

Major and trace element emission rates in hydrothermal plumes in a tropical environment. The case of La Soufrière de Guadeloupe volcano

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Major and trace element emission rates in hydrothermal plumes 1 in a tropical environment. The case of La Soufrière de Guadeloupe 2 volcano 3 Manuel Inostroza^{1,2,3}, Séverine Moune^{1,2,4}, Roberto Moretti^{1,2}, Pierre Burckel¹, Elodie Chilin-Eusebe^{1,2}, Celine Dessert¹, Vincent Robert⁵, Caroline Gorge¹ 4 5 6 ¹Université de Paris Cité, Institut de Physique du Globe de Paris, UMR 7154 CNRS, F75005, Paris, France ²Observatoire Volcanologique et Sismologique de Guadeloupe, Institut de Physique du Globe de Paris, 7 F97113, Gourbeyre, France. 8 9 ³Millennium Institute on Volcanic Risk Research - Ckelar Volcanoes, F1249004, Antofagasta, Chile. 10 ⁴CNRS. IRD, OPCG Laboratoire Magmas et Volcans, Université Clermont Auvergne, F63000, Clermont-11 Ferrand, France 12 ⁵IRD, IMAGO LAMA, F98800 Nouméa, France 13 *Corresponding Author: manuelinostrozap@gmail.com; https://orcid.org/0000-0003-0800-3508 14 Keywords: trace elements, filter packs, emission rates, volcanic-hydrothermal system, La Soufrière de 15 Guadeloupe, pollution ABSTRACT 16 17 Hydrothermal or low-temperature volcanic emissions, most commonly occurring in fumarolic 18 environments, dominate the global volcanic landscape. This work presents physicochemical 19 characterization of the aerosols contained in steam- and H2S-rich plumes discharged from La Soufrière 20 volcano, in conjunction with the first report on their heavy metal degassing emission rates. Our results 21 indicate that the plume is enriched in certain lithophile (K, Ti, Si, Al, Mn, and Mg) and siderophile (Fe) 22 elements, related to hydrothermal rock leaching, and chalcophile (Sb, As, Zn, Pb, and Tl) elements, which 23 are usually degassed from the magma source. Heavy metal emission rates were found to be below 15 g/d, 24 which are modest compared to available worldwide data. Nevertheless, Cr and Sb emission rates were very 25 similar to those of Lascar volcano (Chile), which instead has produced magmatic eruptions in recent times. 26 We propose that the depth of the magma chamber and the input of meteoric waters play an important role 27 in scavenging heavy metals in the hydrothermal system of magmatic-hydrothermal volcanoes. 28 Notwithstanding low heavy metal emission rates, La Soufrière can be regarded as an important pollution 29 source in the Lesser Antilles volcanic arc.

30 1 INTRODUCTION

Surficial volcanic gas emissions indicate the presence of magma chambers evolving in shallower crustal levels and are composed of gases (H₂O, CO₂, SO₂, H₂S, and HCl) and aerosols containing lithophile,

33 siderophile, and chalcophile elements. These can be classified into magmatic and hydrothermal emissions

- according to their chemical compositions, outlet gas temperatures, and the degree of interaction with host 34
- 35 rocks and aquifers hosted in the volcanic edifice (e.g., Giggenbach, 1996; Symonds et al., 2001; Fischer
- and Chiodini, 2015; Moretti and Stefánsson, 2020). Typical magmatic emissions are characterized by 36
- 37 significant concentrations of SO₂ and halides, high outlet gas temperatures (>450 $^{\circ}$ C; Aiuppa et al. 2017),
- 38 and minimal scrubbing processes (Symonds et al. 2001). On the other hand, hydrothermal emissions are
- enriched in H_2S and present lower gas temperatures (<250 °C), suggesting water-rock interactions within a 40 hot water reservoir supplemented with heat and acid fluids from magma underneath. Furthermore,
- 41 hydrothermal emissions with substantial magmatic influence and intermediate temperatures (250-450 °C)
- 42 are usually called magmatic-hydrothermal emissions (e.g., Aiuppa et al. 2017).

39

- 43 Volcanic emissions represent one of the primary trace element sources into the atmosphere, supplying 44 more than 100 kg/day of certain metals and metaloids (e.g., B, As, Cu, Zn, Tl, Pb, among others; e.g., 45 Mather et al. 2003; Moune et al. 2010; Calabrese et al. 2011; Mather 2015; Mandon et al. 2019). These elements include so-called heavy metals, which are toxic even at low concentrations and are degassed as 46 47 chlorides, sulfates, sulfides, or directly as metals (e.g., Moune et al. 2010; Bagnato et al. 2015; Scholtysik 48 and Canil, 2020). Moreover, heavy metals are frequently associated with bioaccumulation in terrestrial and 49 aquatic environments, which then enter the food chain and drinkable water, impacting human health in the surrounding communities (e.g., Varrica et al. 2014; Vigneri et al. 2017; Tomašek et al. 2022). Though 50 51 previous trace element studies have investigated the magmatic emissions (e.g., Crowe et al. 1987; Africano 52 et al. 2002; Aiuppa et al. 2003; Zelenski et al. 2013), hydrothermal fumarolic emissions remain less 53 studied (e.g., Chen et al. 2005; Mandon et al. 2019) primarily because low-temperature and low-flux 54 emissions contain lesser amounts of metals than magmatic emissions, and are more difficult to be 55 characterized. Furthermore, they result from a more complex history in terms of water-rock interaction, 56 that involves numerous physicochemical processes that are known but hard to quantify. These processes, 57 including gas phase condensation, leaching from host rocks, precipitation of secondary mineral phases, and brine evaporation (Africano and Bernard 2000), can scavenge some or add other trace elements. In 58 59 accordance with these processes, unemitted trace elements potentially form ore deposits (Blundy et al. 60 2021). Consequently, hydrothermal emissions are generally less enriched in volatile trace elements and 61 include greater concentrations of rock-forming elements (e.g., Symonds et al. 1990; Obenholzner et al. 62 2003; Inostroza et al. 2022a,b).
- La Soufrière de Guadeloupe (hereafter La Soufrière) is an andesitic volcano in the Lesser Antilles arc, 63 64 formed by the subduction of the Atlantic Plate below the Caribbean Plate (Feuillet et al. 2002). La 65 Soufrière has presented persistent degassing since 1992, which gradually increased in intensity in the last three decades. Currently, fumarolic emissions here are characterized by high amounts of steam ($\sim 200 \text{ t/d}$), 66 67 CO₂ (3-15 t/d), H₂S (0.6-4.0 t/d; Allard et al. 2014; Tamburello et al. 2019; Moune et al. 2022), and low 68 outlet gas temperatures (up to 111 °C on March 23, 2018; Moretti et al. 2020a). Recently, Inostroza et al. 69 (2022a,b) demonstrated that condensed gases collected directly at the vent contained significant amounts

of lithophile and chalcophile elements, along with heavy metals such as Sb, Bi, and Zn. However, the
 behavior and enrichment of these elements in low-temperature plumes are still poorly constrained.

72 This work combines filter pack and MultiGas data collected from low-temperature volcanic plumes at La 73 Soufrière volcano to, i) constrain the physicochemical characteristics of gas and aerosol phases, ii) 74 determine their major and trace element enrichments, and iii) determine heavy metal emission rates 75 degassed from the volcano. This study builds on the previous findings of Inostroza et al. (2022a,b) and 76 their interpretations on major and trace element concentrations in condensed gases, in addition to elemental 77 behavior according to variations in hydrothermal activity. Further, it contributes to the first trace element 78 emission rates in La Soufrière, and as per our knowledge, is one of the first records considering low-79 temperature (~95 °C) volcanic emissions.

80 2 GEOLOGICAL SETTING AND HYDROTHERMAL ACTIVITY

La Soufrière volcano (16.0446 °N, 61.6642 °W, 1467 m.a.s.l.) belongs to the Grande Découverte Volcanic Complex (Fig. 1) and is the highest point in the Lesser Antilles Arc (Komorowski et al. 2005). La Soufrière edifice was developed in the last 11500 years BP (Komorowski et al. 2005; Boudon et al. 2008), after recurrent magmatic and non-magmatic eruptions. The last magmatic eruptions (Vulcanian, VEI 2-3) occurred in 1530 and 1657 CE (Legendre 2012; Metcalfe et al. 2021) and were followed by intermittent phreatic explosions in 1797-98, 1836-37, 1956, and 1976-77 (Legendre 2012; Hincks et al. 2014) which shaped the current fractured appearance of the summit lava dome emplaced in 1530.





90 Figure 1. (a) Over view of La Grande Découverte Volcanic Complex and (b) An aerial photograph 91 showing the volcano summit and hydrothermally altered zones (areas without vegetation), emphasizing the 92 position of primary fumarolic emissions and fractures (white dash lines). Cratere Sud (CS), Gouffre 56 93 (G56), and Napoleon Nord (NapN) vents are situated along fractures and intense soil degassing areas. The 94 wind direction and wind rose information were taken from 2016-2019 data collected by the Sanner weather 95 station (property of the OVSG-IPGP, 16.04497 °N, 61.66272 °W, 1411 m.a.s.l.) and then treated by Rave et al. (In press). The Citerne (CIT), the place where the atmospheric background sample was collected, is 96 97 also shown.

98 The La Soufrière summit presents vigorous fumarolic activity mainly along Cratère Sud (CS) and Gouffre 99 1956 (G56) fractures, with the soil degassing area progressively expanding to the NE (Fig. 1; Jessop et al. 100 2021). This activity is caused by the input of heat and gases from andesitic mush zones located 7-9 km 101 below the summit (Pichavant et al. 2018; Metcalfe et al. 2021) and their subsequent interactions with the 102 hydrothermal system, sustained by up to 6 m of rain per year (Dessert et al. 2015). This hydrothermal

- 103 system appears to be distributed from a few hundred meters up to ~2.5 km below the summit (Rosas-
- 104 Carbajal et al. 2016; Moretti et al. 2020a) and plays a critical role in buffering deep magmatic fluids
- 105 favoring their cooling, condensation, and reactions with surrounding rocks (Brombach et al. 2000; Salaün
- 106 et al. 2011). Such effects have been noted at the summit area given the presence of the Tarissan acid lake,
- 107 relatively stable outlet gas temperatures similar to saturated steam vapor at the pressure of the summit (~95
- [°]C), and intense hydrothermal alteration (Salaün et al. 2011; Heap et al. 2021).
- 109 H₂S has been found to be the predominant sulfur species (0.3-0.6 mol%) in fumarolic emissions at La Soufrière; SO₂ has only been detected through MultiGas measurements with common SO₂/H₂S ratios 110 111 between 0.004 and 0.1 (Tamburello et al. 2019; Moune et al. 2022). Furthermore, HCl has been measured 112 at concentrations of $\sim 0.2 \mod \%$ (Villemant et al. 2014), which have shown notable increase since the early 113 2000s (Bernard et al. 2006; Allard et al. 2014; Inostroza et al. 2022b). Low outlet gas temperatures and the 114 composition of discharged fluids measured by direct sampling and MultiGas suggest the presence of a 115 hydrothermal-dominated system with shallow magmatic influence (Brombach et al. 2000; Villemant et al. 2014; Tamburello et al. 2019; Moretti et al. 2020a; Moune et al. 2022; Inostroza et al. 2022b). Recent 116 117 studies have shown variable spatio temporal behavior in the numerous fumarolic emissions of La 118 Soufrière; these have been attributed to the following: i) different interactions of deep magmatic gases with 119 hydrothermal aquifers (Tamburello et al. 2019), ii) different degassing pathways, that is, fractures versus 120 diffuse degassing (Rosas-Carbajal et al. 2016; Tamburello et al. 2019; Moune et al. 2022); and iii) 121 compositional changes induced by external forces such as extended dry seasons (Moune et al. 2022). These 122 studies suggest that G56 and CS (Fig. 1) are the fumarolic sites with substantial "magmatic" contributions. 123 In contrast, emissions from the Napoleon Nord (NapN) and the entire northeastern summit area of the 124 dome appear to be strongly affected by scrubbing processes, also occurring at a very late stage by 125 interactions with local shallow groundwaters (Tamburello et al. 2019; Inostroza et al. 2022a). Continuous 126 monitoring at CS allowed identification of considerable temperature and compositional changes. These fluctuations suggest that CS could be connected with a deeper portion of the hydrothermal system, 127 128 particularly sensitive to internal (input of magmatic gases and heat) and external (input of meteoric water 129 or changes in the host-rock permeability) forces perturbing the hydrothermal reservoir(s) (Moretti et al. 130 2020a; de Bremond d'Ars and Gibert 2022; Moune et al. 2022).
- 131 Previous studies on gas condensates (Chen et al. 2014; Inostroza et al. 2022a) show that La Soufrière is an important emitter of major and trace elements. According to Inostroza et al. (2022a), most of those 132 133 elements are dispersed as small rock-related solid fragments eroded from fumarolic conduits and tiny 134 aqueous particles containing rock-related and deep-sourced metal/metalloid elements. Transport of tiny aqueous particles is favored by lower outlet gas temperature and more significant steam proportions in La 135 136 Soufrière fumarolic gases compared to typical medium-high temperature volcanic emissions (Inostroza et 137 al. 2022a). In general terms, gas condensates from NapN and CS show elevated S, Sb, B, Cl, Bi, Br, and 138 Zn concentrations relative to andesitic host rocks (Inostroza et al. 2022a).

139 3 SAMPLING AND ANALYTICAL METHODS

140 3.1 Filter pack measurements

141 The filter pack is an active gas and particle filtration method common in atmospheric and volcanological 142 studies, characterized by its lightweight, robust, and small sized instrumentation. In volcanology, this

143 technique consists of the use of alkaline-impregnated filters to trap volcanic acid gases (SO₂, HCl, and HF)

and polytetrafluoroethylene (PTFE) filters for aerosols (Crowe et al. 1987; Finnegan et al. 1989; Gauthier

145 and Le Cloarec 1998; Allen et al. 2000). Given the predominance of H₂S compared to SO₂ in fumarolic

emissions, this study used the modified sampling and analytical methods employed in Aiuppa et al. (2005)

- 147 and described below.
- Before field sampling, ashless paper filters (WathmanTM 1440-047) were impregnated with two solutions to independently trap gaseous SO₂ and H₂S. Gas filters dedicated to trapping SO₂ were impregnated with a solution of 1.2 M NaHCO₃, glycerol (10 wt.%), and methanol (40 wt.%) (Allen et al. 2000), while those for H₂S were impregnated with 1 M AgNO₃ (Sicardi 1955; Natusch et al. 1972; Aiuppa et al. 2005b), and
- 152 glycerol (10 wt.%). Finally, PTFE (FluoroporeTM membrane FALP04700) and gas filters were carefully
- 153 mounted inside a clean box using plastic tweezers.
- 154 Tests at La Soufrière volcano's fumarolic area allowed us to adapt the sampling method according to the high relative humidity (RH ranging from 80 to 100%, Table 1) and the steam- and H₂S-rich chemistry of 155 156 fumarolic gases. These sampling tests helped us make two crucial decisions. First, more attention was paid 157 to climatic conditions, trying to sample only in time intervals without rain or drizzle, and on days with less 158 relative humidity to reduce possible leaching from the filters on the field. Second, it was noted that 159 humidity could affect trapping efficiency on the first gas filter, causing the second gas filter to represent more than 10% of the gas. However, it was assumed that for a measurement to be valid, the last filter must 160 161 contain negligible concentrations (<10%; Mioduszewski and Kress 2008). Subsequently, a third gas filter

162 was included in the holder, ensuring complete entrapment of S-compounds (Fig. 2).

163 Sampling was done using three filter pack holders gathered in parallel (Figs. 2 and 3). Each holder (H_A ,

164 H_{SO2} , and H_{H2S} ; Fig. 2) was assembled using a PTFE filter in front, while for H_{SO2} and H_{H2S} , three gas

165 filters were assembled behind the PTFE filter. Air was drawn through the holders using three diaphragm

166 pumps (one Charles Austen[®] Capex V2 and two Boxer[®] 3K) connected to 12 V portable batteries.

- 167 Filtration of diluted volcanic plumes was carried out at flow rates of 0.72, 0.40, and 0.42 m³/h (Table 1),
- 168 sampling a volume ranging from 0.13 to 0.72 m³. Flow rates were calibrated before sampling, showing
- 169 errors of approximately 5%. H_A were exposed to the plume for longer times (60 min) to trap considerable
- amounts of particles, while H_{H2S} and H_{SO2} were exposed for 15 and 25 min, respectively, to avoid filter
- 171 saturation.
- 172 The plume was sampled from three sites located at <10 m from the vent (3 and 5 m from CS and NapN,
- 173 respectively, and ~10 m from the G56 vent; Table 1) and at 0.5-1.2 m above the soil (Fig. 3a, b) to reduce

the influence of the soil degassing and dust particles blown by the wind. After collection, aerosol and gas filters were stored in sealed plastic holders and left in the fridge. It was noted that $AgNO_3$ -gas filters became brown because of their reaction with H_2S (Fig. 3e), as described by Aiuppa et al. (2005). Additionally, during and after sampling, presence of droplets caused by condensation of the gas phase and humidity were observed on PTFE filters, especially on the wettest days (Fig. 3b, 3d). Atmospheric background for aerosol and gases were collected at La Citerne (CIT; Fig. 1), situated 1400 m SE of the volcano (~1000 m a.s.l.) in an upwind site not affected by the volcanic plume dispersion (Fig. 1).



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Figure 2 Sketch describing filter pack assemblage used for sampling volcanic plumes at La Soufrière volcano. At each site, three filter pack holders called H_A , H_{SO2} , and H_{H2S} were arranged to trap aerosols, aerosols+SO₂, and aerosol+H₂S, respectively. The sequence G1-G2-G3 (Gas 1, Gas 2, and Gas 3) refers to the impregnate gas filter position in the holder.



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Figure 3 Filter pack assemblage for plume sampling procedures at La Soufrière volcano: a) Sampling
during less humid (RH 80 %, August 25, 2021) weather conditions, b) Sampling during humid (RH 92%,
July 19, 2021) conditions, c) View of a PTFE filter exposed 60 min in less humid conditions, d) View of a

190 PTFE filter exposed 60 min in humid conditions, and e) General view of the H_{H2S} after 15 min plume 191 exposure: dark brownish filters denote the reaction of H_2S with AgNO₃ from gas filters.

192 The treatment of gas filters was carried out in the chemistry laboratory of the Observatoire Volcanologique 193 et Sismologique de la Guadeloupe of the Institut de Physique du Globe de Paris (OVSG-IPGP), while 194 analyses for major anions were carried out at the IPGP in Paris. Before analyses, NaHCO₃-treated filters were eluted with 20 ml of Milli-Q water and left at ambient temperatures for one week. Subsequently, the 195 sample was analyzed by ionic chromatography (Dionex IntegrionTM) to determine the concentration of 196 197 sulfate. These filters were not oxidized because NaHCO₃ can react with H₂S producing HS⁻ in the presence 198 of condensed steam or very humid conditions (Garner et al. 1958; Deng et al. 2019); oxidation of 199 NaHCO₃-treated filters would in turn overestimate sulfate concentrations. AgNO₃-treated filters were put into Teflon beakers and eluted twice with a mixture of diluted HNO₃ (19 ml, 2 vol.%) plus H₂O₂ (1 ml, 60 200 vol.%) on a hot plate (~80 °C) until dry. Subsequently, the residue was eluted with 20 ml of Milli-Q to 201 202 determine the concentration of H₂S as sulfate via ionic chromatography. Internal calibrations determined 203 an analytical error of <5%.

204 PTFE filters were treated for analysis in a chemistry clean room hosted in the Laboratoire de Magma et 205 Volcans (Université Clermont Auvergne, France). First, they were hot-leached in clean Teflon beakers 206 using 5 ml of a solution containing HF (0.05 M) and HNO₃ (0.4 M). Then, extracts were transported to the 207 IPGP to be analyzed for trace elements through an Inductively Coupled Plasma Quadrupole Mass 208 Spectrometer (ICP-QMS, Agilent 9000). Internal standards (Sc, In, and Re) were used to control 209 instrument deviation. The analytical error was <10%.

210 Non-treated PTFE filters were cut into -8×8 mm squares, mounted on carbon tape-covered aluminum 211 holders, coated with carbon, and analyzed using Scanning Electron Microscope with Energy Dispersive 212 Spectrometer (SEM-EDS, Quanta 250) in the C3-Mag laboratory at the Université des Antilles (Pointe-à-213 Pitre, Guadeloupe). Following this, highest resolution images were retrieved using a Field Emission Gun 214 (FEG) – SEM (Auriga 40, Zeiss) at the IPGP. Semi-quantitative chemical analyses were performed in the 215 EDS mode using 15 kV of acceleration voltage, 3-5 nA beam current, 40 s dwell time, and 8.5-10 mm working distance. The acquisition of high-resolution imaging and data processing was made using 216 217 INCAEnergy and Spirit2 software.

218	Table 1 Summary of measurements carried out at La Soufrière volcano; the sampling site, holder type,
219	pump flow rate (l/min), filtered volume (m ³), and distance from the vent have been listed.

Date	Fumarole	Set up	Holder type	Pump flow rate (l/min)	Volume (m ³)	Distance from the vent (m)	Relative Humidity (%)
29/01/2021	CS	A+G1+G2* ^{\$}	H _{SO2}	6.7	0.134	5	94
	CS .	A+G1+G2 ^{\$}	H _{H2S}	12	0.18	5	64

20/01/2021	NonN	A+G1+G2* ^{\$}	H _{SO2}	6.7	0.134	2	00
29/01/2021	Inapin	A+G1+G2 ^{\$}	H _{H2S}	12	0.18	5	00
12/02/2021	CIT	A+G1+G2	-	12	0.84	1400**	84
		A+G1+G2+G3	H _{SO2}	6.7	0.1139		
16/03/2021	CS	A+G1+G2+G3	H _{H2S}	7	0.119	5	90
		A*	H_A	12	-		
		A G1+G2+G3	H _{SO2}	7	0.175		
04/06/2021	CS	A+G1+G2+G3	H _{H2S}	6.7	0.1005	5	95
		Р	H _A	12	0.6		
		A+G1+G2+G3	H _{SO2}	7	0.175		
15/06/2021	CS	A+G1+G2+G3*	H _{H2S}	6.7	0.1005	5	85
		А	H _A	12	0.72		
		A+G1+G2+G3*	H _{SO2}	6.7	0.1675		
15/06/2021	NapN	A+G1+G2+G3	H _{H2S}	7	0.105	3	85
	_	А	H _A	12	0.54		
		A+G1+G2+G3	H _{SO2}	7	0.196		
19/07/2021	CS	A+G1+G2+G3*	H _{H2S}	6.7	0.1139	5	91
		A*	H _A	12	-		
		A+G1+G2+G3*	H _{SO2}	7	0.175		
19/07/2021	G56	A+G1+G2+G3	H _{H2S}	6.7	0.1072	10	92
		А	H _A	12	0.744		
		A+G1+G2+G3*	H _{SO2}	7	0.175		
25/08/2021	CS	A+G1+G2+G3	H _{H2S}	6.7	0.1005	5	80
		А	H_A	12	0.72		
		A+G1+G2+G3	H _{SO2}	6.7	0.1675		
25/08/2021	G56	A+G1+G2+G3*	H _{H2S}	7	0.105	10	80
		А	H_A	12	0.72		
		A+G1+G2+G3	H _{SO2}	6.7	0.1675		
22/09/2021	CS	A+G1+G2+G3*	H _{H2S}	7	0.105	5	49
		А	H _A	12	0.72		
		A+G1+G2	H _{SO2}	6.7	0.1675		
22/09/2021	G56	A+G1+G2+G3*	H _{H2S}	7	0.105	10	63
		А	H_A	12	0.72		

*Particle filters used only for SEM observations; **Distance from the volcano summit; ^sGas filters were
only used for sampling tests to constrain humidity effects, sampling time, and filter saturation. The relative
humidity (RH) during sampling was taken from the "Sanner" weather station, which is located at the
volcano summit.

224 3.2 MultiGas

Fluxes of major gas compounds emitted from degassing volcanoes are usually measured by ground-based remote techniques such as Differential Optical Absorption Spectroscopy (DOAS) or UV cameras. These techniques allow reliable fluxes of SO_2 to be obtained. However, these techniques cannot be applied to La Soufrière de Guadeloupe, where fumarolic emissions contain negligible amounts of SO_2 but high concentrations of H_2S . Consequently, we used a MultiGas device (Aiuppa et al. 2005a; Shinohara 2005) to measure H_2S fluxes in the volcanic plume following the method proposed by Allard et al. (2014) and Tamburello et al. (2019).

232 MultiGas is a portable multi-sensor system that allows fast measurement of primary gas compounds in

volcanic plumes. This device included a Gascard IR spectrometer for CO_2 determination (calibration

range: 0–3000 ppmv; accuracy: ± 2%; resolution: 0.8 ppmv) and City Technology electrochemical sensors

for SO₂ (sensor type 3ST/F; calibration range: 0–200 ppm, accuracy: \pm 2%, resolution: 0.1 ppmv) and H₂S

(sensor type 2E; range: 0–200 ppm, accuracy: ±5%, resolution: 0.7 ppmv). It has a GPS attached that 236 237 enables the device's position to be tracked at 1 Hz refresh rate. To determine fumarolic gas fluxes from the 238 two main vents where the fumarolic emissions were strong enough to generate a plume (CS and G56), the 239 horizontal and vertical distributions of gas species in the plume cross-sections were measured at two 240 different heights (typically 0.9 and 2 m) during walking traverses orthogonal to the plume direction, a few 241 meters downwind from the vents. Observations suggest that the fumarolic emissions were mostly flattened 242 to the ground by strong trade winds (up to 14 m/s), and their upper boundary stood at ca. 3-4 m above the ground with a maximum gas density centered at 1.5-2 m above the ground (Gaudin et al. 2016; Tamburello 243 244 et al. 2019). Wind speed was measured with a portable anemometer at the same height as the MultiGas 245 inlet during all traverses. These measurements were carried out contemporaneously with the filter pack 246 sampling.

CO₂/H₂S and SO₂/H₂S gas ratios were processed with the least squared method using the RatioCalc 247 software (Tamburello 2015). We interpolated the concentration measurements for CS and G56 using a 2D 248 spline function and then integrated them over the plume cross section to obtain Integrated Concentration 249 250 Amounts (ICAs) using RatioCalc software (Tamburello 2015). These computations were based on CO_2 as 251 a volcanic marker (ICA CO2; Table 4), given that the IR CO_2 sensor reacts faster than the H₂S sensor and CO₂ measurements are not affected by high humidity conditions (Tamburello et al. 2019). Subsequently, 252 253 CO₂ fluxes were computed by scaling the obtained CO₂ concentration in plume cross sections with the average wind speed. Finally, H_2S was computed by scaling the average H_2S/CO_2 weight ratio with the CO_2 254 255 flux (Moune et al. 2022). These flux computations carry an approximate error of 40% (Tamburello et al. 256 2014), attributed by uncertainties in the average wind speed measurements.

257 4 RESULTS

258 4.1 Physicochemical characterization of solid particles

The type, morphology, and chemistry/mineralogy of particles transported within the plume at La Soufrière volcano were investigated. The appearance of PTFE filters during and after the sampling featured significant amounts of small yellowish particles (Fig. 3c), a few dark particles, and droplets (Fig. 3d). No evident correlation between sampling time and the number of particles was noted. Longer exposures however have the ability to potentially enhance the possible leaching of the filters, resulting in microscopic observations evidencing a circular distribution of solid particles (Fig. 4), a couple of weeks after sampling.

265 Such distribution suggests that droplets gently evaporated during storage.

The size of the solid particles on filters was measured to be up to 310 µm, and found as subrounded droplet marks or scattered on the filter (Fig. 4; Supplementary Material 1). In general, solid particles appeared abundantly in CS filters than in NapN or G56 filtes, likely due to the stronger degassing and hence more erosive contribution at CS. Based on the physicochemical characteristics of particles (Supplementary Material 1), they can be divided into three groups: i) Sulfur-bearing particles that measured up to 310 µm in size and were commonly found in CS samples, corresponding to native sulfur and sulfates interpreted as

- 272 thenardite (Na_2SO_4) and gypsum $(CaSO_4 \cdot 2H_2O; Fig. 5)$. In the case of gypsum, the presence of bassanite 273 (CaSO₄·0.5H₂O) and anhydrite (CaSO₄) cannot be fully discarded; ii) Cl-bearing fragments that reached 274 up to 230 µm in size (were more common in NapN filters), composed of halite (NaCl), sylvite (KCl), and possible akaganeite (Fe³⁺O(OH,Cl); Fig. 5), in addition to several unidentified Cl-bearing particles 275 276 together with Mg, Na, S, and K, suggesting the possible formation of chlorosulfate complexes or small 277 phases with variable chemical composition (Supplementary Material 1); and iii) rock particles (up to 200 278 µm) rich in Si and other lithophile and siderophile chemical elements (Mg, Ca, K, Ti, Mn, and Fe), which 279 appeared in similar proportions as in CS and NapN filters, but predominated in G56 samples.
- 280 It is also important to note that some unusual Fe-bearing particles were found on the filters. For example, a Fe-O (48 and 47 wt.%, respectively) particle with traces of Mn, S, Cl, and K was found on NapN filters, 281 which could be linked with hematite (Fe₂O₃), although EDS analyses were inconclusive. Similarly, <10282 283 µm Fe-Cr (88.3 and 11.7 wt.%, respectively) particles were also found on CS filters, which could 284 correspond to chromferide (Fe₃Cr_{0.4}) or iron-rich particles of unknown origin; their possible anthropogenic origin could be discarded since there is no presence of steelworks or port activities that potentially 285 286 contribute solid particles at the volcano summit. In addition, other heavy metals such as, Cu, Zn, and Sb, 287 occasionally appeared in low concentrations (<15 wt.%; Fig. 5d, e) in one CS and one NapN sample.



Figure 4 General view of PTFE aerosol filters. a) filter non-affected by humidity, while b), c), and d)
correspond to filters collected during more foggy and humid conditions. The filter dryness caused rounded
droplet marks with the distribution of solid particles.



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Figure 5 Morphology (SEM-BSE) and chemistry of representative solid particles on aerosol filters.
Images with "x" marks represent point analyses with noticeable concentrations of Zn. Point EDS analyses
are presented in Supplementary Material 1.

4.2 Major and trace element concentrations

297 Major and trace element concentrations in filter pack holders H_A and H_{H2S} from CS, G56, and NapN 298 plumes and average relative humidity during sampling have been presented in Table 2 and Supplementary 299 Material 2. H_{SO2} holders were not considered because they showed more enhanced Na, Cl, Ca, and Mg 300 concentrations which are likely more related to impurities in our alkaline solution (NaHCO₃) instead of a 301 volcanic source. As expected, and considering their longer sampling duration, H_A aerosol filters displayed 302 higher average concentrations than H_{H2S} aerosol filters, suggesting negligible leaching effects as exposure time increased. Nevertheless, possible leaching effects due to humid climatic conditions at the volcano 303 304 summit, besides the high concentration of steam in fumarolic emissions, cannot be ruled out. Thus major 305 and trace element concentrations presented in this work must be considered as minimum values.

The reliability of the data can be evaluated based on the relative standard deviation (RSD) percentage. This 306 307 expression is a comparison between the standard deviation and the mean of the sample. An RSD >33%308 (value equal to three standard deviations) suggests the presence of concentrations below the detection 309 limit. Consequently, samples with higher RSD should be discarded due to their lower reliability. Chemical 310 analyses from this study reported very low RSD values for various chemical elements. For example, B, Na, Mg, Al, Si, Cl, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Rb, Sr, Y Zr, Sn, Sb, Ba, La, Ce, Pr, and Pb presented 311 312 average RSD <5%, while Li, K, Ni, As, Mo, Cs, Nd, Eu, Tb, Ho, Hf, Tl, Th, and U reported average RSD 313 of 5-10%. S, Ga, Se, Br, Nb, Cd, Te, Sm, Gd, Dy, Er, Tm, Yb, Lu, Ta, W, and Bi presented 10-33% RSD. 314 Moreover, Be, P, Ge, I, and Hg reported higher RSD (>33%), ascribed to concentrations close to or below 315 the detection limit or analytical difficulties (Jian et al. 2000; Badocco et al. 2017). Hence, chemical 316 elements with RSD >33% were removed to attain a representative and confident dataset, and their 317 concentrations were converted into "below detection limit" ("bdl"; Table 2).

Data were processed following chemical and atmospheric background corrections (Supplementary 318 319 Material 2). The chemical blank accounted for 5-10% of average major and trace element concentrations, except for Mo (16%), Sr (20%), Ca (27%), Cr (70%), and Ba (235%). At the same time, the atmospheric 320 321 background (atmospheric blank in Supplementary Material 2) contained concentrations less than 10% of 322 the average major and trace element concentrations, except for U (12%), Li (13%), Ni (13%), Tb (15%), 323 Mn (17%), Cu (20%), Bi (20%), Ta (23%), Co (24%), Mg (28%), V (28%), Rb (28%), Cr (36%), Tl 324 (37%), W (45%), K (51%), and Mo (58%). The average chemical concentrations of Cl and Pb were found to be similar in the atmospheric blank and volcanic plumes. Na and Cd concentrations were removed from 325 326 Table 2 because marine aerosols strongly influence Na, and Cd presented higher concentrations in the 327 atmospheric blank than in aerosol filters (0.84 versus an average of 0.17 ng/m³ of Cd; Supplementary Material 2). These enhanced concentrations suggested that the Guadeloupean atmosphere could be 328 329 enriched in Li, Mg, Na, K, V, Cr, Fe, Cu, Cl, Rb, Mo, Cd, Tb, Ta, W, Tl, Bi, and Pb; careful attention should thus be given to this non-volcanic source of trace elements in fumarolic plumes. Accordingly, blank 330 atmospheric concentrations were subtracted from the total concentrations measured in aerosol filters to 331 332 obtain plume-specific concentrations (Supplementary Material 2).

333 Considering both chemical and atmospheric blanks, the corrected concentration of major and trace elements in the fumarolic plumes at La Soufrière ranged from 10^6 to 10^{-2} ng/m³ (Table 2). Chlorine 334 reached the highest concentrations (10^6 ng/m^3) , followed by concentrations of 10^4 ng/m^3 for Si, S, and Fe. 335 Then, B, Mg, Al, K, Ca, Ti, Cr, Zn, and Br reached plume concentrations of 10²-10⁴ ng/m³. Vanadium. 336 Mn, Ni, Cu, As, Sr, Zr, Mo, Sn, Sb, I, and Pb had in concentrations of $\sim 10^1$ ng/m³, while Li, Co, Ga, Ge, 337 Rb, Y, Nb, REEs, Hf, Ta, Tl, Bi, Th, and U were <1 ng/m³. Compared to G56, fumarolic plumes from 338 339 NapN and CS displayed slight enrichments in the average chemical concentrations compared with G56, likely due to the shorter sampling distance from the vent. Despite the high concentrations of Cl, data 340 curation allowed its purely volcanic recognition only in two (one sample in CS and another from G56) of 341 the eleven samples (Table 2). Ag was only detected in H_{H2S} (Supplementary Material 2), which indicates 342 possible contamination from AgNO3-gas filters; Ag was thus removed from the representative dataset 343 344 (Table 2).

Table 2 Corrected chemical concentration of major and trace elements (expressed in ng/m³) from aerosol
 filters after RSD treatment, chemical, and atmospheric background corrections (Supplementary Material
 2).

Site	CS	CS	CS	CS	CS	CS	G56	G56	G56	NAPN	NAPN
RH	84	90	95	85	80 11	49	92 V	80	<u>63</u>	84	85
Filter	H _{H2S}	H _{H2S}		H _A 15/06/	H _A	H _A	H _A 10/07/	HA 25/09/	H _A	H _{H2S}	H _A 15/06/
Date	29/01/ 2021	2021	2021	2021	25/08/ 2021	2021	2021	25/08/ 2021	2021	29/01/ 2021	2021
Li	0.27	bdl	2.07	1.20	1.10	0.19	0.28	0.40	0.13	0.72	1.35
Be	bdl	bdl	bdl	0.08	bdl	bdl	bdl	bdl	0.02	bdl	bdl
В	bdl	bdl	bdl	52	90	2339	1.26	bdl	6.58	bdl	bdl
Mg	232	153	130	301	828	35	169	302	64	540	361
Al	671	194	565	3874	2989	1331	745	1413	582	1070	3048
Si	2050	203	3383	19257	14520	4642	2439	5142	3104	2458	7421
S	bdl	24254	2657	bdl	5512	4060	2747	1423	12515	9148	bdl
Cl	bdl	840348	bdl	bdl	bdl	bdl	bdl	bdl	87169	bdl	bdl
K	242	bdl	388	307	385	bdl	bdl	67	bdl	856	423
Ca	1036	bdl	4660	48	876	556	883	2403	bdl	6974	1352
Ti	79	42	28	281	204	141	19	1073	70	65	98
V	2.08	3.20	1.23	9.38	7.68	2.34	6.67	12	0.75	2.92	9.19
Cr	411	478	74	8.51	bdl	bdl	bdl	bdl	bdl	262	bdl
Mn	6.82	6.66	14	16	44	8.86	19	27	5.34	15	29
Fe	348	15	1500	5834	6174	3168	10367	13265	1377	1248	10256
Со	0.06	0.79	0.45	0.77	0.86	0.16	0.45	1.03	0.06	0.24	0.89
Ni	2.58	29	48	1.72	5.98	bdl	2.59	1.64	bdl	9.99	13
Cu	1.30	1.67	115	8.26	42	bdl	8.11	bdl	bdl	85	35
Zn	239	122	1352	20	600	2	60	37	/8	938	537
Ga	bdl	bdl	0.29	1.08	0.84	0.51	bdl	0.55	0.21	0.37	1.01
Ge	bdl	bdl	bdl	0.18	0.24	bdl	bdl	bdl	bdl	bdl	bdl
As	7.46	bdl	1.78	0.62	1.44	0.27	0.45	0.50	0.17	21	1.31
Se	bdl	3.04	0.39	bdl	1.55	0.84	2.14	0.89	2.64	1.94	1.10
Br	bdl	bdl	bdl	477	559	4459	321	bdl	bdl	bdl	bdl
Rb	0.30	0.21	0.47	2.25	1.88	0.12	0.04	0.68	0.16	0.91	1.87
Sr	6.45	bdl	4.58	3.12	5.89	4.28	1.38	5.40	1.17	15	5.90
Y	0.21	0.12	0.20	0.50	0.79	0.14	0.23	0.46	0.16	0.29	0.62
Zr	6.76	1.74	13	7.15	4.12	0.69	0.40	2.39	0.78	1.88	2.69
Nb	bdl	bdl	0.09	0.62	0.52	0.11	bdl	0.88	0.10	bdl	0.84
Mo	bdl	5.20	0.28	bdl	0.50	bdl	bdl	3.85	bdl	bdl	1.25
Sn	1.15	0.03	20	1.22	33 10	1.05	12	0.69	0.58	7.04	28
SD	0.71	1/9	9.98	158	10	3.61	0.17	0.15	0.30	3.02	5.19
Te	0.35	bdl	0.02	0.11	0.08	bdl	bdl	0.03	bdl	0.70	bdl
Cs D-	0.44	bdl	0.03	0.16	0.11	0.02	0.02	0.05	0.02	0.75	0.13
ва	Dal		bai	DOI 1.020	2.39	Dal	DOI	bai	bai	Dai	bai
La	0.324	0.208	0.265	1.030	0.965	0.209	0.247	0.802	0.233	0.500	1.022
Ce	0.636	0.442	0.437	2.006	1.8/8	0.454	0.595	1.618	0.493	0.901	2.346

Pr	0.060	0.044	0.037	0.221	0.186	0.047	0.049	0.178	0.050	0.089	0.239
Nd	0.255	0.204	0.184	0.845	0.808	0.199	0.234	0.767	0.204	0.347	0.975
Sm	0.064	0.071	0.072	0.156	0.167	0.047	0.059	0.167	0.042	0.099	0.207
Eu	bdl	bdl	0.009	0.033	0.036	0.014	0.011	0.030	0.010	0.021	0.042
Gd	bdl	bdl	0.044	0.125	0.157	0.043	0.058	0.134	0.038	0.206	0.162
Tb	0.006	0.005	0.006	0.019	0.022	0.004	0.006	0.017	0.005	0.011	0.021
Dy	0.039	0.026	0.036	0.105	0.144	0.025	0.047	0.105	0.032	0.055	0.124
Ho	bdl	bdl	0.007	0.021	0.029	0.005	0.008	0.017	0.006	0.011	0.023
Er	0.032	bdl	0.026	0.066	0.102	0.021	0.034	0.055	0.023	0.045	0.069
Tm	0.004	bdl	0.003	0.010	0.014	0.002	0.004	0.008	bdl	0.007	0.010
Yb	0.021	0.010	0.022	0.062	0.089	0.016	0.028	0.062	0.018	0.025	0.061
Lu	bdl	bdl	0.004	0.009	0.015	0.002	0.004	0.009	0.003	0.004	0.009
Hf	0.17	0.07	0.28	0.19	0.11	0.02	0.01	0.08	0.02	0.07	0.08
Та	bdl	bdl	0.04	0.04	0.01	bdl	bdl	0.14	bdl	0.12	0.11
W	0.22	1.06	0.35	bdl	0.14	bdl	bdl	0.22	bdl	0.87	0.21
Tl	0.10	0.23	0.00	0.01	0.02	bdl	0.00	bdl	0.02	0.20	0.01
Pb	bdl	0.66	4.97	bdl	2.78	bdl	bdl	bdl	bdl	3.94	0.85
Bi	1.09	bdl	0.18	bdl	0.01	bdl	bdl	bdl	bdl	1.98	0.09
Th	bdl	0.06	0.05	0.29	0.24	0.07	0.07	0.42	0.07	0.10	0.28
U	0.01	0.01	0.01	0.06	0.05	0.02	0.03	0.05	0.01	0.04	0.06

348 bdl: below detection limit

349 4.3 Major gas ratios and H₂S volatile fluxes

Gas ratios were measured using filter pack and MultiGas techniques. Plumes were reportedly flat during the sampling period because of persistent west-northwestern wind blowing at 4.2 m/s on average (maximum of 9.5 m/s), while windless days prompted vertical plumes generating unreliable data. Similarly, the high relative humidity may have been responsible for production of partial leaching on the G1 filter (Figs. 2 and 3), as seen at the end of the sampling on the wettest days.

355 Theoretically, chemical concentration should decrease from G1 to G3 (Fig. 3e and Table 1), with G1 containing approximately 90% of the total sulfate concentration (Pennisi and Le Cloarec 1998), whereas 356 357 G2 and G3 having negligible concentrations (<10%). The non-negligible concentration in the last gas filter 358 indicates filter saturation, which does not represent a valid measurement (Wittmer et al. 2014). At La Soufrière, intervals of total sulfate concentrations (i.e., G1+G2+G3 concentrations) in H_{SO2} and H_{H2S} gas 359 filters were 25.7-1486 and 457-4692 ppm (Table 3), respectively, with concentrations generally decreasing 360 from G1 to G3 (Fig. 6). However, six gas samples (four from H_{SO2} and two from H_{H2S}, Fig. 6) displayed 361 saturation because the G3 filter contained sulfate concentrations >10%, and hence, were discarded. In 362 contrast, for the non-saturated samples (G3_{H2S}, G3_{SO2} <10%), G1-H_{SO2} accumulated between 77 and 91% 363 364 of the total sulfate concentration, while G1- and G2-H_{H2S} retained more similar sulfate concentrations (56 365 and 41%, respectively), with G2-H_{H2S} occasionally presenting higher concentrations than G1-H_{H2S}. These equivalent concentrations potentially suggest that the trapping efficiency of G1-H_{H2S} decreased with 366 humidity, while that of NaHCO₃-gas filters remained less affected. We thus reccomend the adoption of 367 368 three gas filters for sampling tropical wet volcanic plumes based on significant concentrations found in 369 G2-H_{H2S} filters.



Figure 6 Sulfate concentration (%) in each gas filter (G1, G2, and G3) with respect to the total amount of sulfate in H_{SO2} and H_{H2S} . The horizontal black dashed line at 90% bounds saturated ("s") filters: when G3 occupies more than 10% of the total concentration of sulfate. Percentages for the G56 sample collected in September 2021 (H_{H2S}) presented concentrations below the detection limit (bdl).

Ratios involving sulfur help constrain magmatic and hydrothermal contributions to gas emissions at 375 quiescent degassing volcanoes. Here we measured SO₂/H₂S molar ratios in air-diluted samples from the 376 377 CS, NapN, and G56 sites using filter packs and MultiGas techniques (Tables 3 and 4, Supplementary 378 Material 3). In the case of CS, SO_2/H_2S ratios determined by filter packs and MultiGas were within the 379 range of 0.18-0.94 and 0.066-0.19, respectively (Table 3), at NapN, they were 0.61 (Table 3) and 0.06 380 (Séverine Moune, personal communication), respectively. Finally, G56 MultiGas ratios ranged from 0.018 to 0.039, while simultaneous filter pack measurements were saturated (Table 3). A comparison of filter 381 382 packs and MultiGas SO₂/H₂S showed evidenced that the results obtained using the filter pack technique 383 were up to one order of magnitude higher than those reported by MultiGas. Such higher SO₂/H₂S ratios in filter packs are not representative of gas, especially considering the low and stable SO₂ concentrations and 384 385 fluxes over the years (Table 4; Moune et al. 2022). Discrepancies can be mainly attributed to sampling 386 issues such as, i) partial oxidation of sulfur species during sample preparation prior to ionic 387 chromatography analyses or ii) enhanced trapping of S-compounds favored by the wetness of gas filters 388 (Mioduszewski and Kress 2008) of the filter pack technique.

 H_2S fluxes measured during discrete field campaigns in 2021 were found to be within the 0.67-2.83 t/d range at CS and 0.27-0.74 t/d at G56. These values have remained stable since mid-2018 after higher fluxes occasionally measured in 2016-2017 (Tamburello et al. 2019). Dry gas fluxes reported in CS were twice higher than those of G56 (Supplementary Material 3).

Table 3 Total sulfate concentration and molar ratios obtained from filter packs in CS, NapN, and G56 plumes (Supplementary Material 3). Holders in which the third gas filter contained more than 10% of the total sulfate concentration are namely "saturated". Total sulfate concentrations are normalized values considering 1 m³ of volcanic plume.

Site	Date	FD	Total sulfate	SO ₂ /H ₂ S molar ratio
Gag	Date		ppm	
CSC	16/03/2021	$P(SO_2)$	saturated	N/A
		$P(H_2S)$	457.15	
CSC	04/06/2021	$P(SO_2)$	saturated	N/A
		$P(H_2S)$	4692.88	
CSC	15/06/2021	$P(SO_2)$	1240.07	0.743
		$P(H_2S)$	3136.53	
NapN	15/06/2021	$P(SO_2)$	266.95	0.610
		$P(H_2S)$	823.09	
CSC	19/07/2021	$P(SO_2)$	213.83	0.184
		$P(H_2S)$	2179.20	
G56	19/07/2021	$P(SO_2)$	Saturated	N/A
		$P(H_2S)$	1634.49	
CSC	25/08/2021	$P(SO_2)$	1486.12	0.942
		$P(H_2S)$	2967.09	
G56	25/08/2021	$P(SO_2)$	36.65	N/A
		$P(H_2S)$	saturated	
CSC	22/09/2021	$P(SO_2)$	684.56	N/A
		$P(H_2S)$	saturated	
G56	22/09/2021	$P(SO_2)$	saturated	N/A
		$P(H_2S)$	bdl	

397 bld: below detection limit; N/A: not applicable.

Table 4 Average wind speed, average SO_2/H_2S molar ratios, and H_2S fluxes emitted from CS and G56 vents. H_2S fluxes were obtained using the Integrated Concentration Amounts (ICA) for CO₂ (ICA CO2), the latter being considered as the volcanic marker (Section 3.2). Dry gas fluxes were obtained by adding the three main fluxes (but not water flux; Supplementary Material 3).

Data	Wind speed*	Wind Molar ratios speed*		H ₂ S max	ICA CO2	Flux (t/d)			
Date	m/s	SO ₂ /H ₂ S	CO ₂ /H ₂ S	ррт	(ppm/m ²)	CO ₂	H_2S	SO ₂	Dry gas
Cratere Sud									
*2006 & 2012	-	0.035	2.50	-	-	-	-	-	-
*2016-2017	-	0.003	3.32	106	7143	5.23	1.87	0.01	7.10
*2018-2020	-	0.067	2.78	75	6923	3.86	1.04	0.05	4.93
16/01/2021	3.8	-	3.300	167	8134	4.81	1.13	-	5.93
29/01/2021	2.35	0.066	2.700	130	6430	2.35	0.67	0.08	3.11
16/03/2021	3.06	0.163	3.060	188	12500	5.95	1.50	-	7.45
04/05/2021	3.48	-	2.005	85	7584	4.10	1.58	0.49	6.17
04/06/2021	4.36	0.166	2.341	116	12662	8.59	2.83	-	11.42
19/07/2021	3.3	0.191	1.855	64	5336	2.74	1.14	0.41	4.29
22/09/2021	2.8	0.162	1.821	111	10861	4.73	2.01	0.61	7.35

27/10/2021	3.2	0.080	1.993	198	11376	5.66	2.20	0.33	8.19
Gouffre 56									
*2006 & 2012	-	-	-	-	-	-	-	-	-
*2016-2017	-	0.012	3.78	33	4165	4.53	1.27	0.02	5.81
*2018-2020	-	0.036	3.49	22	2766	2.01	0.48	0.03	2.52
16/01/2021	8.1	-	5.120	7	2484	3.13	0.47	-	3.60
29/01/2021	2.6	0.062	3.480	27	3040	1.23	0.27	0.03	1.53
16/03/2021	4.52	0.034	3.420	22	4652	3.27	0.74	0.08	4.09
04/05/2021	7.6	-	4.113	17	2004	2.37	0.44	0.03	2.84
04/06/2021	9.47	0.039	3.919	9	2125	3.13	0.62	0.05	3.79
19/07/2021	5.8	0.036	3.898	7	1906	1.72	0.34	0.02	2.08
22/09/2021	2.8	0.030	3.305	29	5417	2.36	0.55	0.03	2.94
27/10/2021	3.9	0.018	3.324	22	4354	2.64	0.61	0.02	3.28
TOTAL (Crater	e Sud + Go	ouffre 56)							
16/01/2021	-	-	-	-	10618	7.94	1.60	0.00	9.53
29/01/2021	-	-	-	-	9470	3.58	0.95	0.12	4.64
16/03/2021	-	-	-	-	17152	9.22	2.24	0.08	11.54
04/05/2021	-	-	-	-	9588	6.47	2.03	0.51	9.01
04/06/2021	-	-	-	-	14787	11.72	3.45	0.05	15.21
19/07/2021	-	-	-	-	7242	4.46	1.48	0.43	6.37
22/09/2021	-	-	-	-	16278	7.09	2.56	0.64	10.29
27/10/2021	-	-	-	-	15730	8.30	2.81	0.35	11.46

* represent average ratios and fluxes previously published from CS and G56 sites (Allard et al. 2014;
Tamburello et al. 2019; Moune et al. 2022).

404 5 DISCUSSIONS

405 5.1 Origin of airborne solid particles

406 The S-, Cl-, and Si-bearing particles on top of La Soufrière appear to be primarily volcanic in origin 407 mainly because these particles were trapped a few meters from fumarolic vents that were already 408 characterized for emitting these particles (Inostroza et al. 2022a, b). However, additional particle sources 409 related to Saharan, marine, or anthropogenic contributions cannot be entirely discarded. The atmospheric 410 background measurement (sample "CIT", Table 1) shows significant concentrations of trace elements, 411 despite the absence of solid volcanic particles on the aerosol filter. Furthermore, the Guadeloupe 412 archipelago have been know to get polluted by sea salt aerosols rich in Na, Cl, K, Mg, S, and Ca (Dessert et al. 2015; Xu-Yang et al. 2022) and affected by Saharan dust every year, especially between April and 413 414 September (Muhs et al. 1990; Pett-Ridge 2009; Dessert et al. 2020; Xu-Yang et al. 2022), transporting 415 solid microparticles through the Atlantic Ocean and enriching the Guadeloupean environment in Si, Al, 416 Ca, K, and Fe.

417 The transport and concentration of non-volcanic aerosols in island environments are mainly governed by 418 wind speed, relative humidity, rainfall regime, altitude above sea level, and particle diameter (Shinozuka et 419 al. 2004; Prather et al. 2013; Murphy et al. 2019). The latter becomes preponderant discriminating non-S-420 rich aerosols found in the volcanic plume at La Soufrière (Dusek et al. 2006). For example, a significant number of solid particles found in the plume (Figs. 5 and 6) display predominantly larger diameter above 421 422 10 μ m and up to 300 μ m in comparison with worldwide marine aerosols that generally are <3 μ m (Chabas 423 and Lefèvre 2000; O'Dowd and de Leeuw 2007) or Saharan particles usually <10 µm (Petit 2005; 424 Euphrasie-Clotilde et al. 2021), suggesting a predominant volcanic origin of the largest particles. However, 425 it is believed that <10 µm aerosols (called PM10) of non-volcanic origin (mainly marine) rich in Na, Cl, K, Mg, S, and Ca could impact the concentration of these elements in the volcanic plume of La Soufrière, 426 substantiating the need for study atmospheric blanks. Moreover, pollution peak events related to Saharan 427 dust provoked PM_{10} concentrations >50 µg/m³ (www.gwadair.fr). Particularly, the event on June 15 and 428 429 July 19, 2021 (www.gwadair.fr) could have influenced the sampled plume's composition. However, such 430 events did not cause noticeable increases in Al, Ca, K, or Fe concentration as could have been expected. 431 Undoubtedly, more detailed information is needed to constrain their contributions and effects during plume 432 sampling.

433 Sulfates and Cl-bearing minerals are usually deposited directly from the gas phase in high temperature 434 (above 400 °C) magmatic emissions (e.g., Getahun et al. 1996; Africano et al. 2002; Nekvasil et al. 2019). 435 However, their presence in low-temperature hydrothermal emissions implies multiple processes, such as 436 gas phase condensation, leaching of host rocks, and precipitation of S-bearing species under more oxidizing conditions (Africano and Bernard, 2000; Zimbelman et al., 2005). Halides can be formed by gas 437 438 phase condensation followed by cooling or evaporation of magmatic-hydrothermal brines (Johnston 1977; 439 Carter et al. 2015; Peretyazhko et al. 2016; Afanasyev et al. 2018); the mineral assemblage found in the 440 volcanic plume of La Soufrière suggests Cl-rich brines circulating in the hydrothermal system interacting 441 with host rocks and magmatic gases containing sulfur. This is supported by the presence of high Cl and S 442 concentrations in gas condensates (Villemant et al. 2014; Inostroza et al. 2022a) and S- and Cl-compounds 443 in the fumarolic gases of La Soufrière (Bernard et al. 2006; Allard et al. 2014; Moretti et al. 2020a, b; 444 Moune et al. 2022). However, the formation mechanism of halide minerals is controversial, and could be 445 explained according to two hypotheses: 1) mineral phases formed at the fumarolic conduit/vent and then 446 transported as solid particles to be subsequently trapped in the aerosol filter, or 2) mineral phases formed 447 because of S- and Cl-rich droplet evaporation during the storage time. Although vent erosion appears as a 448 primary process in La Soufrière emissions, Figures 5 and 6f suggest that the circular distribution of sulfur, 449 sulfates, and Cl-bearing minerals, as well as the delicate and well-formed crystal needles of sulfates and cubic halite, can only be explained by subtle evaporation processes. Furthermore, the clustering of gypsum 450 451 needles (Fig. 5) agrees with droplet evaporation experiments on hydrophobic surfaces comparable with 452 PTFE filters (Shahidzadeh et al. 2015; Zelenski et al. 2020). Therefore, both hypotheses are plausible, and we suggest that their combination explains the occurrence of halides and sulfates in our samples. 453

The amount of ash/rock solid particles in magmatic systems can be accounted for by analyzing Rare Earth Elements (REEs) in aerosol filters (Gauthier and Le Cloarec 1998; Aiuppa et al. 2003). REEs are 456 undoubtedly the indicators of solid particle entrapment due to erosive processes. In addition to particles 457 related to erosive processes, low-temperature emissions also contain acidic hydrothermal solutions enriched in REEs due to variable leaching of the wall rock depending on temperature, pressure, chemical 458 459 composition, and density of carrier fluids (Karpov et al. 2013; Migdisov et al. 2016; Inguaggiato et al. 460 2020; Wan et al. 2021). At La Soufrière, plumes show enrichments in REEs lighter than Eu (Fig. 7), same 461 as for gas condensates collected between 2017 and early 2021 (Inostroza et al. 2022a, b). Such Light REE 462 (LREE) enrichments are well correlated with the significant concentrations and degassing of chlorides and sulfates in volcanic emissions, which are the most common ligands for REE. Cl, particularly, is the most 463 464 enriched element in gas condensates and, therefore, in the hydrothermal reservoir of La Soufrière 465 (Inostroza et al. 2022a), and its presence could be responsible for LREE enrichments given that LREE-466 chlorides are up to 1.5 times more soluble and stable than Heavy REE (HREE)-chlorides in acid and high-467 temperature hydrothermal solutions (Migdisov et al. 2016). Such hypothesis is also supported by the acidic, Cl-rich, and high temperature (>250 °C) conditions predominating in the main hydrothermal 468 469 reservoir beneath La Soufrière summit (Rosas-Carbajal et al. 2016; Moretti et al. 2020a). Besides, the 470 dissolution of sulfates (e.g., jarosite, alunite, or gypsum/anhydrite; Salaün et al., 2011; Heap et al., 2021) in 471 the fumarolic conduit and sulfate-bearing hydrothermally altered andesites could explain part of the 472 enrichment of LREE (Varekamp 2015; Inguaggiato et al. 2020).



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Figure 7 REE patterns normalized to chondrite (Anders and Grevesse 1989) of aerosol filters and andesitic host rocks. REE concentrations in aerosols are those presented in Table 2. In comparison, REE/100000 normalized patterns in andesitic host rocks correspond to the average value of two samples (23CF and SOU-J4) with minimal hydrothermal alteration from the 1530 lava dome and the 1657 scoria fallout deposit presented in Boudon et al. (2008) and Metcalfe et al. (2021), respectively.

479 5.2 SO_2/H_2S gas ratios

480 SO_2/H_2S ratios measured by the MultiGas were slightly higher in 2021 with respect to discrete 481 measurements carried out between 2006 and 2020 (Allard et al. 2014; Tamburello et al. 2019; Moune et al.

- 482 2022). Nevertheless, filter pack measurements gave even higher ratios (as high as 0.94 in August 2021), up 483 to one order of magnitude higher than the MultiGas dataset (Table 3). These high ratios are considered debatable given SO₂-poor and H₂S-rich plumes at La Soufrière. Such high SO₂ concentrations in filter 484 pack measurements may possibly be because the NaHCO₃-impregnated filters could trap S-bearing species 485 other than SO₂ (e.g., H_2S , HS^- , SO_3^{2-}) at high humidity conditions, increasing the concentration of sulfates 486 measured (Mioduszewski and Kress 2008). Therefore, filter wetness could enhance S-species trapping, 487 488 similar to what occurs in coal industries when alkaline traps are used for H₂S removal (e.g., Garner et al., 1958). Consequently, SO₂ concentrations and SO₂/H₂S gas ratios measured by filter packs in humid and 489 490 foggy conditions cannot be fully trusted. Nevertheless, H₂S concentrations can be trusted even if some SO₂ is trapped in H_{H2S} filters, which in any case would be minimal given negligible SO₂ concentrations in the 491 492 plume.
- 493 5.3 Trace element enrichment in the plume

494 Fumarolic plumes at La Soufrière volcano show significant concentrations of major (chemical elements 495 with concentrations above 1000 ppm in host rocks) and trace elements. They include lithophile and 496 siderophile elements, which are well correlated with water-rock interaction in the hydrothermal system and 497 erosive processes in fumarolic conduits, besides chalcophile elements which are usually enriched in 498 volcanic gases given their affinity with sulfur (Symonds et al. 1990; Aiuppa et al. 2003; Inostroza et al. 499 2022a). Among these, a significant proportion of heavy metals is also present in the plume. The most suitable approach to better understand the volatile and non-volatile contribution of trace elements in 500 501 volcanic emissions is the enrichment factor (EF; Duce et al. 1975; Mroz and Zoller 1975), which measures 502 the extent of enrichment (or depletion) of an element based on its concentration in host rocks (Lepel et al. 503 1978; Taran et al. 2001; Gauthier et al. 2016). The EF can be calculated as follow:

504 $EF = (X/Y)_a/(X/Y)_r$

505 where X and Y are the concentrations of the element of interest and the reference element in the aerosol 506 filter (a) and host rocks (r), respectively. Application of the EF in low-temperature hydrothermal emissions 507 such as those in La Soufrière should be cautiously considered if a comparison with other more magmatic 508 volcanic emissions is intended. Usually, EFs are helpful in better understating magma degassing processes, 509 which explains the frequent application of this method in high-temperature magmatic emissions. In the 510 case of La Soufrière, degassing processes are screened by the extensive hydrothermal system produced by 511 the scavenging of significant but undetermined amount of major and trace elements. Therefore, here we 512 used the EF to evaluate variable contributions related to magma degassing, water-rock interaction, and 513 trace element scavenging.

514 The choice of the reference element is critical to better interpret EFs; thus an element of low-moderate 515 volatility and of low abundance in andesitic lavas and aerosol filters is commonly used. Be, Mg, Ti, Th, or

516 Br have been commonly chosen as reference elements in earlier EF computations (Symonds et al. 1987;

517 Taran et al. 1995; Moune et al. 2010; Calabrese et al. 2011; Zelenski et al. 2013), especially in volcanoes 518 with magmatic emissions. However, those reference elements are inappropriate in hydrothermal emissions, 519 given their generally non-negligible concentrations. In our case, Y appears as a good candidate for a 520 reference element, given its low volatility, low concentration in aerosol filters and host rocks, and trusty 521 values according to low RSDs (generally <5 %RSD). Moreover, Y is thoroughly presented in the dataset.</p>

Average Y-based EFs in aerosol samples from CS, G56, and NapN plumes have been presented in Figure 522 8. Chemical elements enriched in the plume (with EF of 10^3 - 10^5) are Br, Fe, K, Sb, Ca, Ti, Bi, Si, Cl, Al, 523 524 Mn, Mg, S, and B. In particular, the enrichment of chalcophiles (Sb, Bi, S) and halogens (e.g., Cl and Br) 525 demonstrate the input of magma-related compounds in the roots of the hydrothermal system (Moune et al. 526 2010; Allard et al. 2014; Zelenski et al. 2014). Conversely, enrichments in Fe and certain lithophiles evidence the importance of water-rock interaction processes in the volcanic edifice (Symonds et al. 1990; 527 528 Inostroza et al. 2022a,b). Moreover, Cr, Zn, Sn, Mo, As, I, Ni, Pb, Tl, W, Cu, Cs, and Ta appear moderately enriched in the plume (EF of 10^{1} - 10^{3}). This group of elements can be interpreted as i) 529 chalcophiles that behave as volatile in magmatic systems, but in La Soufrière, they appear significantly 530 531 scavenged by volcanic groundwaters, and ii) lithophiles and siderophiles leached from host rocks and transported within aqueous droplets. Finally, a third group poorly enriched in the plume (EF< 10^1) is 532 formed by lithophiles and chalcophiles (except for Ga). These elements can be considered less soluble and 533 534 are in minor concentrations in both plumes and host rocks of La Soufrière.

In summary, the CS plume shows the highest EF, closely followed by NapN, while the G56 plume 535 536 occasionally presents EF up to one to two orders of magnitude lower than CS and NapN. Variable EFs at 537 CS, G56, and NapN (Fig. 8) can be explained by, i) artifacts caused by the sampling position and ii) 538 internal magmatic-hydrothermal processes impacting physicochemical characteristics (e.g., flux rates, 539 steam proportion, and outlet temperatures) of fumarolic discharges. We believe that G56 data in this work 540 could be underestimated because of longer sampling distances to the vent and occasionally unfavorable wind direction during sampling, favoring condensation or no collection of certain elements on the filters. 541 542 On the other hand, CS and NapN offer more appropriate sites for sampling at distances <5 m from the 543 vent.

544 CS and NapN filters present direct plume exposure, but NapN shows lower EFs than CS (Fig. 8). This variation can be explained based on different degassing processes affecting these fumaroles. For example, 545 it is believed that the transport of major and trace elements in low-temperature fumarolic emissions can be 546 547 enhanced in the presence of steam-rich fumaroles and high pressure-temperature conditions in the 548 hydrothermal reservoir (Heinrich et al. 1999; Pokrovski et al. 2013). Particularly, NapN differs from CS because of lower steam proportions (75 versus 96 mol%; Tamburello et al. 2019; Moune et al. 2022), 549 550 lower flux rates (Jessop et al. 2021), and lower outlet temperatures (95 versus 100-111 °C; Moretti et al. 551 2020a,b; Inostroza et al. 2022a,b). It has been recently demonstrated that NapN emissions are significantly 552 scrubbed by shallow hydrothermal aquifers, while CS preserves a more profound and magmatic signature

(Tamburello et al. 2019; Moretti et al. 2020a). Consequently, the sampling position and physicochemical processes accounting in the magmatic-hydrothermal system play an essential role in the enrichment of major and trace elements in hydrothermal plumes.

556 Comparison of our computed EF and those recalculated EF from gas condensates collected by Inostroza et 557 al. (2020a; Fig. 8) show a general coherent pattern in plumes and gas condensates, suggesting similar physicochemical processes impacting fumarolic emissions. The main discrepancies are observed in K, Si, 558 Mn, Mg, S, Rb, and Ba, which seem more enriched in condensates than plume measurements, mostly 559 likely due to their transportation within steam condensed droplets or solid particles (Inostroza et al. 2022a) 560 561 and partial deposition closer to the vent (Sainlot et al. 2020). Gas condensates and plumes from La Soufrière also contain significant concentrations of contaminant trace elements such as Sb, Bi, Cr, As, Ni, 562 Pb, and Tl, some even detected in point-EDS particle analyses (e.g., Cr, Ni). The transport of trace 563 564 elements in volcanic plumes is usually correlated with the presence of ligands such as halides, sulfates, or hydroxides (Pokrovski et al. 2013; Mandon et al. 2019: Scholtysic and Canil 2020). However, they are 565 characterized by volatility close to zero at the temperatures found in La Soufrière volcano (up to 111 °C) 566 567 and concentrates in dense and high-temperature brines within the hydrothermal system (Pokrovski et al. 2013). This highlights the important role of water in the transport of metals and metalloids, whose 568 569 significant concentration in fumarolic emissions is more related to the water-rich concentration rather than 570 the concentration of typical ligands (Pokrovski et al. 2013). Consequently, their transport mechanisms 571 would be linked more to transportation within liquid droplets instead of gaseous compounds (Inostroza et 572 al. 2022a).



573

574 **Figure 8** Average Y-based Enrichment Factors (EF_Y) for CS, G56, and NapN plumes. The grey area 575 shows the average EF_Y considering 35 CS and 19 NapN gas condensate samples, respectively, according 576 to the data already published in Inostroza et al. (2022a) (Supplementary Material 2).

- 577 5.4 Trace element emission rates at La Soufrière volcano
- Any trace element emission rate F(X) can be calculated by multiplying gas-normalized ratios in filter 578 packs by the corresponding gas emission rates (Mather et al. 2004). Typically, SO₂ is the normalization gas 579 580 species chosen for this calculation because it has an unambiguously magmatic signature, significative 581 concentrations in volcanic plumes, and a wide range of available techniques to measure its concentration. 582 However, SO₂ concentrations are negligible at La Soufrière. Consequently, we calculated emission rates 583 using H_2S fluxes from MultiGas determination in a way similar to Allard et al. (2014), who used this species to estimate La Soufrière's volatile fluxes released from the magma chamber. Their study 584 585 demonstrated that at La Soufrière, H₂S can be considered as a species of magmatic provenience despite its 586 hydrothermal re-equilibration. Trace element emission rates (F(X)) are then calculated as follows:
- 587 $F(X) = [X/H_2S]_{FP} \times F(H_2S)$
- 588 where $[X/H_2S]_{FP}$ is the mass ratio of any trace element "X" obtained by the filter pack (*FP*) technique and 589 F(H₂S), the H₂S flux measured with the MultiGas.
- 590 Trace element emission rates for La Soufrière volcano have been presented in Table 5. These values are 591 computed considering only the selected heavy metals commonly enriched in volcanic plumes and in most 592 cases, originated by magma degassing. The F(X) values (Table 5) have been calculated for four CS and one G56 samples, using H₂S emission rates of 1.50-2.83 and 0.34 t/d, respectively (Table 4). Heavy metal 593 emission rates range from 2.8×10^{-6} to 15 g/d and 1.8×10^{-6} to 6.1 g/d in CS and G56, respectively, with CS 594 samples presenting higher emission rates than the G56 one (Fig. 9) with the exception of Fe, which 595 596 presents similar emission rates in both CS and G56 plumes. Table 5 and Figure 10 also highlight the high 597 flux of Zn, Ni, and Sb, with emission rates up to $\sim 1 \text{ g/d}$, especially in the sample collected in March 2021. Fe, Zn, Ni, and Sb emission rates are comparable to Hg rates of 2.19 g/d measured at CS in 2006 by 598 599 Bagnato et al. (2009). Emission rates of Sn, Cu, As, Se, Tl, Pb, Ni, Bi, Te, Co, and Mo generally remained below 0.1 g/d. By comparing CS and G56 fumaroles, it can be shown that Fe, Sn, As, Se, and Co presented 600 601 relatively similar average emission rates. Conversely, Cu, Zn, Tl, Ni, and Sb appear with emission rates 602 more than one order of magnitude higher in CS, suggesting that the latter trace elements are scrubbed more 603 than Fe, Sn, As, Se, and Co in the hydrothermal system.
- These emission rates represent the first data obtained from low-temperature steam-rich volcanic emissions and provide valuable information about the efficiency of trace element scavenging by hydrothermal processes. These emission rates must however be considered as minimum values given possible leaching affecting PTFE filters during sampling in the presence of humid climatic conditions and partial deposition of certain soluble elements near the fumarolic vent (Section 3.1).
- 609 **Table 5** Trace element emission rates (g/d) discharged from CS and G56 fumaroles in La Soufrière de 610 Guadeloupe volcano. $F(H_2S)$ is the H_2S flux retrieved from MultiGas (in t/d), and H_2S is the concentration 611 (in g/m³) measured in the aerosol filter using the filter pack technique. Average fluxes in the Caribbean

612 atmosphere (expressed in t/d) are collected from Chester et al. (1979), Morera-Gómez et al. (2019), and

613 Xu-Yang et al. (2022) and presented in Supplementary Material 3. Atmospheric fluxes are converted from

 $kg m^{-2} y^{-1}$ into kg/d using the areal factor of $35\pm 5 m^2$, which corresponds to the average plume cross-

section considering a flattened plume of 3-4 m high and 10 m wide (Gaudin et al., 2016; Allard et al.,

616 2016; Jessop et al., 2021; Moune et al., 2022).

Fumarole	CS	CS	CS	CS	G56	Caribbean Atmosphere *
Filter	H _{H2S}	$\mathbf{H}_{\mathbf{A}}$	$\mathbf{H}_{\mathbf{A}}$	$\mathbf{H}_{\mathbf{A}}$	$\mathbf{H}_{\mathbf{A}}$	-
Date	16/03/2021	04/06/2021	15/06/2021	25/08/2021	19/07/2021	-
F(H ₂ S)	1.50	2.83	2.83	1.57	0.34	-
H_2S	0.16	1.67	1.11	1.05	0.58	-
Fe	1.4×10^{-1}	2.5×10^{0}	1.5×10^{1}	9.2×10^{0}	6.1×10^{0}	4.0×10 ⁻²
Cr	4.4×10^{0}	1.3×10^{-1}	2.2×10 ⁻²	nd	nd	1.0×10^{-4}
Sn	2.7×10^{-4}	4.4×10^{-2}	3.1×10 ⁻³	5.2×10 ⁻²	7.2×10^{-3}	1.2×10^{-5}
Cu	1.5×10^{-2}	2.0×10^{-1}	2.1×10 ⁻²	6.3×10 ⁻²	4.8×10 ⁻³	1.8×10^{-4}
As	nd	3.0×10 ⁻³	1.6×10 ⁻³	2.1×10 ⁻³	2.7×10^{-4}	4.2×10 ⁻⁵
Zn	1.1×10^{0}	2.3×10^{0}	5.1×10 ⁻²	8.9×10^{-1}	3.5×10 ⁻²	1.5×10^{-3}
Se	2.8×10 ⁻²	6.7×10^{-4}	nd	2.3×10 ⁻³	1.3×10 ⁻³	nd
Tl	2.1×10 ⁻³	2.8×10 ⁻⁶	1.9×10 ⁻⁵	2.6×10 ⁻⁵	1.8×10^{-6}	4.6×10 ⁻⁷
Pb	6.1×10 ⁻³	8.4×10 ⁻³	nd	4.1×10 ⁻³	nd	1.3×10 ⁻⁴
Ni	2.7×10^{-1}	8.1×10 ⁻²	4.4×10 ⁻³	8.9×10 ⁻³	1.5×10^{-3}	9.2×10 ⁻⁵
Bi	nd	3.1×10 ⁻⁴	nd	1.3×10 ⁻⁵	Nd	9.8×10 ⁻⁵
Sb	1.7×10^{0}	1.7×10^{-2}	4.0×10 ⁻¹	1.5×10^{-2}	1.0×10^{-4}	8.1×10^{-5}
Te	nd	3.5×10 ⁻⁵	2.9×10 ⁻⁴	1.1×10 ⁻⁴	nd	nd
Со	7.3×10 ⁻³	7.7×10^{-4}	2.0×10 ⁻³	1.3×10 ⁻³	2.7×10^{-4}	1.0×10 ⁻⁵
Мо	4.8×10 ⁻²	4.8×10 ⁻⁴	nd	7.4×10^{-4}	nd	1.1×10^{-5}

617 Nd: not determined/not calculated

618 Comparing La Soufrière emission rates with other quiescently degassing subduction-related volcanoes permits a better understanding of the heavy metal contribution at this volcano and low-temperature 619 620 hydrothermal emissions. Figure 9 shows that La Soufrière's emissions rates are the lowest values reported 621 in the limited literature data for magmatic-hydrothermal emissions. Typical magmatic emissions range 622 between 1 and 2500 kg/d (Moune et al. 2010; Allard et al., 2016), while magmatic-hydrothermal systems 623 such as Lascar (Chile), White Island (New Zealand), and El Chichon (Mexico) emit heavy metal rates ranging from 0.004 to 220 kg/d (Phelan Kotra et al. 1983; Menard et al. 2014; Mandon et al. 2019). 624 625 Emission rates of <15 g/d at La Soufrière (Table 5) represent a modest contribution compared to global heavy metal emission rates in actively degassing volcanoes. Such differences can be explained based on 626 627 variable magmatic and hydrothermal contributions depending on the depth of magma mush and the 628 amount of water inside the volcano edifice. Higher emission rates are well correlated with a more 629 significant magmatic contribution of heavy metals that are degassed directly from shallow crustal magma 630 chambers, as typically observed at volcanoes that have experienced recent magmatic eruptions, such as El

Chichon or White Island (Global Volcanism Program 2022), and also at open vent volcanoes such as 631 632 Masaya and Ambrym. We suggest that low emission rates of heavy metals observed at La Soufrière and Lascar can be attributed to the depth of the magma chamber, which in both is located at >6 km below the 633 634 volcano summit (Díaz et al. 2012; Pichavant et al. 2018). Such considerable depths favor the interaction of 635 heavy metals with host rocks and groundwaters on their rise through the conduit system. Despite similar 636 magma chamber depths beneath La Soufrière and Lascar, these volcanoes differ in the amount of rainwater 637 entering in their hydrothermal systems. For example, Lascar is located in the driest desert on the Earth, while La Soufrière is impacted by huge inputs of rainwater (up to 10 m per year; Dessert et al. 2015). Such 638 639 an input favors widespread hydrothermal emissions at La Soufrière, supported by the predominance of H_2S instead of SO₂, including numerous cold and thermal emissions on volcano flanks. On the other hand, 640 641 Lascar presents fumarolic emissions rich in SO₂, HF, and HCl (Mather et al. 2004; Tassi et al. 2009), and a 642 few thermal springs, and reports of subplinian and vulcanian eruptions in the last decades (Matthews et al. 1997; Global Volcanism Program 2013). Consequently, it is believed that low heavy metal emissions rates 643 at La Soufrière and other low-temperature volcanic emissions are strongly influenced by the location of the 644 645 magma chamber and the extent of scrubbing processes depending on the amount of water inside the 646 volcanic edifice (Blundy et al. 2021).

647 Computed heavy metal fluxes were then compared to average Caribbean atmospheric deposition fluxes 648 reported in Chester et al. (1979), Morera-Gómez et al. (2019), and Xu-Yang et al. (2022) to estimate if volcanic emissions from La Soufrière represent an important pollution source in the Caribbean 649 650 atmosphere. Deposition fluxes represent the amount of material that is deposited in a given area and period 651 of time, without considering chemical species that remain in the atmosphere Thus these fluxes represent 652 only a fraction of the elements in the Caribbean atmosphere and should be considered as a minimum. 653 Average fluxes were used being aware that the Caribbean atmosphere presents heterogeneities in terms of 654 heavy metal content along the Lesser Antilles arc. Furthermore, Morera-Gomez et al. (2019) found anthropogenic influence in Cuba. However, Fe and Zn fluxes (Supplementary Material 3), which are 655 656 elements sensitive to anthropogenic contamination, suggest relatively homogeneous atmospheric chemical 657 composition at the time of these studies. This allowed us to ensure the consistency of the heavy metal data 658 we used for comparison.

Atmospheric fluxes have been converted into kg/d using the areal factor of 35 ± 5 m², which corresponds to 659 the average plume cross-section considering a flattened plume of 3-4 m high and 10 m wide, following the 660 observations made by Allard et al. (2014), Gaudin et al. (2016), Jessop et al. (2021) and Moune et al. 661 (2022). Successively, normalized fluxes ranged between 4.6×10^{-10} and 4.0×10^{-5} kg/d (Fig. 9). These 662 atmospheric fluxes are up to four times lower (e.g., Cr, Sb, Sn, Mo) than La Soufrière fluxes, especially in 663 664 the case of the CS fumarole, which is considered as the primary heavy metal source at this volcano. Notably, atmospheric and volcanic fluxes of Bi displayed closer values, while the G56 fumarole has 665 average fluxes equal to or slightly higher than atmospheric fluxes. Consequently, modest heavy metal 666 667 emissions from La Soufrière can be regarded as a source of pollution in Guadeloupe, although their impact

are very limited in space compared to the major contributors such as dust from the Sahara and marine salts.

669 Moreover, anthropogenic inputs remain poorly constrained and should be carefully considered in future 670 studies, although their influence is believed to be minimal.



671

Figure 9 Heavy metal emission rates (kg/d) compared with other subduction-related and quiescently degassing volcanoes with evidence of hydrothermal activity, such as White Island (Mandon et al. 2019), Lascar (Menard et al. 2014), and El Chichon (Phelan Kotra et al. 1983) volcanoes. The gray area represents emission rates at La Soufrière, and the black dotted and red dashed lines are average emission rates from CS and G56 fumaroles, respectively. The blue dashed area represents the average trace element deposition fluxes in the Caribbean atmosphere according to published bibliographic data (Chester et al. 1979; Morera-Gómez et al. 2019; Xu-Yang et al. 2022).

679 6 CONCLUSIONS

680 This work presented a detailed study on the physicochemical characteristics of volcanic plumes from Cratere Sud, Napoleon Nord, and Gouffre 56 fumaroles, three of the most important degassing sites in La 681 682 Soufrière de Guadeloupe volcano. The sampling was challenging because of harsh weather conditions on the volcano summit and the nature (steamy- and H₂S-rich) of fumarolic emissions, forcing the adaptation 683 of traditional sampling procedures. Given these distinctive characteristics, aerosol filters developed 684 685 droplets during exposure to the plume, following which the partial leaching potentially occurred. 686 Consequently, major and trace element concentrations in the analyzed plumes must be considered 687 minimum concentrations.

Microscopic and chemical analyses identified major and trace elements transported within gas and aerosol 688 phases. Remarkably, volcanic plumes at La Soufrière contain significant concentrations of lithophile or 689 rock-related elements from water-rock interaction processes in the hydrothermal system, in addition to 690 691 significant concentrations of chalcophiles related to a deeper magmatic source. Moreover, La Soufrière is an important source of potentially toxic heavy metals such as Sb, Bi, Cr, As, Ni, Pb, and Tl. Given low 692 693 outlet gas temperatures at La Soufrière's vents, it is believed that most of the elements enriched in the 694 plume are transported within tiny droplets, although the presence of Si-rich and sulfur particles suggests 695 the substantial erosion at the vent. Rock-related and chalcophile elements suggest a variable contribution 696 from hydrothermal sources and magmatic degassing processes.

697 This work also presents the first estimate of heavy metal emission rates discharged at La Soufrière fumaroles. Modest emissions rates (up to 15 g/d) are ascribed to the combination of two physicochemical 698 699 factors: 1) low-temperature fumarolic emissions and 2) small amount of common heavy metal ligands such 700 as chlorides and sulfates in the gas phase. These factors can be explained by a relatively deep location of 701 the magma chamber, the primary source of heavy metals, and the presence of a well-developed 702 hydrothermal system in the volcanic edifice fed by abundant rainfall typical of tropical environments. We 703 suggest that these factors may occur at other volcanoes at the hydrothermal stage whose fluids have a clear 704 magmatic signature. Estimated heavy metal emission rates place La Soufrière as the most modest heavy 705 metal emitter among quiescently degassing subduction volcanoes, but still as an important point of 706 pollution in the Lesser Antilles volcanic arc. Heavy metal degassing at La Soufrière suggests no evident 707 hazard at the volcano summit. However, additional research should be carried out about the transport and 708 evolution of species in low-temperature volcanic plumes released in tropical environments to evaluate their 709 impact on nearby communities.

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726 SUPPLEMENTARY MATERIALS

Supplementary Material 1 provides all SEM-EDS images, including the location of point-chemical analyses. Supplementary Material 2 corresponds to an excel file including chemical and background corrections, besides EF computations. Finally, Supplementary Material 3 provides general information and computations concerning filter packs, MultiGas, and trace element fluxes.

731 CONFLICTS OF INTEREST

The authors declare there are no conflicts of interest.

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