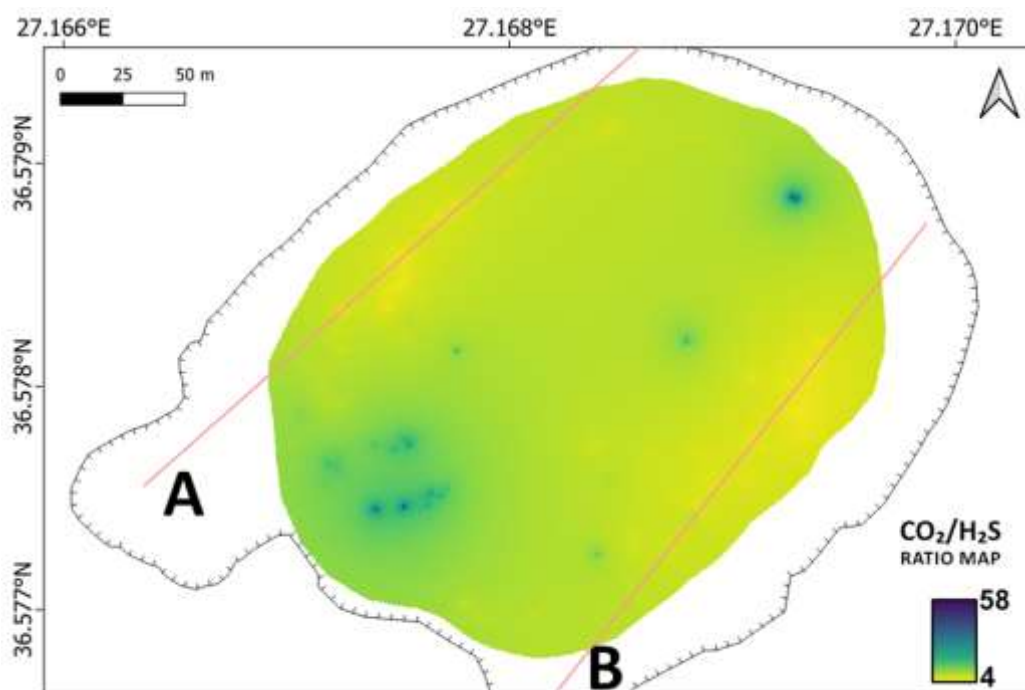


Figure 5.12 A $\text{CO}_2/\text{H}_2\text{S}$ ratio map the in the Stefanos crater, obtained by interpolation (with the IDW method) of results shown in Figure 5.11. Faults (red lines) are taken from Dietrich et al., (2017).

influx of deeply rising gases, hence causing a shorter transit of gases in the hydrothermal gas-liquid-rock interaction zone, and consequently a more reduced scrubbing of sulphur to hydrothermal minerals/solutions.

5.5.2: Temporal evolution of gas composition

Although no magmatic eruption has taken place at Nisyros over the last 10 ka (Bachmann et al., 2010), hydrothermal explosions have been relatively frequent in historical times (Marini et al., 1993). Based on a review of historical chronicles,

Marini et al., (1993) proposed a seismic trigger for these explosions, in which increased rock fracturing during seismic unrests leads to increasing transport of deeply rising volatiles into shallow hydrothermal aquifers, ultimately driving them to the fluid over-pressure conditions that cause hydrothermal explosions.

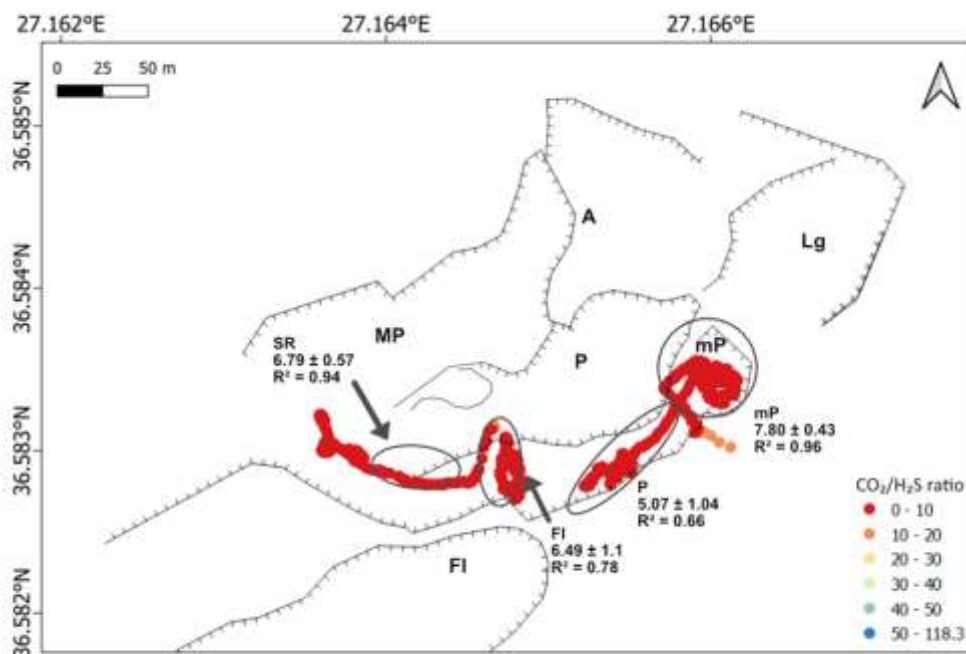


Figure 5.13. Dotted map of CO₂/H₂S ratio map in the walking path along the rim of the explosions craters ontop Lofos dome. A: Ahilleas; Lg: logotethis; mP, P and MP: Mikros Polivotis, Polivotis and Megalos Polivotis craters; FI: Flegethon crater. The point values of the ratios refer to the crater symbols, except for FI and SR, which refer respectively to measurements taken along the crater rim of Polyvotis near Flegethon (FI) and the southern rim of Megalos Polyvotis (SR).

A major seismic unrest in 1996-1997 (Papadopoulos et al., 1998) was followed by large variations in the chemistry of hydrothermal manifestation in 1997-2001 (Chiodini et al., 2002). Chiodini et al. (2002) explained the decreasing CO₂/H₂S ratios and CH₄/CO₂ ratios observed in the fumaroles as caused by a burst of sulphur-rich, hot and oxidized (hence low in CH₄) magmatic fluids into the hydrothermal aquifer(s), hence raising concerns for an increased probability for hydrothermal explosions.

Our CO₂/H₂S results are put in the context of previous gas information at Nisyros obtained using direct sampling of fumaroles (Chiodini et al. 1993; Kavouridis et al. 1999; Marini et al. 2002; Brombach et al. 2003; Fiebig et al. 2004; Marini et al. 2005; D'Alessandro et al. 2013; Fiebig et al. 2013) in the chronogram of Figure 5.14, where also seismic events in range 1989-2025 and $M \geq 2.0$ are highlighted; the seismic events used in this study were downloaded from the Interactive Earthquake Map of the USGS Earthquake Hazards program (USGS 2025): it can be noted that the events highlighted show that the seismic network in Nisyros was unable to detect weak earthquakes ($M < 3$) until 2010. These results make it possible to reconstruct the temporal evolution of the CO₂/H₂S ratio during three decades encompassing the Nisyros seismic/degassing unrest of 1996 to 2001 (Chiodini et al., 2002). Results for (a) all Nisyros fumaroles and (b) for Stefanos and Lofos fumaroles in the specific concur to indicate a progressive CO₂/H₂S decreasing trend from the early 1990s to the early 2000s (e.g., during and shortly after the seismic unrest), followed by a gradual CO₂/H₂S ratio increase from the last 2000s onward. In this context, our 2024 results plot along this increasing trend, revealing some of the highest CO₂/H₂S ratios measured at Stefanos on record (**Fig. 5.14**). Our wide CO₂/H₂S ratio range reflects the larger number of fumaroles analyzed by the Multi-GAS approach, which also includes some mildly emitting fumarole that consistently exhibit more sulphur-scrubbed compositions (e.g., CO₂/H₂S ratios >10)

relative to direct sampling (that typically concentrate on the largest

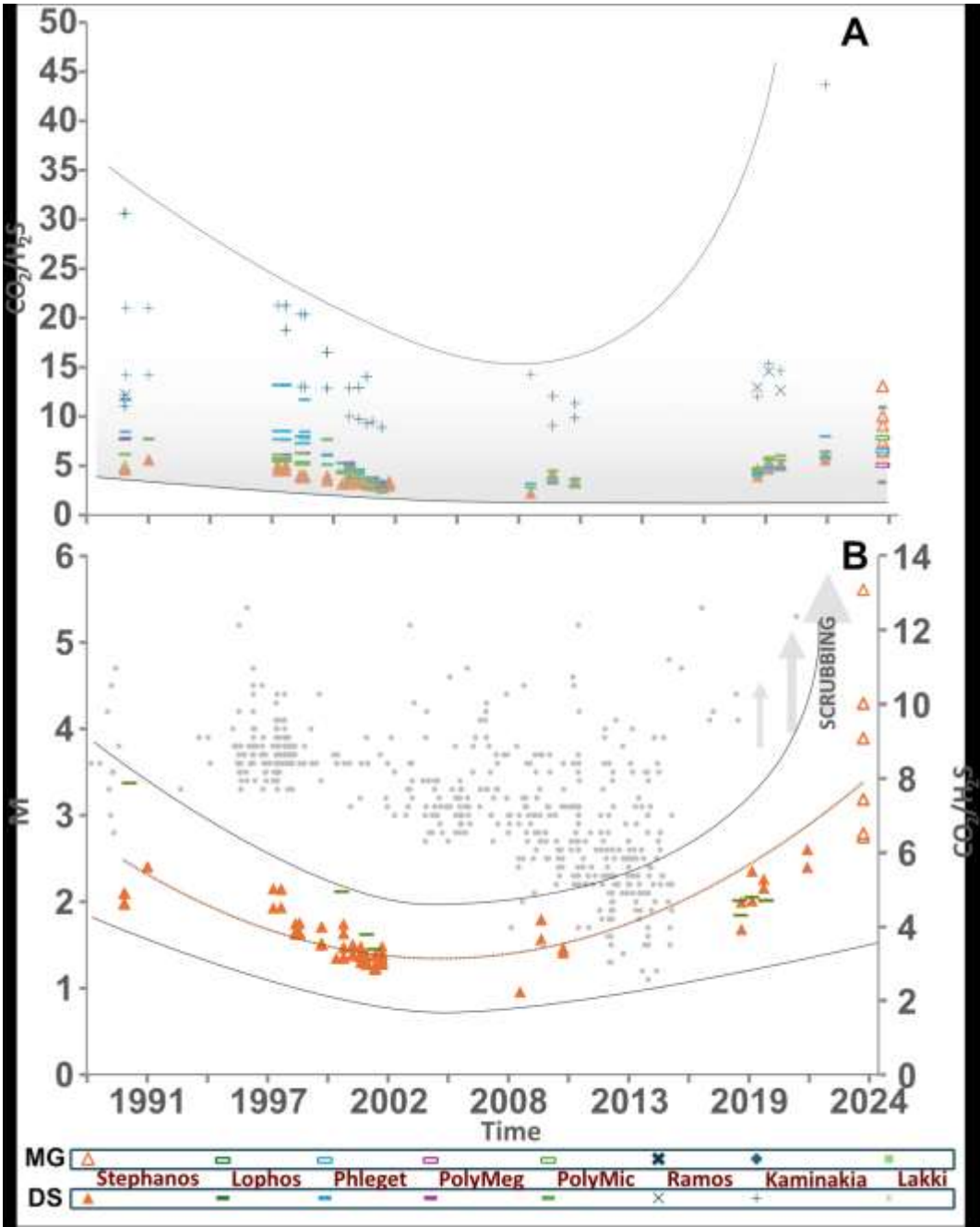


Figure 5.14 (previously page) **A** Time series of CO_2/H_2S in Stefanos and Lofos; Kaminakia and other places in Lakki plain are reported. **B**. Same graphs A with just Stefanos and Lofos. Figure B also exhibits a temporal record of earthquakes. The seismic events analyzed come from the USGS catalog, downloaded via the IRIS Earthquake Browser interface. Data collected with the Multi-GAS system correspond to measurements from 2024 and are highlighted in orange (this study)

fumaroles). We cannot exclude that some of the highest CO₂/H₂S ratios in our dataset reflect some level of H₂S atmospheric processing (e.g., degradation; Massaro et al., 2024) before Multi-GAS sensing, although this possibility is unlikely given the very short plume transits/ages investigated here. Yet, our lowest CO₂/H₂S fumarolic ratios at Stefanos (~6) fall along the same direct sampling trend. Overall, our results with previous work concur to indicate a progressive decline in hydrothermal sulphur transport at Nisyros relative to the restless 1996-2001 period. We tentatively ascribe this to a combination of (i) reduced magmatic gas inflow into the hydrothermal system and (ii) longer residence times in the hydrothermal envelope, and hence more prolonged magmatic gas-hydrothermal interactions, over the last decade.

5.5.3: Implications for gas hazard and human health impact

Nisyros is a popular touristic destination, with circa 60,000 to 75,000 visitors yearly, mostly concentrated in the summer season (Stiros, 2000; Vougioukalakis and Fytikas, 2005; Kinvig et al., 2010; IANOS Project Consortium, 2022). During this time of the year (June to September), hundreds of people are estimated to visit the Nisyros hydrothermal manifestations per day. Our atmospheric gas concentration results here can be used for a first order assessment of the exposure of visitors to potentially toxic hydrothermal gases, and the consequent potential health effects.

As mentioned earlier, carbon dioxide is a major volcanic hazard due to its tendency to accumulate in topographic depressions and confined or poorly ventilated environments. Adverse effects arise from exposure to high concentrations (Baxter, 2000; Viveiros et al., 2024; IVHHN, 2025). In particular, these CO₂-related effects become significant only when/if per cent (%) concentration levels are reached, which are well above those observed in air in proximity to the Nisyros emissions vents (< 2000 ppmv, or 0.2 %; see Figures 5.9 and 5.10).

H₂S is the next most abundant gas in Nisyros fumaroles. Here we reiterate what has already been said regarding gas hazards at Vulcano. Hydrogen sulphide in low concentrations causes loss of smell, irritation of the mucous membranes, gastric and respiratory complaints (20-150 ppm); concentrations exceeding 250 ppm are considered highly harmful and lethal. (Legator 2001; Bates 2002; Balagizi et al. 2018; IVHHN, 2025).

Figure 5.15 is a frequency distribution diagram of H₂S concentrations in the atmospheric plumes of Stefanos fumaroles. The red curve refers to the near-vent fumarolic plume observations (taken at the locations indicated by the red points in

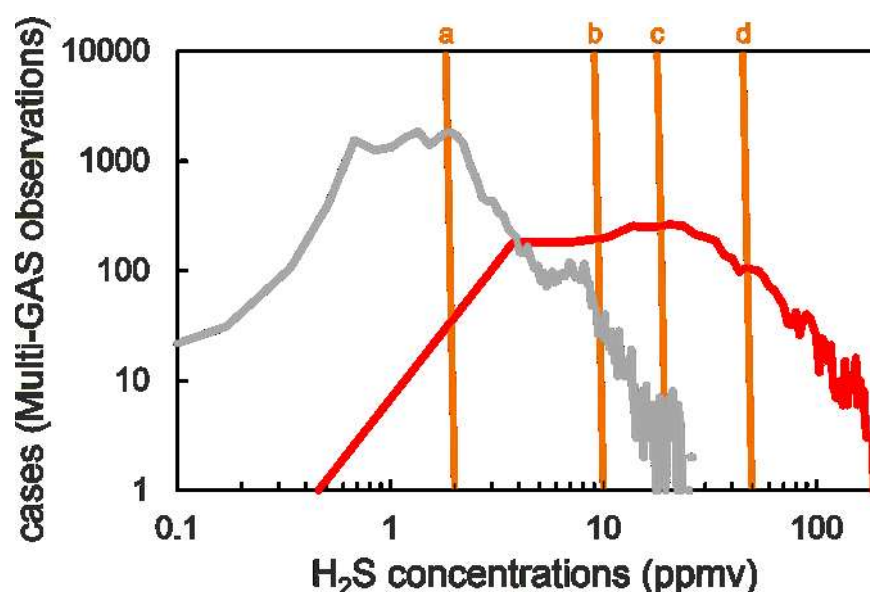


Figure 5.15. Frequency distribution diagram of H₂S concentrations in the atmospheric plumes of Stefanos fumaroles. Red curve: near-vent fumarolic plume observations (taken at the locations indicated by the red points in Fig. 8); grey curve: crater floor and access ramp observations (taken at the locations indicated by the grey points in Fig. 8). The orange vertical bars indicate some H₂S threshold values: a: 2 ppm, health effects include bronchoconstriction in 2/10 of asthmatics and headaches in 3/10 asthmatics (UK Health Security Agency, 2016); b: 10 ppm, short-term (15-minute reference period) maximum exposure limit (MEL) set by the UK Health and Safety Executive (HSE, 2020); c: 20 ppm, health effects include loss of sense of smell to gas, eye irritation (IVHHN); d: 50 ppm, health effects include eye irritation, prolonged exposure may cause pharyngitis and bronchitis (IVHHN). Very high exposures (to more than 200-500 ppm) can cause rapid unconsciousness or death within minutes (IVHHN, 2025).

Fig. 5.8). These exhibit an H₂S distribution with a mode at ~20 ppm, and a mean at ~40 ppm. Considering that the time a tourist typically spends inside the Stefanos crater in a guided tour is circa 30 minutes, we can compare our concentration results with the short-term (15-minute reference period) maximum exposure limit (MEL)

of 10 ppm, set for H₂S (HSE, 2020), as mentioned earlier. In our case, it is expected that the exposure time to proximal fumarolic fumes (the actual time spent by a visitor at less than 1-meter distance from a fumarole) is much shorter and episodic. As an exercise, we can fix this exposure time at 2 minutes, and we can use Haber's law (Gaylor, 2000) to calculate the corresponding maximum exposure limit (MEL_{2 min}). From this, the MEL_{2 min} can be inferred at 75 ppm using the MEL_{15 min} above and the relationship: $[(10 \text{ ppm} \cdot 15 \text{ minutes})/2 \text{ minutes}]$. Our frequency distribution diagram (Fig. 5.15) shows that 85% of our near-vent measurements are below this 75 ppm threshold. Our results hence indicate that a typical visitor would experience discomfort (e.g., exposure to potentially harmful H₂S levels) only in the very unlikely condition of prolonged stays (for more than 2 minutes), without personal protection gears (a gas mask), in a very dense, proximal plume.

A typical visitor/tourist at Nisyros spends most of this visit time within the crater floor, or along the crater access ramp. The grey curve in Figure 5.15 shows the distribution of H₂S concentrations in such crater floor and access ramp areas. Here, the dominant H₂S concentration levels are between ~0.5 and ~2 ppmv (mode: 1.8 ppmv; mean 2.7 ppmv), that are typical of diluted plumes (Oppenheimer et al., 1998) but still well above the background tropospheric levels of 0.00005 to 0.024 ppm (Brimblecombe, 1996). High concentration peaks (up to 23 ppmv) are sporadically observed near small fumaroles. On average, a guided tour of the crater lasts 30 minutes. The MEL_{30 min} is given by $C = (10 \text{ ppm} \cdot 15 \text{ min})/30 \text{ min} = 5 \text{ ppm}$. This indicates that the maximum concentration tolerated in the crater in 30 minutes must not exceed 5 ppm to avoid adverse effects. This concentration threshold is only exceeded in 12% of our measurements.

It is important to keep in mind that the 10-ppm maximum exposure limit (MEL_{15 min}), and other similar thresholds, refer to healthy individuals. However, asthmatics may experience symptoms at concentrations much lower than those tolerated by a health person, with 2 out of 10 showing signs of bronchoconstriction and 3 out of 10 complaining of headaches after exposure to 2 ppm (UK Health Security Agency, 2016). The modal/mean H₂S concentrations in the crater area

(floor and access ramp) are 1.8 and 2.7, implying that asthmatic visitors in the crater are especially exposed to harmful effect from H₂S exposure.

The atmospheric SO₂ concentrations at Stefanos are systematically at sub-ppm levels (Fig. 5.5), which is below the normal application range of the Multi-GAS (Aiuppa et al., 2021). In addition to low accuracy/precision of the used electrochemical sensor at these low concentration levels, concerns remains on if the detected SO₂ reflects a natural process (e.g., caused by rapid atmospheric oxidation of fumarolic H₂S) or rather an analytical artefact (e.g., caused by H₂S oxidation in the Multi-GAS inlet system at high relative humidity conditions in the field) (cfr. 4.1). If reflecting the real atmospheric conditions at Stefanos, these SO₂ concentration levels may reveal dangerous for asthmatics, for which even brief exposures at low doses can cause measurable respiratory effects (Koren 1995; Reno et al., 2015). Our observations of H₂S concentrations and exposure probabilities in the crater area are fully consistent with the models and observations reported by Massaro et al., (2024) (see sections 1-2). As also highlighted by Massaro et al. (2024), while healthy visitors are generally unlikely to experience adverse effects during typical short-term visits, individuals with pre-existing respiratory conditions may be exposed to non-negligible concentrations, even for brief periods. The results of Massaro et al (2024) also confirm that the eastern and western sectors of the crater rim are systematically impacted by fumarolic plume fumigation, with significant probabilities of exceeding potentially harmful H₂S thresholds of 0.03 ppm (for 1 h exposure) and 0.01 ppm (for 24h exposures). These results, and those presented in this study, suggest the potential exposure to toxic H₂S levels during routine touristic visits.

5.6: Conclusions

We have analyzed the atmospheric concentrations of volcanogenic gas species (CO₂, H₂S, H₂ and SO₂) in the proximal (< 1m) plumes of the hydrothermal fumaroles of Stefanos and Lofos on top of Nisyros volcano.

Our spatially resolved measurements allow mapping the main gas emission vents as spots of high CO₂ (< 1000 ppmv) and H₂S (> 80 ppmv) concentrations. At Stefanos, these cluster along a ring-shaped structure corresponding to the outer margins of the crater floor. These gas-rich spots are especially concentrated along two roughly parallel, NE-trending zones in the north-western and south-eastern segments of the ring, suggesting a dominant structural control on gas ascent and discharge. In these area, CO₂/H₂S ratios are typically <10 (the lowest ratios, in the 5.1±1.0 to 7.8±0.4 range, are measured at Lofos), suggesting small degrees of magmatic-hydrothermal interactions with fluids and rocks in the fumaroles' ascent conduits (hydrothermal reactions typically scavenge H₂S from gas relative to less reactive CO₂). For comparison, more H₂S-depleted (CO₂/H₂S >> 10) are observed in the more modest (in terms of surface expression) fumaroles of the south-western portion of the Stefanos ring structure.

Comparison with literature results indicate higher CO₂/H₂S ratios in 2025 relative to 1996-2001, confirming progressive vanishing of the hydrothermal unrest of the late 1990s. The H₂S atmospheric concentration levels inside the Stefanos crater, a popular touristic destination, are potentially harmful for visitors with chronic respiratory diseases.

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6: CONCLUDING REMARKS

In this PhD dissertation, I investigated the potentialities of the use of chemical mapping of fumarolic fields as an effective tool to study and monitor hydrothermal volcanoes in unrest. By using portable Multi-component Gas Analyzer Systems (Multi-GAS), I obtained high-spatial- and high-temporal-resolution measurements that allowed reconstructing the chemical heterogeneity of fumarolic fields and tracking their evolution through time.

This approach was applied to two quiescent volcanic systems that have experienced recent unrest: La Fossa crater on Vulcano Island (Italy) and Nisyros Island (Greece). These two case studies provided complementary insights into the behavior of hydrothermal systems under different geological and unrest conditions.

At Vulcano, repeated gas surveys were carried out between 2021 and 2024, spanning the major degassing unrest that began in autumn 2021. Chemical mapping revealed a clear compositional contrast between crater-rim and inner-crater fumaroles. Rim fumaroles were characterized by relatively stable, magmatic-dominated gas signatures, with high concentrations of CO_2 , SO_2 , H_2S and H_2 and consistently low CO_2/SO_2 ratios, indicating limited chemical processing of magmatic gases upon their ascent through the hydrothermal system. In contrast, inner-crater fumaroles displayed larger temporal variations in gas composition and a wide heterogeneity of CO_2/SO_2 ratios. These variations are interpreted as the result of alternating phases of expansion and contraction of the degassing gas feeding conduit system sustaining the unrest, which is suggested to be located in correspondence to the partially buried rim of the 1888-1890 eruption crater. The persistence of intermediate, below-background CO_2/SO_2 ratios in the crater-rim area throughout the 2021-2024 period, together with elevated SO_2 fluxes, indicate that hydrothermal conditions have not yet fully returned to background levels, despite the overall decline of degassing activity following the peak of unrest in fall 2021.

At Nisyros, the chemical mapping technique was applied through walking traverses conducted across the fumarolic fields of Stefanos and Lofos, two of the most active hydrothermal areas on the island. Measurements acquired at high spatial and temporal resolution allowed the identification of the main degassing zones. These are highlighted as spots with elevated CO₂ and H₂S concentrations that align along a ring-shaped degassing structure corresponding to the inner rim of the Stefanos crater. The spatially resolved gas ratios, obtained for a far larger number of fumaroles than typically achievable through direct sampling, revealed an overall compositional homogeneity across the fumarolic fields. Comparison with the multi-decadal geochemical record of Nisyros showed that fumarolic gases measured in 2025 were characterized by higher CO₂/H₂S ratios relative to those emitted during the 1996-2001 seismic and degassing unrest, suggesting a gradual recovery of the volcanic system toward background hydrothermal conditions. Because Stefanos is a popular touristic destination, visited by thousands of visitors yearly, the possible health impact on tourists, visitors and operators, exercised by the exposure to potentially hazardous volcanic gases such as CO₂ and H₂S, was also evaluated.

Overall, the results of this study demonstrate that rapid, spatially extensive Multi-GAS surveys represent a useful complement to traditional direct sampling methods. By enabling the reconstruction of the chemical diversity of fumarolic fields and their temporal evolution, Multi-GAS mapping can provide valuable constraints on the drivers, dynamics and evolution of volcanic unrest in hydrothermal systems.

