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**Crust-mantle interactions and
connections with the geodynamic system
in the origin and circulation of fluids in
the Comoros Archipelago - Indian Ocean**

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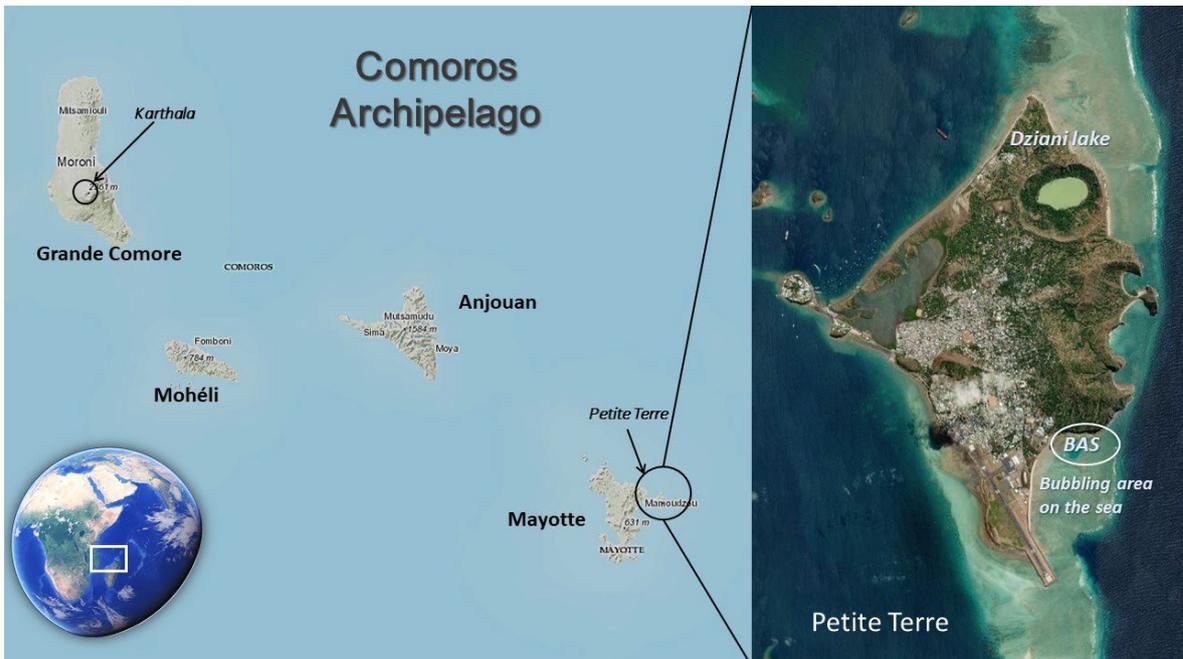
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Map of the Comoros Archipelago with in evidence the two target areas of study: Grande Comore and Petite Terre (Mayotte) islands



Summit crater of Karthala

Introduction

The role of fluids in crust-mantle interactions is of crucial importance in providing information regarding the definition of the origin of magmas, the identification of their depths of origin, and the nature of the interaction processes that determine their characteristics. Complex geodynamic systems may therefore have an articulated history of processes that can be reconstructed by studying the fluids emitted in such areas, and by analysing the fluids included in the rocks that characterise these geological regions. In short, we can cite the thoughtful metaphor of Sadao Matsuo, the first leader of the Commission on the Chemistry of Volcanic Gases (CCVG), who referred to volcanic gas emissions as a “telegram from the Earth’s interior”. This research represents an attempt to read and interpret as much as possible from such complex messages with regard to an area of extreme geological pertinence and interest to contemporary volcanic geochemistry.

The chosen area of study for the present work focuses on two islands of the Comoros Archipelago: Grande Comore and Mayotte, located within the Mozambique Channel within a complicated geodynamic system of great interest due to the currently existing volcanic and seismic activity, of which a complete descriptive picture is currently lacking. In particular, especially with regard to fluid geochemistry, very little knowledge of gas and fluid emissions yet exists. In this sense, it is now even more compelling to understand these characteristics, not only in consideration of the high level of activity of the Karthala volcano in Grande Comore, but also with regard to the volcanic and seismic activity recently recorded at Mayotte Island, which is very close to the recent submarine volcano formed only 50 km South-East off-shore of Mayotte, and by far the largest known submarine eruption until now (Feuillet et al., 2021; Berthod et al., 2021).

The specific aim of this study is to investigate the existing outgassing conditions on both islands in order to include this knowledge within a broader and multidisciplinary framework that will facilitate the understanding of the volcanic dynamics of this particular area of the Indian Ocean.

Karthala volcano, located on Grande Comore Island, is the most active volcano in the western Indian Ocean after Piton de la Fournaise at La Reunion. Karthala is a basaltic shield volcano which has erupted regularly in the last century; fourteen eruptions are listed from 1904 to today, where the last eruptive activity occurred in

2007 (Bachèlery et al., 2016). Owing to its remote location, it is still under-studied and, in particular, little is known about its diffuse outgassing. The study of the diffuse outgassing of the Karthala volcano, with particular attention to the emission of CO₂ from the flanks of the volcano, is therefore crucial for the assessment of the state of activity of the volcano. In addition, as two significant persistent fumarolic fields are present in its summit crater area, both soil and fumarolic gas emission are investigated in terms of gas-geochemistry in this work.

Geochronological data recognize Mayotte as the earliest starting point of magmatic activity among the islands of the archipelago, which dates back to at least 10.58 Ma ago. The islands of Mohéli and Anjouan then follow at around 3.9 and 5 Ma ago, respectively, and finally Grande Comore at around 0.13 Ma (Michon, 2016). No recent eruptions have been recorded at Mayotte since the last occurred around 2050 BCE ± 500 (Smithsonian Institution - <https://volcano.si.edu>). ; however, stable volcanic activity at Mayotte is still present in the form of a large area of subaerial and underwater outgassing near its south-eastern coast at the Dziani Lake, which is situated in the north part of the island on the small island of Petite Terre. Significantly, Petite Terre was recently affected by a seismic crisis that lasted for several months, and was accompanied by the formation of the largest underwater volcano in recent centuries, about 50 km from its coast (see Ship spies largest underwater eruption ever - <https://www.sciencemag.org/news/2019/05/>; Berthod et al., 2021a, 2021b; Cesca et al., 2020; Feuillet et al., 2021; Lemoine et al., 2020; REVOSIMA, 2019).

The thesis is divided into two sections: the first will focus on the Karthala and Petite Terre gas emissions, considering fumarolic fields, soil emissions and bubbling areas, with the purpose of identifying the main characteristics, similarities and differences, of gas chemistry and isotopic variability in the two islands; the second section of the thesis focuses on the difference between the two known bubbling areas at Petite Terre, where I include the further study of the Lake Dziani gas emissions that have been investigated only in the most recent surveys.

In this study, I attempt to address the existing gap in knowledge regarding gas geochemistry on the islands focusing specifically on gas emissions, using an approach that combines different research objectives, and fieldwork and laboratory techniques, in order to:

- 1) define the chemical and isotopic characteristics of magmatic fluids in terms of the major gas components (CO₂, CH₄, H₂S, H₂ and H₂O) in free gases, noble gases (He-Ne-Ar) and C isotope ratios;
- 2) measure soil CO₂ concentration and identifying their $\delta^{13}\text{C}$ isotope signatures;
- 3) identify the similarities and differences regarding the volatiles emitted from the main volcanic and geothermal areas in both Grande Comore and Mayotte Islands;
- 4) conceptualise a geochemical model of the complex geodynamic framework of the Archipelago, integrating the gas geochemistry results obtained through the processes entailed in points 1-3;
- 5) evaluate the impact of volcanic emissions in the local area for monitoring purposes.

The success of such an approach has been previously demonstrated with regard to other magmatic systems worldwide, such as Mount Etna (Paonita et al. 2012, 2021), but particularly in relation to La Reunion, which is located in the Indian Ocean in a comparable geodynamic system of intraplate volcanism (Liuzzo et al., 2015; Boudoire et al. 2016, 2018, 2020).

In terms of gas geochemistry, the various findings of this thesis converge towards the recognition of some notable peculiarities with regard to the two target islands, which can be summarised according to the following four points:

First, the soil CO₂ emissions are spatially distributed along the main structural features of both Grande Comore and Petite Terre; however, the carbon isotopic signature of soil CO₂ emissions highlights a low magmatic contribution at distal areas of Karthala volcano, and a significantly higher magmatic contribution in CO₂ emissions at Petite Terre. This difference may be ascribed to the different states of volcanic activity on the two islands at the time of the surveys.

Second, with regard to the helium isotopic signature, the $^3\text{He}/^4\text{He}$ data are within the range of measurements in fluid inclusions of Grande Comore (Class et al., 2005), indicating for the gas emissions a low level of $^3\text{He}/^4\text{He}$ values ($\sim 6 \leq \text{Rc/Ra} \leq \sim 7.5$ Petite Terre; $\sim 4.6 \leq \text{Rc/Ra} \leq \sim 5.8$ Karthala), if compared with La Reunion signature ($\sim 12 \leq \text{Rc/Ra} \leq \sim 15$ Boudoire et al. 2020).

Third, the bubbling area on the sea (BAS) and Lake Dziani are likely fed by a common source (about 17 km below Petite Terre); however, Dziani lake is significantly affected by secondary processes that are mainly related to biotic

activities in the lake, which result in the higher variability of gas chemistry, $\delta^{13}\text{C}$ in methane and CO_2 than BAS.

Fourth, the increased value of R_c/R_a between 2008 and 2018-19, and a not-reached isotopic equilibrium of $\delta^{13}\text{C}_{\text{CH}_4}$ from the hydrothermal fluid, may be ascribed to the volcanic activity that generated the new submarine volcano 50 km offshore from Petite Terre. This consideration is also consistent with the final interpretation of this work, where the input of heated CO_2 -rich fluid into the Petite Terre hydrothermal system is a consequence of the perturbation of the shallow plumbing system by the offshore submarine eruption, resulting in higher equilibrium temperatures in 2018 and subsequent cooling down during and after the seismo-volcanic activity.

This work is expected to make a significant step forward in the current knowledge of the gas geochemistry of the Comores Archipelago, and, in particular, results in a better knowledge of the main characteristics of the emitted volcanic fluids. More importantly, it will assist in the recognition of which geochemical markers may be of potential relevance for volcanic monitoring purposes, thereby improving the understanding of the present state of its volcano activity. This latter aspect is especially important for the Karthala volcano, with regard to the ongoing sub-marine volcanic activity close to Mayotte. This would be of great support for local observation infrastructures and contribute to the improvement of applications in volcanic and environmental monitoring of this populated area.

Finally, this work would also provide a valuable case study that may be applicable to other similar contexts worldwide, allowing the definition of a comprehensive model considering volcanological effect and social impacts within the same framework.



The Soufrière area at Karthala volcano



The Bubbling Area on the Sea (BAS) at Petite Terre

SECTION 1

Spatial distribution of gases emissions and gas geochemistry analysis of Grande Comore and Mayotte Islands

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GAS GEOCHEMISTRY AT GRANDE COMORE AND MAYOTTE VOLCANIC ISLANDS (COMOROS ARCHIPELAGO), INDIAN OCEAN

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Abstract

The Comoros archipelago is an active geodynamic region of intra-plate volcanism within which the youngest and oldest islands (Grande Comore and Mayotte respectively) are characterized by recent volcanic activity. The frequent eruptions of the large shield volcano Karthala on Grande Comore (last eruption 2007), and the recent birth of a large submarine volcano since 2018 at the submarine base of Mayotte are associated with permanent fumarolic emissions, bubbling gas seeps, and soil gas emissions, which are studied in detail here for the first time. CO₂ fluxes and chemical and isotopic gas compositions acquired during two surveys in 2017 and 2020 are integrated with older datasets collected between 2005 and 2016, permitting the identification of a possible influence of the recent volcanic and magmatic activity at Mayotte.

At Karthala, high gas fluxes with high temperature, and a marked magmatic signature are concentrated close to the summit crater area, while only weaker emissions with a stronger biogenic signature are found on the volcano flanks. At Mayotte, lower temperature and higher CH₄ content are recorded in two main seep areas of CO₂-rich fluid bubbling, while soil emissions on land record a higher proportion of magmatic fluids compared to Karthala. Our preliminary results reveal two quite separate gas emission patterns for each island that

are distinct in composition and isotopic signatures, and well-correlated with the present state of volcanic activity. This work may potentially provide support for local observation infrastructures and contribute to the improvement in volcanic and environmental monitoring.

1. Introduction

Comoros archipelago is located in the Mozambique Channel between the east coast of Africa and the north-western coast of Madagascar. The formation of a huge submarine volcanic edifice since 2018, about 50 km offshore east of Mayotte, has prompted a renewal of multidisciplinary researches on the seismo-volcanic activity of the Comoros archipelago by the international volcanological community (Bachèlery et al., 2019; Berthod et al., 2020; Cesca et al., 2020; Feuillet et al., 2019; Lemoine et al., 2020; REVOSIMA, 2019). The archipelago consists of four main islands from NW to SE: Grande Comore, Mohéli, Anjouan, and Mayotte (Figure 1), amongst which Grande Comore hosts the large and frequently active basaltic Karthala volcano (last eruption in 2007). Subaerial Holocene volcanic activity related to a range of alkaline magma compositions (from basanite to phonolite) has been documented in the other islands (Bachèlery et al., 2016; Michon, 2016; Tzevahirtzian et al., 2021 and references therein). Comoros archipelago is considered as the potential diffuse Lwandle-Somali sub-plate boundary and part of the SE extension of the East African Rift System (Famin et al., 2020; Michon, 2016). The recent review of morphological, geological and chronological data of Tzevahirtzian et al. (2021) suggests that Mayotte and Moheli are the oldest islands, while Anjouan and Grande Comore are the most recent ones. The recent volcanism of Karthala in Grande Comore has been interpreted as hot-spot-related by geochemical studies (e.g. Class et al., 1998). Grande Comore and Anjouan are high altitude volcanic islands, intersected by well developed triple-armed volcanic rifts. On the contrary, Moheli and Mayotte are lower islands, with less well developed rift zones, and a wide insular shelf, which is very narrow on Grande Comore and Anjouan. Karthala is the second most active volcano in the Indian Ocean, after Piton de la Fournaise in La Réunion island, with permanent hydrothermal and fumarolic emissions close to its summit area (Bachèlery and Coudray, 1993; Bernabeu et al., 2018). Two years after the last summit Karthala eruption, Bernabeu et al. (2018) document high CO₂ fluxes in the soil close to the eruptive vent. However, the absence of chemical or isotopic analysis did not permit to attribute these emissions to the recently emplaced magma or to deeper sources. Seep areas of low-

temperature CO₂-rich bubbling gases have been reported for the first time between 1993 and 1998 at Mayotte, on the small island (Petite Terre) located on its eastern side (Traineau et al., 2006 and references therein).

In this work, we focus on the gaseous emissions on the oldest (Mayotte) and youngest (Grande Comore) islands, which are also the two recently active volcanic systems of the Comoros archipelago, with the aim at constraining the extent and spatial distribution of the outgassing areas and the geochemical signature of the gas emissions. Data were collected by a team of researchers from IPGP/OVVF and INGV who carried out surveys on the two islands between 2017 and 2020. In addition, we included data from older measurement campaigns which were undertaken for different purposes between 2005 and 2014. The results of the geochemical investigation highlight the differences in outgassing characteristics between the two volcanic islands and their link with the recent volcanic activity. We perform a comparison with the gas geochemistry of La Réunion island, where a deep and plume-like undegassed mantle contribution has long been identified.

Grande Comore and Mayotte are densely populated islands and in view of the high level of seismic and volcanic activity and the related hazards, these first results represent a significant contribution to pave the way for future activities on geochemical monitoring and hazard mitigation.

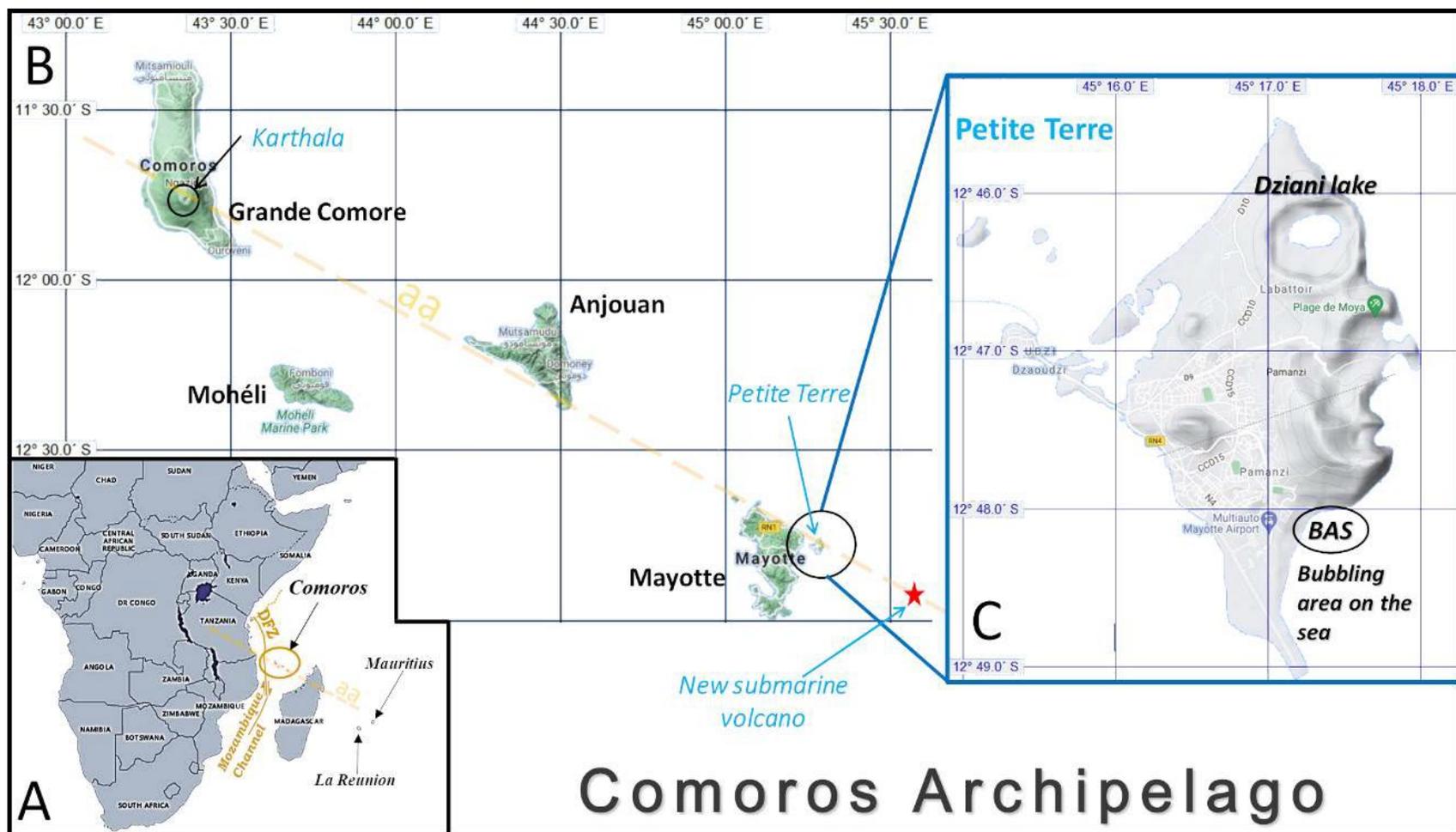


Figure 1. Map of the Comoros archipelago, which is located on the northern zone of the Mozambique Channel (A), in which is also shown the Davie Fracture zone (DZF). The elongated trend N120° “a-a” of the islands (B) corresponds to the recognised regional structural trend well defined by distribution of the 1901–2018 seismicity for $M > 4$ in Lemoine et al. (2020). In (C) highlighted on the map is the little island on the east coast of Mayotte called Petite Terre, where have been acquired all the measurements (both from the soil and from the bubbling area on the sea) mentioned in this paper regarding Mayotte island. The red star is the approximate location of the new submarine volcano.

2. Geological context

The islands of the Comorian archipelago are located within the Mozambique Channel in a particularly complex geodynamic region where the tectonic features are yet to be unambiguously defined. The main and better known tectonic structure, the Davie Fracture Zone (DFZ) (Phethean, 2016), is considered the kinematic hinge that allowed the southward drift of Madagascar following the Gondwana breakup. Despite its well defined structure, the DFZ has been described as either a western transform fault (Coffin et al., 1986) or as a continent-ocean transform margin (Gaina et al., 2013) of the Western Somali Basin (Figure 1A). The alignment of the islands is NW-SE (Figure 1B) and coincident with the main seismic zone of the archipelago (Lemoine et al., 2020). This orientation of islands separates the North Somali basin, which is agreed to be oceanic, and the South Somali basin, which for some authors is thought to be oceanic crust (e.g. Klimke et al., 2016; Rabinowitz et al., 1983), while other authors identify this as a thinned continental crust (e.g. Bassias & Leclaire, 1990; Roach et al., 2017).

The two main hypotheses that have been developed over time to explain the origin of the Comoros volcanism are:

- a) a mantle plume, which interacts with the oceanic lithosphere (Claude-Ivanaj et al., 1998; Class et al., 2005; Deniel, 1998; Emerick and Duncan, 1982; Hajash and Armstrong, 1972; Nougier et al., 1986). The link with a deep mantle hot spot has been invoked to explain the eastward migration of volcanism age, but also to explain the variability of geochemical magma composition measured along the archipelago. Karthala lavas are those recording a stronger hot spot signature (Bachèlery and Hémond, 2016; Claude-Ivanaj et al., 1998; Class et al., 2009; Coltorti et al., 1999). Recent seismic tomography (French and Romanowicz, 2015) fails to unambiguously identify a deep plume rooted in the mantle below Comoros archipelago.
- b) the reactivation of regional lithospheric structures, which interact with asthenospheric processes. This hypothesis rejects the previous model because it is inconsistent with the current volcanic activity which includes both Karthala volcano and the recent and still ongoing submarine volcanic activity eastward of Mayotte and with the absence of a clear age decrease along the archipelago (Famin et al.,

2020; Lemoine et al., 2020; Michon, 2016; Nougier et al., 1986; Tzevahirtzian et al., 2021)

At Mayotte, the volcanic activity becomes increasingly older from the eastern side (Petite Terre island), to the western main island (Grande Terre) (Nehlig et al., 2013). The still ongoing (at the time of writing), large-volume and long-lasting sub-marine eruption of Mayotte, the largest submarine event ever detected by monitoring networks (Cesca et al., 2020; Lemoine et al., 2020), challenges current models on the origin of Comoros volcanism. Since 2018, several km³ of evolved basanite lava have been emitted on the 3.5 km deep seafloor 50 km east from Mayotte from a deep source located in the upper lithospheric mantle (Bachèlery et al., 2019; Berthod et al., 2020; Lemoine et al. 2020). The new volcano grows on a N120° oriented volcanic ridge, which runs along the eastern submarine flank of Mayotte and whose western subaerial tip is the small island of Petite Terre (Tzevahirtzian et al., 2021; Figure 1B). On Petite Terre, recent volcanic activity has built on the coral reef a set of Holocene basaltic scoria cones and phonolitic maars (Nehlig et al., 2013; Zinke et al., 2001), and two main areas of low-temperature CO₂-rich gas bubbling seeps. A first bubbling area occurs in the NE part of Petite Terre inside the intracrateric lake of the Dziani phonolitic maar, where several CO₂- and CH₄- rich bubbling spots have been identified (Milesi et al., 2020). A second area, first described in 1998 on the eastern tidal flat of Petite Terre is located close to the “Airport beach” (BAS site; Sanjuan et al., 2008; Traineau et al., 2006). There, tens of bubbling spots occur at the southern feet of the large “Vigie” phonolitic maar, on a muddy flat area exposed to significant tide and extended for about 250x300 m from the beach (see also Figure 2).

In Grande Comore, at least three volcanic massifs have been identified: the old and inactive M’Badjini massif in the southernmost part of Grande Comore, the rarely active La Grille volcano in the north (last dated eruption: 1029-1424 CE) and in between the frequently active Karthala shield volcano (last eruption: 2007) (Bachèlery et al., 2016 and references therein). Karthala volcano is a large (summit elevation 2361 m) basaltic shield volcano, the highest relief of the Comoros archipelago, and exhibits well-developed rift zones diverging from a 3.6 x 2.7 km wide summit polylobate caldera. The average frequency of its eruptions, occurring both at the volcano summit and on the flanks, is of one eruption every 6-8 years over the past 100 years and the volcano was frequently active in the 1991-2007 period (Bachèlery et al., 2016). The self-potential studies of the summit caldera performed by

Lénat et al. (1998) and Bernabeu et al. (2018) show that the main hydrothermal activity of the volcano does not occur below the main summit crater (Choungou-Chahalé), but on the northern part of the summit caldera, where several recent eruptions have occurred. We sampled two main areas, the first one corresponds to steaming grounds and fumaroles located close to the Choungou-Chagnoumeni pit crater located in the northern part of the caldera and filled by the lavas of the last eruption in 2007 (see Figure 10B site CC) and a second one, the “Soufrière” fumarolic area (Figure 3) located on recent lavas 1.7 km north of the summit caldera, along the northern rift zone (see Figure 10B site LS).



Figure 2: Tidal area (BAS) in which the numerous emergence of bubbling gases are found



Figure 3 – La Soufriere: Site Ka-Su-01, free gas sampling in fumarole

3. Materials and Methods

3.1 Previous datasets

In this study, we present the results of our 2017-2020 surveys on soil gas fluxes and their composition as well as on the composition of Mayotte gas bubbling and Grande Comore fumarolic areas (Figures 10 and 11). Our dataset is integrated with older and partly unpublished surveys acquired on the two islands.

At Mayotte, the BAS bubbling site has been first studied by BRGM in November 2005 (Traineau et al., 2006; BRGM report) and April 2008 (Sanjuan et al., 2008; BRGM report) in terms of spatial distribution, gas fluxes, temperature, pH and chemical and isotopic composition. In the BRGM campaigns, $\delta^{13}\text{C}$ and δD data were not acquired on methane and preliminary noble gases data were produced by the IPGP laboratory (M. Moreira). A rich biological, chemical and isotopic dataset (C-H-S species, not including the noble gases) of the Dziani intracrateric lake and of its bubbling was acquired in the period 2012-2018 (Cadeau et al., 2020; Gérard et al., 2018; Hugoni et al., 2018; Jovovic et al., 2017; Leboulanger et al., 2017; Milesi et al., 2019; 2020). Milesi et al. (2020) collected fluids in August 2016 by focusing on the spatial distribution and C-H chemical and isotopic composition of bubbling gases in the Dziani lake, while only a single analysis (G7 sample) is reported for the BAS area.

On Karthala volcano, the summit steaming grounds and fumarole have been first described (but not sampled) by Bachèlery and Coudray (1993). Soil CO_2 and temperature profiles were measured between March 2008 and January 2010 in the hot grounds (40-80°C) close to the summit 2007 pit crater by Bernabeu et al. (2018). The first detailed study of the gas emissions in Grande Comore was performed in 2014 in the frame of an international geothermal exploration project (Benavente and Brotheridge, 2015; Chaheire et al., 2016).

3.2 Gas sampling and analysis

Grande Comore field work were performed in December 2017 (volcano flanks) and October 2018 (volcano flanks and summit area). Mayotte surveys were carried out on Petite Terre (Figure 1) in four campaigns, i.e. in December 2018, April 2019, September 2019 and November 2020 (Table 1 and Table 2).

Soil gas samples for isotopic ($\delta^{13}\text{C}$ in CO_2) and chemistry analysis were collected by introducing a steel probe into the ground (50 cm long) and collected in 10 mL Exetainer glass vials and in two-stopcock glass bottles 100mL.

Dry gases from fumarolic fields at Karthala were collected using a steel probe (the same as for soil sampling) introduced into the ground and connected to a three-way valve equipped of a syringe and a tube connected to the bottles for gas storage. Bubbling gases at Mayotte have been taken using a steel funnel connected to a three-way valve equipped with a syringe and a tube connected to two-stopcock glass bottles 250mL (chemistry and C-H isotopic analysis), two-stopcock steel bottles 100mL (noble gases elemental and isotopic analysis), and pre-weighed evacuated bottles containing absorbing alkaline solution (4N NaOH) following the method of Giggenbach and Goguel (1989).

All the gas samples were analysed at the laboratories of INGV (Istituto Nazionale di Geofisica e Vulcanologia), Sezione di Palermo, for their chemistry and for the isotopic compositions of noble gases (He, Ne, and Ar), C of CO_2 , and C and H of CH_4 . Analyses are reported in Table 1. The chemical composition of He, H_2 , O_2 , N_2 , CO, CH_4 , and CO_2 was measured by a gas chromatograph (Clarus 500, Perkin Elmer) equipped with a 3.5-m column (Carboxen 1000) and double detector (hot-wire detector and flame ionization detector [FID]), for which the analytical errors were < 3%.

The C-isotope composition of CO_2 (expressed as $\delta^{13}\text{C}$ ‰) vs. V-PDB (Vienna-Pee Dee Belemnite) was determined using a continuous-flow isotope-ratio mass spectrometer (Thermo Delta Plus XP, Finnigan), connected to a gas chromatograph (Trace GC) and interface (Thermo GC/C III, Finnigan). The gas chromatograph and its column (length = 30 m and i.d. = 0.32 mm; Poraplot-Q) were operated at a constant temperature of 50°C using He as the carrier gas. The analytical errors were <0.1‰. The same instrument has been used for C and H isotope determination in CH_4 , where a combustion interface (Thermo GC III, Finnigan) was used to produce CO_2 from CH_4 and a gas-chromatograph/thermal-conversion interface provided online high-temperature conversion of CH_4 into H. The SDs for the $\delta^{13}\text{C}$ and δD measurements of CH_4 were <0.2 and <2.5‰, respectively.

Noble gas (He, Ne, Ar) isotopes were analyzed at the noble-gas laboratory at INGV-Palermo. ^3He and ^4He were measured into a split flight tube mass spectrometer (GVI-Helix SFT), after purification of the sample from the major gaseous species and separation from the other

noble gases. ^{20}Ne was determined by admitting Ne into a multicollector mass spectrometer (Thermo-Helix MC plus), after purification procedure into a stainless steel ultra-high vacuum line distinct from that of He and Ar, as above described for helium. The $^3\text{He}/^4\text{He}$ ratio is expressed as R/R_a (being R_a the He isotope ratio of air and equal to $1.39 \cdot 10^{-6}$) with an analytical uncertainty (1σ) below 0.3%. Hereafter we discuss the $^3\text{He}/^4\text{He}$ ratio corrected for atmospheric contamination using the measured $^4\text{He}/^{20}\text{Ne}$ ratio (e.g., Sano and Wakita, 1985) that is reported in units of R_c/R_a , as follows:

$$\frac{R}{R_a} = \frac{\left(\frac{R_m}{R_a}\right) \cdot \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_m - \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_a}{\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_m - \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_a} \quad (1)$$

where subscripts m and a refer to measured and atmosphere theoretical values, respectively [$(\text{He}/\text{Ne})_a = 0.318$] (Ozima and Podosek, 1983). We highlight that the correction on the $^3\text{He}/^4\text{He}$ ratio is small or negligible for most of the gas samples [$(^4\text{He}/^{20}\text{Ne})_m \gg (^4\text{He}/^{20}\text{Ne})_a$].

The Ar elemental and isotopic compositions (^{36}Ar , ^{38}Ar , and ^{40}Ar) were quantified in a multicollector mass spectrometer (Helix MC-GVI). The analytical uncertainty (1σ) for single $^{40}\text{Ar}/^{36}\text{Ar}$ measurements was $<0.1\%$. ^{40}Ar was corrected for air contamination ($^{40}\text{Ar}^*$) in samples showing $^{40}\text{Ar}/^{36}\text{Ar} > 315$ assuming that the ^{36}Ar present derived from atmosphere, as follows:

$$^{40}\text{Ar}^* = ^{40}\text{Ar}_{\text{sample}} - ^{36}\text{Ar}_{\text{sample}} \cdot \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{\text{air}} \quad (2)$$

Typical blanks for He, Ne, and Ar were $<10^{-15}$, $<10^{-16}$, and $<10^{-14}$ mol, respectively, and are at least two orders of magnitude lower than the sample signals at the relative mass spectrometers. Further details on samples purification and analysis are described by Rizzo et al. (2019) and Boudoire et al (2020).

3.3 Soil CO₂ fluxes

The soil CO₂ emissions data presented in this study have been acquired drawing on two different methods (Figure 4): dynamic concentration (Gurrieri and Valenza, 1988) and accumulation chamber (Chiodini et al. 1998). The methods differ owing to the fact that different teams carried out measurement surveys on different islands at different times. However, each single measurement campaign is consistent for the method used (Table 2, Table 3).

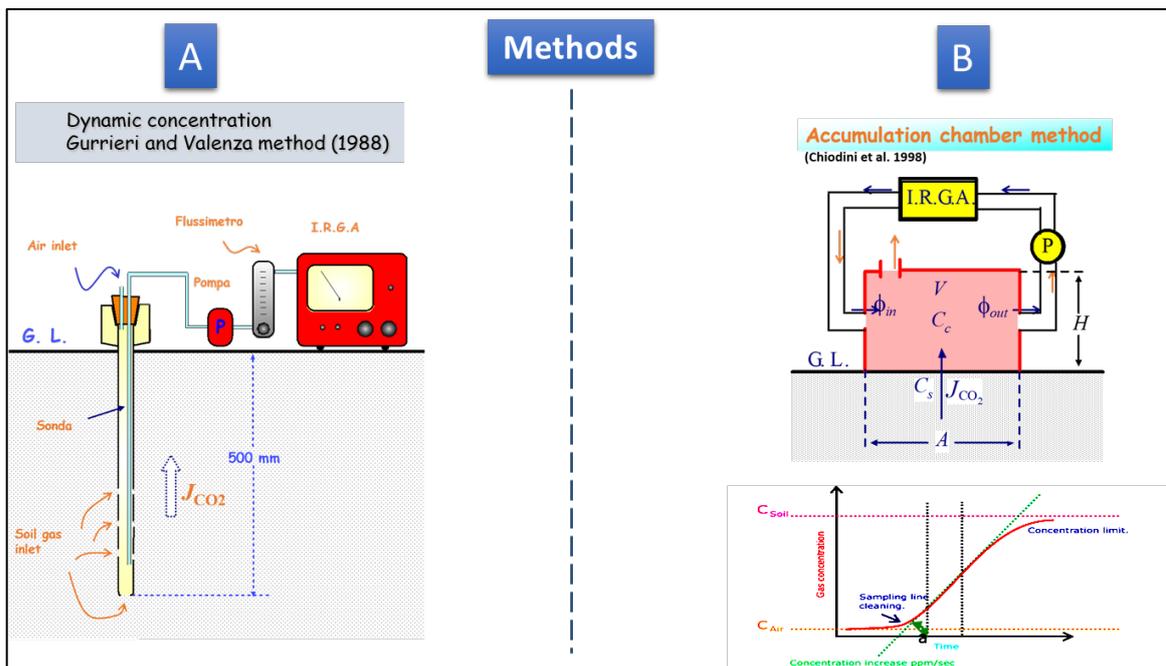


Figure 4: Diagram of the two methods of sampling soil CO₂ emission: A) Dynamic Method and B) Accumulation Chamber method. The two measurement methods are suitable for CO₂ sampling in similar environmental contexts; however, the specific characteristics of the two methods may make either one or the other approach more suitable depending on the soil characteristics and the variable density of vegetation that may be covering the ground. It should be noted that the two measurement methods obtain information that are not directly comparable: (A) being obtained at a depth of 50 cm, and the other (B) obtained from a gas flow passing at the soil-atmosphere interface. For this reason, the measurements carried out in this study were always treated by distinguishing the sampling method used on the relative area, and not by integrating measurements obtained with both methods.

3.3.1 Accumulation chamber method

Both Benavente and Brotheridge, (2015) surveys in Grande Comore and two of our surveys at Mayotte (September 2019 and November 2020) adopted the accumulation chamber method for measurements of soil CO₂ flux emissions using two different portable accumulation chamber each of them equipped with different IR spectrometers. Benavente and Brotheridge's campaign used a West System portable instrument with a LI-COR 820 IR and a 200 mm diameter chamber (West System chamber B), which introduces soil gas through the infrared spectrometer via tubing with an inline Mg(ClO₄)₂ filter (avoiding the absorption of moisture which may cause interference in CO₂ concentration). Our campaigns in 2019 and 2020 at Mayotte Island used a West Systems portable accumulation chamber equipped with a Dräger Polytron IR sensor and a chamber with the same geometry as the one used by Benavente and Brotheridge in Grande Comore (West system chamber B). We recorded soil temperature at each measurement location using a handheld Type K thermocouple probe inserted to 10 cm below ground level. In addition, pressure measurements and other weather parameters were recorded by a hand-held instrument meter (Kestrel 5000 series). Soil CO₂ flux ($g\ m^{-2}\ d^{-1}$) from each site were calculated using the following equation (1):

$$\phi CO_2 = 44.01 \cdot \frac{86400 \cdot P}{10^6 \cdot R \cdot T_k} \cdot \frac{V}{A} \cdot \frac{\delta_c}{\delta_t} \quad (3)$$

where δ_c/δ_t is the change in the CO₂ concentration with time (ppm s⁻¹), P is the measured pressure in mbar, R is the gas constant (bar L K⁻¹ mol⁻¹), T is the measured temperature (K), V is the chamber net volume (0.006186 m³) and A is chamber inlet net area (0.0314 m²). The measurement accuracy of the CO₂ flux measurements method is ±12.5 % (Evans et al., 2001)

3.3.2 Dynamic concentration method

In our Grande Comore surveys, we focused on CO₂ soil emissions on the volcano flanks, where the Benavente and Brotheridge (2015) surveys failed in identifying significant anomalies using the accumulation chamber method. Therefore, we performed most of our measurements using the dynamic concentration method in our 2017 and 2018 field works and compared them with a subset acquired on the same sites using the accumulation chamber technique. This approach permits us to compare the Karthala dataset with that acquired on the Piton de la Fournaise volcano (Liuzzo et al., 2015). The dynamic concentration method (Gurrieri and Valenza, 1988) is based on an empirically identified

relationship between soil CO₂ flux and CO₂ concentration in a gas mixture obtained by diluting soil gas with air (dynamic concentration), by means of a specific 50 cm probe inserted into the soil. Through a constant flux rate of 0.8 l/m, the gas from the soil is pumped to an IR spectrophotometer which measures CO₂ concentration. The spectrophotometer used was manufactured by Edinburgh Instruments Ltd. (range 0–10%; accuracy ±2%; digital resolution 0.01%) pressure and temperature corrected and it is the same used in the surveys on Piton de la Fournaise volcano. The CO₂ flux is derived from the CO₂ dynamic concentration value through an empirical relationship (4) verified experimentally in the laboratory for a range of applicable permeability 0.36–123 μm² and pumping flux 0.4–4.0 L/min:

$$\phi CO_2 = (32 - 5.8 \cdot k^{0.24})C_d + 6.3 \cdot k^{0.6} \cdot C_d^3 \quad (4)$$

where ϕCO_2 is the soil CO₂ flux expressed in kg m⁻² d⁻¹, k is the numerical values of the gas permeability (μm²), and C_d is the numerical value of molar fraction of the diluted CO₂ concentration. In this work, ϕCO_2 is converted into g m⁻² d⁻¹. For more details on the method, see Camarda et al. [2006a, 2006b]. In this work we used a k value of 30, which is very close to the k value (35) used at Reunion island in previous studies on Piton de la Fournaise (Boudoire *et al.*, 2017; Liuzzo *et al.*, 2013; Liuzzo et al., 2015). In consideration of the typical range of permeability in volcanic soils, $k=30$ value is a reasonable value limiting the error into less than 7% of the measurement (see table S1 supplementary materials).

4. Results

4.1 Gas composition of fumaroles and bubbling gases

4.1.1 Chemistry

Karthala gases (CC, from the summit caldera fumaroles; LS from the Soufrière area. For the locations see figure 10) show a general higher degree of air contamination with respect to Mayotte samples (table 1), with the exception of sample Ka-Su-01 from Soufrière that shows the highest CO₂ concentration (up to 92.2%), a significant content of H₂ (25,992 ppm), low concentrations of CH₄ (346 ppm). With regard to noble gases, He varies in a narrow concentration range (10.0-12.7 ppm), ²⁰Ne is between 0.03 (sample Ka-Su-01) and 7.7 ppm, ⁴⁰Ar 32.8 (sample Ka-Su-01) and 5,152.8 ppm. In the Mayotte sample set noble gases show a variable concentration, with He ranging between 8.2 and 113.2 ppm, ²⁰Ne between 0.052 and 7.65 ppm, ⁴⁰Ar in the range 55.1-3346.6 ppm. Among the other samples taken from high flux pools, only the sample CI-1a has a significant air contamination, showing concentrations of N₂ and O₂ of 54.9% and 14.9% respectively. The BAS bubbling gases from the tidal flat show a CO₂ dominant composition up to 98.69% and a variable concentration in CH₄ ranging between 416 and 2982 ppm. The concentration of CH₄ increases significantly in the “MAN” samples, taken from low-flux pools located close to littoral mangroves (up to 4621 ppm). In the BAS samples, H₂ and CO are generally in low concentrations ranging between 2.2 and 318 ppm for H₂ and 0.7 and 18 ppm for CO.

The chemical composition of Karthala and Mayotte gases is plotted in the ternary diagrams of Figure 5. The relative proportions of N₂, He and Ar, display a mixing trend between a He-rich component and an atmospheric component (air or air-saturated water – ASW). Both gases from the fumarolic Karthala areas (CC and LS) and the bubbling gases from Mayotte (BAS) show a variable degree of contamination by an atmospheric endmember, and its contribution is higher for air than for ASW. On the whole, the He-Ar-N₂ variability falls within a typical compositional range of crustal gases of which the two dominant mixing sources appear to be atmospheric and MORB-type mantle, well distinguished from typical subduction-related gases. An exception is the sample Ka-Su-01 which is significantly different from the present Karthala database, where only the samples SKM182 and SKM183 (fumarole 6 - survey 2014 Benavente and Brotheridge, 2015) show some similarity in low ⁴⁰Ar and He/N₂ ratio. Another exception is sample SKM70, (sampled in 2010 by Benavente and Brotheridge, 2015) over-enriched in Ar and therefore placed in the corresponding vertex of the ternary diagram. However, the apparent excess in Ar is actually

due to an anomalous absence in N₂ (Table 1). This sample can reasonably be considered an outlier in which analytical problems were encountered during lab analysis and therefore will not be discussed further.

The chemical composition in relation to the plot of CO₂-CH₄-He highlights that low temperature gas seeps of Mayotte have a larger CH₄ proportion with respect to Karthala fumarolic gases. In the plot, it is also reported the field of variability of La Reunion bubbling gases that allows to argue that Comoros gases are in general CH₄-enriched.

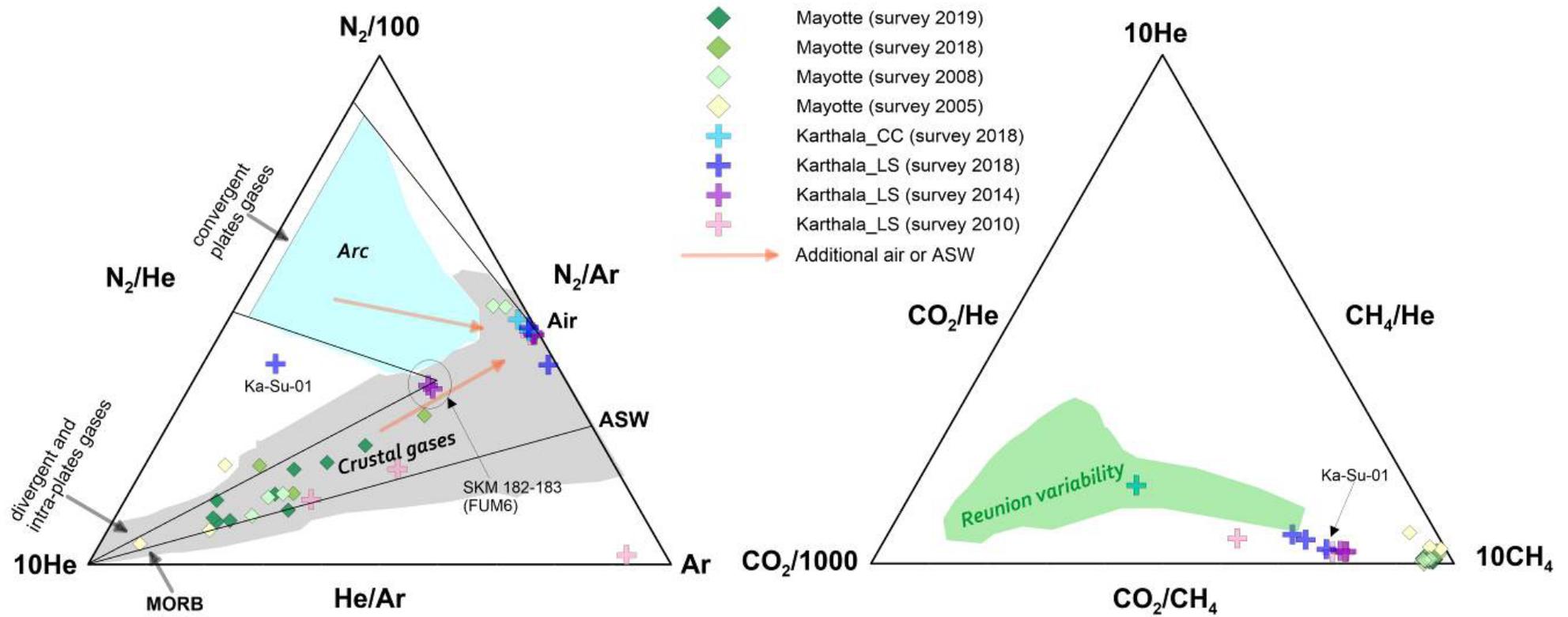


Figure 5. Relative proportion of He-Ar-N₂ in a ternary diagram on the left showing also the areas of crustal gases and arc volcanism from literature. Data collected at Grande Comore and Mayotte show a variable air and ASW contamination. CO₂-CH₄-He ternary diagram on the right displays a relatively CH₄-enrichment of Grande Comore and particularly in Mayotte. For comparison is also shown the field of variability of La Reunion gases.

4.1.2 Isotopic ratios of noble gases, CO₂ and CH₄

Table 1 reports the isotopic compositions of noble gases CO₂, and CH₄ of the sampled gases. Karthala gases have R/Ra values ranging from 3.8 (Ka-Su-02) to 5.7 Ra (Ka-Su-01), with no significant variation between CC and LS emissions. After correction for the contamination by atmospheric fluids (Rc/Ra), the ³He/⁴He value (5.7) is still measured in the sample Ka-Su-01, since it has the minor air contamination. Instead, the other samples range from 4.7 to 5.9 Ra due to a variable atmospheric contribution. In gases from Karthala, the ⁴He/⁴⁰Ar* ratio calculated after the correction of ⁴⁰Ar for atmospheric contamination (see eq. 2 in section 3.2) is available only for sample Ka-Su-01 and is 1.5. The relatively higher air contamination in Karthala gases, than in Mayotte gases, is also highlighted by the ⁴He/²⁰Ne (⁴He/²⁰Ne_{air}=0.31), which is generally low with an average of 1.5 (with exception of Ka-Su-01, ⁴He/²⁰Ne = 356.6), and ⁴⁰Ar/³⁶Ar (⁴⁰Ar/³⁶Ar_{air}=295.5), which is in average 303.2 (with exception of Ka-Su-01, ⁴⁰Ar/³⁶Ar = 378).

In the BAS bubbling gases there is the lack of a strong air contamination as previously indicated by the chemistry of these gases since the ⁴He/²⁰Ne ratios (up to 1663) are orders of magnitude higher the ratio in air (0.318), therefore no significant changes can be observed in the comparison between R/Ra and Rc/Ra values, except for only one sample (MAR-1) sampled in 2018. In fact, this sample shows a ³He/⁴He ratio of 3.2 Ra and a ³He/⁴He ratio of 4.2 (Rc/Ra) after correction for air contamination. The latter value strongly differs from the rest of the dataset of BAS gases, thus we suspect that this sample underwent some storage and transport to the laboratory issues that fractionated the ³He/⁴He, leading us to exclude it for the following discussion. In support of this, we highlight that the sample MAR-3 collected in April 2019 from the same degassing area yielded an Rc/Ra value of 7.2 (Table 1). The ⁴He/⁴⁰Ar* values of BAS gases range between 1.2 and 1.7 with a general overlap of the values among the different emissions and surveys. ⁴He/²⁰Ne in Mayotte samples vary up to 1660 and only the MAR-1 and MAN-2 (⁴He/²⁰Ne = 1.07 and 43.59, respectively) samples, both taken from pools with a relatively low flux, show significant air contamination. The variability of ⁴⁰Ar/³⁶Ar span up to 434, with MAR-1 and MAN-2 again showing the highest air contamination (⁴⁰Ar/³⁶Ar = 290 and 308, respectively).

The C-isotope composition of CO₂ (δ¹³C_{CO2}) of Karthala gases varies between -4.98‰ and -4.48‰, except for sample Ka-Su-02 that shows the most positive value of -3.91‰. At Mayotte the δ¹³C_{CO2} values of BAS gases vary from -5.74‰ and -3.5‰, whereas the most negative ratios are measured in samples from MAN.

The C and H pair isotope in methane were measured only in BAS gases. In detail, the C-isotope composition of CH₄ ($\delta^{13}\text{C}_{\text{CH}_4}$) was determined in most of the samples and varies between -24.4‰ and -18.7‰ , except for two samples from MAN 1 and 2 that showed the less negative ratios of -12.4‰ and -11.7‰ . The hydrogen isotopic composition of CH₄ ($\delta\text{D}_{\text{CH}_4}$) was measured only in C1-2 and DIST-1 that were sampled in 2019 through Giggenbach bottles to enrich the concentration of CH₄ of dry gases. These samples yielded a δD of -118.1‰ and -137.8‰ V-SMOW, respectively.

5. Discussion

5.1 Light noble gas signature

Our new He-isotopic data for Karthala and Mayotte span a significant range of $^3\text{He}/^4\text{He}$ signatures (4.18-7.53 Ra), with systematic differences between the two islands of Comoros archipelago. In detail, gases from Mayotte show Rc/Ra values higher than those from Karthala. Interestingly, the Rc/Ra variability we measured in 2017-2020 gases from Mayotte (7.5-6.4 Ra) and Karthala (5.9-4.7 Ra) matches that found in fluid inclusions from the two active volcanic edifices of the Grande Comore, la Grille and the Karthala (6.9 and 5.2 Ra respectively; Class et al., 2005). In Figure 6, we modelled two air-magma mixing curves considering data from Class et al. (2005) at Grande Comore and considering the average of the values for La Grille and Karthala fluid inclusions as representative of possible mantle reservoirs end-members. According to Class et al. (1998, 2005, 2009) that propose the presence of a plume contribution in the mantle beneath Gran Comore, our data show that Comoros gases have a low-He signature, like the fluid inclusions in lavas from the same volcanic systems (Karthala volcano). This low $^3\text{He}/^4\text{He}$ signature is well distinct from that documented in typical hot-spot contexts like the adjacent Afar region (R/Ra up to 19.6; Hilton et al., 2011; Marty et al., 1996) and la Réunion (R/Ra = 14.5-12; Boudoire et al., 2020; Marty et al., 1993). In Figure 6, data of bubbling gases of Piton des Neiges from La Reunion are plotted together with two mixing curves that explain their variability, showing that they fall within the range of Rc/Ra values measured in fluid inclusions of eruptive products of the island.

Ocean island basalts (OIB) from the Comoros archipelago display geochemical features different from the other Indian OIB (Bachèlery and Hemond, 2016; Class and Goldstein, 1997; Class et al., 1998; Class et al., 2009; Claude-Deniél, 1998; Claude-Ivanaj et al., 1998;

Pelleter et al., 2014; Späth et al., 1996). Comoros volcanism has produced a suite of variably silica-undersaturated, alkaline lavas (from melilitites and basanites, to alkali basalts to phonolites), enriched in incompatible trace elements and with variable relative depletion in K. With the exception of La Grille lavas, most lavas on the archipelago record the signature of variable degrees of fractionation during their storage and ascent to the surface after their emission from the deep garnet-bearing mantle source (Bachèlery et al., 2016). Several geochemical models have been proposed to explain the elongated array of their Sr-Nd-Pb isotopic signature, whose end-members range from i) mixing between heterogeneous deep plume sources (EMI, HIMU) and a shallower depleted convective ambient mantle or ii) mixing between a homogeneous deep plume sources (EMI component), plus a variable contribution of the shallower heterogeneous and old metasomatised oceanic lithosphere. Whatever the source of the mantle heterogeneities, all authors agree that Karthala lavas and rare old samples from Mayotte record the strongest EM1 contribution of the Comorian plume (Pelleter et al., 2014). According to Class et al. (1998), the alkali basalts of Karthala reflect mainly plume derived melts, while the basanites of La Grille are the products of interaction of plume melts with the metasomatised oceanic lithosphere. Class et al. (2005) show that olivines in Grande Comore lavas span a relatively small range of low- $^3\text{He}/^4\text{He}$ compositions. La Grille “lithosphere-dominated” lavas have preserved a nearly MORB signature ($6.75\text{--}7.08 R_A$) suggesting that amphibole forming metasomatism occurred before the arrival of the plume. All samples show good correlations between Sr–Nd–He isotope ratios, indicating that the Grande Comore $^3\text{He}/^4\text{He}$ ratios are not significantly influenced by crustal contamination and reflect recent mixing between plume- and lithosphere-derived melts. These authors highlight that the deep plume component has a low and well constrained $^3\text{He}/^4\text{He}$ signature of $5.2 \pm 0.2 R_A$. On the basis of the correlation with Osmium isotopes, Class et al. (2009) argue that the low-He signature does not record contribution from subcontinental lithospheric mantle, but that of a deep plume interacting with oceanic lithosphere. In this frame, the Comoros plume would represent a “low $^3\text{He}/^4\text{He}$ – high $^{187}\text{Os}/^{186}\text{Os}$ ” hotspot whose deep source is dominated by recycled ^4He -rich material.

A detailed treatment of this topic is out of the scope of this paper and will be treated in ongoing studies. Whatever the specific process producing the low- $^3\text{He}/^4\text{He}$ signature, we show that Karthala gases record a signature consistent with that recorded in the fluid

inclusions of its lavas. On the contrary, Mayotte gases have a slightly higher $^3\text{He}/^4\text{He}$ signature, which matches that of la Grille lavas. These findings are consistent with the barometric results of previous works (Bachèlery et al., 2019; Berthod et al., 2020) on the lavas of Mayotte submarine eruption, showing that these evolved basanite magmas are extracted by large shallow mantle reservoirs (50-20 km depth) located between the Moho and the upper oceanic lithosphere.

The $^4\text{He}/^{40}\text{Ar}^*$ values measured in Karthala (only one reliable value) and Mayotte gases vary in a narrow range (1.2-1.7), falling within that typical of fertile mantle ($^4\text{He}/^{40}\text{Ar}^* = 1-5$; Marty, 2012) and magmatic values from other geodynamic settings (e.g., Boudoire et al., 2018b; Bräuer et al., 2013; Paonita et al., 2012; Rizzo et al., 2019). In magmatic environments, this ratio varies during melts degassing and is indicative of relative entrapment pressures (e.g., Boudoire et al., 2018b; Paonita et al., 2012). Focusing on Mayotte gases for which $^4\text{He}/^{40}\text{Ar}^*$ is available for different gas emissions and surveys dates, we do not notice systematic variations. This leads us to two important deductions: the first is that this ratio is not modified by gas-water interaction as e.g. He/CO_2 (see section 5.2) and thus can be used to track temporal variations eventually related to changes in magmatic dynamics; the second is that Mayotte gas emissions reflect a magmatic degassing occurring in a narrow range of depth. In other words, we could consider a homogeneous (in terms of depth) source of degassing. If we consider the findings of a recent study carried out at La Reunion, in which Boudoire et al. (2018b) constrained a range of $^4\text{He}/^{40}\text{Ar}^* = 2.1 \pm 0.4$ for fluids exsolved at underplating (10-15 km below Piton de la Fournaise), assuming a comparable ratio in primary magmas below Mayotte, we could speculate that BAS emissions reflect the degassing of a melt ponding at comparable depths. Finally, the lack of evident temporal variations leads us to consider limited depth variations of the melt feeding the discharge of BAS emissions.

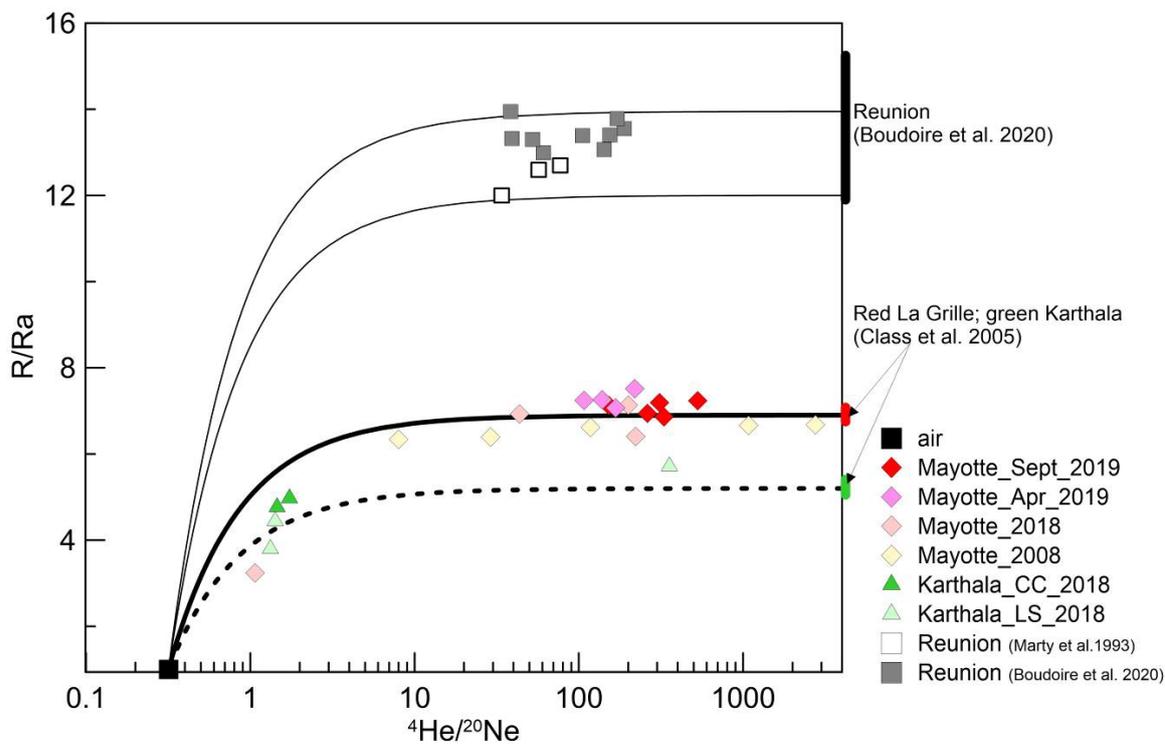


Figure 6. $^4\text{He}/^{20}\text{Ne}$ versus $^3\text{He}/^4\text{He}$ (R/Ra) in fumaroles and bubbling gas from Grande Comore and Mayotte. For comparison are shown data from bubbling gases at La Reunion from Bouidoire et al., (2020) and Marty et al., (1993). Thick and dash black lines indicating air-magma mixing are calculated from the average value [from Class et al., (2005)] of La Grille and Karthala fluid inclusions respectively. Thin black lines are calculated as the minimum and maximum of bubbling gases at La Reunion. At the right side of the diagram are also indicated three solid black red and green bars, corresponding to the range of the R/Ra variability of La Reunion, La Grille and Karthala fluid inclusions respectively.

5.2 Evidences of gas-water interaction and origin of CO₂ and CH₄

To evaluate the carbon origin of CO₂ in Karthala and Mayotte gases, $\delta^{13}\text{C}$ is diagnostic of the original geochemical environment, being able to discriminate between a magmatic source ($-8\text{‰} < \delta^{13}\text{C} < -4\text{‰}$; Sano and Marty, 1995), the contribution from subducted marine limestone with $\delta^{13}\text{C}=0\text{‰}$, and matter of organic origin with much lighter $\delta^{13}\text{C}=-25\text{‰}$ (Hoefs, 2015). Thus, we correlated the variation of the CO₂/³He versus $\delta^{13}\text{C}$ ratio based on the approach proposed by Sano and Marty (1995 and references therein). In order to evaluate the secondary processes of gas-water interaction, we have considered data corrected for air only for samples having N₂<22%. This is because for samples having N₂>22%, the correction would have yielded unrealistic ratios (Table 1). Figure 7A plots two mixing curves modelled considering both an organic and a limestone endmember, in which the mantle corresponds to CO₂/³He= 5.0x10⁹ and $\delta^{13}\text{C}=-4.4\text{‰}$, which result from the average values of our data and data from literature. For both organic and limestone endmembers, a value of CO₂/³He=1.0x10¹³ is assumed, whereas for organic and limestone $\delta^{13}\text{C}$ endmember is assumed $\delta^{13}\text{C}=-25\text{‰}$ and $\delta^{13}\text{C}=0\text{‰}$ respectively (Sano and Marty, 1995). As known from other studies in hydrothermal gases (Capasso et al., 2005;; Gilfillan et al., 2009; Rizzo et al., 2019), the CO₂/³He, He/CO₂, CH₄/CO₂ ratios and $\delta^{13}\text{C}$ isotopic signature can be potentially modified by gas-water interaction in which CO₂ dissolves preferentially with respect to the other species. These effects need to be evaluated and eventually filtered out in order to calculate the thermobarometric conditions of the hydrothermal system feeding the gas seeps (Figures 5 and 7). In Mayotte gases, we observe only a modest variability of the He/CO₂ ratio (Figure 7), which overlaps with that found in Karthala fluids, with the exception of two 2018 samples from the “MAN” pools with low gas flux that show He/CO₂>1.0x10⁻⁴. Similar evidences were observed by BRGM in 2005 samples 9a,b,c over the whole Mayotte tidal flat (Traineau et al., 2006) and might suggest an increase in gas fluxes after 2005. In order to constrain the pristine C isotopic signature of CO₂ in Karthala and Mayotte, we modelled a Rayleigh fractionation assuming a dissolution under equilibrium conditions based on the approach used in Rizzo et al. (2019). The Clark and Fritz (1997) equation is as follows:

$$\delta^{13}C_{CO_2} = (\delta^{13}C_{CO_2})_0 + \varepsilon \ln(f) \quad (5)$$

where the subscript 0 indicates the initial CO₂ isotope composition and f is the fraction of the residual gas phase, while ε is the fractionation factor between DIC (dissolved inorganic

carbon) and gaseous CO₂ (CO_{2(g)}). In turn, ε depends on water temperature and pH, which are unknown, therefore, for our purpose the values of temperature and pH has been chosen which better approximate our dataset corresponding to T=32°C and pH=5.71. These values correspond to those measured in the marine water of the Mayotte tidal flat by BRGM surveys (Sanjuan et al., 2008; Traineau et al., 2006). Our results show that Karthala gases are not evidently affected by interaction with shallow waters, as well as most Mayotte bubbling gases record only a minor partial dissolution of CO₂ (Figure S1 supplementary materials, where data plotted refer to air-corrected data - Table 1). The modest effect of preferential dissolution of CO₂ in water with respect to CH₄ and He is evident in Figure 7B, where He/CO₂ vs Rc/Ra are shown. Therefore, not considering the samples MAN affected by minor dissolution effects, the general variability of Mayotte and Karthala gases falls well within the range of mantle values (Figure 7A). In spite of streaming through a thick carbonate sequence of the coral reef or of the extensive bacterial contribution recorded in the nearby gas bubbling of the Dziani lake (Milesi et al., 2019, 2020), the gases of Mayotte tidal flat do not show any obvious limestone or organic contributions. Their magmatic signature can be constrained at $\delta^{13}\text{C}\approx-4.3\text{‰}$, which can also represent the magmatic signature of Karthala gases. This statement is supported by the narrow variability of $\delta^{13}\text{C}$ range both at Karthala fumaroles ($-4.9\text{‰}\leq\delta^{13}\text{C}\leq-3.9\text{‰}$) and Mayotte BAS high flux bubbling pools least affected by gas-water interaction ($-4.9\text{‰}\leq\delta^{13}\text{C}\leq-3.5\text{‰}$), as well as by their relatively stability in time considering data from BRGM of 2006 and 2008 campaigns ($-4.3\text{‰}\leq\delta^{13}\text{C}\leq-3.2\text{‰}$) as well as in 2016 with $\delta^{13}\text{C}=-3.2\text{‰}$ (G7 point by Milesi et al., 2020). Therefore, a $\delta^{13}\text{C}\approx-4.3\pm 0.2\text{‰}$ is a reasonable approximation of a possible $\delta^{13}\text{C}$ magmatic signature for the archipelago.

If compared to the bubbling springs of La Réunion (Figure 7A), we notice that the $\delta^{13}\text{C}$ signature of Mayotte and Karthala gases is slightly less negative and shows a minor variability. It is worth noting that La Réunion gases with $\delta^{13}\text{C}\approx-6\text{‰}$ display a trend of decrease of CO₂/³He suggesting the occurrence of a process of selective dissolution of CO₂ in water, which is observed in Mayotte only for the samples MAN 1 and 2.

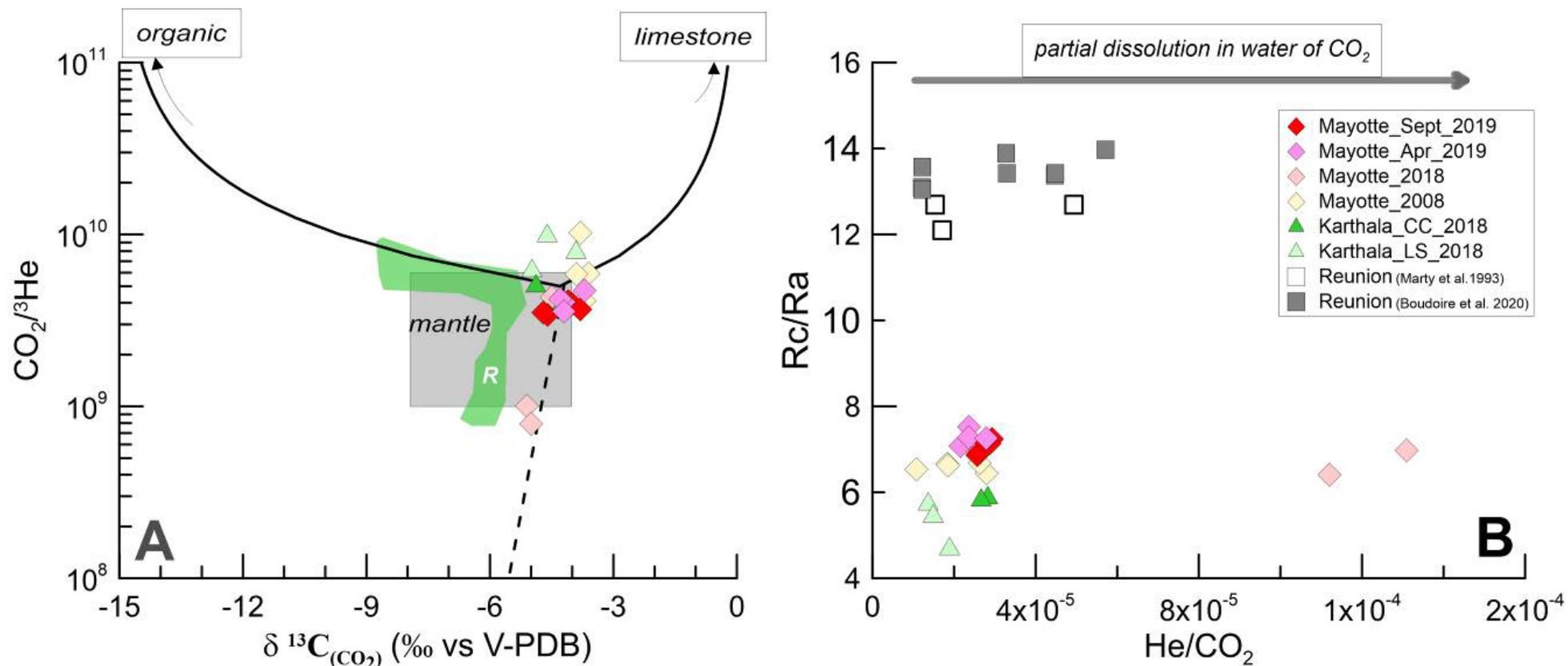


Figure 7. A: $\delta^{13}\text{C}$ of CO_2 versus $\text{CO}_2/{}^3\text{He}$ diagram of fumaroles and bubbling gases at Grande Comore and Mayotte. B: He/CO_2 versus R_c/R_a . For comparison is indicated also the variability of corresponding gases at La Reunion (R). Diagram 4A shows that gases at Comore archipelago are in the field of Mantle-like origin with no evident organic or limestone contributions. Solid lines are mixing curves between organic, mantle and limestone endmembers, while the dashed line indicates a Rayleigh fractionation dissolution. Diagram 4B displays a variable degree of water-gas interaction affecting CO_2 variability.

Even if the Karthala and Mayotte fluids are CO₂ dominated, we recall that they show a progressive enrichment in CH₄ up to concentrations of 2982 ppm in gases from Mayotte, which allowed to measure its isotopic composition of C and H (δ D of methane was measured only in DIST-1 and C1-2, table 1). Following the classification proposed by Schoell (1980) (Figure S2 supplementary materials), samples DIST-1 and C1-2 could be considered of abiogenic origin, coherently with the G3 bubbling spot with the highest gas flux in the Dziani lake, recently documented by Milesi et al. (2020). The same authors report of a G7 sample in the BAS area which shows similar $\delta^{13}\text{C}$ of DIST-1 and C1-2 but very negative δ D of methane (-250‰). However, it must be stressed that distinguishing between methanogenesis processes of biological origin or thermogenic processes at the origin of CH₄ (Mazzini et al, 2011; Schoell, 1980; Welhan, 1988) is complicated by possible mixing between endmembers with different isotopic signature (Taran et al. 2010) or by the occurrence of oxidation processes (e.g., Batista Cruz et al., 2019). It is therefore clear that further data are needed to better constrain the origin of methane in the BAS area of Mayotte.

5.3 CO₂ degassing from soil

Volcanic areas are often places where diffuse outgassing of CO₂ emission occurs, facilitated by tectonic structures which locally increase soil permeability. On seismically and volcanically active areas like the Comoros, soil CO₂ emissions have been investigated in order to identify hidden tectonic structures driving fluid emissions to the surface (e.g., Bonforte et al., 2013; Boudoire et al., 2017; Giammanco et al., 2006; Gurrieri et al., 2008; Irwin and Barnes, 1980; Liuzzo et al., 2013). In volcanic tropical settings like the Comoros, the presence of significant fraction of soil CO₂ emissions can also be ascribed to biogenic activity, which may be mixed with gas originating from magmatic sources and whose relative proportion may evolve in time as affected by seasonal effects and the evolution of the seismic and volcanic activity (e.g., Boudoire et al., 2018a; Chiodini et al. 2008; Liuzzo et al., 2015).

While rift zones are marked by well defined alignments of volcanic cones in Grande Comore, they are much less defined in Mayotte, where a set of mafic scoria cones and phonolite maars are scattered on the Petite Terre island (Famin et al., 2020; Michon, 2016; Nehlig et al., 2013; Tzevahirtzian et al., 2021). In Grande Comore, volcano flanks are often

resurfaced by the frequent emplacement of lava flows, nevertheless thick soils and sand covers are found in most locations, suitable for the measurement of soil CO₂ fluxes. At Petite Terre, the recent explosive activity of phonolitic maars emplaced a widespread cover of several meters thick fine grained ashes that, together with the low altitude of the island and the widespread urban context, limit the areas suitable for CO₂ flux measurements. In our survey strategy, we aimed at characterizing the CO₂ fluxes from the soil on the territory and linking them with known or hidden tectonic structures and with the main degassing areas (summit of Karthala in Grande Comore and Dziani lake and Airport tidal flat in Mayotte). Measurements on Mayotte tidal flat were performed at low tide, when the sandy/muddy flat is wet but without a continuous water cover, excepted some large bubbling pools. Samples of soil gas were taken alongside the soil CO₂ flux measurements to investigate the isotopic signature of carbon in CO₂ and thus constrain the sources of the soil CO₂ emission. As previously mentioned in 3.1, as the soil CO₂ dataset was acquired using two different methods and at different times, it is not uniform and therefore our choice in data analysis was to consider each area separately. Even if acquired in different seasons and times, all the measurements were carried out on dry sunny days and generally stable weather conditions. Where possible, measurements were performed at a spacing of ca. 50 m or less, though in some cases distances between individual sites and length and orientation of the tracks were dependent upon local urban density, morphological obstacles, and vegetation cover. Concerning vegetation cover, we point out that in the summit area of Karthala, where the measurements were carried out, vegetation was almost absent. In the peripheral areas of Karthala and at Petite de Terre, the vegetation cover was typically tropical with a prevalence of C₃ type plants (Hoefs, 2015). At the measurement sites, however, the density of the cover was on average low and estimated at about 30% within an average 10 m radius of each measurement and never more than 50%.

5.3.1 Grande Comore

At Grande Comore three campaigns were conducted for the measurement of soil CO₂ using two different methods: a) Accumulation chamber, b) Dynamic concentration (Figure 10).

The first survey at Grande Comore (4-8 November 2014) was conducted by Benavente and Brotheridge, (2015) and focused on exploring the potential geothermal resources of the

island. Using the accumulation chamber method (Chiodini et al., 1998), the survey concentrated on the summit area of Karthala volcano, providing a total of 155 measurements of CO₂ flux (table 2), and only a subset of measurements was performed on the volcano flanks showing very low soil degassing rates. In the summit caldera, the survey by Benavente and Brotheridge, (2015) focused on the northern and recently active (2007) part of the caldera, consistently with previous geophysical and CO₂ surveys of Lénat et al. (1998) and Bernabeu et al. (2018), showing that the strongest hydrothermal activity occurs in this area (CC area). In addition, Benavente and Brotheridge, (2015) provide the first dataset on the most active and high temperature Soufrière area, on the northern rift (LS area). The results of the 2014 survey are plotted in Figure 10B. The soil CO₂ flux ranges from background air (0 flux) up to 17,364 g m⁻² d⁻¹. The grid of points in the area investigated by Benavente and Brotheridge, (2015) was suitable for the estimation of the total budget of CO₂ flux emission at that period, which was calculated by using the GSA method (Chiodini et al., 1998), resulting in an average of ~291.2 Mg d⁻¹ and ~695.8 Mg d⁻¹ at the crater and La Soufrière areas respectively. The remaining summit area investigated of Karthala volcano is characterized by a general very low average of CO₂ flux.

In 2017 (28 Nov – 07 Dic) and 2018 (11-16 Oct), the second and the third soil CO₂ measurement surveys were carried out by IPGP and INGV teams (Figure 8), using the Dynamic method (Gurrieri and Valenza, 1988) and focusing on the volcano flanks and La Grille area. The unknown *k* value, necessary for the application of the dynamic method (equation 2), has been chosen from those which give the minimum percentage deviation between the most probable range of *k* values in volcanic soils (Camarda et al., 2006a) and in consideration of the similarity with soil CO₂ emission measured at La Reunion (Boudoire et al., 2017; Liuzzo et al., 2015). For all the measurements at Karthala a *k* value of 30 μm² has been chosen (see supplementary materials Table, S2). Considering reasonable that the probable range of permeability in volcanic soil ranges between 20 and 40 μm², the percentage deviation is less than 6.5% in all the measurements carried out at Karthala.

87 measurements were taken during the 2017 campaign in the distal area of the Karthala volcano, with soil CO₂ flux ranging between approximately 9 and 450 g m⁻² d⁻¹ (table 2). During the 2018 campaign, we carried out 65 measurements, where some were partially overlapping the previously surveyed area, however most were in new areas not covered by the 2017 survey (Figure 10A). In 2018, minimum and maximum fluxes are around 5 and 950

g m⁻² d⁻¹ respectively, and confirmed that the maximum fluxes occur inside the summit caldera, close to the CC hot ground and fumarolic field. The findings of these two campaigns (Figure 10C and 10D) show a possible correlation between the main structures (Bachèlery and Coudray, 1993) and the highest flux emissions, confirming that the spatial distribution of the soil CO₂ flux is tightly linked to the tectonic structures of Grande Comore. The Soufrière fumaroles and the maxima on the volcano flank fall on the main rift zones previously identified on the basis of the alignment of volcanic cone. Interestingly, anomalous areas of high CO₂ soil flux extend at low altitude, both in the northern and western part, where a recent seismic and volcanic activity has occurred, while relatively lower fluxes are measured in the southern part of the island, which corresponds to the oldest little active part of Grande Comore (see Bachèlery et al., 2016 for a recent review).

It is interesting to note the similarity in the rate of soil CO₂ flux measured in the Grande Comore with those measured on a tropical island with comparable characteristics, such as La Reunion. In Liuzzo et al. (2015) the soil CO₂ flux documented on the Piton de la Fournaise volcano were in the range of 5.52 to 701.56 g m⁻² d⁻¹ and were measured during quiescence phases. In spite of its strong eruption rate, Piton de la Fournaise lacks an area of strong degassing near its summit, which instead occurs on the older and quiescent Piton des Neiges volcano (Boudoire et al., 2020; Marty et al., 1993).



Figure 8. Sampling soil CO₂ gas by the dynamic method in the Karthala summit area



Figure 9. Sampling soil CO₂ gas by the accumulation chamber method at Petite Terre

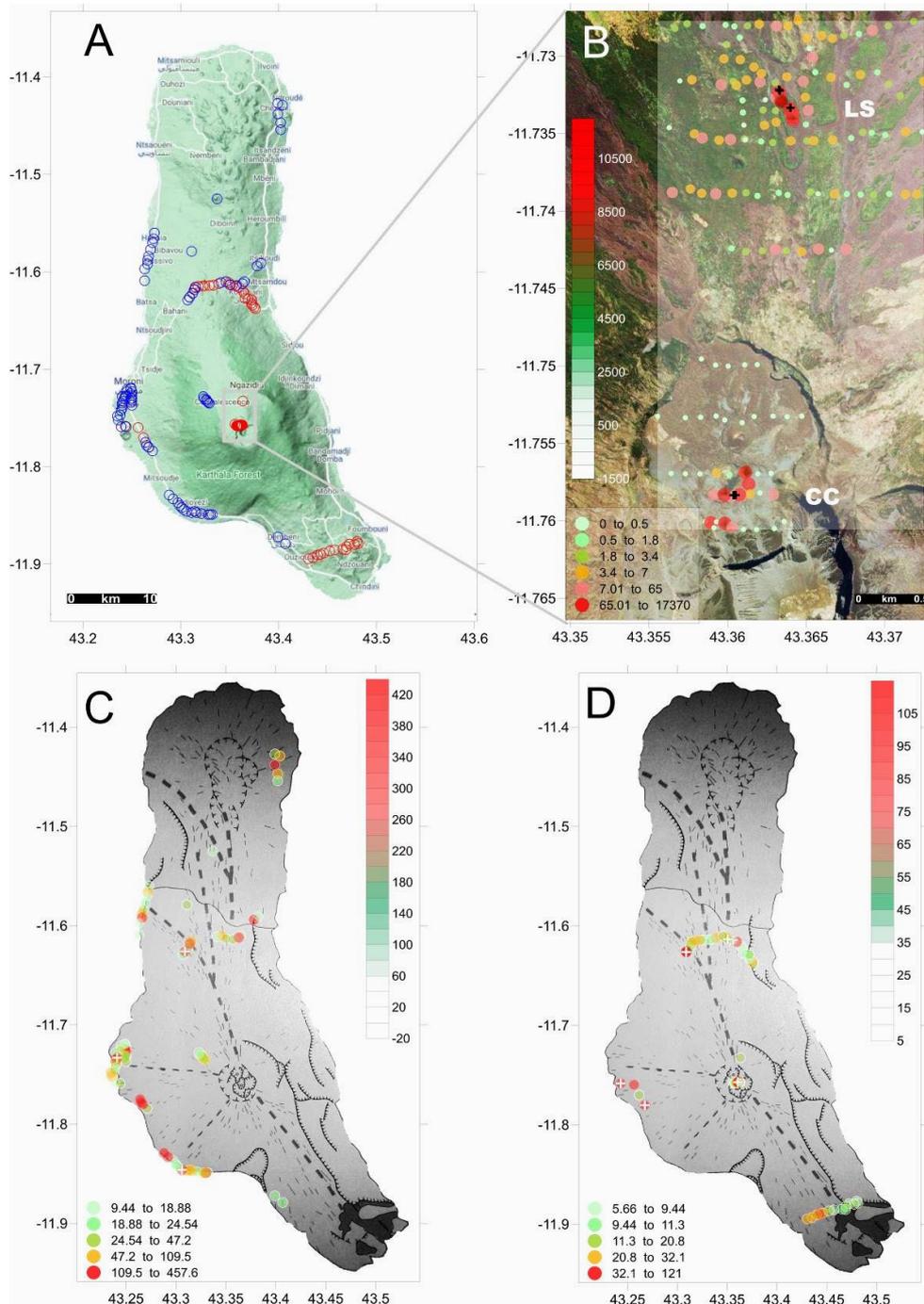


Figure 10. Soil CO₂ measurements at Grande Comore. In A site of measurements distinct in blue and red for 2017 and 2018 surveys respectively (this study). Inside the white rectangle are indicated the 2018 sites of measurements not indicated in B. In figure 10B a classed post map (where soil CO₂ flux is expressed in range of g m⁻² d⁻¹) and a contour plot of soil CO₂ emission of the 2014 survey at the summit of Karthala volcano realized using the accumulation chamber method. CC indicates the Central Caldera area; LS indicates La Sufriere; the sites of the gas sampling of 2018 reported in table1 are indicated as black crosses. Figures 10C and D are related to 2017-2018 surveys respectively realized using the "Dynamic concentration method" [Gurrieri and Valenza (1988)]; the white crosses in 5B and 5C are the sites of soil CO₂ sampling for isotopic analysis. On both maps it has overlapped the structural map from Bachèlery and Coudray (1993).

5.3.2 Mayotte - Petite Terre

The occurrence of a widespread ash cover makes the dynamic concentration method not suitable for most CO₂ flux measurements at Petite Terre, Mayotte, where surveys were performed using the accumulation chamber method (Figure 9) in 2019 (9-13 September) and in 2020 (11 November) (Figure 11). On this island, a total of 166 measurements of CO₂ flux were taken from the soil and 53 on the tidal flat of the Airport (BAS: bubbling area in the sea Figure 11B). We did not perform a CO₂ survey inside the Dziani crater, however it represents a target of future investigations. Not surprisingly the strongest CO₂ soil emissions were measured in the Airport tidal flat, where the CO₂-rich bubbling pools are located, with a range of values between 12 and 70,485 g m⁻² d⁻¹. Peak emissions are thus 4 times higher than those measured at Karthala. The grid of points for this initial exploration did not lend itself to estimating the overall CO₂ flux budget, which will instead be the focus of future investigations. On land, we measured fluxes that span from background levels (corresponding to the air values concentrations) to 173.4 g m⁻² d⁻¹, being much lower than in the volcano flanks of Karthala or of la Réunion. Our surveys show that at Mayotte the underlying hydrothermal system is the main source of the outgassing of the island and the bubbling area on the tidal flat is an important area of high CO₂ flux. This could arise from a combination of high fluxes focused in two areas (Airport tidal flat and Dziani) and the widespread and poorly permeable fine ash cover on Petite Terre. The possible influence of the ash cover on soil CO₂ fluxes is however not straightforward. At Petite Terre, the thickness of fine ashes increases from west to east and the soil CO₂ fluxes as well, together with the occurrence of the two main areas of gas bubbling, which are located on the eastern side of the island. Even if the on land soil CO₂ emissions are generally modest compared with other sites, their spatial distribution still permits to identify preferential areas of CO₂ emissions on the ground and to discuss their possible link with hidden tectonic structures, not always recognisable with other methods of investigation. Available datasets (Famin et al., 2020; Tzevahirtzian et al., 2021) show that Petite Terre is the tip of a huge and mostly submarine volcanic ridge with a broad regional alignment in the N120° direction, corresponding to the main regional structure of Comoros archipelago and interpreted as a right-lateral shear in the lithosphere (Famin et al., 2020; Michon, 2016). Results from our surveys (Figure 11A) show a distribution of soil CO₂ degassing which might be overlapped to a possible structural scheme in which a system of fractures is determined by a combination of the main structural trends along N120° and a combination of Riedel's

structures coherent with the right shear (Figure 11C). In this scheme, the N120° is well correlated to the alignment of Holocene tephritic scoria cones corresponding to the oldest phase of the recent volcanism of Petite Terre (Nehlig et al., 2013). A NNE-SSW (R') trend of soil CO₂ emission is overlapped on the most recent volcanism of the phonolitic maars, where the principal evidence of outgassing is shown by the BAS zone at the feet of the large "Vigie" maar and the bubbling manifestation inside the Dziani lake (Milesi et al., 2020). A possible trend corresponding to R structures is also appreciable in the central area of the island. Even if this first approach proposes an interpretative evaluation of the spatial outgassing distribution, however it must be stressed that future investigations on larger areas are needed to better understand the detailed structural pattern on Mayotte Island.

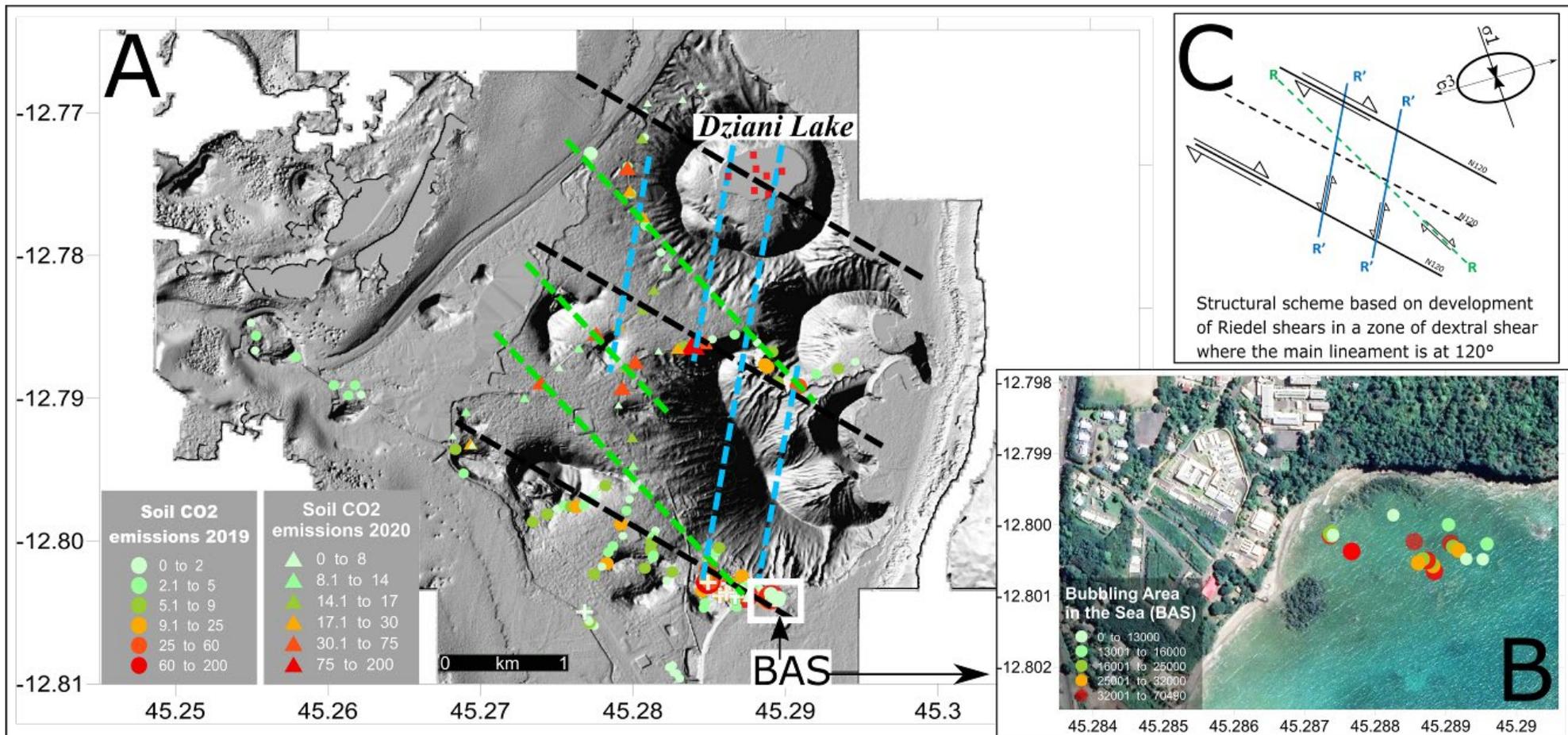


Figure 11. (A) Digital elevation map of Petite Terre highlighting the volcanic cones and the soil CO₂ emissions by a classed post map (where soil CO₂ flux is expressed in range of $\text{g m}^{-2} \text{d}^{-1}$) showing 2019 and 2020 surveys. The white crosses are the sites of soil CO₂ sampling for isotopic analysis. The red squares within the Dziani lake are the bubbling sites investigated by Milesi et al., (2020). BAS indicates the bubbling area in the sea, which is magnified in (B) as a classed post map of the CO₂ flux measurements carried out in 2019. The structural trend in (A) is adapted to the Mayotte soil emissions from the theoretical structural scheme exposed in figure (C) based on a dominant shear zone N120°.

5.4 Equilibrium temperature of hydrothermal gases

In the previous paragraphs, we have shown that the fumarolic and bubbling gases of Grande Comore and Mayotte have relatively high methane contents with the proportion of methane being highest at Mayotte. We also highlighted the effect on gas chemistry of partial dissolution of CO₂ in water, as well as identified the samples that showed the most evident effects of this process.

Data of CO₂ and CH₄ poorly or not affected by the dissolution of CO₂ in water allowed us to evaluate the possible gas equilibrium conditions among different gas species in hydrothermal environments. In several geothermal systems, the Fischer-Tropsch process has been successfully used to define the origin of methane since the 60s (D'Amore and Panichi, 1980; Hulston and McCabe, 1962). Nowadays an extensive scientific literature exists that explores the conditions of equilibrium among gas species in hydrothermal environments in order to obtain useful geo-indicators for temperature and pressure (Chiodini and Marini, 1998; Fischer and Chiodini, 2015). Assuming that in the hydrothermal system an equilibrium is attained between the dominant species H₂O-H₂-CO₂-CO-CH₄, methane can form inorganically from the reaction:



where the formation of methane is favoured by the decreasing temperature. For this system we assumed as a condition of thermal equilibrium between CH₄ and CO₂ the equation proposed by Giggenbach (1992):

$$\log (X_{\text{CH}_4} / X_{\text{CO}_2}) = 4625 / (t_e + 273) - 10.4 \quad (7)$$

where t_e is the equilibrium temperature (°C) while X_{CH_4} and X_{CO_2} are the molar fraction of CH₄ and CO₂ respectively.

Under these assumptions, equilibrium temperatures range between around 381 and 460°C at Karthala (Figures S2 supplementary m.) which is consistent with data from Benavente and Brotheridge, (2015). At Mayotte temperature vary between 314 and 339 °C (excluding MAN 1 and 2 which are recognized as affected by a severe dissolution of CO₂ in water). Interestingly, we do not record a change neither in equilibrium temperature nor in outlet temperature (in equilibrium with sea water temperature) in bubbling gases of the BAS Mayotte tidal flat in the period 2005-2019 in spite of the large magmatic event occurring at ca. 50 km from its coast.

To explore possible evidences of recent input of deep fluids in Mayotte hydrothermal system we evaluated the thermal equilibrium in combination with their isotopic signatures on the basis of their $\delta^{13}\text{C}$ isotopic fractionation factor between CO_2 and CH_4 . In our BAS samples, $\delta^{13}\text{C}_{\text{CH}_4}$ ranges from -24.4 to -11.7‰, the most positive values corresponding to the MAN samples collected by a low-flux pool close to the mangrove area (Figures S2 supplementary m.). To this aim, we have combined the temperatures obtained from (7) with the temperatures (t_e) calculated using the equation proposed by Bottinga (1969) valid for temperatures ranging between 0-700 °C:

$$\Delta = 22166 / (t_e + 273) - 13.8 \quad (8)$$

where Δ is the difference between $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ values. The relation (8) provides on the whole higher temperatures, ranging between 370 and 515°C (Figures S2 supplementary materials), where the samples MAN-1 and MAN-2 – (16-12-2018), which have been hypothesized to be affected by a strong fluid-water interaction, provide a much higher apparent equilibrium temperature up to 940°C and therefore they are not discussed further.

It is known that temperatures calculated from the CO_2 - CH_4 isotopic geothermometer are generally higher than temperatures obtained from geothermometers based on chemical equilibrium (Horita, 2001). This difference is attributable to several process which can affect the final equilibrium and various hypotheses have been invoked to account for outcomes. If external factors able to affect the hydrothermal system cannot be excluded (e.g. an external sources of gas interacting with the hydrothermal system) amongst the causes that might determine discrepancy on the estimation of temperature, a sort of "quenching effect" on the isotopic signature of hydrothermal gases may be considered relevant. Under this assumption, CO_2 and CH_4 were initially in isotopic equilibrium attained at the original source (supposed to be deep) however, during the ascent of the gas to shallow depths, there may not be enough time for the isotopic readjustment thus preserving the original isotope ratios. Such a quenching effect is also justifiable by the faster rate of reequilibration (about 100 times) of the chemical system than the isotopic system (Giggenbach, 1982).

In order to understand if the different temperature obtained by the chemical and isotopic geothermometers could be an expression of a quenching effect acting on the BAS area at

Mayotte we plotted the log of the concentration ratio of CH₄ and CO₂ versus the δ¹³C of both methane and CO₂ (Ono et al., 1993). In Figure 12 the thick black lines were modelled assuming that both chemical and isotopic equilibrium is maintained with a fixed δ¹³C_{CO2} corresponding to the range of magmatic signature, here -4‰ and -8‰ (dashed black lines) by coupling the equations (7) and (8):

$$\log\left(\frac{X_{CH_4}}{X_{CO_2}}\right) = \frac{4625 (\Delta+13,8)}{22166} - 10.4 \quad (9)$$

In addition, the equilibrium temperature calculated using the equation (7) (green line) is shown. The trend of the continuous black lines therefore should represent the variation of the δ¹³C_{CH4} expected if equilibrium conditions are attained by gases injected in the hydrothermal system. However, our data show a significant shift of the methane toward heavier isotopic concentrations. Bacterial oxidation of thermogenic CH₄ can explain isotopic fractionation determining an increase of the isotopic ratio (Baker and Fritz, 1981; Coleman et al., 1981). For instance, this process may be probable in the Dziani lake, where Milesi et al. (2020) have underlined a probable mixing between gas of biogenic and magmatic origin.

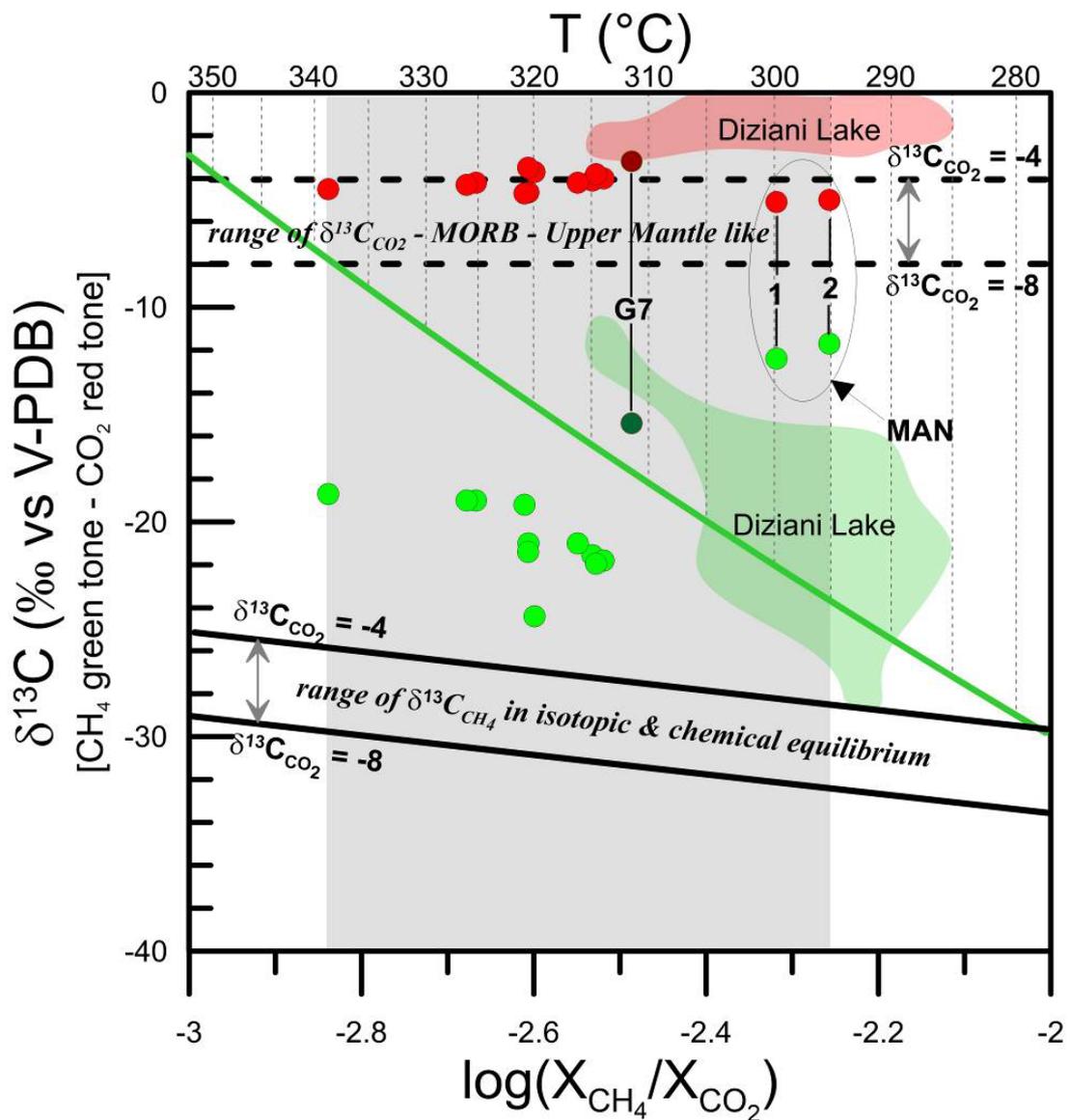


Figure 12. $\delta^{13}\text{C}$ for CO_2 (red) and CH_4 (green) versus $\log(X_{\text{CH}_4}/X_{\text{CO}_2})$ of Mayotte bubbling gases. Dark red and green symbols are referred to the G7 sample of Milesi et al., (2020) mentioned in the text, also the red and green area are referred to the variability of the Diziani lake samples from the same authors. The green line correspond to the CH_4 and CO_2 thermal equilibrium expressed in equation (7) (Giggenbach, 1992), the thick black lines are calculated as the equation (9) for isotopic and chemical equilibrium between CH_4 and CO_2 for two cases of $\delta^{13}\text{C}(\text{CO}_2)$ corresponding at -4‰ and -8‰ which in turn are indicated as dashed lines.

Although a carbon isotopic fractionation of methane cannot be excluded, some important differences between the gases of the BAS area and Diziani Lake should be underlined. The range of variability of $\delta^{13}\text{C}_{\text{CH}_4}$ of the BAS samples is consistent with an abiogenic source (Schoell, 1980). Moreover, the δD values of the samples DIST -1 and C1-2 are -137.8‰ and -118.05‰ , respectively, being much higher than the value of G2 (-272‰) methane-rich pool of Diziani lake reported by Milesi et al. (2020), confirming a probable abiotic origin of methane at BAS. Chemical equilibrium temperatures are systematically higher at BAS than

at Dziani (<290°C), further suggesting an inorganic origin of BAS methane, or a more magmatic contribution in the hypothesis of a binary mixing between biotic and abiogenic methane. The methane-rich geochemical environment of the Dziani gases is definitely conditioned by the microbial activity in lacustrine waters, very different from the CO₂-rich geochemical environment of the BAS area. It is therefore likely that a quenching effect could explain the shift towards more positive $\delta^{13}\text{C}$ values of methane in the BAS data that "freezes" the isotopic equilibrium at corresponding higher temperatures. Assuming that a quenching effect is significant on the BAS samples, the consequences are equally important; under this hypothesis the temperature would have a corresponding isotopic equilibrium in the range estimated by the equation (8), that is between 370 and 515°C and, in turn, such high temperatures can be explained by deep magmatic inputs.

5.5 Temporal variations of $^3\text{He}/^4\text{He}$ in gases from Mayotte

In order to have further evidences of possible variations of geochemical parameters that may have recorded the ongoing submarine volcanic activity, we evaluated the time variation of the helium isotope ratio. This tracer was found to be crucial in defining magmatic recharge in deep reservoirs in many volcanic systems on Earth (Boudoire et al., 2020; Caracausi et al., 2003; Paonita et al., 2016; Rizzo et al., 2015, 2016; Sano et al., 2015). Figure 13 shows values from the 2008 (BRGM repository) and the 2018-2019 surveys. As discussed before, the interpretation of this parameter is quite complex in the Comoros context, because of the possible "low- $^3\text{He}/^4\text{He}$ " signature of the deeper undegassed asthenospheric source. Our data suggests that the helium isotopic signature of the BAS fluids (Figure 13) was relatively low in the 2008 samples and it becomes significantly higher (average increase of 0.58 Rc/Ra) in the samples from the 2018 survey. This shift is consistent with the drainage of large volumes of evolved basanite magma from shallow mantle lithospheric depth feeding the Mayotte gaseous emissions at least in 2008, whose potential signature is very close to that recorded by fluid inclusions at La Grille (Class et al., 2005). Since the beginning of the eruption, the Rc/Ra signature of BAS fluids approaches that conventionally accepted for convective MORB mantle (8 ± 1 Ra, Graham, 2002). Thus, we can tentatively speculate that this time evolution is associated with the emplacement of sub-lithospheric magmas at shallower depth along the large Mayotte volcanic ridge.

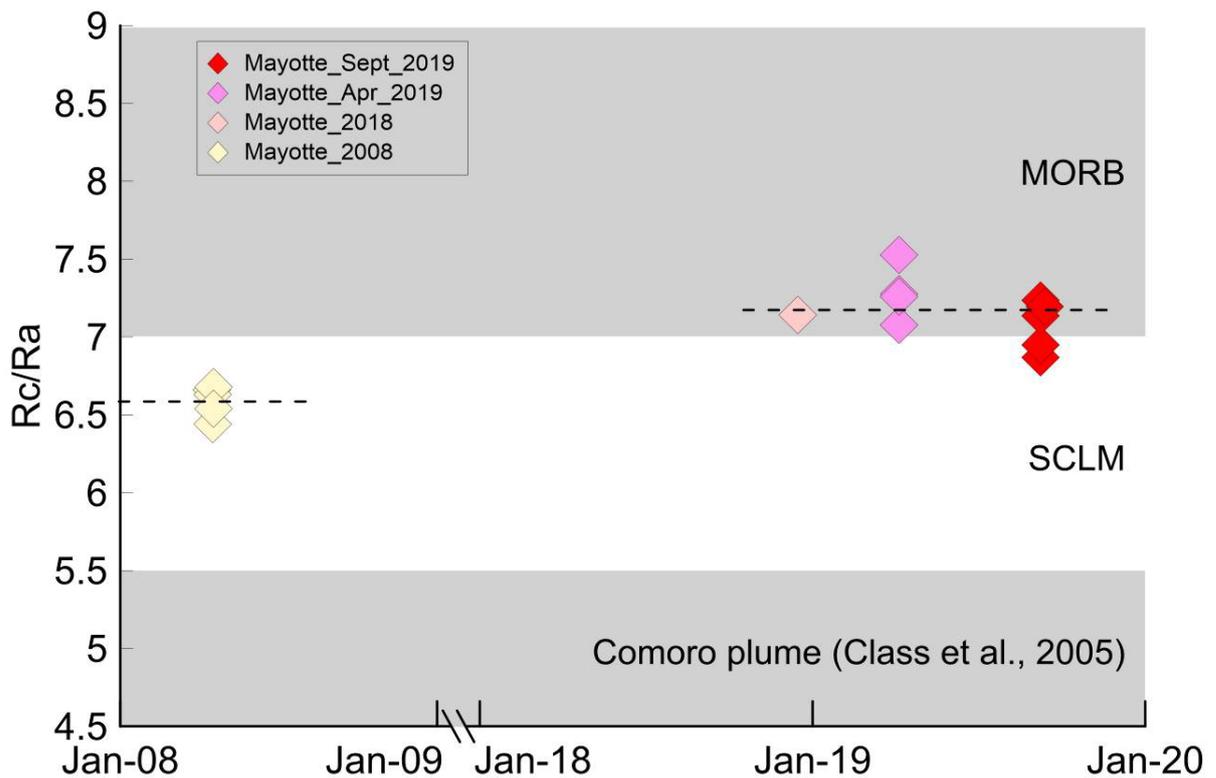


Figure 13. Rc/Ra time series. Rc/Ra has increased by an average 0.5 of between 2008 and 2018-2019. Black dashed lines indicate the averages Rc/Ra for the two distinct periods.

5.6 Gas emissions from the soil

Soil CO₂ emission can be ascribed to various origins and generally the total outgassing budget results from a mixture of different sources (Amundson et al., 1998; Cerling et al., 1991; Chiodini et al., 2008; Liuzzo et al. 2015). With the aim at quantifying the different contributions other than those of magmatic origin, such as biogenic source or air contamination in soil CO₂ flux, 22 gas samples were collected at Grande Comore and at Mayotte for CO₂ concentration and carbon isotopic analysis ($\delta^{13}\text{C}_{\text{CO}_2}$) (table 1). All the samples were taken directly at 0.5 m depth in the soil, as described in section 3.2. The results of their CO₂ concentration and C isotopic signature are shown in Figure 14, and are modelled as a mixing of three possible endmembers: atmospheric, biogenic and magmatic. Figure 14 also reports $\delta^{13}\text{C}$ of gas from fumarolic fields at Karthala (central crater CC and La Soufrière LS, Figure 10B) and from the bubbling marine area off the coast at Mayotte (BAS, Figure 11B), both obtained from the 2017-2018 surveys. Included in Figure 14 are also data collected at Mayotte by BRGM in 2005-2008 (BRGM/RP-568082 Final reports 2008) and in 2016 from Milesi et al. (2020) at the Dziani volcanic lake, with the exception of sample G7 that was collected in 2016 at the bubbling area BAS. We report the endmembers of

atmospheric ($\delta^{13}\text{C} = -8\text{‰}$) and “biogenic” ($\delta^{13}\text{C} = -25\text{‰}$; Hoefs, 2015) carbon (corresponding to organic matter). In Figure 14, we report the mixing curves between the three endmembers reported above. The “magmatic” endmember was fixed considering the $\delta^{13}\text{C}$ average values of CO_2 of fumarolic and bubbling gases from Karthala and Mayotte, which we considered representative of the magmatic signature beneath these islands of the Comore archipelago ($\delta^{13}\text{C} = -4.3\text{‰}$). This choice is supported by the small narrow variability of $\delta^{13}\text{C}$ range of variation both in at Karthala fumaroles ($-4.9\text{‰} \leq \delta^{13}\text{C} \leq -3.9\text{‰}$) and Mayotte BAS high flux bubbling pools least affected by gas-water interaction ($-4.9\text{‰} \leq \delta^{13}\text{C} \leq -3.5\text{‰}$, slightly higher values up to 5.7 being those of the MAN low flux pool), and their relatively stability in time considering data from BRGM of 2006 and 2008 campaigns ($-4.3\text{‰} \leq \delta^{13}\text{C} \leq -3.2\text{‰}$) as well as in 2016 with $\delta^{13}\text{C} = -3.2\text{‰}$ (G7 point by Milesi et al., 2020), thus a reasonable approximation of a possible $\delta^{13}\text{C}$ magmatic signature for the archipelago.

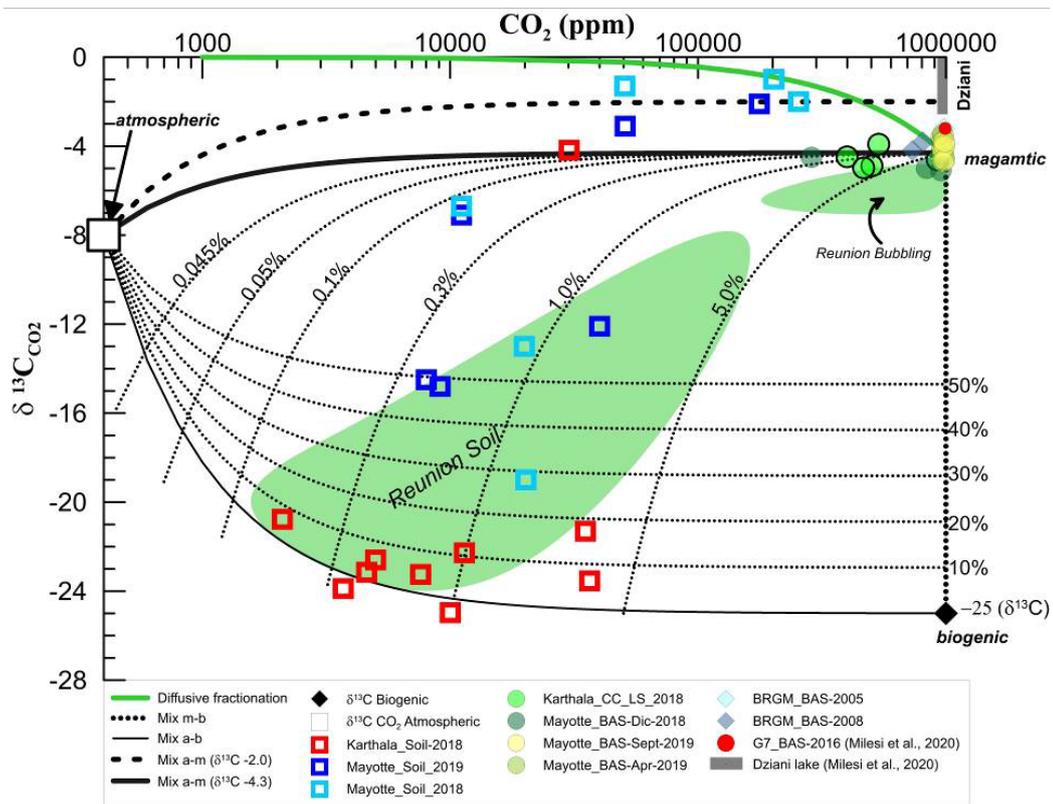


Figure 14. Diagram plotting carbon isotopic composition of soil CO_2 versus soil CO_2 log-concentrations (ppm) showing the theoretical binary mixing curves between three endmembers: atmospheric, biogenic and magmatic. Also shown are the binary mixing curves (hyphen curve) which allow a differentiation in the percentage of the magmatic component (M) in the hypothesis that the biogenic contribution could be extended up to $\delta^{13}\text{C} = 25\text{‰}$ (Hoefs, 2015). Green areas are referred to La Reunion soil and bubbling gases data repository, while the grey bar is the $\delta^{13}\text{C}_{\text{CO}_2}$ Dziani lake’s variability from Milesi et al., (2020).

The Karthala isotopic signature regarding $\delta^{13}\text{C}$ in CO_2 from the soil is much wider than in the fumaroles and ranges in the interval $-24.9\text{‰} \leq \delta^{13}\text{C} \leq -4.2\text{‰}$. Almost all of the isotopic

values show a low contribution of magmatic gas and a variable degree of air contamination. A few samples showing high CO₂ concentration have however a modest magmatic contribution (less than 20%) and correspond to sites close to the main structural lineaments showed in Figure 10. The vegetation cover at Karthala, as on all Comorian islands, is essentially tropical and therefore predominantly characterized by C₃ plants. Isotopically, C₃ plants have an isotopic signature which range between -35 and -20 (Hoefs, 2015). Therefore, a possible impact on soil CO₂ could result in generally very negative $\delta^{13}\text{C}$ values, which seems significant in the Karthala flanks soil emissions. A single $\delta^{13}\text{C}$ value from the soil at Karthala has an isotopic signature close to the magmatic endmember and the corresponding site is very close to the steaming fumarolic field inside the summit CC caldera. These results allow us to conclude that during the 2017 and 2018 surveys, which were performed during a phase of quiescence of the volcano, soil CO₂ emission on the flanks at Grande Comore was predominantly of biogenic origin, while clear evidence of volcanic origin CO₂ emission was detectable only at the summit crater of Karthala. This overall picture of gas fluxes and isotopic signature at Karthala is in strong contrast with that found during a similar quiescence period at Piton de la Fournaise (Liuzzo et al., 2015). On Piton de la Fournaise, only weak emission of low-temperature fluids and low CO₂ fluxes occur in the central summit area during quiescence periods, while diffuse CO₂ emissions with a clear and strong magmatic contribution (up to 60% of the diffuse fluid composition) have been detected along the main rift zones on the flanks of the volcano. On both volcanoes deep fluid percolation is focused on the main rift zones crossing the volcano edifice. However, the much lower rate of volcanic activity and longer quiescence duration at Karthala translates in low soil CO₂ fluxes with a dominant organic signature. The absence of permanent CO₂-rich emissions below the summit area of Piton de la Fournaise has been attributed to the geometry of its deep plumbing system, which is laterally shifted with respect to the central summit area (Liuzzo et al., 2015; Michon, 2016).

At Mayotte the isotopic values of soil gases taken on land are much more scattered than the Karthala data sampled on the volcano flanks. The range of isotopic variation spans the $-19.0\text{‰} \leq \delta^{13}\text{C} \leq -1\text{‰}$ range at various CO₂ concentrations. Even considering a possible impact of the vegetative cover of C₃ plants, the $\delta^{13}\text{C}$ results at Mayotte, show a significant magmatic contribution in contrast to the isotopic signature of Karthala soil emissions. It is interesting to notice a scattered distribution similar to that previously reported for $\delta^{13}\text{C}$ in

soil emission at La Reunion (Boudoire et al, 2017; Liuzzo et al, 2015). The Comoros archipelago is located in the Equatorial rainforest climate zone and La Réunion in a rainy tropical context. Therefore it is reasonable to consider that the soil of these islands is characterised by similar pedogenesis and biogenic processes to those identified in other tropical zones (Basile-Doelsch et al., 2005; Frank et al., 2002, 2006; Rouff et al., 2012), which in turn can significantly affect the isotopic signature of carbon in soil CO₂, as reported at La Reunion by Liuzzo et al. (2015). It is therefore not surprising that $\delta^{13}\text{C}$ of CO₂ distribution in Mayotte lies within a comparable range of values as those reported for isotopic soil CO₂ measurements at La Reunion in previous works (Boudoire et al 2017, Liuzzo et al. 2015).

The less negative $\delta^{13}\text{C}$ values ($-3\text{‰} < \delta^{13}\text{C} < -1\text{‰}$) were recorded at several soil CO₂ sampling areas that were taken on the beach or on a cliff very close to the BAS bubbling zone. However, these values cannot be explained as a mixing of atmospheric and magmatic CO₂ fixed at -4.3‰ . The less negative $\delta^{13}\text{C}$ values for these two sites elicit three possible hypotheses: either 1) they may lie in a mixing curve between atmospheric and magmatic endmember where the magmatic signature is more positive (around $\delta^{13}\text{C} = -2\text{‰}$); 2) they can be affected by isotopic fractionation on the aquifer; or 3) they are affected by kinetic fractionation due to a process of CO₂ diffusion through the soil as observed in other studies (Capasso et al., 2001; Cerling, 1984; Hesterberg and Siegenthaler, 1991; Severinghaus et al., 1996). We stress that we identify this process only in a limited area, very close to the BAS tidal flat, which is affected by a process determining a significant modification of the isotopic signature that ends with less negative $\delta^{13}\text{C}$ value. Regarding the first hypothesis, a mixing curve between air and magmatic endmember fixed at $\delta^{13}\text{C} = -2\text{‰}$ seems to correlate well to these more positive isotopic data (black dashed curve in Figure 14). In addition, the mixing curve at $\delta^{13}\text{C} = -2\text{‰}$ lies in the range of isotopic signatures of Dziani lake (Milesi et al., 2020). However, Dziani lake lies within a closed volcanic crater that receives a significant volcanic CO₂ contribution. According to Milesi et al. (2019) also in such lacustrine site biogenic and microbial methanogenesis CO₂ reduction is particularly significant (thus potentially affecting the isotopic signature of CO₂ shifting $\delta^{13}\text{C}$ toward more positive signature. These microbial processes have not been identified in our beach context. The similarity of the $\delta^{13}\text{C}$ signature between Dziani lake and these few ground sites discussed is unrealistic also because the mentioned soil degassing area is far from Dziani lake, while

instead very close to the BAS (a few tens of meters). As a consequence, we should expect an isotopic signature closer to that measured in BAS fluids. Moreover, it is difficult to explain alongside the entire dataset presented here, especially considering that the Karthala data fall within a range comparable to the bubbling data at Petite Terre. The second hypothesis invokes an isotopic fractionation that may be ascribed to the interference with the (salty) aquifer, which in turn should determine more negative isotopic values. In addition, the composition of soil gas samples collected at Mayotte do not show detectable CO₂ dissolution in water (see Figure S1 supplementary), therefore the interference of the aquifer at this site seems to be very modest. Regarding the third hypothesis, a curve of diffusive fractionation was modelled (green line in Figure 14) following Capasso et al. (2001):

$$\delta_i = -\Delta x \cdot \left(\frac{D_{j-a}}{D_{i-a}} - 1 \right) \cdot 10^3\text{‰} \quad (9)$$

where δ_i is the expected fractionated isotopic value of soil CO₂ sample; Δx is the variable molar fraction between CO₂ in air and in the sample; D is the binary diffusion coefficient of CO₂ in air; where specifically, D_j is related to ¹²C, and D_i is related to ¹³C. In our case, the diffusivity ratio of carbon in CO₂ (by the way D_{j-a}/D_{i-a}) is equal to 1.0044 (from Reid et al., 1977). For these samples, which were collected in the area close to the bubbling zone, it is therefore reasonable to consider a variable grade of isotopic diffusive fractionation that modified gases with a starting isotopic signature probably close to the bubbling gas thus leading to the conclusion that a kinetic diffusive fractionation might be the main process acting in this specific zone of the island.

We are aware that a wider dataset would certainly contribute to a more comprehensive understanding of the various processes responsible of the isotopic signature in soil CO₂ gas at Petite Terre. We however underline that the most significant results from this dataset support the hypothesis of a clear fingerprint of an active magmatic source into soil CO₂ emissions which has not been clearly identified on the volcano flanks of Karthala. Consequently, we conclude that the high CO₂ fluxes from the BAS tidal area and the time evolution of their He isotopic signature, together with the stronger magmatic CO₂ contribution emissions diffused on land at Petite Terre, potentially record the large magmatic and volcanic event occurring on the submarine flanks of the island. On the contrary, we can anticipate that the future reactivation of Karthala volcano should be

recorded by a significant change in CO₂ emissions from the soil in terms of both fluxes, areal distribution and isotopic composition, as observed on other active volcanoes (Liuzzo et al. 2013).

6. Conclusions

This work presents the results of recent campaigns for the measurement of soil, fumarolic and bubbling gas emissions in two islands within the Comoros archipelago: Grande Comore and Mayotte. Although the measurement campaigns of soil CO₂ emissions are not exhaustive for the entire territory of these two islands, the first results show that they are spatially distributed along the main structural features of both Grande Comore and Petite Terre. A significant difference is found in the origin of the CO₂ emitted from the soil. The carbon isotopic signature of soil CO₂ emissions highlights evidence of a low magmatic contribution at distal areas of Karthala volcano, and a significantly higher magmatic contribution in CO₂ emissions at Petite Terre.

Gas geochemistry of fumarolic fields at Karthala (Grande Comore), and bubbling gases at Mayotte fall within the typical range of MORB-type mantle source. Compared with La Reunion dataset (Boudoire et al., 2018a; Boudoire et al., 2018b; Liuzzo et al., 2015), the Comoros islands dataset shows a CH₄ enrichment, and a variable degree of air contamination.

The isotopic signature of helium (³He/⁴He) in gas emissions confirms relatively low Rc/Ra values (4.18-7.53) for the entire archipelago compared to other volcanic systems in the Indian Ocean such as Reunion (12-14.6). ³He/⁴He data are consistent with average values of fluid inclusions for both Karthala and Petite Terre, spanning in the interval of $6.41 \leq Rc/Ra \leq 7.53$ at Petite Terre and $4.68 \leq Rc/Ra \leq 5.87$ at Karthala. The origin of CO₂ in the fumarolic emissions is basically magmatic (-5.7; -3.2) with no evidence of significant organic or sedimentary contribution for both Grande Comore and Mayotte.

Based on the CO₂, H₂, H₂O and CH₄ contents, a hydrothermal system below Mayotte has been recognized with an equilibrium temperature of ~ 300°C. Water-gas interaction process has been detected in Mayotte resulting in a partial CO₂ dissolution in water. The methane of the hydrothermal system seems to be abiogenic in origin.

The differences recognized between Grande Comore and Mayotte may be ascribed to the different states of volcanic activity at the two islands at the time of the surveys. Soil CO₂ emissions at Grande Comore are generally dominated by biogenic origin while there is a clear magmatic CO₂ contribution in Petite Terre.

Moreover, the increased value of R_c/R_a between 2008 and 2018-19 at Mayotte coupled to a not fully-reached isotopic equilibrium of the pair $\delta^{13}C_{CO_2}-\delta^{13}C_{CH_4}$ in the hydrothermal fluids may be ascribed to the recent volcanic activity which generated the new submarine volcano 45 km offshore from Petite Terre.

Further investigations and a suitable geochemical monitoring program are needed to better understand the complex volcanic system of Comoros archipelago. Nevertheless, our results show some clues of a potential volcano activity of Mayotte which opens important scenarios for the implication regarding procedures aimed to reduce volcanic hazard in this region.

TABLES OF DATA

Table 1: Chemical composition of major and minor gaseous components and isotopic values from fumaroles, bubbling area and soil emission of Grande Comore and Mayotte.

Sampling Date	Sample	Lat	Long	Site	Major (Raw)								$\delta^{13}\text{C}$ (‰)		δD (‰)
					T (°C)	CO ₂ (Vol%)	CO (ppmv)	CH ₄ (ppmv)	N ₂ (Vol%)	O ₂ (Vol %)	H ₂ (ppmv)	He (ppmv)	CO ₂	CH ₄	CH ₄
08/09/2019	Dist N	-12.80064	45.28883	BAS		97.1		2854.0	0.3	0.04		25.0	-4.1	-21.6	
08/09/2019	Dist N	-12.80064	45.28883	BAS		98.5		2982.0	0.4	0.04	112.0	26.0	-4.0	-21.8	
08/09/2019	C1-2	-12.80015	45.28736	BAS		98.7		2444.0	0.3	0.06		29.0	-4.7	-21.0	
08/09/2019	C1-2	-12.80015	45.28736	BAS		97.3		2384.0	0.5	0.07	16.0	28.0	-4.7	-19.2	
13/09/2019	Dist 2	-12.8005	45.28871	BAS		98.3	1.2	2914.0	0.3	0.10		27.0	-3.8	-22.0	
08/09/2019	DIST-1	-12.80064	45.28883	BAS			18.0	390000.0	43.1	15.81	8.0	3558.0		-22.1	-137.8
08/09/2019	C1-2	-12.80015	45.28736	BAS			4.1	455400.0	48.0	2.96	11.0	5528.0		-19.6	-118.1
06/04/2019	Dist 1-A	-12.80064	45.28883	BAS	39.2	97.1	1.2	2442.0	0.5	0.16	<1	21.0	-3.7	-24.4	
06/04/2019	Dist 1-B	-12.80064	45.28883	BAS	39.1	95.8	2.4	2426.0	1.7	0.51	<1	20.0	-3.6		
06/04/2019	Dist 2	-12.8005	45.28871	BAS	nd	97.3	2.1	2406.0	0.3	0.11	<1	19.0	-3.5	-21.4	
06/04/2019	C 1 -1	-12.80015	45.28736	BAS	43	97.0	2.1	2088.0	0.8	0.20	<1	23.0	-4.2	-19.0	
06/04/2019	C 1 -3	-12.80015	45.28736	BAS	43.2	97.0	5.0	2036.0	0.9	0.21	<1	23.0	-4.3	-19.0	
06/04/2019	MAR 3	-12.80051	45.28740	BAS	42	96.5	10.0	2725.0	1.6	0.36	<1	27.0	-4.2	-21.0	
16/12/2018	MAR-1	-12.80036	45.28766	BAS	30.2	63.3	1.6	1209.0	27.8	7.50	2.2	7.0			
16/12/2018	MAR-1	-12.80036	45.28766	BAS	30.2								-4.8		
16/12/2018	CI-1a	-12.80015	45.28736	BAS	29.5	28.7	2.1	416.0	55.0	14.95	<1	bdl	-4.5	-18.7	
16/12/2018	C1-b	-12.80015	45.28736	BAS	29.5	97.9	1.7	2130.0	0.7	0.10	318.0	23.0	-4.5		
16/12/2018	CI-1	-12.80015	45.28736	BAS	29.5								-4.9		
16/12/2018	CI-2	-12.80015	45.28736	BAS	29.4										
16/12/2018	MAN-1	-12.80064	45.28705	BAS	30.1	95.5	0.7	4587.0	2.5	0.21	<1	107.0	-5.1	-12.4	
16/12/2018	MAN-1	-12.80064	45.28705	BAS	30.1								-5.6		
16/12/2018	MAN-2	-12.80064	45.28705	BAS	30.1	83.5	8.0	4621.0	12.0	2.69	<1	110.0	-5.0	-11.7	
16/12/2018	MAN-2	-12.80064	45.28705	BAS	30.1								-5.7		
12/10/2018	Karthala 1	-11.75833	43.360518	CC		50.3	74.9	40.7	37.1	9.38	63.2	16.6	-4.9		
12/10/2018	Karthala 2	-11.75834	43.360379	CC		39.9	23.1	0.0	44.9	11.53	88.1	13.5	-4.5		
13/10/2018	Ka-Su-01	-11.73217	43.363274	LS		92.2	24.1	345.8	1.0	0.21	25992.2	12.7	-4.6		
13/10/2018	Ka-Su-02	-11.73222	43.363317	LS		53.5	22.6	149.6	33.4	8.71	14000.0	12.3	-3.9		
13/10/2018	Ka-Su-03	-11.73334	43.364004	LS		46.6	15.5	145.8	39.6	10.13	11600.0	9.5	-5.0		

Sampling Date	Sample	Site	Noble gases isotopes											
			R/Ra	⁴ He/ ²⁰ Ne	⁴ He ppm	²⁰ Ne ppm	Rc/Ra	⁴⁰ Ar ppm	³⁸ Ar ppm	³⁶ Ar ppm	⁴⁰ Ar* ppm	⁴⁰ Ar atm	⁴⁰ Ar/ ³⁶ Ar corr	³⁸ Ar/ ³⁶ Ar corr
08/09/2019	Dist N	BAS	6.9	329.4	24.4	0.07	6.9	59.3	0.028	0.15	14.9	44.4	392.0	0.1863
08/09/2019	Dist N	BAS	6.9	261.6	25.1	0.10	6.9	55.2	0.025	0.13	16.4	38.8	418.0	0.1878
08/09/2019	C1-2	BAS	7.2	529.1	27.5	0.05	7.2	62.8	0.027	0.14	20.2	42.6	434.1	0.1872
08/09/2019	C1-2	BAS	7.1	152.4	26.0	0.17	7.1	125.3	0.067	0.36	19.6	105.7	348.1	0.1871
13/09/2019	Dist 2	BAS	7.2	310.7	25.7	0.08	7.2	72.0	0.036	0.19	15.4	56.6	374.4	0.1865
08/09/2019	DIST-1	BAS												
08/09/2019	C1-2	BAS												
06/04/2019	Dist 1-A	BAS	7.1	167.7	21.2	0.13	7.1	87.3	0.045	0.24	15.1	72.2	354.9	0.1856
06/04/2019	Dist 1-B	BAS		1663.9										
06/04/2019	Dist 2	BAS												
06/04/2019	C 1 -1	BAS	7.5	219.3	22.5	0.10	7.5	105.5	0.055	0.30	16.2	89.3	347.4	0.1842
06/04/2019	C 1 -3	BAS	7.3	138.9	22.5	0.16	7.3	141.9	0.079	0.43	15.9	126.0	331.8	0.1852
06/04/2019	MAR 3	BAS	7.2	107.8	27.2	0.25	7.3	239.0	0.139	0.75	17.4	221.5	318.1	0.1861
16/12/2018	MAR-1	BAS	3.2	1.1	8.2	7.65	4.2	3346.6	2.146	11.53	-	-	290.7	0.1861
16/12/2018	MAR-1	BAS												
16/12/2018	CI-1a	BAS												
16/12/2018	C1-b	BAS	7.1	200.3	23.2	0.12	7.1	75.1	0.035	0.19	18.5	56.6	390.3	0.1875
16/12/2018	CI-1	BAS												
16/12/2018	CI-2	BAS												
16/12/2018	MAN-1	BAS	6.4	222.2	102.0	0.46	6.4	497.8	0.263	1.41	81.3	416.4	352.8	0.1873
16/12/2018	MAN-1	BAS												
16/12/2018	MAN-2	BAS	6.9	43.6	113.3	2.60	7.0	1762.8	1.072	5.71	74.6	1688.2	308.8	0.1879
16/12/2018	MAN-2	BAS												
12/10/2018	Karthala 1	CC	5.0	1.7	12.3	7.11	5.9	3827.3	2.475	13.06			296.3	0.1894
12/10/2018	Karthala 2	CC	4.8	1.5	12.7	8.75	5.8	5152.8	3.301	17.42			295.9	0.1894
13/10/2018	Ka-Su-01	LS	5.7	356.6	11.9	0.03	5.7	32.9	0.013	0.08	8.5		378.3	0.1810
13/10/2018	Ka-Su-02	LS	3.8	1.3	10.4	7.88	4.7	5047.3	3.068	16.38			308.3	0.1872
13/10/2018	Ka-Su-03	LS	4.4	1.4	10.0	7.06	5.4	4450.6	2.671	14.26			312.3	0.1873

Sampling Date	Sample	Site	Corrected for air contamination					
			He ppm	H ₂ ppm	N ₂ %	CH ₄ ppm	CO ppm	CO ₂ %
08/09/2019	Dist N	BAS	25.6		0.15	2925.3		99.6
08/09/2019	Dist N	BAS	26.2	113.0	0.29	3008.4		99.4
08/09/2019	C1-2	BAS	29.3		0.12	2467.3		99.6
08/09/2019	C1-2	BAS	28.6	16.4	0.22	2438.3		99.5
13/09/2019	Dist 2	BAS	27.4			2958.4	1.22	99.8
08/09/2019	DIST-1	BAS						
08/09/2019	C1-2	BAS						
06/04/2019	Dist 1-A	BAS	21.6			2512.6	1.23	99.9
06/04/2019	Dist 1-B	BAS	20.7			2532.0	2.50	100.0
06/04/2019	Dist 2	BAS	19.5			2469.4	2.15	99.8
06/04/2019	C 1 -1	BAS	23.6		0.01	2148.0	2.16	99.8
06/04/2019	C 1 -3	BAS	23.6		0.14	2090.7	5.13	99.6
06/04/2019	MAR 3	BAS	27.7		0.22	2809.4	10.31	99.5
16/12/2018	MAR-1	BAS						
16/12/2018	MAR-1	BAS						
16/12/2018	CI-1a	BAS						
16/12/2018	C1-b	BAS	23.3	322.8	0.38	2162.0	1.72	99.4
16/12/2018	CI-1	BAS						
16/12/2018	CI-2	BAS						
16/12/2018	MAN-1	BAS	109.6		1.72	4699.5	0.71	97.8
16/12/2018	MAN-1	BAS						
16/12/2018	MAN-2	BAS	127.3		2.27	5378.5	9.27	97.2
16/12/2018	MAN-2	BAS						
12/10/2018	Karthala 1	CC	27.1	120.1	4.00	76.2	142.71	96.0
12/10/2018	Karthala 2	CC						
13/10/2018	Ka-Su-01	LS	13.3	27324.5	0.27	363.5	25.37	97.0
13/10/2018	Ka-Su-02	LS	18.1	25073.9	1.60	266.6	40.24	95.9
13/10/2018	Ka-Su-03	LS	14.0	23402.3	3.71	292.4	31.05	93.9

Sampling Date	Sample	Lat	Long	Site	Major (Raw)								$\delta^{13}\text{C}$ (‰)	
					T (°C)	CO ₂ (Vol%)	CO (ppmv)	CH ₄ (ppmv)	N ₂ (Vol%)	O ₂ (Vol %)	H ₂ (ppmv)	He (ppmv)	CO ₂	
05/12/2017	KA171206 1A	-11.733	43.241	Soil		1.1	13.0	0.5	78.2	19.57	163.0		-22.3	
06/12/2017	KA171205 1A	-11.626	43.309	Soil		1.0	9.0	0.5	78.5	19.18	126.0		-25.0	
07/12/2017	KA171207 1B	-11.846	43.306	Soil		3.7	7.0	0.5	78.4	16.79	125.0		-23.5	
12/10/2018	KART 181012 -1	-11.757155	43.360631	Soil		3.0	16.6	336.0	80.0	21.40	44.0	10.7	-4.2	
15/10/2018	KART 64 A	-11.780161	43.267323	Soil		0.5	5.2	2.8	78.2	20.70	25.3	8.4	-23.2	
15/10/2018	KART 61 A	-11.626042	43.30893	Soil		3.5	7.8	2.9	70.1	17.74	24.8	10.5	-21.3	
15/10/2018	KART 47 A	-11.614397	43.355913	Soil		0.4	8.0	2.3	73.1	19.36	22.6	8.7	-23.9	
15/10/2018	KART 49 A	-11.613266	43.350659	Soil		0.2	6.7	3.0	72.6	17.49	13.4		-20.8	
15/10/2018	KART 63 A	-11.626137	43.308888	Soil		0.8	6.7	4.6	74.5	19.22	25.7	9.0	-23.3	
16/10/2018	KART 67 A	-11.758396	43.242995	Soil		0.5	8.4	1.5	74.5	19.64	33.9	15.9	-22.6	
09/09/2019	MAY 1582	-12.800208	45.286703	Soil		5.1	7.0	2.5	73.9	19.39	2.8	5.0	-3.1	
10/09/2019	AEROPORTO	-12.801281	45.276823	Soil		4.0			76.6	17.26			-12.1	
10/09/2019	MAY 1590	-12.800167	45.285713	Soil		0.8	5.0	1.3	76.7	19.92			-14.5	
10/09/2019	MAY 1603	-12.799336	45.286335	Soil		1.1	4.7	1.3	76.9	20.12			-7.1	
10/09/2019	MAY 1599	-12.799945	45.286118	Soil		0.9	4.4	1.2	76.7	19.84			-14.8	
10/09/2019	MAY 1631	-12.799228	45.284923	Soil		17.7	7.0	1.6	65.0	16.04	2.4	4.2	-2.1	
15/12/2018	V-1	-12.80019	45.28664	Soil	32.2	5.1	11.0	1.8	74.2	19.54	11.0	bdl	-1.3	
15/12/2018	V-2	-12.80019	45.28664	Soil	32.5	1.1	14.0	1.8	76.7	20.39	9.0	bdl	-6.7	
15/12/2018	V-3	-12.80019	45.28664	Soil	32.0	20.2	13.0	1.8	62.7	16.24	11.0	bdl	-1.0	
15/12/2018	V-4	-12.80019	45.28664	Soil	31.9	25.4	12.0	1.9	57.9	14.86	14.0	bdl	-2.0	
16/12/2018	PAF-1	-12.80009	45.28598	Soil		2.0	9.0	1.0	77.6	19.12	5.0	bdl	-19.0	
16/12/2018	PAF-2	-12.80013	45.28596	Soil		2.0	9.0	0.8	77.1	19.47	8.0	bdl	-13.0	

Sampling Date	Sample	Lat	Long	Site	Major (Raw)					
					CO ₂ (Vol%)	CH ₄ (ppmv)	N ₂ (Vol%)	O ₂ (Vol %)	H ₂ (ppmv)	He (ppmv)
16/04/2008	G1			BAS - [BRGM (2008)]	97.4	1900.0	0.4	0.58	<50	18.0
17/04/2008	G2			BAS - [BRGM (2008)]	73.3	1900.0	21.9	5.88	<50	22.0
17/04/2008	G3			BAS - [BRGM (2008)]	96.7	2300.0	0.4	0.47	<50	18.0
18/04/2008	G4			BAS - [BRGM (2008)]	98.0	2700.0	0.4	0.45	<50	25.9
18/04/2008	G5			BAS - [BRGM (2008)]	80.7	1600.0	16.4	4.77	<50	9.9
18/11/2005	9a	-12.801715	45.289816	BAS - [BRGM (2008)]	87.7	11300.0	9.9	2.69	<50	340.0
23/11/2005	9b	-12.801625	45.289724	BAS - [BRGM (2008)]	98.4	3700.0	1.2	0.53	<50	130.0
20/11/2005	9c	-12.800144	45.287327	BAS - [BRGM (2008)]	97.1	1900.0	0.6	0.15	<50	130.0
18/11/2005				BAS - [BRGM (2008)]	0.1	<50	78.1	20.90	<50	<50
19/11/2005				BAS - [BRGM (2008)]	0.4	<50	76.8	20.90	<50	<50
13/07/2010	SKM70			LS - [Benavente and Brotheridge (2015)]	93.6	370.0	0.3	0.00	41000.0	11.0
13/07/2010	SKM53			LS - [Benavente and Brotheridge (2015)]	94.1	430.0	0.3	0.00	42000.0	13.0
13/07/2010	SKM72			LS - [Benavente and Brotheridge (2015)]	93.9	430.0	0.6	0.00	40000.0	12.0
14/07/2010	SKM67			LS - [Benavente and Brotheridge (2015)]	63.2	110.0	27.0	6.40	23000.0	9.0
02/09/2014	SKM180 (Fum 4)	-11.75810318	43.36108294	CC - [Benavente and Brotheridge (2015)]	37.3		48.7	13.30		11.0
02/09/2014	SKM183 (Fum 6)	-11.73236085	43.36335423	LS - [Benavente and Brotheridge (2015)]	94.5	410.0	1.9	0.11	25000.0	13.0
02/09/2014	SKM182 (Fum 6)	-11.73236085	43.36335423	LS - [Benavente and Brotheridge (2015)]	94.3	440.0	1.9	0.00	25900.0	13.0
03/09/2014	SKM185 (Fum 7)	-11.73390178	43.36406988	LS - [Benavente and Brotheridge (2015)]	41.8		44.4	11.60	13800.0	9.0
03/09/2014	SKM66 (Fum 8)	-11.73390178	43.36406988	LS - [Benavente and Brotheridge (2015)]	41.7		44.4	11.60	13800.0	9.0
03/09/2014	SKM72 (Fum 8)	-11.73390178	43.36406988	LS - [Benavente and Brotheridge (2015)]	44.5		42.6	10.80	12600.0	9.0

Sampling Date	Sample	Site	$\delta^{13}\text{C}$ (‰)	Noble gases isotopes							Corrected for air contamination		
			CO ₂	R/Ra	⁴ He/ ²⁰ Ne	⁴ He ppm	²⁰ Ne ppm	Rc/Ra	⁴⁰ Ar ppm	He ppm	N ₂ %	CH ₄ ppm	CO ₂ %
16/04/2008	G1	BAS - [BRGM (2008)]	-3.6	6.7	1083.0	18.0	0.02	6.7	70.0	18.6		1983.1	101.7
17/04/2008	G2	BAS - [BRGM (2008)]	-4.2	6.4	29.0	22.0	0.76	6.4	1900.0	27.9		2585.7	99.8
17/04/2008	G3	BAS - [BRGM (2008)]	-3.9	6.6	118.0	18.0	0.15	6.6	80.0	18.7		2405.8	101.2
18/04/2008	G4	BAS - [BRGM (2008)]	-3.7	6.7	2750.0	25.9	0.01	6.7	90.0	26.6		2784.5	101.1
18/04/2008	G5	BAS - [BRGM (2008)]	-3.8	6.3	8.0	9.9	1.24	6.5	1500.0	11.0		2012.8	101.5
18/11/2005	9a	BAS - [BRGM (2008)]				340.0			700.0	382.2		12729.1	98.8
23/11/2005	9b	BAS - [BRGM (2008)]	-3.2			130.0			300.0	132.6		3776.8	100.4
20/11/2005	9c	BAS - [BRGM (2008)]	-4.3			130.0			100.0	133.5	0.04	1951.8	99.7
18/11/2005		BAS - [BRGM (2008)]							9000.0				
19/11/2005		BAS - [BRGM (2008)]							9000.0				
13/07/2010	SKM70	LS - [Benavente and Brotheridge (2015)]				11.0			1501.0				
13/07/2010	SKM53	LS - [Benavente and Brotheridge (2015)]				13.0			75.0				
13/07/2010	SKM72	LS - [Benavente and Brotheridge (2015)]				12.0			140.0				
14/07/2010	SKM67	LS - [Benavente and Brotheridge (2015)]				9.0			3199.0				
02/09/2014	SKM180 (Fum 4)	CC - [Benavente and Brotheridge (2015)]				11.0			5690.0				
02/09/2014	SKM183 (Fum 6)	LS - [Benavente and Brotheridge (2015)]				13.0			230.0				
02/09/2014	SKM182 (Fum 6)	LS - [Benavente and Brotheridge (2015)]				13.0			220.0				
03/09/2014	SKM185 (Fum 7)	LS - [Benavente and Brotheridge (2015)]				9.0			5310.0				
03/09/2014	SKM66 (Fum 8)	LS - [Benavente and Brotheridge (2015)]				9.0			5300.0				
03/09/2014	SKM72 (Fum 8)	LS - [Benavente and Brotheridge (2015)]				9.0			5000.0				

Table 2 – Soil CO₂ flux (g m⁻² d⁻¹) surveys at Grande Comore and Mayotte

Grande Comore 4-8 Nov 2014			CO ₂ flux [g m ⁻² d ⁻¹]	Grande Comore 4-8 Nov 2014			CO ₂ flux [g m ⁻² d ⁻¹]	Grande Comore 4-8 Nov 2014			CO ₂ flux [g m ⁻² d ⁻¹]	Grande Comore 4-8 Nov 2014			CO ₂ flux [g m ⁻² d ⁻¹]
Latitude	Longitude														
1	-11.760030	43.358620	0.00	41	-11.753260	43.355550	0.00	81	-11.730710	43.361680	4.80	121	-11.730080	43.365400	9.00
2	-11.760120	43.358940	992.60	42	-11.753240	43.359270	0.00	82	-11.731120	43.362160	6.60	122	-11.731050	43.365570	1.20
3	-11.760440	43.359140	0.00	43	-11.753320	43.358290	0.00	83	-11.733480	43.362250	2.10	123	-11.731370	43.366580	5.50
4	-11.760070	43.359300	0.00	44	-11.753340	43.357310	0.00	84	-11.734470	43.362340	6.70	124	-11.731860	43.367570	0.50
5	-11.760150	43.359830	5378.00	45	-11.734620	43.356290	0.00	85	-11.734260	43.363090	3.40	125	-11.731190	43.368440	4.00
6	-11.760410	43.360290	8.90	46	-11.731600	43.356970	0.00	86	-11.733520	43.363050	2.70	126	-11.731050	43.369530	1.10
7	-11.760550	43.361020	0.00	47	-11.728210	43.356650	2.50	87	-11.732700	43.363090	8.50	127	-11.731810	43.370240	3.00
8	-11.760560	43.361840	0.00	48	-11.727900	43.357430	2.60	88	-11.731730	43.363020	2.80	128	-11.732570	43.370970	2.20
9	-11.760500	43.362970	0.00	49	-11.728070	43.358410	1.10	89	-11.731340	43.363770	6.00	129	-11.738900	43.372030	4.40
10	-11.760040	43.363590	0.00	50	-11.727990	43.359880	1.50	90	-11.731630	43.364810	8.20	130	-11.738920	43.371310	4.20
11	-11.758290	43.362920	30.20	51	-11.728090	43.360430	1.40	91	-11.732660	43.364940	6.10	131	-11.738890	43.370270	1.60
12	-11.758200	43.362060	0.00	52	-11.728050	43.361270	1.90	92	-11.733500	43.365130	7.50	132	-11.738950	43.369280	2.70
13	-11.757630	43.361340	1242.70	53	-11.727940	43.362010	4.70	93	-11.734420	43.364980	1.30	133	-11.738940	43.368460	1.50
14	-11.758260	43.361440	5.70	54	-11.728060	43.363120	9.10	94	-11.735480	43.365060	2.90	134	-11.738900	43.367580	1.30
15	-11.758390	43.360850	24.50	55	-11.728050	43.363840	3.60	95	-11.735480	43.364010	5.40	135	-11.738890	43.366800	4.20
16	-11.758310	43.360750	153.50	56	-11.727720	43.364480	3.80	96	-11.734120	43.364140	313.40	136	-11.738880	43.365750	0.00
17	-11.758460	43.360220	7.90	57	-11.732320	43.363310	21.50	97	-11.733950	43.364120	8994.00	137	-11.738770	43.365270	2.50
18	-11.758430	43.359810	0.00	58	-11.732320	43.363260	796.70	98	-11.733710	43.364130	553.70	138	-11.738960	43.363820	1.10
19	-11.758320	43.359130	21.30	59	-11.732820	43.362400	0.00	99	-11.733580	43.364050	175.80	139	-11.738840	43.363260	1.50
20	-11.758320	43.359790	6931.00	60	-11.731670	43.362060	10.10	100	-11.733390	43.363960	3046.10	140	-11.739020	43.361900	1.40
21	-11.756940	43.356410	0.00	61	-11.731540	43.361200	6.10	101	-11.732920	43.363410	17364.40	141	-11.738830	43.361170	1.90
22	-11.756960	43.357310	0.00	62	-11.731630	43.360350	3.30	102	-11.732400	43.363310	396.10	142	-11.738850	43.360300	4.60
23	-11.756970	43.358240	0.00	63	-11.731850	43.359590	7.20	103	-11.735470	43.365470	4.50	143	-11.738890	43.359250	8.90
24	-11.756920	43.359290	4.00	64	-11.731530	43.357740	4.10	104	-11.735410	43.366680	4.20	144	-11.738860	43.358360	3.60
25	-11.757020	43.360120	1.30	65	-11.735020	43.357890	5.30	105	-11.735290	43.367860	1.60	145	-11.738570	43.357640	3.70
26	-11.756930	43.361020	4.60	66	-11.735290	43.358390	8.10	106	-11.734920	43.368590	2.70	146	-11.738800	43.356490	21.10
27	-11.756870	43.361130	9811.10	67	-11.735430	43.359460	4.90	107	-11.734950	43.369160	1.50	147	-11.742410	43.360250	1.30
28	-11.756960	43.361920	0.00	68	-11.735390	43.360180	8.00	108	-11.735100	43.370020	1.30	148	-11.742630	43.361150	2.20
29	-11.756930	43.362760	0.00	69	-11.735350	43.361070	3.20	109	-11.734880	43.371330	4.30	149	-11.742560	43.362230	2.90
30	-11.753250	43.364720	0.00	70	-11.735510	43.362140	1.30	110	-11.734890	43.372370	0.00	150	-11.742500	43.363040	7.20
31	-11.753290	43.363780	0.00	71	-11.735580	43.362880	3.00	111	-11.731630	43.372480	5.30	151	-11.742550	43.363730	3.30
32	-11.753240	43.362890	0.00	72	-11.735400	43.361130	0.00	112	-11.727760	43.371830	2.70	152	-11.742620	43.364710	6.00
33	-11.753270	43.361690	0.00	73	-11.734460	43.361040	0.00	113	-11.728050	43.370230	3.00	153	-11.742450	43.365780	10.00
34	-11.753660	43.360930	0.00	74	-11.733640	43.360980	1.30	114	-11.728340	43.369200	13.50	154	-11.742530	43.366600	0.00
35	-11.753490	43.359830	0.00	75	-11.732860	43.360950	1.60	115	-11.728570	43.368350	1.30	155	-11.742480	43.367530	7.80
36	-11.749920	43.361890	0.00	76	-11.731890	43.360570	5.80	116	-11.728670	43.367390	2.60				
37	-11.749930	43.361090	0.00	77	-11.730180	43.359770	6.30	117	-11.728860	43.366670	5.70				
38	-11.750010	43.360040	0.00	78	-11.729260	43.359940	1.80	118	-11.728690	43.365970	4.80				
39	-11.749950	43.359240	0.00	79	-11.728800	43.360780	1.60	119	-11.728840	43.365040	4.40				
40	-11.749550	43.358340	0.00	80	-11.730240	43.360810	4.80	120	-11.729510	43.365180	0.00				

Grande Comore 28 Nov-07 Dic 2017		CO ₂ flux [g m ⁻² d ⁻¹]	
Latitude	Longitude		
1	-11.579000	43.311000	32.10
2	-11.525000	43.337000	15.10
3	-11.879000	43.407000	22.66
4	-11.872000	43.399000	18.88
5	-11.735000	43.329000	18.88
6	-11.735000	43.329000	47.20
7	-11.734000	43.328000	33.98
8	-11.733000	43.327000	18.88
9	-11.732000	43.326000	52.86
10	-11.731000	43.326000	45.31
11	-11.730000	43.324000	16.99
12	-11.728000	43.323000	22.66
13	-11.723000	43.250000	24.54
14	-11.725000	43.249000	168.07
15	-11.727000	43.250000	239.87
16	-11.730000	43.250000	32.10
17	-11.730000	43.249000	20.77
18	-11.732000	43.250000	30.21
19	-11.734000	43.249000	33.98
20	-11.737000	43.250000	24.54
21	-11.720000	43.249000	13.22
22	-11.849000	43.332000	20.77
23	-11.849000	43.330000	256.89
24	-11.849000	43.328000	41.54
25	-11.849000	43.328000	98.18
26	-11.848000	43.321000	18.88
27	-11.847000	43.316000	49.09
28	-11.846000	43.314000	79.30
29	-11.847000	43.311000	54.75
30	-11.846000	43.306000	179.40
31	-11.844000	43.303000	22.66
32	-11.842000	43.301000	18.88
33	-11.840000	43.299000	18.88
34	-11.837000	43.297000	11.33
35	-11.833000	43.292000	120.84
36	-11.829000	43.288000	145.40
37	-11.784000	43.271000	30.21
38	-11.780000	43.267000	226.64
39	-11.778000	43.265000	160.51
40	-11.775000	43.264000	457.58
41	-11.719000	43.249000	16.99
42	-11.721000	43.245000	22.66
43	-11.723000	43.245000	16.99

Grande Comore 28 Nov-07 Dic 2017		CO ₂ flux [g m ⁻² d ⁻¹]	
Latitude	Longitude		
44	-11.727000	43.244000	60.42
45	-11.728000	43.243000	22.66
46	-11.728000	43.240000	22.66
47	-11.730000	43.242000	15.10
48	-11.733000	43.241000	226.64
49	-11.735000	43.240000	118.96
50	-11.737000	43.240000	94.41
51	-11.740000	43.240000	43.42
52	-11.742000	43.239000	16.99
53	-11.747000	43.238000	22.66
54	-11.748000	43.235000	50.98
55	-11.752000	43.236000	52.86
56	-11.759000	43.239000	11.33
57	-11.759000	43.244000	37.76
58	-11.560000	43.273000	9.44
59	-11.566000	43.272000	94.41
60	-11.570000	43.271000	13.22
61	-11.577000	43.269000	18.88
62	-11.584000	43.267000	35.87
63	-11.588000	43.266000	103.85
64	-11.592000	43.266000	109.51
65	-11.597000	43.263000	11.33
66	-11.609000	43.263000	13.22
67	-11.629000	43.307000	20.77
68	-11.626000	43.309000	306.06
69	-11.622000	43.312000	20.77
70	-11.618000	43.314000	135.95
71	-11.616000	43.315000	62.31
72	-11.594000	43.378000	147.29
73	-11.591000	43.382000	16.99
74	-11.429000	43.404000	98.18
75	-11.427000	43.399000	39.65
76	-11.438000	43.399000	120.84
77	-11.447000	43.402000	100.07
78	-11.454000	43.402000	22.66
79	-11.610000	43.365000	16.99
80	-11.612000	43.363000	228.53
81	-11.614000	43.357000	24.54
82	-11.613000	43.350000	24.54
83	-11.610000	43.346000	71.75
84	-11.611000	43.341000	13.22

Grande Comore 11-16 Oct 2018		CO ₂ flux [g m ⁻² d ⁻¹]	
Latitude	Longitude		
1	-11.876616	43.480066	7.55
2	-11.878802	43.481346	7.55
3	-11.879880	43.477517	13.22
4	-11.879253	43.472302	7.55
5	-11.882023	43.469274	13.22
6	-11.885114	43.468817	9.44
7	-11.884848	43.465353	11.33
8	-11.885446	43.457200	7.55
9	-11.886513	43.452216	18.88
10	-11.888558	43.445997	28.32
11	-11.890019	43.442657	33.98
12	-11.890607	43.440029	22.66
13	-11.893221	43.435186	20.77
14	-11.894565	43.430336	28.32
15	-11.756312	43.355270	7.55
16	-11.758078	43.357018	9.44
17	-11.757963	43.357585	7.55
18	-11.757925	43.357977	9.44
19	-11.758013	43.358559	9.44
20	-11.757705	43.358812	7.55
21	-11.757610	43.359170	16.99
22	-11.757605	43.359566	30.21
23	-11.757513	43.359916	22.66
24	-11.757327	43.360275	11.33
25	-11.757155	43.360631	802.29
26	-11.757020	43.360974	951.98
27	-11.756931	43.361213	45.31
28	-11.756826	43.361449	283.36
29	-11.756816	43.361700	32.10
30	-11.756957	43.362062	9.44
31	-11.757067	43.362450	7.55
32	-11.757152	43.362882	7.55
33	-11.732509	43.363215	15.10
34	-11.637843	43.376308	11.33
35	-11.636014	43.375007	22.66
36	-11.634025	43.373187	7.55
37	-11.632313	43.371923	7.55
38	-11.628818	43.372358	9.44
39	-11.628904	43.372267	13.22
40	-11.627732	43.368685	9.44
41	-11.627151	43.365583	7.55
42	-11.622232	43.365063	5.66
43	-11.619964	43.363529	5.66
44	-11.615842	43.359638	47.20

Grande Comore 11-16 Oct 2018		CO ₂ flux [g m ⁻² d ⁻¹]	
Latitude	Longitude		
45	-11.614397	43.355913	7.55
46	-11.613988	43.352644	7.55
47	-11.613266	43.350659	16.99
48	-11.611125	43.349181	30.21
49	-11.609914	43.345950	11.33
50	-11.612037	43.338725	28.32
51	-11.613682	43.333515	9.44
52	-11.614027	43.329282	7.55
53	-11.614261	43.324552	9.44
54	-11.614549	43.322405	20.77
55	-11.614855	43.317845	20.77
56	-11.615610	43.314634	16.99
57	-11.618371	43.313629	28.32
58	-11.621824	43.312271	9.44
59	-11.626042	43.308930	105.74
60	-11.625871	43.309033	56.64
61	-11.626137	43.308888	120.84
62	-11.780161	43.267323	67.97
63	-11.770174	43.261717	11.33
64	-11.759701	43.256409	37.76
65	-11.758396	43.242995	84.96

Mayotte 9-13 Sept 2019		CO ₂ flux [g m ⁻² d ⁻¹]	
Latitude	Longitude		
1	45.286856	-12.799818	50.66
2	45.286886	-12.799780	3.50
3	45.286808	-12.799860	7.62
4	45.286780	-12.799913	4.02
5	45.286777	-12.799973	9.68
6	45.286748	-12.799982	5.70
7	45.286731	-12.800008	5.66
8	45.286717	-12.800075	3.90
9	45.286699	-12.800123	4.26
10	45.286686	-12.800178	3.95
11	45.286703	-12.800208	30.90
12	45.286661	-12.800261	2.92
13	45.286664	-12.800280	4.80
14	45.286662	-12.800339	2.04
15	45.286693	-12.800380	0.52
16	45.286672	-12.800439	1.64
17	45.286711	-12.800493	2.28
18	45.285713	-12.800167	5.28

Mayotte 9-13 Sept 2019			CO ₂ flux [g m ⁻² d ⁻¹]
Latitude	Longitude		
19	45.285764	-12.800136	4.86
20	45.285806	-12.800110	12.65
21	45.285844	-12.800085	8.40
22	45.285883	-12.800070	17.57
23	45.285907	-12.800087	5.70
24	45.286072	-12.800006	22.82
25	45.286160	-12.800000	9.00
26	45.286118	-12.799945	17.06
27	45.286107	-12.799880	7.76
28	45.286142	-12.799805	5.36
29	45.286244	-12.799578	21.54
30	45.286335	-12.799336	41.57
31	45.286491	-12.799352	14.70
32	45.286694	-12.799469	19.13
33	45.286883	-12.799525	6.48
34	45.287022	-12.799293	11.90
35	45.287079	-12.799116	8.10
36	45.287149	-12.798782	12.95
37	45.282678	-12.805537	0.45
38	45.282875	-12.805612	1.18
39	45.283069	-12.805955	0.00
40	45.282586	-12.805040	1.63
41	45.282379	-12.805167	1.00
42	45.277490	-12.802276	0.00
43	45.277386	-12.802210	0.00
44	45.277352	-12.802227	0.00
45	45.277246	-12.802167	4.45
46	45.277162	-12.802143	4.36
47	45.277292	-12.802176	1.21
48	45.277152	-12.802055	8.00
49	45.277126	-12.801957	1.64
50	45.277061	-12.801850	0.52
51	45.276823	-12.801281	15.70
52	45.276858	-12.801248	4.21
53	45.284543	-12.799820	11.56
54	45.284848	-12.799386	37.94
55	45.284923	-12.799228	173.44
56	45.285052	-12.799154	39.81
57	45.285033	-12.797719	0.00
58	45.285041	-12.797734	11.98
59	45.284897	-12.797933	4.84
60	45.284909	-12.798320	27.11
61	45.284959	-12.798641	13.28

Mayotte 9-13 Sept 2019			CO ₂ flux [g m ⁻² d ⁻¹]
Latitude	Longitude		
62	45.284912	-12.798811	42.42
63	45.284776	-12.799008	9.62
64	45.285290	-12.797520	1.69
65	45.285442	-12.797118	2.12
66	45.285659	-12.796799	6.87
67	45.284645	-12.801006	2.36
68	45.284708	-12.800662	3.18
69	45.286793	-12.800945	3.26
70	45.288012	-12.799281	2.55
71	45.287850	-12.799243	0.49
72	45.287528	-12.799367	0.00
73	45.287306	-12.799543	4.04
74	45.287123	-12.799624	1.61
75	45.281475	-12.795606	1.99
76	45.281311	-12.796021	4.06
77	45.281218	-12.796457	6.18
78	45.281190	-12.797037	6.81
79	45.281312	-12.797480	2.53
80	45.281154	-12.798122	2.03
81	45.280780	-12.798222	7.22
82	45.281349	-12.797331	2.60
83	45.282582	-12.798498	5.60
84	45.282209	-12.799108	1.80
85	45.280079	-12.792672	1.06
86	45.279778	-12.793405	1.45
87	45.279577	-12.794203	3.39
88	45.279207	-12.795135	13.83
89	45.279342	-12.795964	0.00
90	45.278689	-12.796682	3.46
91	45.278386	-12.797120	2.67
92	45.278279	-12.797905	16.76
93	45.277967	-12.798124	0.00
94	45.277448	-12.798648	7.81
95	45.255220	-12.782986	1.97
96	45.255288	-12.781948	3.81
97	45.254958	-12.781035	0.00
98	45.257887	-12.783449	2.11
99	45.260400	-12.785424	3.47
100	45.261339	-12.786133	2.61
101	45.262178	-12.786088	0.00
102	45.261778	-12.785416	3.32
103	45.264903	-12.787605	5.05
104	45.268356	-12.789905	5.71

Mayotte 9-13 Sept 2019			CO ₂ flux [g m ⁻² d ⁻¹]
Latitude	Longitude		
105	45.268894	-12.791590	2.73
106	45.273430	-12.794984	8.00
107	45.274379	-12.794448	5.34
108	45.275029	-12.794076	1.03
109	45.275483	-12.793842	2.43
110	45.275939	-12.793916	7.21
111	45.276297	-12.793910	12.45
112	45.276781	-12.793827	3.11
113	45.277189	-12.793428	2.68
114	45.277539	-12.792994	1.97
115	45.278188	-12.792446	5.57
116	45.280727	-12.766360	0.00
117	45.280762	-12.768051	0.39
118	45.279645	-12.770106	2.52
119	45.279858	-12.771997	3.38
120	45.280814	-12.774220	2.93
121	45.281827	-12.776119	1.50
122	45.294567	-12.783769	1.70
123	45.293457	-12.784258	6.53
124	45.292021	-12.784650	3.35
125	45.290841	-12.785500	26.03
126	45.289486	-12.785186	6.06
127	45.288814	-12.784143	10.06
128	45.288652	-12.783974	11.54
129	45.289141	-12.783073	6.76
130	45.288129	-12.782416	1.27
131	45.286670	-12.781859	4.26
132	45.285204	-12.782200	0.00
133	45.283348	-12.782728	6.09
Mayotte BAS 9-13 Sept 2019			CO ₂ flux [g m ⁻² d ⁻¹]
Latitude	Longitude		
1	45.288840	-12.800657	33304.40
2	45.288840	-12.800657	33304.40
3	45.288818	-12.800576	29549.64
4	45.288818	-12.800576	29549.64
5	45.288787	-12.800533	20025.38
6	45.288787	-12.800533	20025.38
7	45.288766	-12.800518	21481.59
8	45.288766	-12.800518	21481.59
9	45.288766	-12.800518	21481.59
10	45.288766	-12.800518	21481.59
11	45.288734	-12.800502	34896.13

Mayotte 9-13 Sept 2019			CO ₂ flux [g m ⁻² d ⁻¹]
Latitude	Longitude		
12	45.288734	-12.800502	34896.13
13	45.288676	-12.800483	22764.99
14	45.288611	-12.800534	27874.64
15	45.288257	-12.799866	12330.93
16	45.288257	-12.799866	12330.93
17	45.288257	-12.799866	12330.93
18	45.288257	-12.799866	12330.93
19	45.288257	-12.799866	12330.93
20	45.288257	-12.799866	12330.93
21	45.288257	-12.799866	12330.93
22	45.288257	-12.799866	12330.93
23	45.288257	-12.799866	12330.93
24	45.288257	-12.799866	12330.93
25	45.288257	-12.799866	12330.93
26	45.288257	-12.799866	12330.93
27	45.287666	-12.800374	35046.24
28	45.287666	-12.800374	35046.24
29	45.287666	-12.800374	35046.24
30	45.287666	-12.800374	35046.24
31	45.287666	-12.800374	35046.24
32	45.287666	-12.800374	35046.24
33	45.287361	-12.800153	18028.15
34	45.287361	-12.800153	18028.15
35	45.287361	-12.800153	18028.15
36	45.287361	-12.800153	18028.15
37	45.287364	-12.800154	47932.23
38	45.287370	-12.800155	12824.78
39	45.287392	-12.800154	13008.43
40	45.287356	-12.800126	18762.74
41	45.287356	-12.800126	18762.74
42	45.287388	-12.800106	23629.43
43	45.287388	-12.800106	23629.43
44	45.287388	-12.800106	23629.43
45	45.287402	-12.800144	136.21
46	45.288553	-12.800236	35046.24
47	45.289069	-12.800259	70485.66
48	45.289104	-12.800310	17064.31
49	45.289178	-12.800359	26435.94
50	45.289290	-12.800481	8730.58
51	45.289524	-12.800485	5952.67
52	45.289584	-12.800270	15537.98
53	45.289039	-12.800000	14289.19

Mayotte 11 Nov 2020			CO ₂ flux [g m ⁻² d ⁻¹]
	Latitude	Longitude	
1	45.28444	-12.7644	4.81
2	45.28326	-12.7654	6.69
3	45.28096	-12.7656	5.95
4	45.28058	-12.7681	15.93
5	45.27964	-12.7702	34.82
6	45.27978	-12.7718	17.22
7	45.28066	-12.7736	26.00
8	45.28116	-12.7753	17.04
9	45.28222	-12.7771	13.72
10	45.28137	-12.7787	16.14
11	45.28062	-12.7801	15.93
12	45.27904	-12.7812	29.44
13	45.27759	-12.7818	39.00
14	45.27644	-12.7828	8.52
15	45.27516	-12.7842	4.78
16	45.27395	-12.7852	48.00
17	45.27289	-12.7863	8.96
18	45.26905	-12.7873	10.93
19	45.26936	-12.7895	19.95
20	45.26946	-12.7896	3.85
21	45.26819	-12.789	7.94
22	45.2847	-12.7824	62.91
23	45.28392	-12.7826	159.30
24	45.28293	-12.7828	28.73
25	45.28168	-12.783	6.07
26	45.28016	-12.7838	48.72
27	45.27952	-12.7842	14.55
28	45.27929	-12.7856	13.95
29	45.2793	-12.7856	37.36
30	45.27905	-12.7868	4.03
31	45.27994	-12.7891	15.85
32	45.28001	-12.7911	12.56
33	45.28612	-12.7999	29.08

Table 3 – Synopsis of soil CO₂ results and relative method used and year of measurements

CO ₂ flux [g m ⁻² day ⁻¹]	Grande Comore		Grande Comore		Mayotte		Mayotte Bubbling Sea
	2014		2017	2018	2019	2020	2019
Min	0.0		9.44	5.66	0.0	3.85	12.2
Max	17364.4		457.58	951.98	173.4	159.3	70485.7
Average	365.6		67.61	51.91	8.2	23.90	21084.0
σ	1886.3		79.41	153.91	17.0	28.39	12045.2
	<i>Accumulation Chamber</i>		<i>Dynamic Concentration (K=30)</i>		<i>Accumulation Chamber</i>		<i>Accumulation Chamber</i>

SUPPORTING INFORMATION

Table S1. Evaluation of the best k used for the CO₂ flux determination (equation 4 in the text) and estimation of the percentage deviations

CO ₂ flux [g m ⁻² day ⁻¹] calculation at different k values								Percentage deviations of k=30			
		K=1	K=10	K=20	K=30	K=35	K=40	K=50	%+	%-	
2018	min	7.86	6.58	6.03	5.66	5.52	5.38	5.15	38.77	9.06	k=1 - k=50
	max	1313.41	1101.38	1011.61	951.98	927.80	906.14	868.43	37.97	8.78	
	media	71.85	60.18	55.22	51.91	50.57	49.37	47.28	38.40	8.93	
2017	min	13.10	10.96	10.05	9.44	9.19	8.97	8.58	38.77	9.06	k=1 - k=50
	max	634.13	530.84	486.87	457.58	445.68	435.01	416.41	38.58	9.00	
	media	93.79	78.48	71.96	67.61	65.84	64.25	61.49	38.74	9.05	
Common range of k values in volcanic soil											
2018	min			6.03	5.66	5.52	5.38		6.44	4.97	k=20 - k=40
	max			1011.61	951.98	927.80	906.14		6.26	4.82	
	media			55.22	51.91	50.57	49.37		6.36	4.90	
2017	min			10.05	9.44	9.19	8.97		6.44	4.97	k=20 - k=40
	max			486.87	457.58	445.68	435.01		6.40	4.93	
	media			71.96	67.61	65.84	64.25		6.44	4.96	

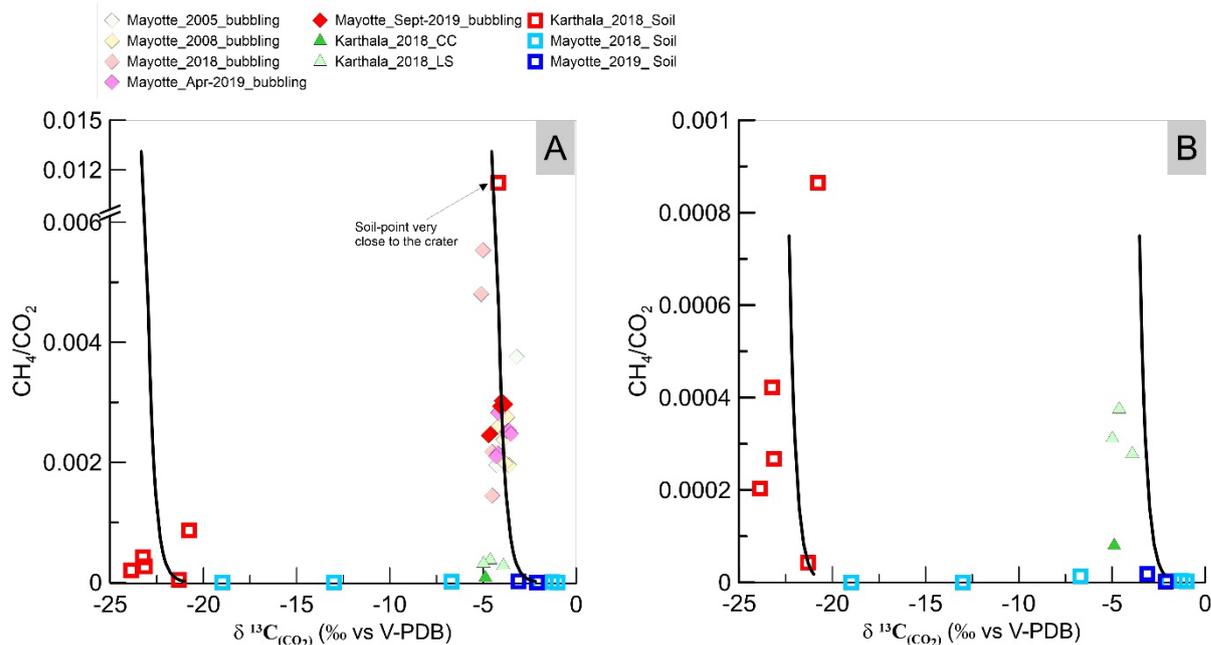


Figure S1. Binary diagram of $\delta^{13}\text{C}_{(\text{CO}_2)}$ versus CH_4/CO_2 . In figure (A) soil, fumaroles and bubbling gases from Grande Comore and Mayotte. In (B) the same diagram in which the data are magnified at a very low CH_4/CO_2 ratio. Black equilibrium curves modelled fitting two endmembers for Karthala soil emissions and for fumaroles and bubbling gases (Karthala and Mayotte) at $\delta^{13}\text{C}_{(\text{CO}_2)} = -21\text{‰}$ and -2.2‰ respectively, in both cases at $T=32^\circ$ and $\text{pH}_{(\text{H}_2\text{CO}_3)}=5.71$.

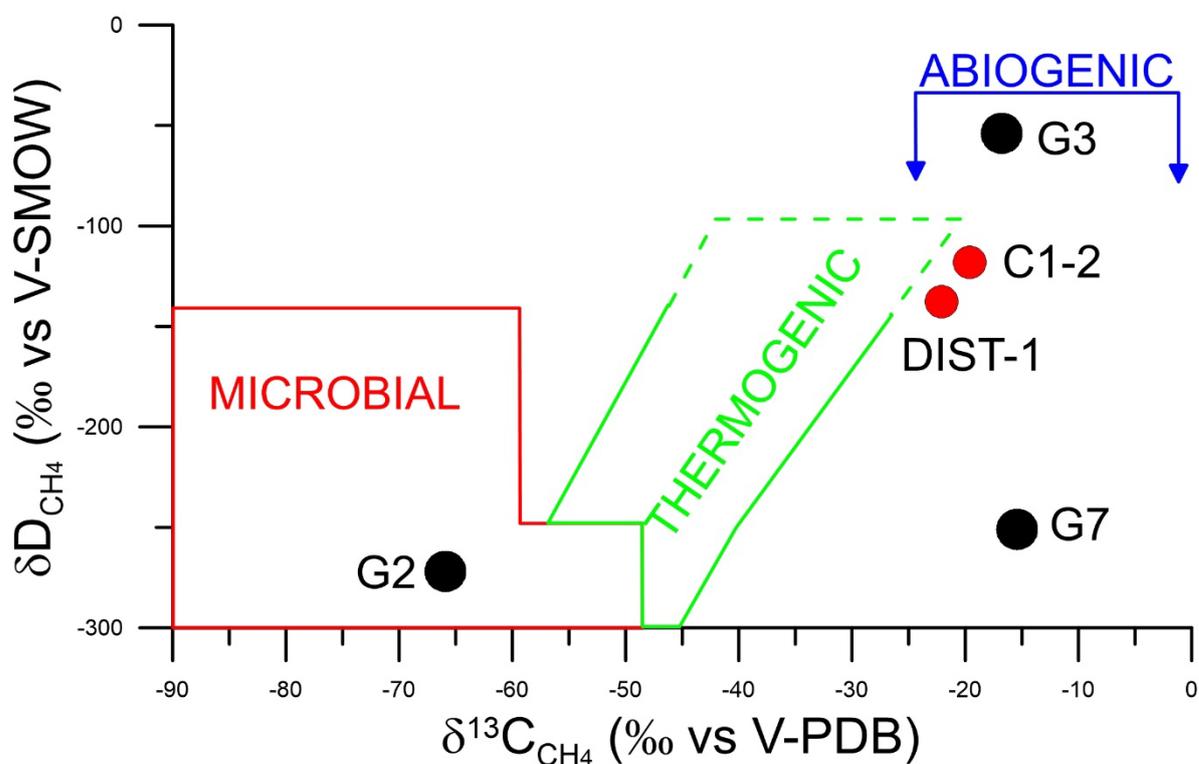


Figure S2. $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta\text{D}_{\text{CH}_4}$ diagram (modified from Schoell (1980) and Mazzini et al. (2011)). G2, G3 and G7 data from Milesi et al., (2020).

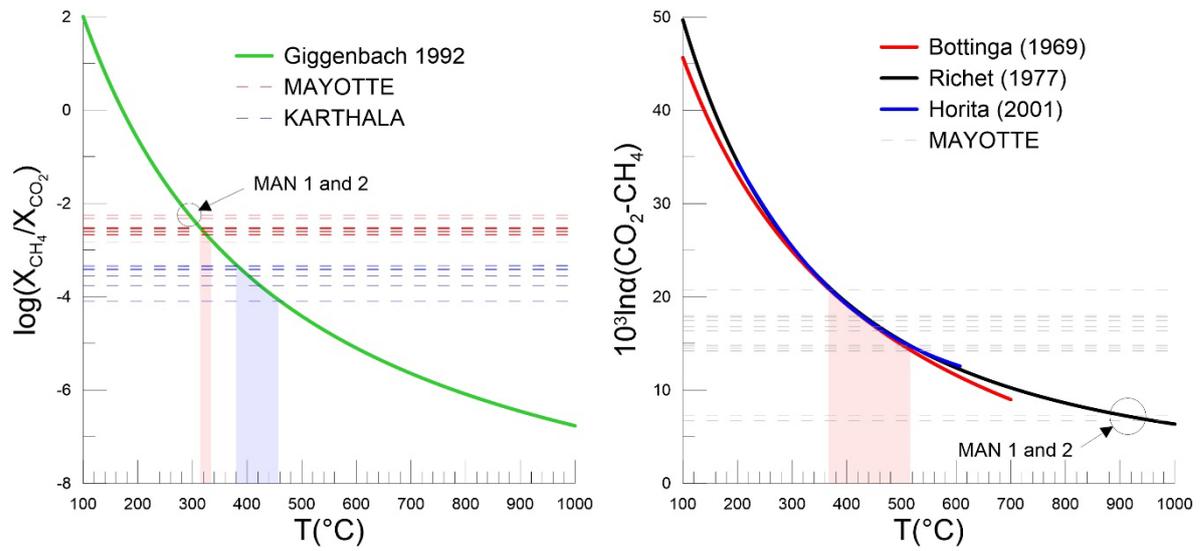


Figure S3. On the left plot of the relationship for thermal equilibration between CH₄ and CO₂ from Giggenbach, (1992). On the right plot temperature equilibrium related to difference in $\delta^{13}\text{C}$ values between CO₂ and CH₄ ($10^3 \ln \alpha$) from Bottinga, (1969); Horita, (2001) and Richet et al. (1977).

SECTION 2

CO₂ CH₄ and noble gas emissions at Petite Terre (Mayotte) – Indications of magmatic fingerprints in gas emission and recognition of secondary process in the differentiation of gas from their pristine composition

This section includes part of the paper submitted in Comptes Rendus Geoscience – Académie des sciences:

The composition of gases emissions at Petite Terre (Mayotte, Comoros): Inference on magmatic fingerprints

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This second section of the thesis is dedicated to a more in-depth study of degassing at Petite Terre, where it has been possible to broaden the area of investigation to include Lake Dziani (Dziani Dzaha). Added to this is a closer assessment of the temporal evolution of some geochemical parameters, such as the helium ratio and the temperature of the hydrothermal system, which were acquired and collected over the four years, with the aim of providing further clues to the volcanic processes taking place in the study area. Indeed, this time series analysis allows a further step forward in the interpretation of the degassing of Mayotte within a broader geodynamic framework, which also considers the possible effects of ongoing submarine volcanic activity.

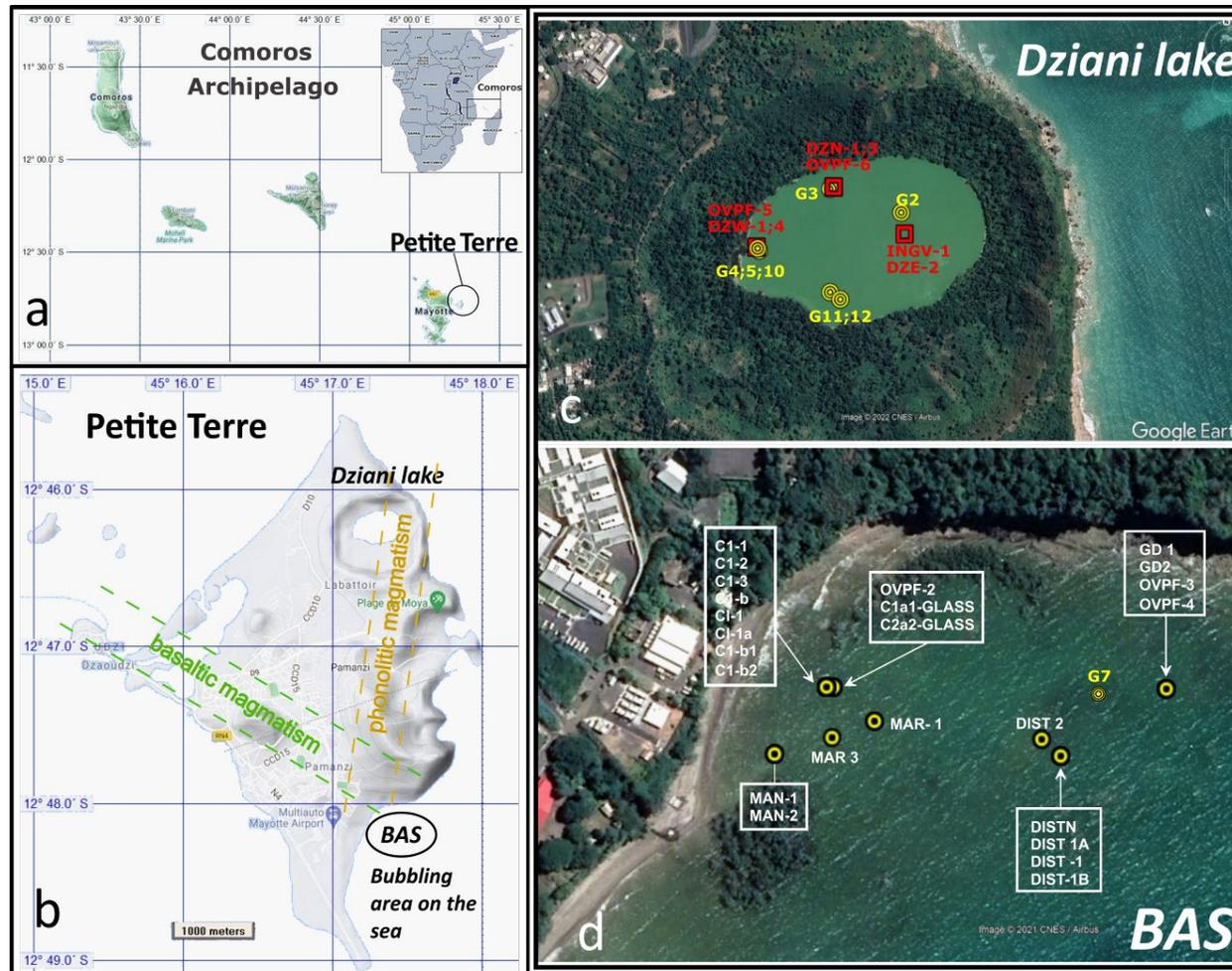


Figure 15. Map of the Comoros archipelago located on the northern zone of the Mozambique Channel between continental African and Madagascar. In (b) map of the little island on the east coast of Mayotte called Petite Terre, where have been acquired all the measurements. In (c) and (d) the Dziani Lake and bubbling area on the sea BAS respectively, where the locations of the sampling sites are indicated.

7. Introduction and geological context of Petite Terre (Mayotte)

The large-volume and long-lasting sub-marine eruption of Mayotte, the largest submarine event ever detected by monitoring networks (Berthod et al., 2021; Cesca et al., 2020; Famin et al., 2020; Lemoine et al., 2020), challenges current models on the origin of Comoros volcanism. Since 2018, about 6.5 km³ of evolved basanite lava have been emitted on the 3.5 km deep seafloor, 50 km east south-east from Mayotte, from a deep source located in the upper lithospheric mantle (Bachèlery et al., 2019; Berthod et al., 2021; Lemoine et al., 2020). The new volcano is located on a N120° oriented volcanic ridge, which runs along the eastern submarine flank of Mayotte, whose western subaerial tip is the small island of Petite Terre (Tzevahirtzian et al., 2021). The occurrence of this submarine eruptive activity requires urgent investigation into the origin of bubbling fluids and their potential genetic relation with the seismo-volcanic activity.

At Mayotte, the volcanic activity becomes increasingly older from the eastern side (Petite Terre island), to the western main island (Grande Terre) (Nehlig et al., 2013). On Petite Terre, more recent volcanic activity has resulted in a set of Holocene basaltic scoria cones and phonolitic maars formed upon the existing coral reef (Zinke et al., 2001; Nehlig et al., 2013), as well as two main areas of low-temperature CO₂-rich gas seeps (Figure 15). In this work, we focus on these two bubbling emission zones on Petite Terre, with the aim of constraining the geochemical signature of their gas emissions.

The first bubbling area occurs in the NE part of Petite Terre (Figure 15c) inside the crater lake of the Dziani Dzaha phonolitic maar. Dziani Dzaha lake is a meromictic lake in a sub-central narrow depression with a maximum depth ranging between 4,5 m to around 18 m (Figure 16 and 17). The bubbling emissions are heterogeneously distributed around the lake margins and within the central area, therefore passing through different water column depths. The lake is located in a volcanic crater formed by a phreatomagmatic eruption, which may correspond to one of the most recent volcanic events of the island of Petite Terre. Several CO₂-rich and high-flux bubbling areas occur around the lake margins, and a main CH₄-rich spot featuring myriads of small bubbles occurs close to the deepest part of the lake (Milesi et al., 2020). With regard to the physical and chemical characteristics, the salinity of the lake water reaches up to 52 psu, and the alkalinity is ca 0.2 mol·L⁻¹, with pH values up to 9.4 (Cadeau et al., 2020). Facilitated by such physical-chemical conditions of

the lake, is the uniquely elevated presence of Microbialites, benthic sedimentary deposit formed in close association with micro-organisms (Cadeau et al., 2020; Milesi et al., 2020) A second bubbling area, first described in 1998, on the eastern tidal flat of Petite Terre is located close to the “Airport beach” (Figure 15d BAS site; Traineau, 2006; Sanjuan, 2008), where many bubbling spots with variable flux occur at the southern part of the large “Vigie” phonolitic maar, situated on a muddy flat area exposed to significant tide and extending about 250x300m from the beach (Liuzzo et al., 2021).



Figure 16. Lake Dziani seen from the edge of the formation crater



Figure 17. Detail of Lake Dziani showing one of the several bubbling sites near the emergence of microbialite formations.

8. Data Results

All data discussed in the text refer to Table 4. This is a supplement to Table 1 with data from the 2020-2021 surveys. The figures below include data from both tables (1, 4).

8.1 Gas composition

The Mayotte noble gas samples show a more variable composition for the Dziani Dzaha Lake than for BAS (Table 4), with ^4He ranging between 8.2 and 113 ppm at BAS and between 42.5 and 1139.5 for the Dziani Dzaha Lake. ^{20}Ne values for the BAS zone range from 0.1 to 7.7 ppm and ^{40}Ar is in the range 55.2-3346.6 ppm, while for the Dziani Lake has ^{20}Ne in the range 0.8-18.6 and ^{40}Ar in the range 281.4-2055.1. Some of the samples have a significant air contamination showing concentrations of N_2 and O_2 up to 76.4% and 20.4% respectively (Table 4, Figure 18a).

The BAS bubbling gases from the tidal flat show a CO_2 dominated composition with concentrations up to 98.8% and a variable concentration in CH_4 ranging between 16 and 5291ppm with the lowest value related to an air-contaminated sample (C2a2-glass). In the BAS samples, H_2 and CO are generally in low concentrations, ranging between below detection limit and 11 ppm for H_2 and b.d.l and 18 ppm for CO (higher values for H_2 and CO in Table 4 refer to samples collected in steel samplers, which we do not consider reliable, as mentioned in section 2.). At Dziani Dzaha Lake, CO_2 is also the dominant gas species in two of the three analysed spots, with values up to 97.3%, while CH_4 is variable between 3897 and 81900 ppm, except in the third spot where it is dominant. H_2 and CO are generally present in low concentration.

The chemical composition of Mayotte gases is plotted in the ternary diagrams of Figure 18a, indicating the relative proportions of N_2 , He and Ar, which display a mixing trend between a He-rich component and an atmospheric component (air or air-saturated water – ASW). The bubbling gases from both areas at Mayotte show a variable degree of contamination by an atmospheric end-member, and its contribution is probably slightly higher for air than for ASW at least in BAS. On the whole, the He-Ar- N_2 variability falls within a typical compositional range of crustal gases, of which the two dominant mixing sources appear to be atmospheric and MORB-type mantle, and are well distinguished from typical

subduction-related gases, which have higher N_2/Ar ratios. With regard to the helium variability, the similarity between Dziani Lake and BAS is interesting, as there seems to be no appreciable difference in the air-MORB mixing. This suggests that shallow processes do not significantly affect helium abundances at Petite Terre.

The chemical composition in relation to the plot of CO_2-CH_4-He (Figure 18b) highlights that low temperature gas seeps of Petite Terre have a general high CH_4 concentration.

A relatively higher abundance of CH_4 in Dziani than in BAS tidal flat is likewise evident. Since 2020, the CO_2 -rich bubbling spots of the two sites show comparable abundances of CH_4 , and Dziani still hosts the only CH_4 -dominated bubbling area. The INGV-1 sample in Dziani is the most enriched in methane; however, it should also be noted that this specific sample is also affected by air contamination (Figure 15c, Table 4).

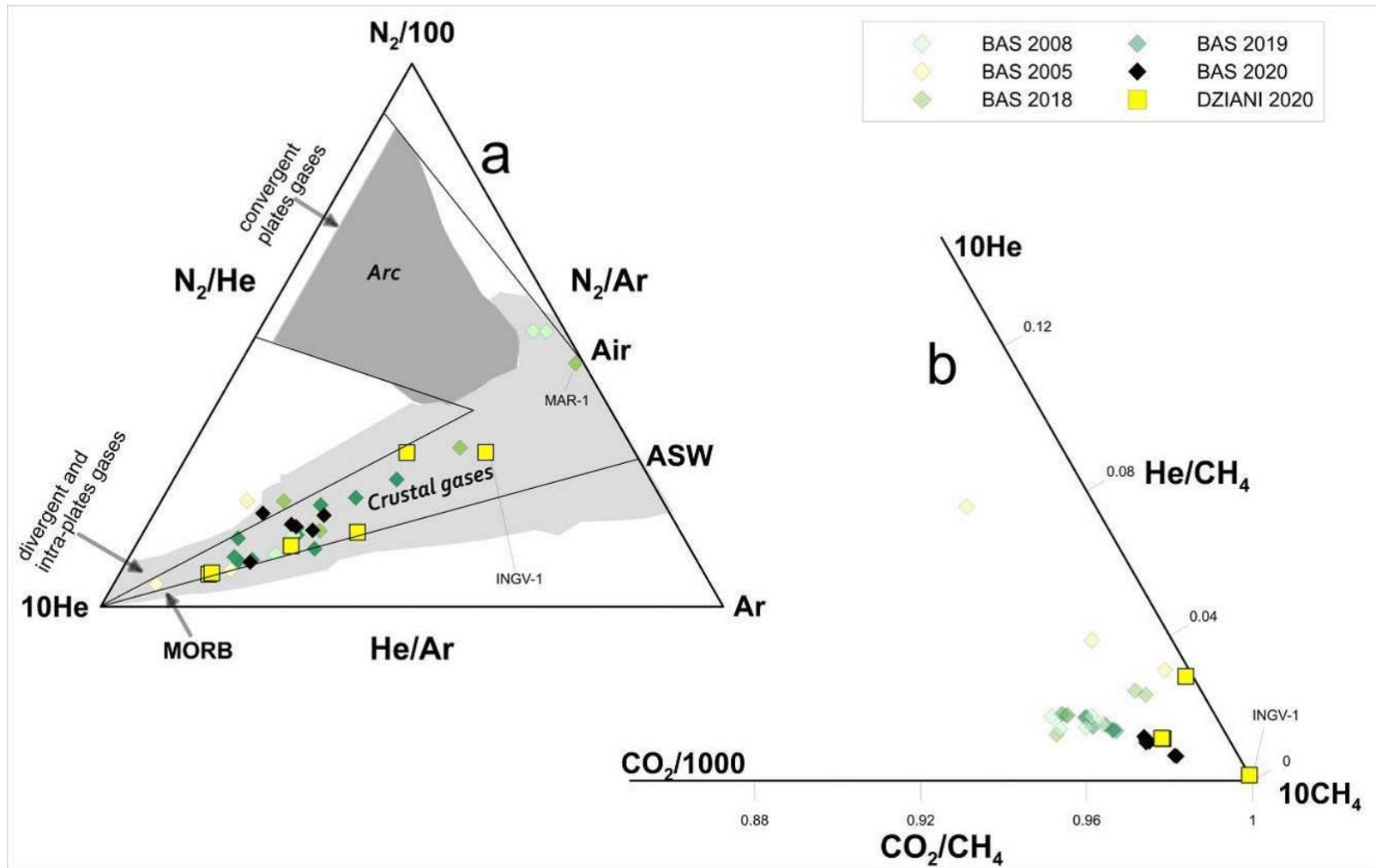


Figure 18 Relative proportion of He-Ar-N₂ in a ternary diagram on the left (a) showing also the areas of crustal gases and arc volcanism from literature. Data collected at Petite Terre show variable air and ASW contamination. In (b) CO₂-CH₄-He ternary diagram displays a relatively CH₄-enrichment of Petite Terre gases. Areas in different shades of grey distinguish gases from arc- and crustal geodynamic environments - from literature data.

8.2 Systematics of noble gas isotope ratios, CO₂ and CH₄ isotopes

Table 4 reports the isotopic compositions of noble gases, CO₂ and CH₄ of the sampled gases in the two bubbling areas of Petite Terre. Regarding the measured ³He/⁴He ratios, these vary between 5.45 and 7.5 Ra in BAS, and between 5.3 and 6.8 Ra in Dziani Dzaha Lake (Figure 19). It is worth of note that the range of R/Ra values is very similar between BAS and Dziani Lake, although it should be noted that less data are available for Dziani Dzaha and that they are only related to the 2020 campaign. In both BAS and Dziani Dzaha lake, a few samples show a clear air contamination as recorded by relatively high content of N₂ and O₂. It is possible that these samples underwent some issues during storage and transport to the laboratory that fractionated the ³He/⁴He, (for example MAR-1 Figure 19) leading us to exclude them for further discussion. Noble gases of the majority of the samples confirm a lack of a significant air contamination as previously indicated by the chemistry of these gases (Table 4). For instance, the ⁴He/²⁰Ne ratios is at least 2 orders of magnitude higher than the ratio in air (0.318). In the BAS area it reaches up to 1663 in our 2018-2020 dataset, and up to 2750 in BRGM Final report 2008, while it reaches up to 2122 in the Dziani Dzaha lake.

The ⁴⁰Ar/³⁶Ar values ranges from the atmospheric ratios up to 434 in BAS, and up to 468 in the Dziani Dzaha. The few air contaminated samples have lower ratios, like MAR-1 and MAN-2 in BAS site (⁴⁰Ar/³⁶Ar = 290 and 308; and ⁴He/²⁰Ne = 1.07 and 43.59, respectively), and INGV-01 in the Dziani Lake (⁴⁰Ar/³⁶Ar=306 and ⁴He/²⁰Ne = 33.3).

With the exception of a few air-contaminated samples, R/Ra and Rc/Ra bias is almost negligible.

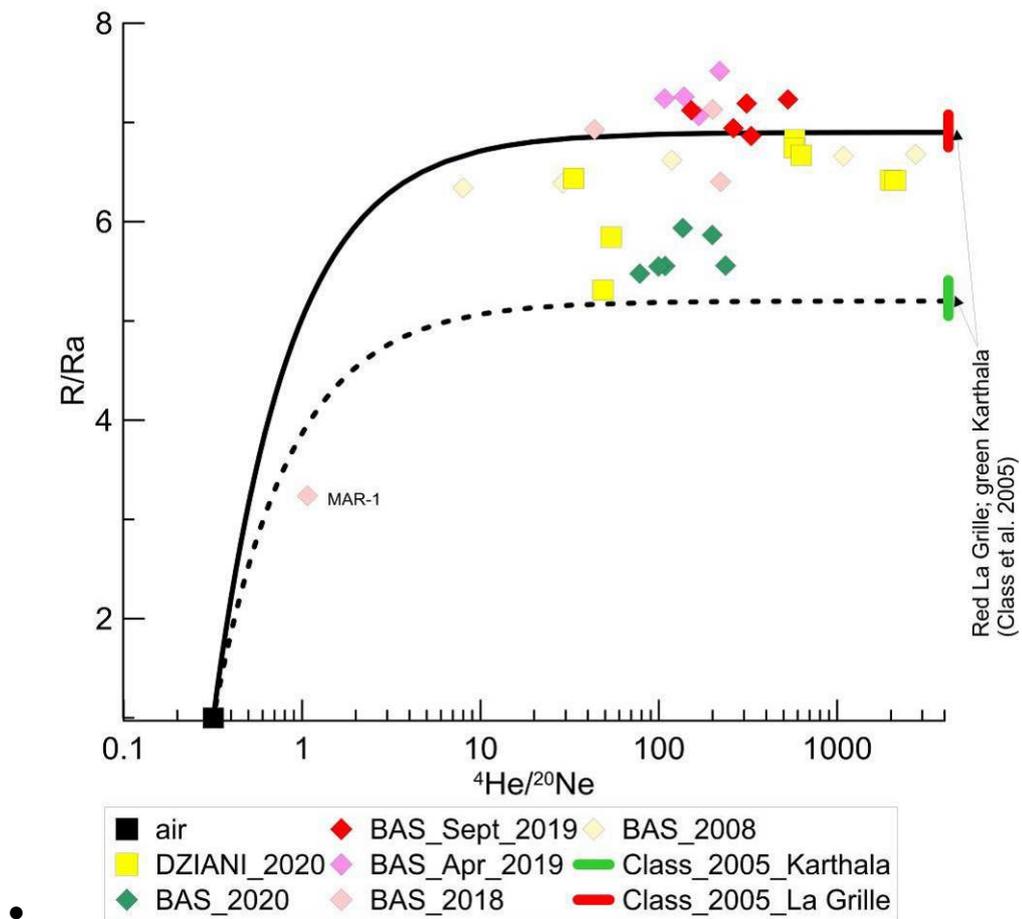


Figure 19 $^4\text{He}/^{20}\text{Ne}$ versus $^3\text{He}/^4\text{He}$ (R/Ra) in Mayotte bubbling gas. Thick and dash black lines indicating air-magma mixing are calculated from the average value [from Class et al., (2005)] of La Grille and Karthala fluid inclusions respectively [see also Liuzzo et al., 2021]. At the right side of the diagram are also indicated two solid red and green bars, corresponding to the range of the R/Ra variability of La Grille and Karthala fluid inclusions respectively [Class et al., (2005)].

The $^4\text{He}/^{40}\text{Ar}^*$ ratios of BAS gases range between 1.3 and 1.7, with a general overlap of values between different emissions and sampling periods, and they are within 1.1 and 1.5 in Dziani Lake, irrespective of the variable CH_4/CO_2 ratios. These values fall within the typical range of mantle production ratio ($^4\text{He}/^{40}\text{Ar}^* = 1-5$; Marty, 2012) and magmatic values from other geodynamic settings (e.g., Boudoire et al., 2018; Bräuer et al., 2013; Paonita et al., 2012; Rizzo et al., 2019).

The $^4\text{He}/^{40}\text{Ar}^*$ variability is commonly used to track magmatic degassing processes (e.g., Boudoire et al., 2018). $^4\text{He}/^{40}\text{Ar}^*$ ratios at Petite Terre do not show systematic variations as a function of location or time. Liuzzo et al. (2021) suggest that this homogeneous signature reflects that all bubbling spots are related to a single degassing source and pressure, likely related to magmas stored close to the mantle-crust underplating depth (15-20 km). This depth range corresponds to the shallower part of the magmatic plumbing system below

Mayotte, where evolved basanitic magma differentiate to form phonolitic melts (Berthod et al. 2021a,b);).

The C-isotope compositions of CO₂ ($\delta^{13}\text{C}_{\text{CO}_2}$) at BAS gases vary from -5.7‰ and -3.5‰ , where the most negative ratios are those measured in samples from MAN-1 and MAN-2 a sampling spot with relatively low gas flux and located close to a dense area of Mangrove trees. At Dziani Dzaha Lake the variability is much wider with $\delta^{13}\text{C}_{\text{CO}_2}$ spanning between -0.9 and -6.3‰ (data from this work), where the most negative value is that of the sample INGV-01 from the CH₄-rich plume. Previous data collected in 2016 from Milesi et al., (2019) show an even higher variability with $^{13}\text{C}_{\text{CO}_2}$ between -0.3 and -20.1 (the most negative correspond to G2 sample in Milesi et al., 2019). Figure 20a shows the $\delta^{13}\text{C}_{\text{CO}_2}$ distribution and highlights a significant separation of the isotope signature between the two bubbling areas, where Dziani Lake seem systematically more positive than BAS (with the exception of G2 not represented in the plot) and where the $\delta^{13}\text{C}_{\text{CO}_2}$ in BAS are confined in a narrow range of about 2 delta units.

With regard to the distribution of the C-isotope composition of CH₄ ($\delta^{13}\text{C}_{\text{CH}_4}$) (Figure 20b), the signature of BAS and Dziani partly overlaps each other with the BAS site showing a fairly narrow range of variability, (between about -25‰ and -10‰). At BAS, the least negative values are found in the MAN site (MAN-1 and MAN-2 samples), the latter of which is considered affected by gas-water dissolution by Liuzzo et al. (2021). Dziani lake shows a wider variation in $\delta^{13}\text{C}_{\text{CH}_4}$ fluctuating from minimum values of more than -65‰ (in G2 of Milesi et al., 2019) and maximum values of -11‰ . The different isotopic variability of carbon in a $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ space is evident in Figure 21, where the two markers are linearly and negatively correlated ($R^2 = 0.7$) in the BAS site and positively correlated in the Dziani lake. Interestingly our new dataset on Dziani lake clearly shows more negative $\delta^{13}\text{C}_{\text{CH}_4}$ values with respect to that of Milesi (2020).

The hydrogen isotopic composition of CH₄ ($\delta\text{D}_{\text{CH}_4}$) was measured in samples collected through Giggenbach bottles to enrich the concentration of CH₄ of dry gases. These samples yielded a δD of -118.1‰ and -137.8‰ V-SMOW, respectively in BAS and -124‰ and -184‰ V-SMOW in Dziani Lake.

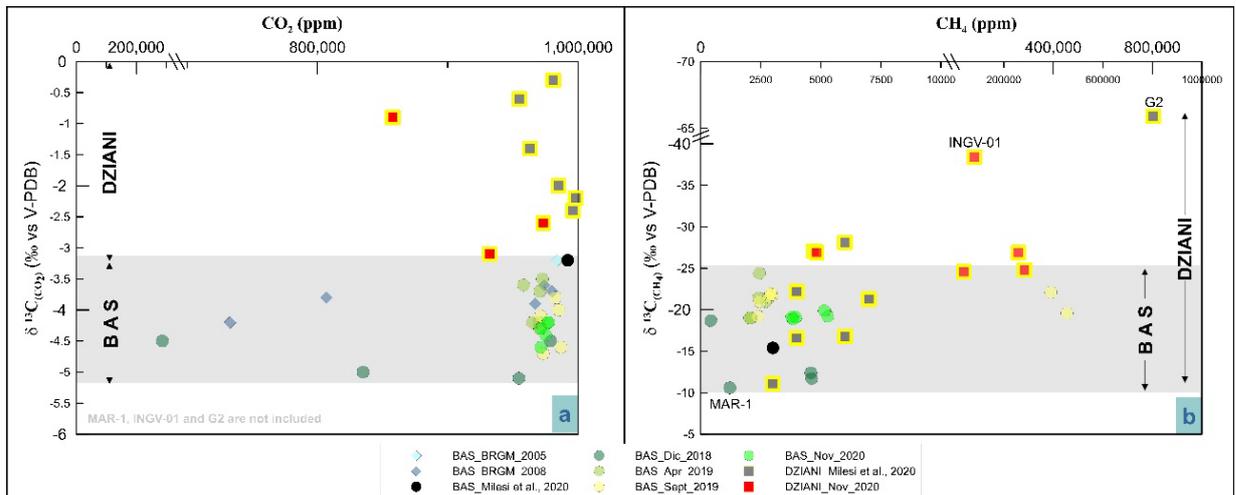


Figure 20. Comparison of carbon isotopic variability in CO_2 and CH_4 between BAS and Dziani Lake

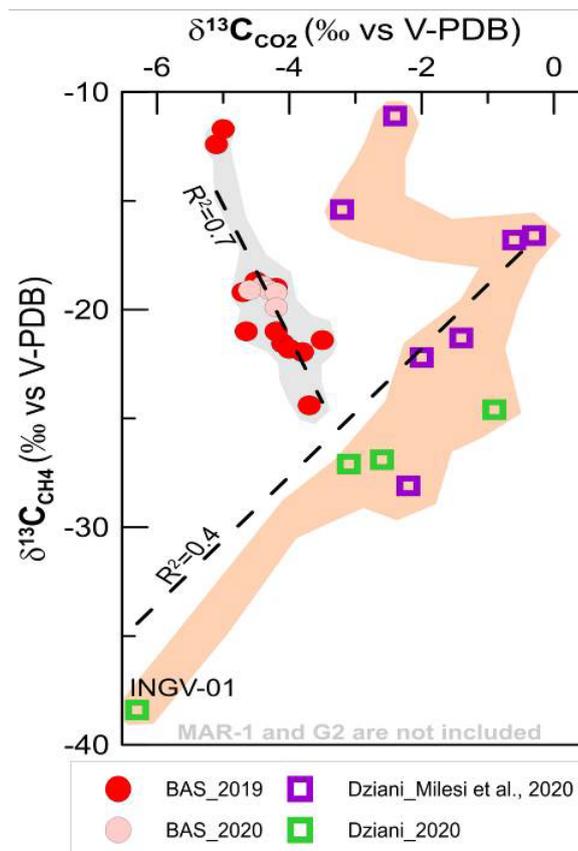


Figure 21. CO_2 vs CH_4 at BAS and Dziani Lake. It is noticeable the difference between BAS and Dziani Lake with the latter showing a much more scattered range of variability.

9. Discussion

9.1 CO₂ origin and gas-water interaction

In order to assess the origin of CO₂ and CH₄ rich gas emissions in Mayotte, we followed the approach used in Sano and Marty (1995) and we extended the dataset from the BAS area discussed in Liuzzo et al. (2021) with new gas acquisitions made in 2020 in BAS and in the Dziani Dzaha Lake. Therefore, to discriminate possible contributions from various origins (magmatic, organic and marine sediments), we considered the isotopic variability of carbon in CO₂ versus CO₂/³He ratio (Figure 22). The two mixing curves were modelled between the local mantle endmember resulting from the average values of our data (in which we only considered data that were not modified by secondary processes), data from literature (CO₂/³He= 5.0x10⁹ and δ¹³C=-4.3‰, Liuzzo et al., 2021) and an organic (δ¹³C=-25‰) and limestone endmember (δ¹³C=0‰) from Hoefs, (2015). For both organic and limestone carbon endmembers, a value of CO₂/³He=1.0x10¹³ is assumed. Finally, in order to evaluate the secondary processes of gas-water interaction, we have considered data corrected for air only for samples having N₂<22%, following the approach in Liuzzo et al. (2021).

The distribution of the data for the two degassing areas at Petite Terre shows clear differences. With the exception of the MAN-1 and MAN-2 samples, the BAS area shows little variability in bulk chemistry and C isotopy and are reasonably interpretable as being related to a mantle-like outgassing process. Conversely, the gas samples from the Dziani Lake area have a larger scattering.

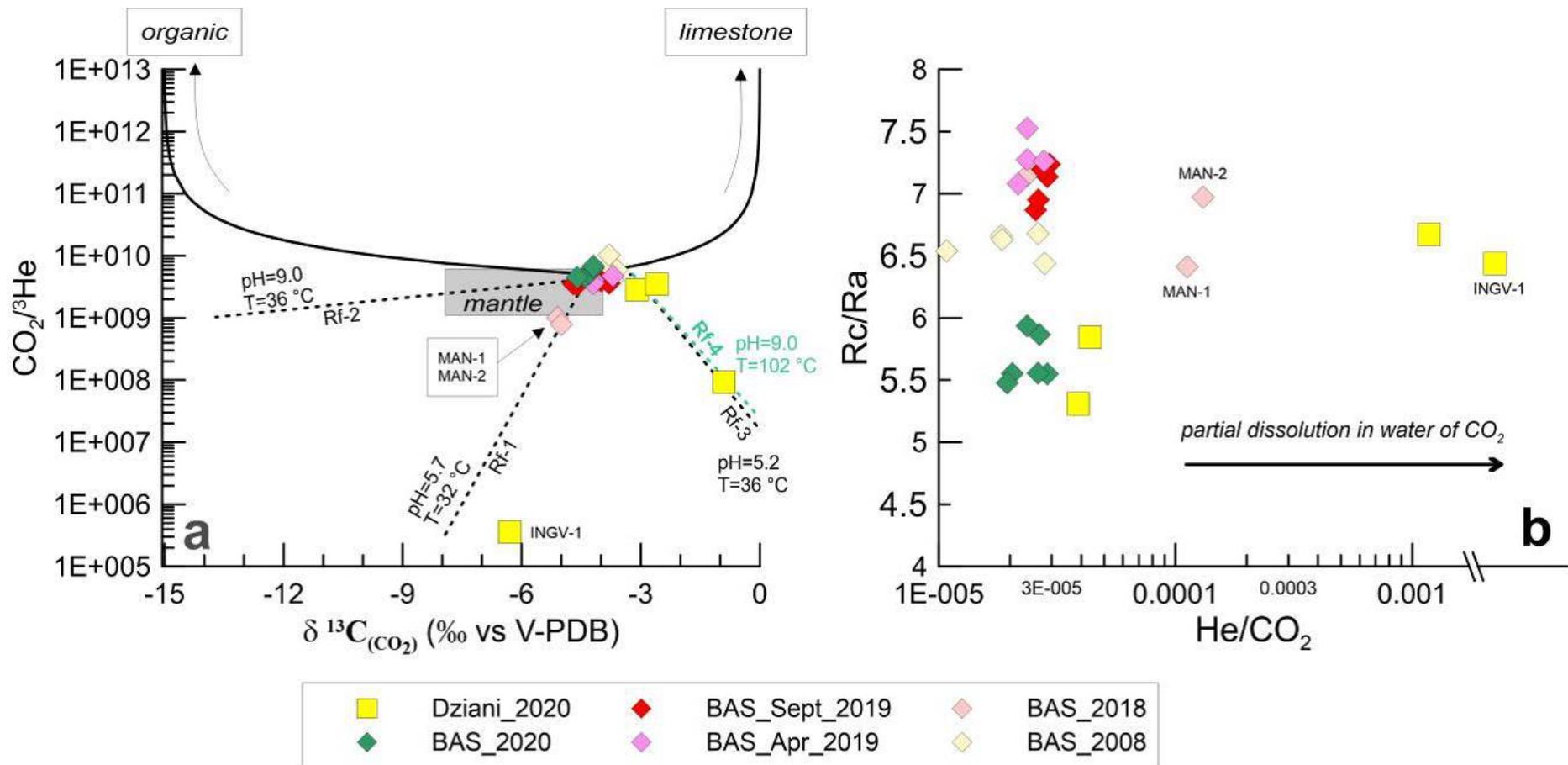


Figure 22. In (a): $\delta^{13}\text{C}$ of CO_2 versus $\text{CO}_2/{}^3\text{He}$ diagram of fumaroles and bubbling gases at Petite Terre (Mayotte). In (b): He/CO_2 versus R_c/R_a . Diagram 6a shows that gases at Petite Terre are in the field of mantle-like origin with no evident organic or limestone contributions. Solid lines are mixing curves between organic, mantle and limestone endmembers, while the dashed line indicates a Rayleigh fractionation (Rf) related to gas dissolution in water having four different pH-T conditions (see text for interpretation). Diagram 6b displays a variable degree of water-gas interaction controlling CO_2 variability.

In the case of gases from the Dziani Dzaha lake, gas-water interaction may have had an important effect as also highlighted in Liuzzo et al. (2021) for some samples of the BAS area. In fact, the variability of He/CO₂ vs Rc/Ra shown in Figure 22b, evidences a possible CO₂ partial dissolution in water played a role in the Dziani Lake emissions. Four possible Rayleigh fractionation curves were modelled assuming a gas dissolution in water under equilibrium conditions (Appendix A equation 3). However, whereas in the case of the BAS zone a simple dissolution process can be assumed (MAN 1-2 curve Rf-1) (Liuzzo et al., 2021), in the case of Dziani Lake, a single dissolution step underlying the measured scattering is not realistic. In fact, if we consider the typical parameters of the Dziani lake (pH=9 and temperature of 36 °C from Milesi et al. (2020)) the corresponding curve Rf-2 calculated clearly does not fit with any Dziani data. A possible balance between temperature and pH that can fit with the Dziani gases might be achieved at temperatures of 32-36°C, but requires a much more acid pH of about 5.2-5.7. This condition excludes the possibility of fractionation occurring in the water column of the Dziani lake. If, on the other hand, a possible fractionation in equilibrium with the lake's pH of about 9 is taken into account, the temperature required to obtain a good fit on the data (Rf-4 path) should be about 102°C. However, these temperatures are not realistic, nor have such temperature anomalies ever been found in any of the surveys performed in the lake before or after the beginning of the seismic crisis. This leads to the conclusion that the gaseous emissions from Dziani Dzaha may undergo gas-water interaction processes under non-equilibrium conditions and/or the occurrence of other fractionation processes. Among these, in Lake Dziani Dzaha an isotope exchange between $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{TDIC}}$ could lead to less negative isotopic values measured at Dziani Dzaha if we consider that water lake reaches DIC concentrations up to 0,2 mol/L and $\delta^{13}\text{C}_{\text{TDIC}}$ up to +13‰ (Cadeau et al., 2020). This hypothesis remains speculative at this time, but could be better evaluated with future data acquisition that might define possible clearer trends. Nevertheless, the variability of He/CO₂ vs Rc/Ra shown in Figure 22b, evidences that a possible partial dissolution in water played a role in the Dziani Lake emissions, and appears to be notably extreme in the CH₄-rich INGV-1 sample. In particular, this sample is collected in correspondence of the deepest portion of the lake (Figure 15c), and as already noted for sample G2 in Milesi et al. (2020), may have been significantly affected by the higher water column. All of these effects need to be evaluated and eventually filtered out in order to calculate the thermobarometric conditions of the hydrothermal system feeding the gas seeps (see next section), as it has been recognized in

other studies of hydrothermal gases (Capasso et al., 2005; Gilfillan et al., 2009; Rizzo et al., 2019). In fact, the $\text{CO}_2/{}^3\text{He}$, He/CO_2 , CH_4/CO_2 , ratios and $\delta^{13}\text{C}$ isotopic signature can be potentially modified by oxydation/reduction reactions and/or by gas-water interaction in which CO_2 dissolves preferentially with respect to the other species.

9.2 CH_4 origin and $\delta^{13}\text{C}$ versus δD variability

For the data collected in the 2019-2020 campaigns, it was possible to define the isotopic signature of carbon and hydrogen in methane in both BAS and the Dziani Dzaha Lake sites and compare them with previous data of Dziani Dzaha Lake from Milesi et al. (2020). The results are plotted a classification diagram proposed by Schoell (1980) (Figure 23). It must be stressed that distinguishing between methanogenesis processes of biological origin, or thermogenic processes at the origin of CH_4 (Mazzini et al, 2011; Schoell, 1980; Welhan, 1988) is complicated by the possible mixing between endmembers with different isotopic signatures (Taran et al. 2010), or by the occurrence of oxydation processes (e.g., Batista Cruz et al., 2019).

Although with some relative variability, the isotopic signature of methane in BAS is placed in the field of abiogenic origin, together with sample G7, acquired in 2016 in this area by Milesi et al. (2020). This confirms that outgassing in the BAS tidal area originate from a homogeneous and unique source, particularly if we also take into account the stable and low variability of Rc/Ra and $\delta^{13}\text{C}-\text{CO}_2$ values (Figures 19, 20 and 21). The situation in the Dziani Dzaha Lake seems to be different. The CH_4 -rich G2 sample corresponds to a gas that has clearly undergone a reduction process by microbial methanogenesis, as already highlighted in Milesi et al. (2020). Our INGV-01 sample from this area (Table 4), as shown in Figure 22b, has probably undergone a strong interaction in water or in the sediments (the bubbling in INGV-1 emerges from the deeper portion of the lake). The isotopic characteristics of methane for this sample can be consistent with a thermogenic origin or mixing between abiogenic and biogenic end-members. In the Dziani lake, the isotopic signature of the CH_4 -rich bubbling is thus distinct from that of the CO_2 -rich area, like G3, which have similar abiogenic characteristics to the samples in BAS, but with the less negative proportion of δD . The remaining samples from the 2020 campaign in Dziani Lake appear to be intermediate between abiogenic and thermogenic fields (DZN 1 -2; OVPF-5;

DZW 1-4). The variability of methane isotopic characteristics with respect to outgassing in Dziani Lake thus appears to be much more complex than measured in BAS, which is confirmed also by the wider variability in $\delta^{13}\text{C}$ signature in CO_2 (Figures 20, 21). That again suggests that several processes may operate in the lake to produce a larger chemical and isotopic variability with respect to the more homogeneous BAS area.

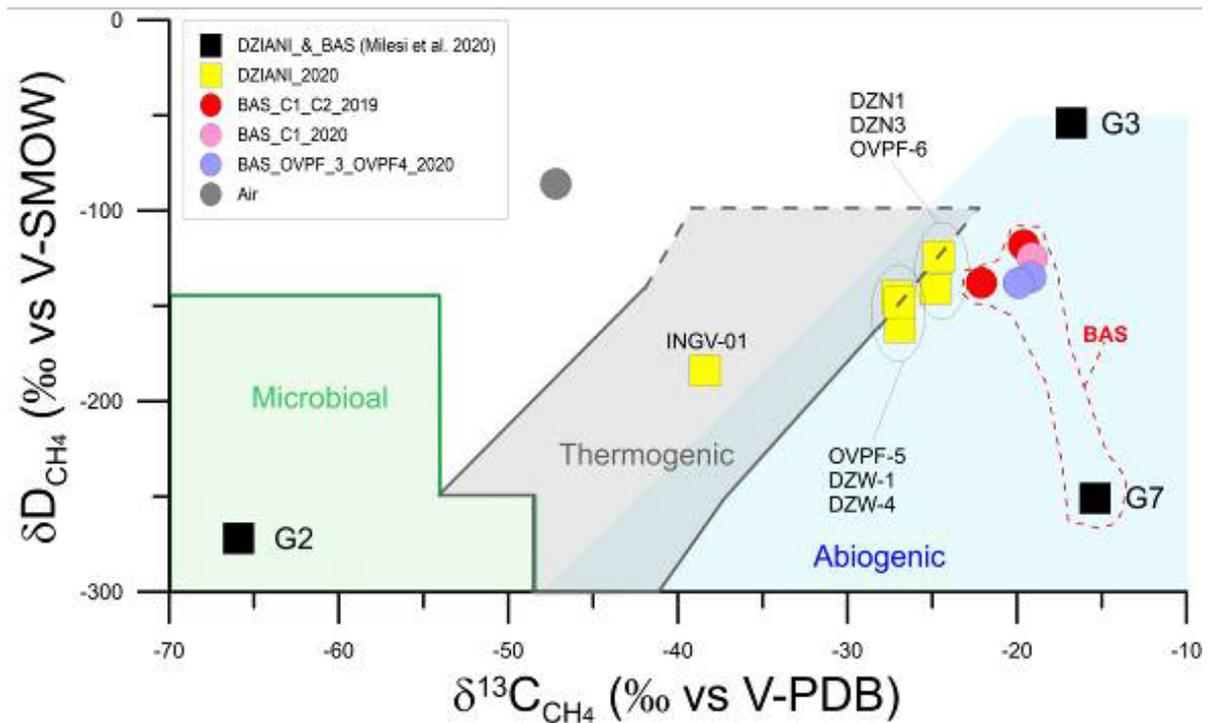


Figure 23. $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta\text{D}_{\text{CH}_4}$ diagram (modified from Schoell (1980)). G2, G3 and G7 data acquired in 2016 from Milesi et al., (2020).

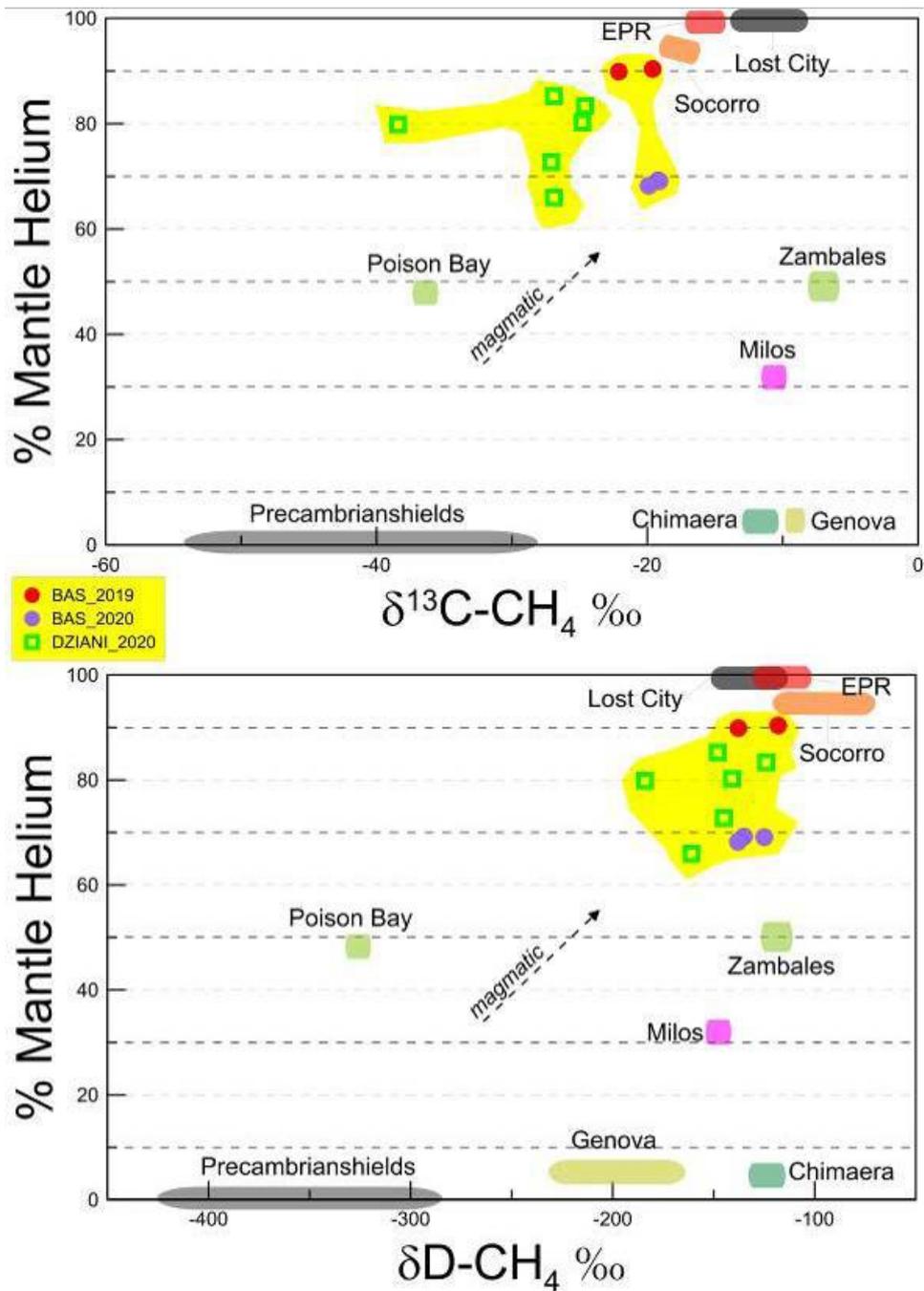


Figure 24. $\delta^{13}\text{C}$ and δD in CH_4 vs mantle %He. The Petite Terre data are compared with a larger dataset of various geodynamic origins from Etiope & Sherwood Lollar (2013), and appear consistent with environments where methane of magmatic origin is recognised.

It is therefore clear that further data are needed to better constrain the origin of methane in the Dziani Dzaha lake, and we are aware that the debate on methane origin is open within the scientific community, in particular in order to justify its possible abiotic origin assuming a “magmatic” or “late magmatic” origin (Etiope & Sherwood Lollar, 2013). However, answering this question is not trivial, considering that the recent submarine eruption only 50 km off-shore from Petite Terre represents by far the largest known

submarine eruption until now (Feuillet et al., 2021; Berthod et al., 2021). In this context, a further clue is given by the isotopic signature of helium involved in the outgassing process at Petite Terre, which can be useful in discerning and assessing the deep origin of the gas. Therefore, we considered the isotopic variability of methane by comparing it with the percentage of mantle-related helium, following the approach indicated in Etiope & Sherwood Lollar (2013) (Figure 24). In our case, the Petite Terre gases fall within the area where magmatic CH₄ inputs are recognised (EPR - East Pacific Rise, Socorro, Lost City (Proskurowski et al., 2008; Taran et al., 2010a; Welhan and Craig, 1983)). This leads us to conclude that it is not improbable that input of gas of magmatic origin may reasonably have contributed to the general outgassing at Petite Terre, and specifically even regarding a not negligible contribution of methane, which in turn, particularly in the Dziani Dzaha lake area, has undergone further transformation processes by microbial activity.

9.3 Equilibrium temperature of hydrothermal gases

The elemental composition of the gases of Petite Terre show a general low concentration of H₂ and CO in both BAS and Dziani Lake areas. Therefore, although H₂ and CO are considered useful geo-indicators for equilibrium temperature and pressure in the hydrothermal system, we did not consider here it suitable for thermobarometric purposes. On the contrary, the amounts of CO₂ and methane (Table 4) are high enough to have good analytical precision in both concentration and isotopic data. Therefore, we used the approach adopted by Liuzzo et al. (2021), assuming that in the hydrothermal system an equilibrium is attained between the dominant species H₂O-H₂-CO₂-CO-CH₄, in which the formation of methane is favoured by the decreasing temperature from the reaction (4) indicated in Appendix A.4. For this system, the temperature has been calculated assuming a condition of thermal equilibrium between CH₄ and CO₂ by the equation (5) in Appendix A.4 as proposed by Giggenbach (1992). Moreover, to explore the possible evidence of recent input of deep fluids in the Mayotte hydrothermal system, we evaluated the thermal equilibrium in combination with their isotopic signatures based on their $\delta^{13}\text{C}$ isotopic fractionation factor between CO₂ and CH₄. To this aim, we combined the temperatures obtained from the equation (5) with the temperatures calculated using the equation (6) proposed by Bottinga (1969), valid for temperatures ranging between 0-700 °C (Appendix A.4), following the approach proposed in Ono et al. (1993), and recently applied in the

Comoros area by Liuzzo et al. (2021), finally obtaining the equation (7). On this basis, the curves of thermal equilibrium were modelled assuming that both chemical and isotopic equilibrium is maintained with a fixed $\delta^{13}\text{C}_{\text{CO}_2}$ representative of the possible range of magmatic signature; here we considered a range of $\delta^{13}\text{C}_{\text{CO}_2}$ magmatic signatures from -4‰ to -8‰ when coupling the equations (5) and (6).

The results are shown in Figure 25, which allows to extend the preliminary study made by Liuzzo et al. (2021), considering recent gas sampling in 2020 at both BAS and the Dziani Dzaha lake areas of Petite Terre. The data considered are those in which there are no obvious secondary variations and/or gas-water interactions.

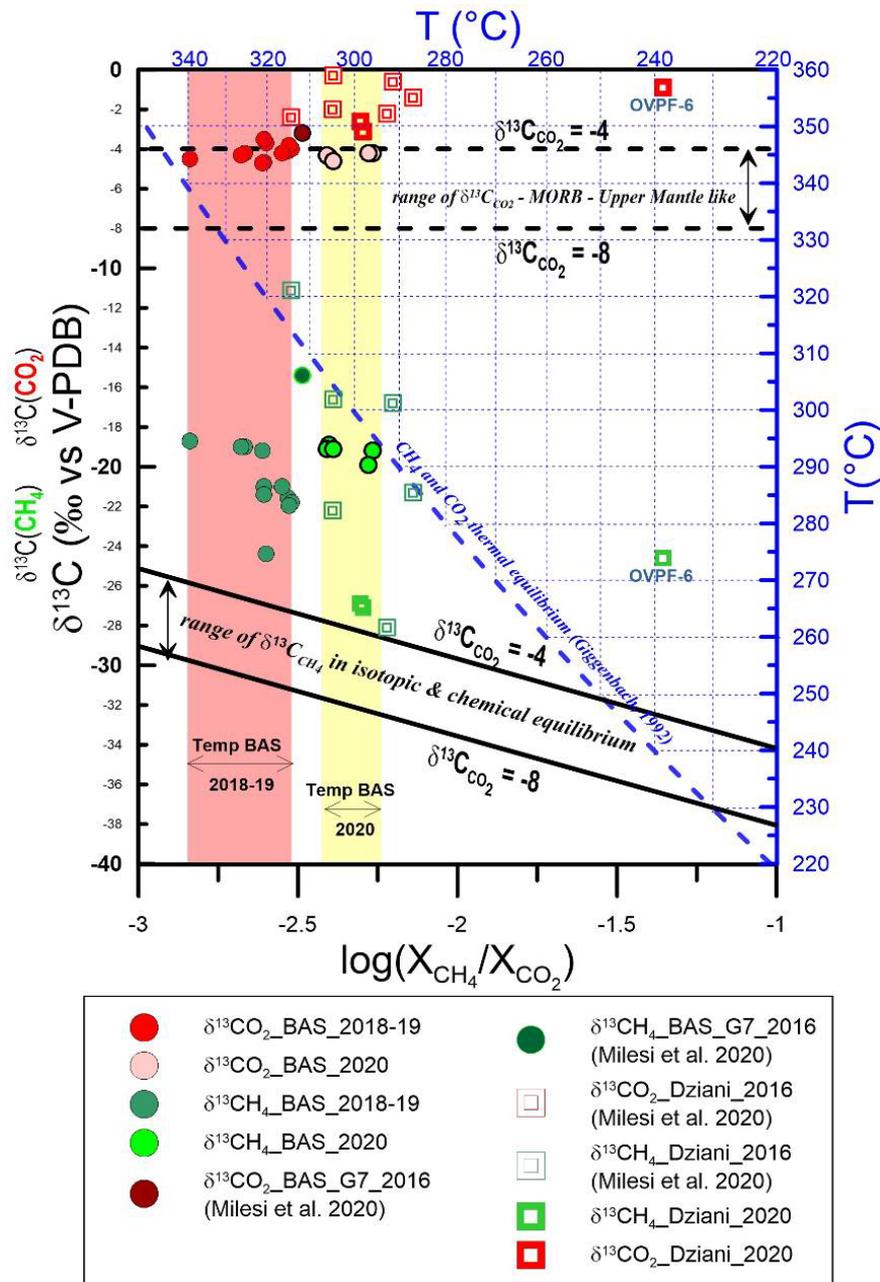


Figure 25.- $\delta^{13}\text{C}$ for CO_2 (red) and CH_4 (green) versus $\log(X_{\text{CH}_4}/X_{\text{CO}_2})$ of Petite Terre bubbling gases. Red and yellow area are referred to the range of temperature of the samples in collected in BAS area between 2018 and 2020. The blue dashed line correspond to the CH_4 and CO_2 thermal equilibrium expressed in equation (5) Appendix A.4 (Giggenbach, 1992), the thick black lines are calculated as the equation (7) Appendix A.4 for isotopic and chemical equilibrium between CH_4 and CO_2 for two cases of $\delta^{13}\text{C}(\text{CO}_2)$ corresponding at -4% and -8% which in turn are indicated as black dashed lines.

The methane-rich gases at the Dziani Lake are certainly conditioned by the microbial activity in lacustrine waters and sediments; the range of variability of $\delta^{13}\text{C}_{(\text{CH}_4)}$ and δD is high, and the values are generally scattered. The variability of $\delta^{13}\text{C}_{(\text{CO}_2)}$ is less extensive than for $\delta^{13}\text{C}_{(\text{CH}_4)}$; however, Dziani Lake $\delta^{13}\text{C}_{(\text{CO}_2)}$ gases show a wider range of variability than BAS. As noted in the previous sections, this leads us to conclude that outgassing in Dziani Lake is probably affected by several phenomena and not due to a single source of degassing. It is rather a variable degree of mixing between organic and abiotic components which may

probably have determined the measured isotopic variability (Milesi et al., 2020). Figure 25 also shows that isotopic equilibrium is not reached between CO₂ and CH₄, as all sampled gases at Dziani Lake have variable $\delta^{13}\text{C}_{(\text{CH}_4)}$ values above the calculated equilibrium curves. Bacterial oxidation of CH₄ can explain isotopic fractionation, determining an increase in the isotopic ratio in the residual methane (Baker and Fritz, 1981; Coleman et al., 1981; Horita, 2001), and this process may be significant in the Dziani lake, where the widest isotopic variability is recorded.

Regarding the BAS area, the range of variability of $\delta^{13}\text{C}_{(\text{CH}_4)}$ is consistent with an abiogenic source (Schoell, 1980), and the data also show moderate variability in their isotopic signature. Therefore, the degassing source at BAS can be reasonably considered unique. In the 2020 samples, however, a significant shift of the methane toward heavier isotopic concentrations, as observed in Liuzzo et al. (2021) is still evident. Although a carbon isotopic fractionation of methane cannot be excluded in BAS area as in Dziani Lake, Liuzzo et al. (2021) has shown that a possible quenching effect may be considered relevant on the isotopic signature of hydrothermal gases at BAS area. This assumption considers CO₂ and CH₄ initially in isotopic equilibrium at their original source, supposed to be from significant depth. However, during the ascent of the gas to shallow crustal layers, there may not be enough time for the isotopic readjustment, thus preserving the original isotope ratios. Such a quenching effect is also justifiable by the faster rate of re-equilibration (about 100 times) of the chemical system than the isotopic system (Giggenbach, 1982). This possible quenching effect appears to have continued in 2020 where the thermal isotopic disequilibrium between CO₂ and CH₄ is comparable to the 2018-19 samples. Hence, as assumed in Liuzzo et al. (2021) also for the 2020 samples, the corresponding source gas temperatures could be even higher than those calculated from the equilibrium obtained from equation (5).

While these assumptions may remain speculative, it seems reasonable to suppose that the hydrothermal system at BAS may have received deep-hot CO₂ and CH₄-rich gas inputs at the beginning of the volcanic activity in 2018.

In addition, the thermal variation over time is particularly significant. Figure 26 shows the trends over time of the temperature calculated with equation (5) in both BAS and Dziani Lake. The most relevant fact is that, at least for BAS, a well-defined and decreasing trend can be observed between 2018 and 2021. The temperature of Lake Dziani appears to follow

the same decreasing trend as BAS, however it should be noted that any interpretation here is difficult because the gas at Dziani may have undergone secondary processes, mentioned earlier, and that less data are available. However, it is noteworthy here to mention that the seismic activity progressively decreased since May 2018 together with the magma extrusion rate (Bachèlery et al., 2019; Berthod et al., 2021a, 2021b; Cesca et al., 2020; Feuillet et al., 2021; Lemoine et al., 2020; REVOSIMA, 2019; REVOSIMA Monthly Bulletin, December 2021). It is therefore reasonable to assume that a deep fluid input, which was somehow related to the most intense phase of submarine eruptive activity, may have reached the outgassing areas of Petite Terre, resulting in the increase of temperature in the hydrothermal system, which then over time fell steadily, as the eruptive intensity decreased.

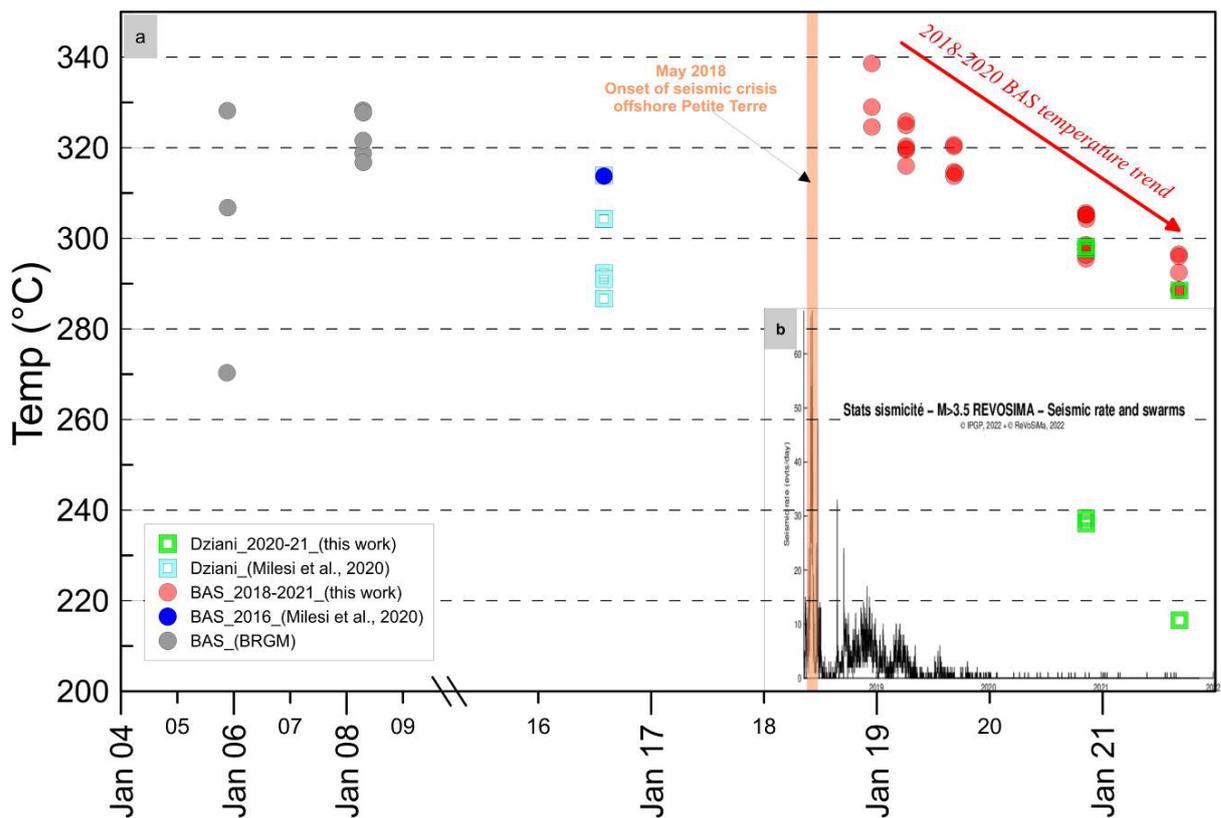


Figure 26 – (a) Temperature-time variations calculated by using equation 4 from Giggenbach, 1992 (Appendix A.4) for all the samples of Petite Terre. In box (b), overlaid in time, the seismicity rate (event/day) for M>3.5 earthquakes [from REVOSIMA Monthly Bulletin - December 2021]

10. Conclusions

This study has investigated the geochemistry of the two low-T bubbling areas at Petite Terre, BAS (Airport tidal flat) and Dziani Lake, and has given insights into the origin of the emitted hydrothermal fluids.

It seems plausible that the gas reaching Petite Terre is connected to the shallower part of the magmatic plumbing located near the Moho at about 17 km b.s.l. (Berthod et al., 2021a, 2021b) (Figure 27a). This inference stems from the homogeneous and low He/Ar* ratios of Mayotte gases and the absence of crustal signature in their chemical and isotopic signatures. The magmatic system located at crustal underplating depth seems to have been affected by an arrival of CO₂-He rich fluids from the deeper plumbing system (around 36-50 km depth), which is at the origin of the ongoing basanitic volcanism (Berthod et al. 2021a, 2021b). Both the deep and the shallow plumbing systems were involved in the recent submarine eruptive activity responsible for the construction of the recent volcanic edifice about 50 km offshore Petite Terre (Berthod et al., 2021a ; Cesca et al., 2020; Feuillet et al., 2019; Lemoine et al., 2020). The change in fluid input and composition translates also in higher equilibrium temperatures of the crustal hydrothermal system in 2018, which then recorded a constant cooling over time during the decrease of the seismo-volcanic activity.

The gases detected in both the BAS and Lake Dziani reflect primarily the signature of deep gases in terms of geochemical tracers such as R/Ra $\delta^{13}\text{C}$ in carbon and methane (Figure 27b), however they were also affected by secondary effects that produce the variability we observe in the two areas. The Dziani Dzaha lake gases, which range from CO₂- to CH₄-dominated, are variably and in some cases significantly affected by microbial activity in a meromictic lake environment. In the BAS tidal area, the influence of the microbial activity and of the gas-water interaction is certainly less significant. This resulted in a significant difference in the methane isotopic signal and pH, which is quite distinct in the two degassing environments. Conversely, the He content and signature seems less affected by late-stage processes.

An important implication of the recognition of deep gases related to the several stages of the magmatic plumbing system in the BAS area, make this area an extremely important sector for volcano monitoring purposes.

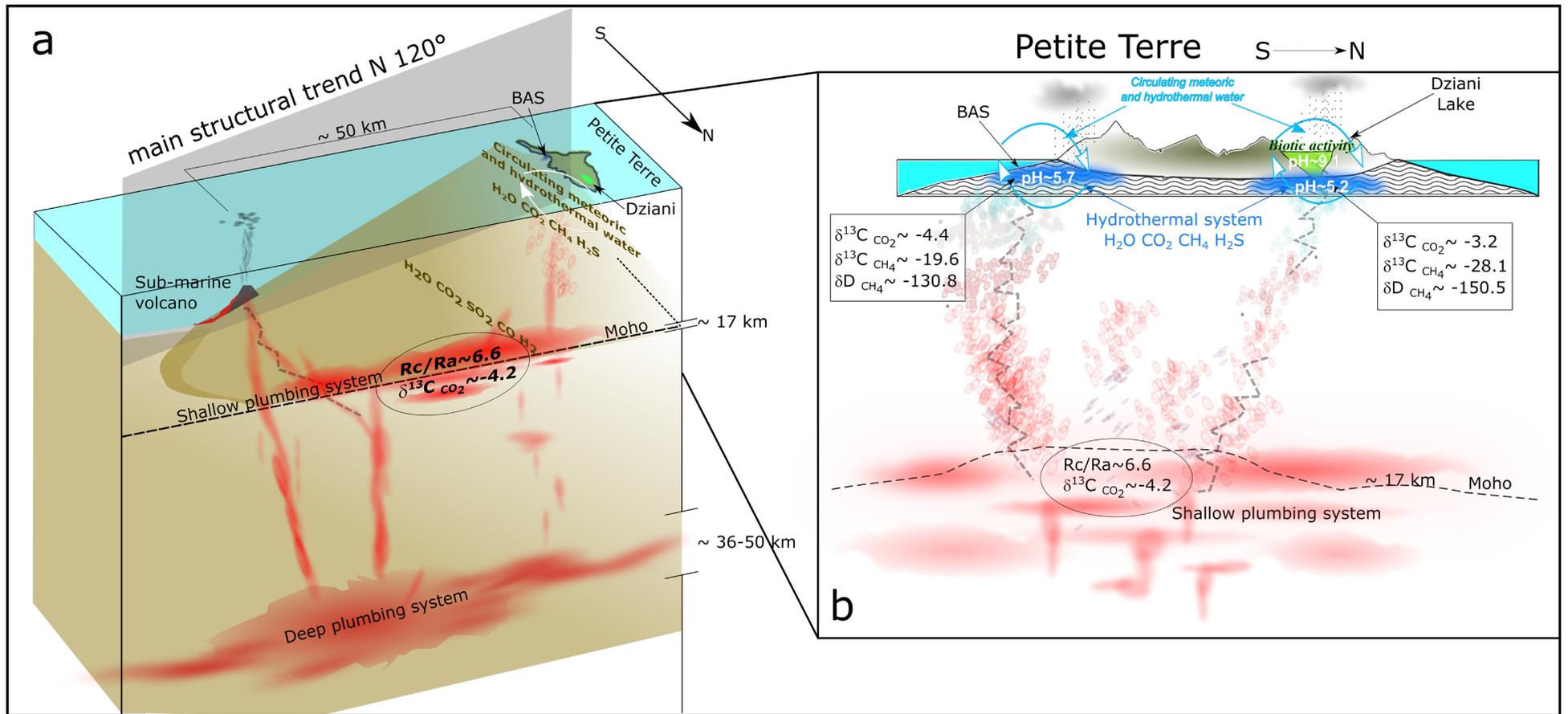


Figura 27 - (a) Conceptual diagram of the deep and shallow hydraulic system (modified by Berthod et al., 2021a and 2021b) beneath Petite Terre Island. (b) Detail of the interaction of magmatic fluids reaching the two outgassing areas BAS and Lake Dziani.

Appendix

A1. Rc/Ra calculation

The $^3\text{He}/^4\text{He}$ ratio is expressed as R/Ra (being Ra the He isotope ratio of air and equal to $1.39 \cdot 10^{-6}$) with an analytical uncertainty (1σ) below 0.3%. The $^3\text{He}/^4\text{He}$ ratio corrected for atmospheric contamination has been calculated using the measured $^4\text{He}/^{20}\text{Ne}$ ratio following Sano and Wakita, (1985) and is reported in units of Rc/Ra, as follows:

$$\frac{R_c}{R_a} = \frac{\left(\frac{R_m}{R_a}\right) \cdot \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_m - \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_a}{\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_m - \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_a} \quad (1)$$

where subscripts m and a refer to measured and atmosphere theoretical values respectively [(He/Ne) $_a$ = 0.318 (Ozima and Podosek, 1983)]. As consequence of a very low air contamination the correction on the $^3\text{He}/^4\text{He}$ ratio is small or negligible for most of the gas samples ($^4\text{He}/^{20}\text{Ne})_m \gg (^4\text{He}/^{20}\text{Ne})_a$.

A2. Argon correction

^{40}Ar was corrected for air contamination ($^{40}\text{Ar}^*$) in samples showing $^{40}\text{Ar}/^{36}\text{Ar} > 315$ assuming that the ^{36}Ar present derived from atmosphere, as follows:

$$^{40}\text{Ar}^* = ^{40}\text{Ar}_{\text{sample}} - ^{36}\text{Ar}_{\text{sample}} \cdot \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{\text{air}} \quad (2)$$

A3. $\delta^{13}\text{C}_{\text{CO}_2}$ calculation in a Rayleigh fractionation under dissolution equilibrium

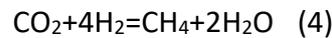
In order to constrain the pristine C isotopic signature of CO_2 in Mayotte, we modelled a Rayleigh fractionation assuming a dissolution under equilibrium conditions based on the approach used in Rizzo et al. (2019) and Liuzzo et al. (2021) for the application in the previous study for Comoros Archipelago. The Clark and Fritz (1997) equation is as follows:

$$\delta^{13}\text{C}_{\text{CO}_2} = (\delta^{13}\text{C}_{\text{CO}_2})_0 + \varepsilon \ln(f) \quad (3)$$

where the subscript 0 indicates the initial CO_2 isotope composition and f is the fraction of the residual gas phase, while ε is the fractionation factor between DIC (dissolved inorganic carbon) and gaseous CO_2 ($\text{CO}_{2(g)}$). In turn, ε depends on water temperature and pH, which are unknown, therefore, for our purpose the values of temperature and pH has been chosen which better approximate our dataset corresponding to $T=32^\circ\text{C}$ and $\text{pH}=5.7$ and it is plotted in figure 22a +as curve Rf-1. These values correspond to those measured in the marine water of the Mayotte tidal flat by BRGM surveys (Sanjuan, 2008; Traineau, 2006). The curve Rf-2 have been calculated using a $\text{pH}=9$ and $T=36^\circ\text{C}$, while for Rf-3 $\text{pH}=5.2$ and $T=36^\circ\text{C}$; and for Rf-4 $\text{pH}=9$ and $T=102^\circ\text{C}$ (where $\text{pH}=9$ and $T=36$ have been measured in Dziani Lake water by Milesi et al. (2020)).

A4. Equilibrium temperature

Assuming that in the hydrothermal system an equilibrium is attained between the dominant species $\text{H}_2\text{O}-\text{H}_2-\text{CO}_2-\text{CO}-\text{CH}_4$, methane can form inorganically from the reaction:



where the formation of methane is favoured by the decreasing temperature. For this system we assumed as a condition of thermal equilibrium between CH_4 and CO_2 the equation proposed by Giggenbach (1992):

$$\log (X_{\text{CH}_4} / X_{\text{CO}_2}) = 4625/(t_e+ 273) -10.4 \quad (5)$$

The equilibrium temperature for the isotopic fractionation of $\delta^{13}\text{C}$ between CO_2 and CH_4 is calculated using the equation proposed by Bottinga (1969) valid for temperatures ranging between $0-700^\circ\text{C}$:

$$\Delta=22166/(t_e+273)-13.8 \quad (6)$$

where Δ is the difference between $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ values.

In Figure 25 the thick black lines were modelled assuming that both chemical and isotopic equilibrium is maintained with a fixed $\delta^{13}\text{C}_{\text{CO}_2}$ corresponding to the range of magmatic signature, here -4‰ and -8‰ (dashed black lines) by coupling the equations (5) and (6):

$$\log \left(\frac{X_{\text{CH}_4}}{X_{\text{CO}_2}} \right) = \frac{4625 (\Delta+13,8)}{22166} - 10.4 \quad (7)$$

TABLE OF DATA

Table 4: Chemical composition of major and minor gaseous components and isotopic values from bubbling area at Petite Terre.

Sampling Date	Sample	Lat	Long	Site	Major (Raw)							δ13C (‰)		δD (‰)
					CO2 (Vol%)	CO (ppmv)	CH4 (ppmv)	N2 (Vol%)	O2 (Vol %)	H2 (ppmv)	He (ppmv)	CO2	CH4	CH4
08/11/2020	OVPF-1	-12.8002	45.2874	BAS	97.5	0.8	3859.0	0.7	0.1	18.0	26.0	-4.4	-18.9	
08/11/2020	C1a1-glass	-12.8002	45.2874	BAS	51.8	1.3	2046.0	36.9	10.0	3.8	13.0			
08/11/2020	OVPF-2	-12.8002	45.2874	BAS	97.2	0.6	3787.0	0.6	0.2	17.0	23.0	-4.3	-19.1	
08/11/2020	C2a2-glass	-12.8002	45.2874	BAS	0.9	1.4	16.0	76.4	20.4	4.0	4.7			
08/11/2020	OVPF-3	-12.8002	45.2895	BAS	97.7	36.0	5291.0	0.5	0.0	82.0	20.0	-4.2	-19.2	-135.0
08/11/2020	GD-1	-12.8002	45.2895	BAS	49.5	1.5	2495.0	38.7	10.4	3.7	9.0			
08/11/2020	OVPF-4	-12.8002	45.2895	BAS	97.7	bdl	5145.0	0.6	0.1	218.0	19.0	-4.2	-19.9	-138.0
08/11/2020	GD-2	-12.8002	45.2895	BAS	73.6	bdl	3600.0	20.7	5.4	2.4	13.0			
10/11/2020	C1-b1	-12.8002	45.28736	BAS	97.1	bdl	3958.0	0.7	0.1	28.0	28.0	-4.6	-19.1	-125.0
10/11/2020	C1-b2	-12.8002	45.28736	BAS	98.8	bdl	3907.0	0.4	0.1	bdl	26.0			
09/11/2020	OVPF-5	-12.7708	45.2858	DZIANI	93.2	bdl	4707.0	3.3	1.2	11.0	41.0	-3.1	-27.1	-145
09/11/2020	DZW-1	-12.7708	45.2858	DZIANI	97.3	0.3	4825.0	1.1	0.9	8.0	38.0	-2.6	-26.9	-161
09/11/2020	DZW-4	-12.7708	45.2858	DZIANI	bdl	8.0	258400.0	40.8	31.0	392.0	2322.0		-26.9	-148
09/11/2020	DZW4-dupl	-12.7708	45.2858	DZIANI										
09/11/2020	OVPF-6	-12.7694	45.2877	DZIANI	85.8	bdl	37800.0	8.5	0.3	12.0	1013.0	-0.9	-24.6	-124
09/11/2020	DZN-1	-12.7694	45.2877	DZIANI	85.8	bdl	39700.0	9.1	0.5	bdl	958.0			
09/11/2020	DZN-3	-12.7694	45.2877	DZIANI	bdl	bdl	283500.0	64.5	2.6	24.0	7823.0		-24.8	-141
09/11/2020	DZN-3-dupl	-12.7694	45.2877	DZIANI										
09/11/2020	INGV-01	-12.7710	45.2903	DZIANI	0.2	6.0	81900.0	73.6	16.5	39.0	478.0	-6.3	-38.4	-184
09/11/2020	DZE-2	-12.7710	45.2903	DZIANI	0.3	1.2	3897.0	77.6	20.6	3.8	9.0			

Sampling Date	Sample	Lat	Long	Site	Noble gases isotopes											
					R/Ra	4He/20Ne	[4He] ppm	[20Ne] ppm	Rc/Ra	40Ar ppm	38Ar ppm	36Ar ppm	40Ar* ppm	40Ar atm	40Ar/36Ar corr	38Ar/36Ar corr
08/11/2020	OVPF-1	-12.8002	45.2874	BAS	5.86	199.45	28.25	0.14	5.87	110.71	0.06	0.31	18.86	91.85	355.50	0.19
08/11/2020	C1a1-glass	-12.8002	45.2874	BAS												
08/11/2020	OVPF-2	-12.8002	45.2874	BAS	5.92	136.09	24.49	0.18	5.94	91.41	0.05	0.25	18.86	72.55	371.61	0.19
08/11/2020	C2a2-glass	-12.8002	45.2874	BAS												
08/11/2020	OVPF-3	-12.8002	45.2895	BAS	5.54	108.44	19.72	0.18	5.55	90.47	0.05	0.26	13.30	77.17	345.67	0.19
08/11/2020	GD-1	-12.8002	45.2895	BAS												
08/11/2020	OVPF-4	-12.8002	45.2895	BAS	5.46	78.22	19.89	0.25	5.48	98.17	0.05	0.29	13.31	84.86	341.19	0.19
08/11/2020	GD-2	-12.8002	45.2895	BAS												
10/11/2020	C1-b1	-12.8002	45.28736	BAS	5.53	99.83	26.99	0.27	5.55	72.16	0.03	0.18	19.54	52.62	404.40	0.19
10/11/2020	C1-b2	-12.8002	45.28736	BAS	5.55	237.19	31.63	0.13	5.56	87.63	0.04	0.23	18.54	69.08	373.95	0.19
09/11/2020	OVPF-5	-12.7708	45.2858	DZIANI	5.82	54.00	42.51	0.79	5.85	405.89	0.24	1.24	39.52	366.37	326.89	0.19
09/11/2020	DZW-1	-12.7708	45.2858	DZIANI	5.28	48.62	42.45	0.87	5.31	281.37	0.16	0.85	31.40	249.97	331.99	0.19
09/11/2020	DZW-4	-12.7708	45.2858	DZIANI	6.82	577.25	2322.33	4.02	6.83	9088.27	4.72	25.11	1669.59	7418.68	362.06	0.19
09/11/2020	DZW4-dupl	-12.7708	45.2858	DZIANI	6.74	575.22	2438.49	4.24	6.74	9634.94	5.01	26.56	1786.22	7848.72	362.81	0.19
09/11/2020	OVPF-6	-12.7694	45.2877	DZIANI	6.67	628.12	1139.54	1.81	6.67	2055.13	0.82	4.42	749.02	1306.11	463.77	0.19
09/11/2020	DZN-1	-12.7694	45.2877	DZIANI												
09/11/2020	DZN-3	-12.7694	45.2877	DZIANI	6.42	1994.54	8223.72	4.12	6.42	15342.65	6.07	32.85	5636.66	9705.99	467.01	0.18
09/11/2020	DZN-3-dupl	-12.7694	45.2877	DZIANI	6.42	2122.31	8439.59	3.98	6.42	15764.01	6.22	33.62	5828.82	9935.20	468.76	0.19
09/11/2020	INGV-01	-12.7710	45.2903	DZIANI	6.39	33.31	620.22	18.62	6.44	12340.99	7.63	40.26	444.49	11896.50	306.44	0.19

Sampling Date	Sample	Lat	Long	Site	Corrected for air contamination						
					He ppm	H2 ppm	O2 %	N2 %	CH4 ppm	CO ppm	CO2 %
08/11/2020	OVPF-1	-12.8002	45.2874	BAS	26.47	18.34	0.00	0.24	3932.82	0.81	99.37
08/11/2020	C1a1-glass	-12.8002	45.2874	BAS	20.30	6.85	0.00	-0.46	3949.21	2.28	100.07
08/11/2020	OVPF-2	-12.8002	45.2874	BAS	23.53	17.42	0.00	0.04	3881.17	0.61	99.57
08/11/2020	C2a2-glass	-12.8002	45.2874	BAS	-31.26	270.09	0.00	29.85	1112.06	89.66	70.00
08/11/2020	OVPF-3	-12.8002	45.2895	BAS	20.27	83.16	0.00	0.33	5365.96	36.51	99.11
08/11/2020	GD-1	-12.8002	45.2895	BAS	12.90	6.93	0.00	-0.38	5033.43	2.78	99.88
08/11/2020	OVPF-4	-12.8002	45.2895	BAS	19.26	221.11	0.00	0.38	5218.42	0.00	99.07
08/11/2020	GD-2	-12.8002	45.2895	BAS	15.62	3.03	0.00	0.81	4825.20	-0.09	98.70
10/11/2020	C1-b1	-12.8002	45.28736	BAS	28.60	28.63	0.00	0.27	4047.28	0.00	99.32
10/11/2020	C1-b2	-12.8002	45.28736	BAS	26.17	0.00	0.00	0.04	3936.47	0.00	99.57
09/11/2020	OVPF-5	-12.7708	45.2858	DZIANI	44.00	11.86	0.00	-1.28	5089.07	-0.02	100.76
09/11/2020	DZW-1	-12.7708	45.2858	DZIANI	39.50	8.34	0.00	-2.26	5044.09	0.30	101.75
09/11/2020	DZW-4	-12.7708	45.2858	DZIANI							
09/11/2020	DZW4-dupl	-12.7708	45.2858	DZIANI							
09/11/2020	OVPF-6	-12.7694	45.2877	DZIANI	1043.35	12.35	0.00	7.64	38935.48	0.00	88.36
09/11/2020	DZN-1	-12.7694	45.2877	DZIANI	984.77	-0.01	0.00	7.63	40814.10	-0.01	88.19
09/11/2020	DZN-3	-12.7694	45.2877	DZIANI							
09/11/2020	DZN-3-dupl	-12.7694	45.2877	DZIANI							
09/11/2020	INGV-01	-12.7710	45.2903	DZIANI	2301.87	187.42	0.00	59.24	397823.18	28.19	0.73
09/11/2020	DZE-2	-12.7710	45.2903	DZIANI	257.75	219.69	0.00	54.91	260997.01	63.93	18.94

Sampling Date	Sample	Lat	Long	Site	Major (Raw)						
					CO2 (Vol%)	CO (ppmv)	CH4 (ppmv)	N2 (Vol%)	O2 (Vol %)	H2 (ppmv)	He (ppmv)
5/9/2021	C1-2	-12.800117	45.2873	BAS	97.7	0.8	5099	0.25	0.0705	bdl	22
5/9/2021	C1-1	-12.80015	45.28736	BAS	97.45	0.9	5158	0.68	0.27	bdl	2021
5/9/2021	MAN	-12.80064	45.28705	BAS	96.94	1.5	6654	1.59	0.45	bdl	38
5/9/2021	MAR	-12.80045	45.28873	BAS	97.73	0.9	5838	0.43	0.23	bdl	15
5/9/2021	DIST	-12.799917	45.28612	BAS	97.62	1.4	6637	0.5	0.24	bdl	2021
7/9/2021	DZW	-12.770833	45.28582	DZIANI	97.28	1.1	6126	1.2021	0.73	bdl	54
7/9/2021	DZN	-12.769403	45.28771	DZIANI	89.71	1	24400	6.5	1.98	bdl	330

Sampling Date	Sample	Lat	Long	Site	Corrected for air contamination						
					He ppm	H2 ppm	O2 %	N2 %	CH4 ppm	CO ppm	CO2 %
5/9/2021	C1-2	-12.800117	45.2873	BAS	22.384		0.07	0.254368318	5188.096214	0.814	99.2
5/9/2021	C1-1	-12.80015	45.28736	BAS	21.34		0.27	0.691000802	5241.444318	0.9146	98.5
5/9/2021	MAN	-12.80064	45.28705	BAS	37.834		0.45	1.583044892	6624.89353	1.4934	97.3
5/9/2021	MAR	-12.80045	45.28873	BAS	15.172		0.23	0.434934814	5904.998706	0.9103	98.7
5/9/2021	DIST	-12.799917	45.28612	BAS	21.28		0.24	0.506657787	6725.375469	1.4186	98.6
7/9/2021	DZW	-12.770833	45.28582	DZIANI	58.525		0.79	1.311395671	6639.347007	1.1922	97.2
7/9/2021	DZN	-12.769403	45.28771	DZIANI	1026		6.16	20.20949473	75863.33407	3.1092	65.9

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11. Concluding remarks

The research carried out in this doctoral thesis aimed to deepen the existing knowledge of gaseous emissions on two islands of the Comoros archipelago, Grande Comore, and Mayotte (Petite Terre), and set out to specifically address a research gap in the understanding of gas geochemistry of the archipelago from a volcanological perspective. In particular, the study highlights similarities and differences between Grande Comore and Mayotte, and strongly suggests that the gas-geochemical dissimilarities may arguably be linked to a different "state of activity" of the volcanic processes affecting the two islands, and source heterogeneities.

The results of the thesis converge in several conclusions, the main ones of which are summarised as follows:

- The regional and local structural/tectonic framework appears to facilitate the diffusive degassing of CO₂ from the soil. This condition results in spatially distributed soil gas emissions along the main structural features of Grande Comore and Petite Terre. The analysis of the isotopic composition of carbon in soil CO₂ emissions made it possible to distinguish between a magmatic and an organic contribution on the two islands. $\delta^{13}\text{C}$ signatures of soil CO₂ emissions highlight evidence of a low magmatic contribution at distal areas of Karthala volcano ($-25 < \delta^{13}\text{C} < -20.8$), and a significantly higher magmatic contribution in CO₂ emissions at Petite Terre ($-19 < \delta^{13}\text{C} < -1$). This difference may be ascribed to the different states of volcanic activity at the two islands at the time of the surveys, and indicates that Karthala volcano is in a state of quiescence.
- Gas geochemistry of Karthala and Petite Terre falls within the typical range of crustal magmatism. The $^3\text{He}/^4\text{He}$ data for both Karthala and Petite Terre are consistent with average values of fluid inclusion of Grande Comore, and are fixed at a relatively low level for typical OIB: $6.41 \leq R_c/R_a < \leq 7.53$ Petite Terre; $4.68 \leq R_c/R_a \leq 5.87$ Karthala. The $^4\text{He}/^{40}\text{Ar}^*$ values measured at Petite Terre gases vary within a narrow range (1.2-1.7), falling within that typical of a fertile mantle and do not show systematic variations. This leads to the conclusion that Mayotte gas emissions reflect a magmatic degassing occurring in a narrow range of depth, which coincides with the shallow plumbing system

(approximately 17-20 km depth) and is consistent with recent studies based on petrological monitoring.

- A hydrothermal system below Petite Terre has been identified, with CO₂, H₂, H₂O CH₄ equilibrium characteristics and temperature ranging between about 280°C and 300°C. The gases detected in both the BAS and Lake Dziani reflect primarily the signature of deep gases in terms of geochemical tracers such as R/Ra, δ¹³C in CO₂ and methane. However, Dziani Dzaha lake CO₂ and CH₄ gases, both for ratio of concentration and isotopic signature, are more variable and in some cases significantly affected by microbial activity in a meromictic lake environment.
- Both the deep and the shallow plumbing systems involved in the recent submarine eruptive activity offshore Petite Terre result in a change in the input and composition of fluids reaching Petite Terre, with some significant consequences:
 - an increase in the value of Rc/Ra between 2008 and 2018-19, and a subsequent decline coinciding with the waning of the submarine eruptive activity;
 - a not-reached isotopic equilibrium of δ¹³C_{CH₄} from the hydrothermal fluid
 - higher equilibrium temperatures of the hydrothermal system in 2018, which then recorded a constant cooling down more or less coinciding with the decrease of Rc/Ra values above described.

Such improved understanding of the main characteristics of the emitted volcanic fluids enables the recognition of which geochemical markers may be of potential relevance for volcanic monitoring purposes, and thereby strengthen the understanding of the present state of the magmato-volcano activity at Karthala and at Mayotte. This would therefore provide valuable support for local observation infrastructures, and contribute to the improvement of applications in volcanic and environmental monitoring protocols of this populated area.

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