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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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ABSTRACT

Hydrothermal or low-temperature volcanic emissions, most commonly occurring in fumarolic environments, dominate the global volcanic landscape. This work presents physicochemical characterization of the aerosols contained in steam- and H₂S-rich plumes discharged from La Soufrière volcano, in conjunction with the first report on their heavy metal degassing emission rates. Our results indicate that the plume is enriched in certain lithophile (K, Ti, Si, Al, Mn, and Mg) and siderophile (Fe) elements, related to hydrothermal rock leaching, and chalcophile (Sb, As, Zn, Pb, and Tl) elements, which are usually degassed from the magma source. Heavy metal emission rates were found to be below 15 g/d, which are modest compared to available worldwide data. Nevertheless, Cr and Sb emission rates were very similar to those of Lascar volcano (Chile), which instead has produced magmatic eruptions in recent times. We propose that the depth of the magma chamber and the input of meteoric waters play an important role in scavenging heavy metals in the hydrothermal system of magmatic-hydrothermal volcanoes. Notwithstanding low heavy metal emission rates, La Soufrière can be regarded as an important pollution source in the Lesser Antilles volcanic arc.

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

34 according to their chemical compositions, outlet gas temperatures, and the degree of interaction with host
35 rocks and aquifers hosted in the volcanic edifice (e.g., Giggenbach, 1996; Symonds et al., 2001; Fischer
36 and Chiodini, 2015; Moretti and Stefánsson, 2020). Typical magmatic emissions are characterized by
37 significant concentrations of SO₂ and halides, high outlet gas temperatures (>450 °C; Aiuppa et al. 2017),
38 and minimal scrubbing processes (Symonds et al. 2001). On the other hand, hydrothermal emissions are
39 enriched in H₂S 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).

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
46 elements include so-called heavy metals, which are toxic even at low concentrations and are degassed as
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
50 surrounding communities (e.g., Varrica et al. 2014; Vigneri et al. 2017; Tomašek et al. 2022). Though
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
58 brine evaporation (Africano and Bernard 2000), can scavenge some or add other trace elements. In
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).

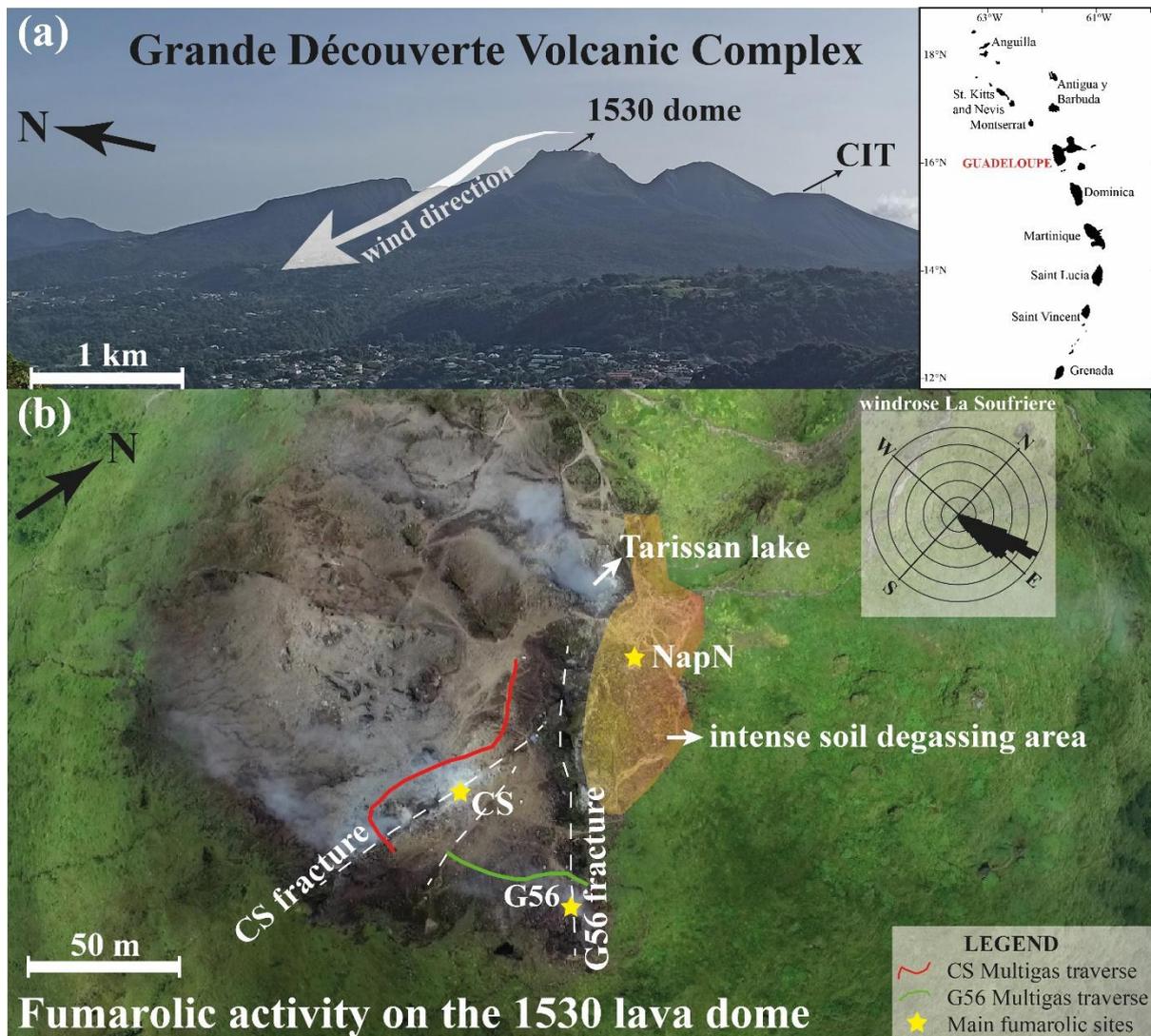
63 La Soufrière de Guadeloupe (hereafter La Soufrière) is an andesitic volcano in the Lesser Antilles arc,
64 formed by the subduction of the Atlantic Plate below the Caribbean Plate (Feuillet et al. 2002). La
65 Soufrière has presented persistent degassing since 1992, which gradually increased in intensity in the last
66 three decades. Currently, fumarolic emissions here are characterized by high amounts of steam (~200 t/d),
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

70 of lithophile and chalcophile elements, along with heavy metals such as Sb, Bi, and Zn. However, the
71 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

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



89

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 856
 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
 96 et al. (In press). The Citerne (CIT), the place where the atmospheric background sample was collected, is
 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
108 °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
110 Soufrière; SO₂ has only been detected through MultiGas measurements with common SO₂/H₂S ratios
111 between 0.004 and 0.1 (Tamburello et al. 2019; Moune et al. 2022). Furthermore, HCl has been measured
112 at concentrations of ~0.2 mol% (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.
116 2014; Tamburello et al. 2019; Moretti et al. 2020a; Moune et al. 2022; Inostroza et al. 2022b). Recent
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
127 fluctuations suggest that CS could be connected with a deeper portion of the hydrothermal system,
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
132 important emitter of major and trace elements. According to Inostroza et al. (2022a), most of those
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
135 aqueous particles is favored by lower outlet gas temperature and more significant steam proportions in La
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)
144 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
146 emissions, this study used the modified sampling and analytical methods employed in Aiuppa et al. (2005)
147 and described below.

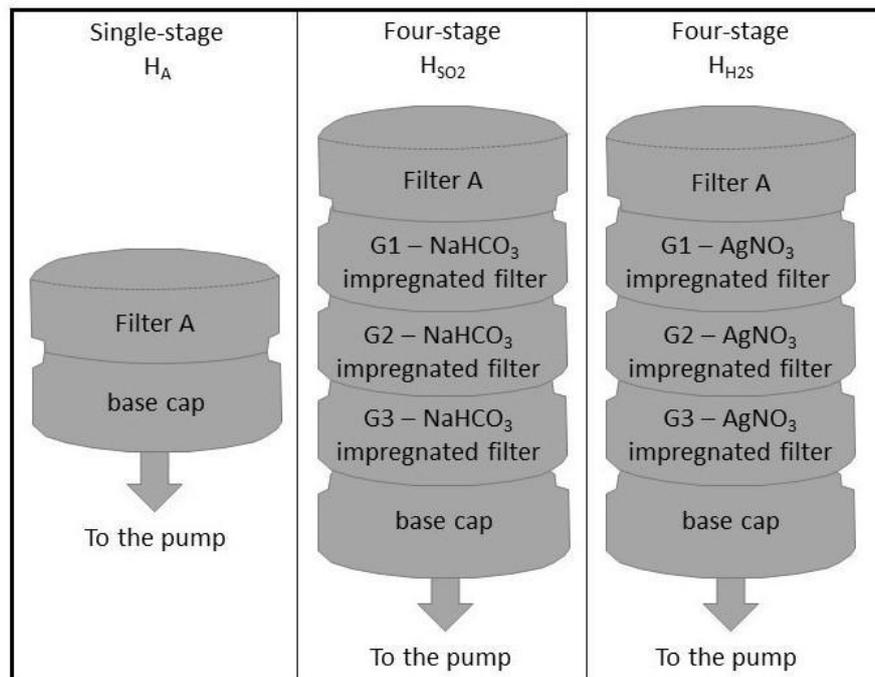
148 Before field sampling, ashless paper filters (Wathman™ 1440-047) were impregnated with two solutions
149 to independently trap gaseous SO₂ and H₂S. Gas filters dedicated to trapping SO₂ were impregnated with a
150 solution of 1.2 M NaHCO₃, glycerol (10 wt.%), and methanol (40 wt.%) (Allen et al. 2000), while those
151 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 (Fluoropore™ 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
155 high relative humidity (RH ranging from 80 to 100%, Table 1) and the steam- and H₂S-rich chemistry of
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
160 more than 10% of the gas. However, it was assumed that for a measurement to be valid, the last filter must
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
170 amounts of particles, while H_{H2S} and H_{SO2} were exposed for 15 and 25 min, respectively, to avoid filter
171 saturation.

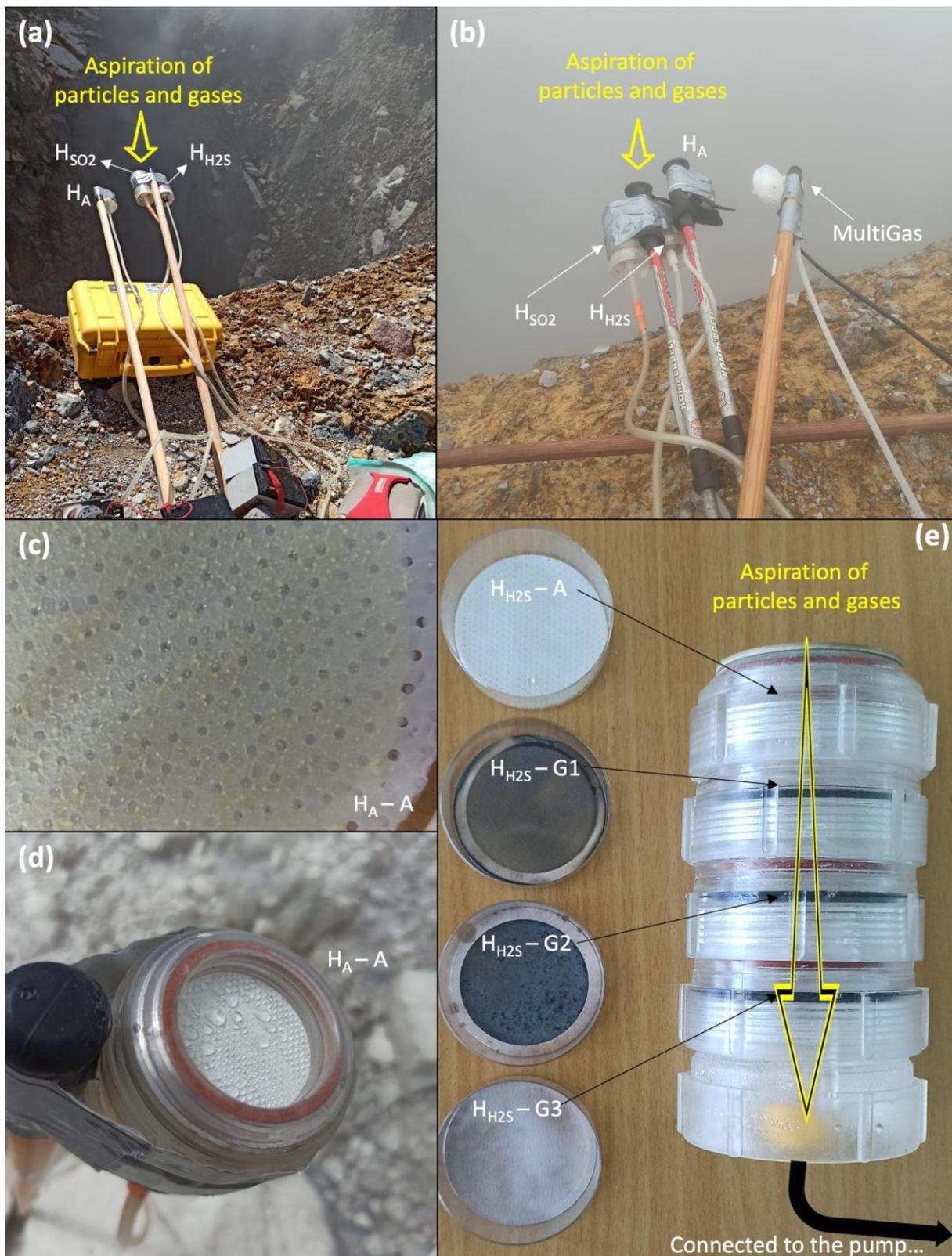
172 The plume was sampled from three sites located at <10 m from the vent (3 and 5 m from CS and NapN,
173 respectively, and ~10 m from the G56 vent; Table 1) and at 0.5-1.2 m above the soil (Fig. 3a, b) to reduce

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



181

182 **Figure 2** Sketch describing filter pack assemblage used for sampling volcanic plumes at La Soufrière
 183 volcano. At each site, three filter pack holders called H_A , H_{SO_2} , and $H_{\text{H}_2\text{S}}$ were arranged to trap aerosols,
 184 aerosols+ SO_2 , and aerosol+ H_2S , respectively. The sequence G1-G2-G3 (Gas 1, Gas 2, and Gas 3) refers to
 185 the impregnate gas filter position in the holder.



186

187 **Figure 3** Filter pack assemblage for plume sampling procedures at La Soufrière volcano: a) Sampling
 188 during less humid (RH 80 %, August 25, 2021) weather conditions, b) Sampling during humid (RH 92%,
 189 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 H₂S after 15 min plume
191 exposure: dark brownish filters denote the reaction of H₂S 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
195 were eluted with 20 ml of Milli-Q water and left at ambient temperatures for one week. Subsequently, the
196 sample was analyzed by ionic chromatography (Dionex Integrion™) to determine the concentration of
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
200 into Teflon beakers and eluted twice with a mixture of diluted HNO₃ (19 ml, 2 vol.%) plus H₂O₂ (1 ml, 60
201 vol.%) on a hot plate (~80 °C) until dry. Subsequently, the residue was eluted with 20 ml of Milli-Q to
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
216 working distance. The acquisition of high-resolution imaging and data processing was made using
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 (m³), 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	84
		A+G1+G2 [§]	H _{H2S}	12	0.18		

29/01/2021	NapN	A+G1+G2* [§]	H _{SO2}	6.7	0.134	3	88
		A+G1+G2 [§]	H _{H2S}	12	0.18		
12/02/2021	CIT	A+G1+G2	-	12	0.84	1400**	84
16/03/2021	CS	A+G1+G2+G3	H _{SO2}	6.7	0.1139	5	90
		A+G1+G2+G3	H _{H2S}	7	0.119		
		A*	H _A	12	-		
04/06/2021	CS	A G1+G2+G3	H _{SO2}	7	0.175	5	95
		A+G1+G2+G3	H _{H2S}	6.7	0.1005		
		P	H _A	12	0.6		
15/06/2021	CS	A+G1+G2+G3	H _{SO2}	7	0.175	5	85
		A+G1+G2+G3*	H _{H2S}	6.7	0.1005		
		A	H _A	12	0.72		
15/06/2021	NapN	A+G1+G2+G3*	H _{SO2}	6.7	0.1675	3	85
		A+G1+G2+G3	H _{H2S}	7	0.105		
		A	H _A	12	0.54		
19/07/2021	CS	A+G1+G2+G3	H _{SO2}	7	0.196	5	91
		A+G1+G2+G3*	H _{H2S}	6.7	0.1139		
		A*	H _A	12	-		
19/07/2021	G56	A+G1+G2+G3*	H _{SO2}	7	0.175	10	92
		A+G1+G2+G3	H _{H2S}	6.7	0.1072		
		A	H _A	12	0.744		
25/08/2021	CS	A+G1+G2+G3*	H _{SO2}	7	0.175	5	80
		A+G1+G2+G3	H _{H2S}	6.7	0.1005		
		A	H _A	12	0.72		
25/08/2021	G56	A+G1+G2+G3	H _{SO2}	6.7	0.1675	10	80
		A+G1+G2+G3*	H _{H2S}	7	0.105		
		A	H _A	12	0.72		
22/09/2021	CS	A+G1+G2+G3	H _{SO2}	6.7	0.1675	5	49
		A+G1+G2+G3*	H _{H2S}	7	0.105		
		A	H _A	12	0.72		
22/09/2021	G56	A+G1+G2	H _{SO2}	6.7	0.1675	10	63
		A+G1+G2+G3*	H _{H2S}	7	0.105		
		A	H _A	12	0.72		

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

224 3.2 MultiGas

225 Fluxes of major gas compounds emitted from degassing volcanoes are usually measured by ground-based
226 remote techniques such as Differential Optical Absorption Spectroscopy (DOAS) or UV cameras. These
227 techniques allow reliable fluxes of SO₂ to be obtained. However, these techniques cannot be applied to La
228 Soufrière de Guadeloupe, where fumarolic emissions contain negligible amounts of SO₂ but high
229 concentrations of H₂S. Consequently, we used a MultiGas device (Aiuppa et al. 2005a; Shinohara 2005) to
230 measure H₂S fluxes in the volcanic plume following the method proposed by Allard et al. (2014) and
231 Tamburello et al. (2019).

232 MultiGas is a portable multi-sensor system that allows fast measurement of primary gas compounds in
233 volcanic plumes. This device included a Gascard IR spectrometer for CO₂ determination (calibration
234 range: 0–3000 ppmv; accuracy: ± 2%; resolution: 0.8 ppmv) and City Technology electrochemical sensors
235 for SO₂ (sensor type 3ST/F; calibration range: 0–200 ppm, accuracy: ± 2%, resolution: 0.1 ppmv) and H₂S

236 (sensor type 2E; range: 0–200 ppm, accuracy: $\pm 5\%$, resolution: 0.7 ppmv). It has a GPS attached that
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
243 ground with a maximum gas density centered at 1.5–2 m above the ground (Gaudin et al. 2016; Tamburello
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.

247 $\text{CO}_2/\text{H}_2\text{S}$ and $\text{SO}_2/\text{H}_2\text{S}$ gas ratios were processed with the least squared method using the RatioCalc
248 software (Tamburello 2015). We interpolated the concentration measurements for CS and G56 using a 2D
249 spline function and then integrated them over the plume cross section to obtain Integrated Concentration
250 Amounts (ICAs) using RatioCalc software (Tamburello 2015). These computations were based on CO_2 as
251 a volcanic marker (ICA CO_2 ; Table 4), given that the IR CO_2 sensor reacts faster than the H_2S sensor and
252 CO_2 measurements are not affected by high humidity conditions (Tamburello et al. 2019). Subsequently,
253 CO_2 fluxes were computed by scaling the obtained CO_2 concentration in plume cross sections with the
254 average wind speed. Finally, H_2S was computed by scaling the average $\text{H}_2\text{S}/\text{CO}_2$ weight ratio with the CO_2
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

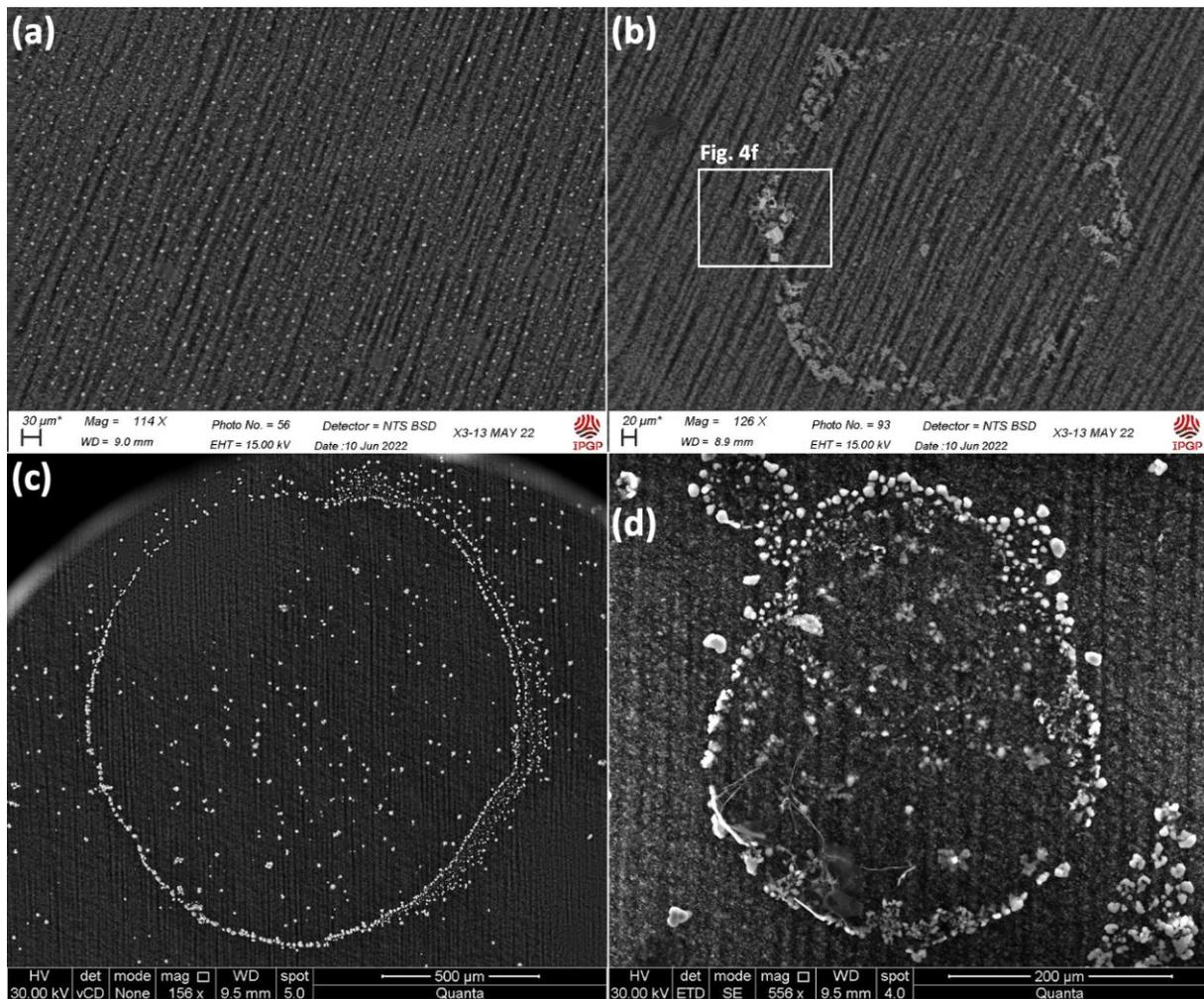
258 4.1 Physicochemical characterization of solid particles

259 The type, morphology, and chemistry/mineralogy of particles transported within the plume at La Soufrière
260 volcano were investigated. The appearance of PTFE filters during and after the sampling featured
261 significant amounts of small yellowish particles (Fig. 3c), a few dark particles, and droplets (Fig. 3d). No
262 evident correlation between sampling time and the number of particles was noted. Longer exposures
263 however have the ability to potentially enhance the possible leaching of the filters, resulting in microscopic
264 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.

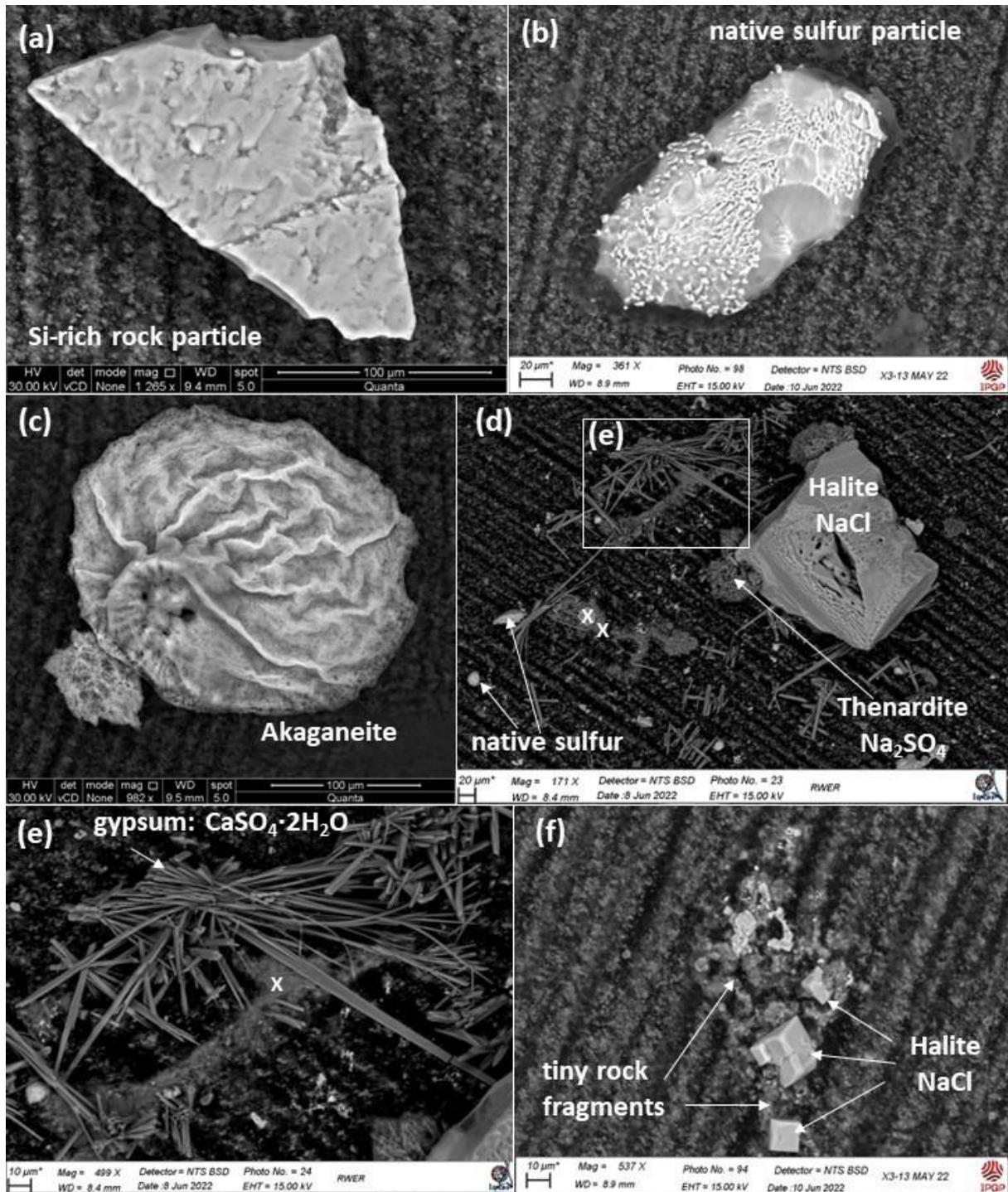
266 The size of the solid particles on filters was measured to be up to 310 μm , and found as subrounded droplet
267 marks or scattered on the filter (Fig. 4; Supplementary Material 1). In general, solid particles appeared
268 abundantly in CS filters than in NapN or G56 filters, likely due to the stronger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

272 thenardite (Na_2SO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Fig. 5). In the case of gypsum, the presence of bassanite
 273 ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4) 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
 275 possible akaganeite ($\text{Fe}^{3+}\text{O}(\text{OH},\text{Cl})$; Fig. 5), in addition to several unidentified Cl-bearing particles
 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
 281 Fe-O (48 and 47 wt.%, respectively) particle with traces of Mn, S, Cl, and K was found on NapN filters,
 282 which could be linked with hematite (Fe_2O_3), although EDS analyses were inconclusive. Similarly, <10
 283 μm Fe-Cr (88.3 and 11.7 wt.%, respectively) particles were also found on CS filters, which could
 284 correspond to chromferide ($\text{Fe}_3\text{Cr}_{0.4}$) or iron-rich particles of unknown origin; their possible anthropogenic
 285 origin could be discarded since there is no presence of steelworks or port activities that potentially
 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.



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



292

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

296 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 ($NaHCO_3$) 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
303 time increased. Nevertheless, possible leaching effects due to humid climatic conditions at the volcano
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.

306 The reliability of the data can be evaluated based on the relative standard deviation (RSD) percentage. This
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,
311 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
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).

318 Data were processed following chemical and atmospheric background corrections (Supplementary
319 Material 2). The chemical blank accounted for 5-10% of average major and trace element concentrations,
320 except for Mo (16%), Sr (20%), Ca (27%), Cr (70%), and Ba (235%). At the same time, the atmospheric
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
325 to be similar in the atmospheric blank and volcanic plumes. Na and Cd concentrations were removed from
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/m^3 of Cd; Supplementary
328 Material 2). These enhanced concentrations suggested that the Guadeloupean atmosphere could be
329 enriched in Li, Mg, Na, K, V, Cr, Fe, Cu, Cl, Rb, Mo, Cd, Tb, Ta, W, Tl, Bi, and Pb; careful attention
330 should thus be given to this non-volcanic source of trace elements in fumarolic plumes. Accordingly, blank
331 atmospheric concentrations were subtracted from the total concentrations measured in aerosol filters to
332 obtain plume-specific concentrations (Supplementary Material 2).

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

345 **Table 2** Corrected chemical concentration of major and trace elements (expressed in ng/m³) from aerosol
 346 filters after RSD treatment, chemical, and atmospheric background corrections (Supplementary Material
 347 2).

Site	CS	CS	CS	CS	CS	CS	G56	G56	G56	NAPN	NAPN
RH	84	90	95	85	80	49	92	80	63	84	85
Filter	H _{H2S}	H _{H2S}	H _A	H _{H2S}	H _A						
Date	29/01/ 2021	16/03/ 2021	04/06/ 2021	15/06/ 2021	25/08/ 2021	22/09/ 2021	19/07/ 2021	25/08/ 2021	22/09/ 2021	29/01/ 2021	15/06/ 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
B	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
Co	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	78	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	26	1.22	35	1.03	12	0.69	0.58	7.04	28
Sb	0.71	179	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	0.44	bdl	0.03	0.16	0.11	0.02	0.02	0.05	0.02	0.75	0.13
Ba	bdl	bdl	bdl	bdl	2.59	bdl	bdl	bdl	bdl	bdl	bdl
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	1.878	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
Ta	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

350 Gas ratios were measured using filter pack and MultiGas techniques. Plumes were reportedly flat during
351 the sampling period because of persistent west-northwestern wind blowing at 4.2 m/s on average
352 (maximum of 9.5 m/s), while windless days prompted vertical plumes generating unreliable data.
353 Similarly, the high relative humidity may have been responsible for production of partial leaching on the
354 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
356 containing approximately 90% of the total sulfate concentration (Pennisi and Le Cloarec 1998), whereas
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
359 Soufrière, intervals of total sulfate concentrations (i.e., G1+G2+G3 concentrations) in H_{SO2} and H_{H2S} gas
360 filters were 25.7-1486 and 457-4692 ppm (Table 3), respectively, with concentrations generally decreasing
361 from G1 to G3 (Fig. 6). However, six gas samples (four from H_{SO2} and two from H_{H2S}, Fig. 6) displayed
362 saturation because the G3 filter contained sulfate concentrations >10%, and hence, were discarded. In
363 contrast, for the non-saturated samples (G3_{H2S}, G3_{SO2} <10%), G1-H_{SO2} accumulated between 77 and 91%
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
366 equivalent concentrations potentially suggest that the trapping efficiency of G1-H_{H2S} decreased with
367 humidity, while that of NaHCO₃-gas filters remained less affected. We thus recommend the adoption of
368 three gas filters for sampling tropical wet volcanic plumes based on significant concentrations found in
369 G2-H_{H2S} filters.

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

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

398 **Table 4** Average wind speed, average SO₂/H₂S molar ratios, and H₂S fluxes emitted from CS and G56
399 vents. H₂S fluxes were obtained using the Integrated Concentration Amounts (ICA) for CO₂ (ICA CO₂),
400 the latter being considered as the volcanic marker (Section 3.2). Dry gas fluxes were obtained by adding
401 the three main fluxes (but not water flux; Supplementary Material 3).

Date	Wind speed*	Molar ratios		H ₂ S max	ICA CO ₂	Flux (t/d)			Dry gas
	m/s	SO ₂ /H ₂ S	CO ₂ /H ₂ S	ppm	(ppm/m ²)	CO ₂	H ₂ S	SO ₂	
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 (Cratere Sud + Gouffre 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

402 * represent average ratios and fluxes previously published from CS and G56 sites (Allard et al. 2014;
403 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
413 et al. 2015; Xu-Yang et al. 2022) and affected by Saharan dust every year, especially between April and
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.

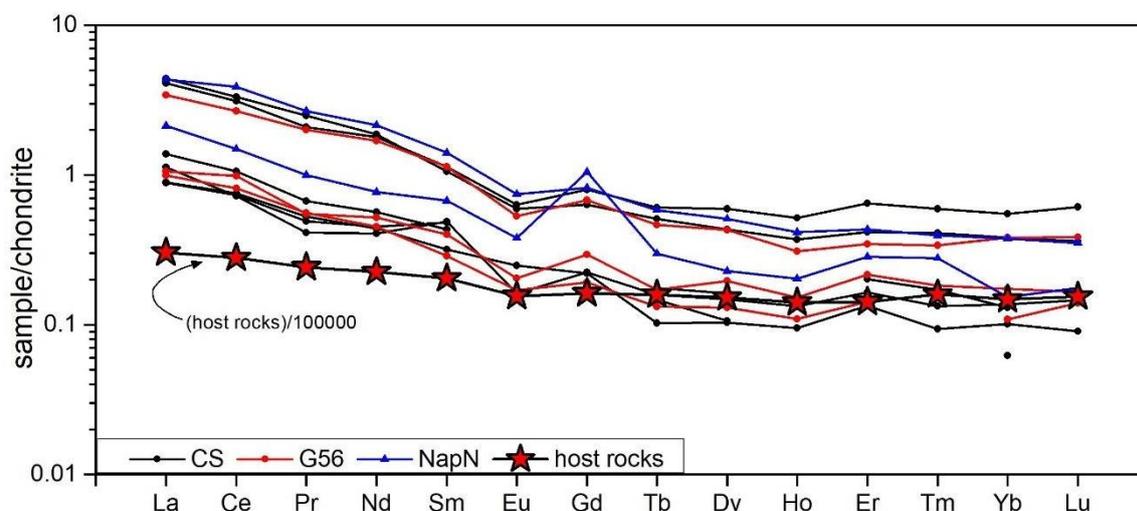
417 The transport and concentration of non-volcanic aerosols in island environments are mainly governed by
418 wind speed, relative humidity, rainfall regime, altitude above sea level, and particle diameter (Shinozuka et

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
421 number of solid particles found in the plume (Figs. 5 and 6) display predominantly larger diameter above
422 10 μm and up to 300 μm in comparison with worldwide marine aerosols that generally are $<3 \mu\text{m}$ (Chabas
423 and Lefèvre 2000; O'Dowd and de Leeuw 2007) or Saharan particles usually $<10 \mu\text{m}$ (Petit 2005;
424 Euphrasie-Clotilde et al. 2021), suggesting a predominant volcanic origin of the largest particles. However,
425 it is believed that $<10 \mu\text{m}$ aerosols (called PM₁₀) of non-volcanic origin (mainly marine) rich in Na, Cl, K,
426 Mg, S, and Ca could impact the concentration of these elements in the volcanic plume of La Soufrière,
427 substantiating the need for study atmospheric blanks. Moreover, pollution peak events related to Saharan
428 dust provoked PM₁₀ concentrations $>50 \mu\text{g}/\text{m}^3$ (www.gwadair.fr). Particularly, the event on June 15 and
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
437 oxidizing conditions (Africano and Bernard, 2000; Zimbelman et al., 2005). Halides can be formed by gas
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
450 cubic halite, can only be explained by subtle evaporation processes. Furthermore, the clustering of gypsum
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
453 we suggest that their combination explains the occurrence of halides and sulfates in our samples.

454 The amount of ash/rock solid particles in magmatic systems can be accounted for by analyzing Rare Earth
455 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
 458 enriched in REEs due to variable leaching of the wall rock depending on temperature, pressure, chemical
 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
 463 sulfates in volcanic emissions, which are the most common ligands for REE. Cl, particularly, is the most
 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
 468 acidic, Cl-rich, and high temperature (>250 °C) conditions predominating in the main hydrothermal
 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).



473
 474 **Figure 7** REE patterns normalized to chondrite (Anders and Grevesse 1989) of aerosol filters and andesitic
 475 host rocks. REE concentrations in aerosols are those presented in Table 2. In comparison, REE/100000
 476 normalized patterns in andesitic host rocks correspond to the average value of two samples (23CF and
 477 SOU-J4) with minimal hydrothermal alteration from the 1530 lava dome and the 1657 scoria fallout
 478 deposit presented in Boudon et al. (2008) and Metcalfe et al. (2021), respectively.

479 5.2 SO₂/H₂S gas ratios

480 SO₂/H₂S 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
484 debatable given SO₂-poor and H₂S-rich plumes at La Soufrière. Such high SO₂ concentrations in filter
485 pack measurements may possibly be because the NaHCO₃-impregnated filters could trap S-bearing species
486 other than SO₂ (e.g., H₂S, HS⁻, SO₃²⁻) at high humidity conditions, increasing the concentration of sulfates
487 measured (Mioduszewski and Kress 2008). Therefore, filter wetness could enhance S-species trapping,
488 similar to what occurs in coal industries when alkaline traps are used for H₂S removal (e.g., Garner et al.,
489 1958). Consequently, SO₂ concentrations and SO₂/H₂S gas ratios measured by filter packs in humid and
490 foggy conditions cannot be fully trusted. Nevertheless, H₂S concentrations can be trusted even if some SO₂
491 is trapped in H_{H2S} filters, which in any case would be minimal given negligible SO₂ concentrations in the
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
500 suitable approach to better understand the volatile and non-volatile contribution of trace elements in
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:

$$504 \text{ EF} = (X/Y)_a / (X/Y)_r$$

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.

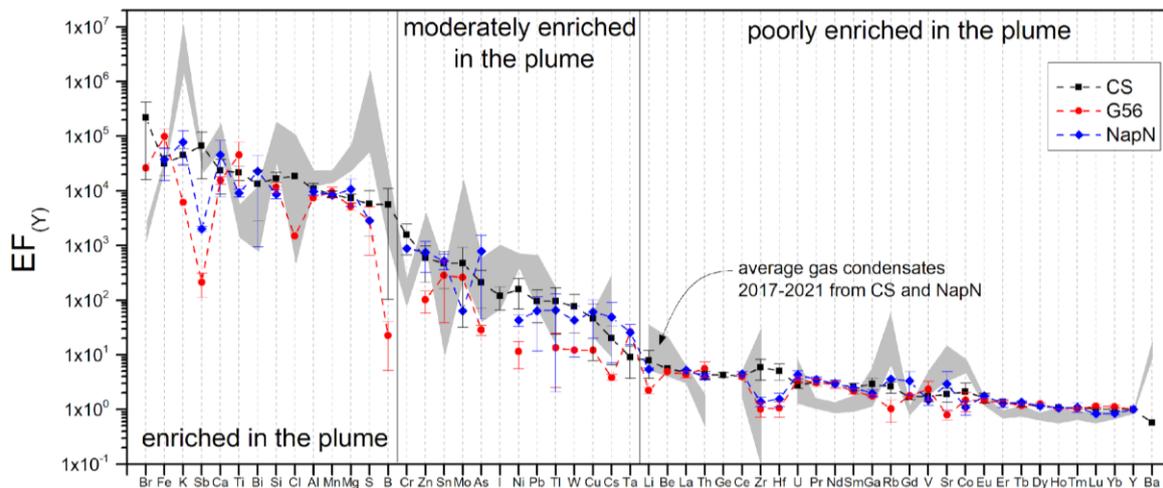
522 Average Y-based EFs in aerosol samples from CS, G56, and NapN plumes have been presented in Figure
523 8. Chemical elements enriched in the plume (with EF of 10^3 - 10^5) are Br, Fe, K, Sb, Ca, Ti, Bi, Si, Cl, Al,
524 Mn, Mg, S, and B. In particular, the enrichment of chalcophiles (Sb, Bi, S) and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

535 In summary, the CS plume shows the highest EF, closely followed by NapN, while the G56 plume
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
541 wind direction during sampling, favoring condensation or no collection of certain elements on the filters.
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
545 variation can be explained based on different degassing processes affecting these fumaroles. For example,
546 it is believed that the transport of major and trace elements in low-temperature fumarolic emissions can be
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
549 because of lower steam proportions (75 versus 96 mol%; Tamburello et al. 2019; Moune et al. 2022),
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

553 (Tamburello et al. 2019; Moretti et al. 2020a). Consequently, the sampling position and physicochemical
 554 processes accounting in the magmatic-hydrothermal system play an essential role in the enrichment of
 555 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
 558 physicochemical processes impacting fumarolic emissions. The main discrepancies are observed in K, Si,
 559 Mn, Mg, S, Rb, and Ba, which seem more enriched in condensates than plume measurements, mostly
 560 likely due to their transportation within steam condensed droplets or solid particles (Inostroza et al. 2022a)
 561 and partial deposition closer to the vent (Sainlot et al. 2020). Gas condensates and plumes from La
 562 Soufrière also contain significant concentrations of contaminant trace elements such as Sb, Bi, Cr, As, Ni,
 563 Pb, and Tl, some even detected in point-EDS particle analyses (e.g., Cr, Ni). The transport of trace
 564 elements in volcanic plumes is usually correlated with the presence of ligands such as halides, sulfates, or
 565 hydroxides (Pokrovski et al. 2013; Mandon et al. 2019; Scholtysic and Canil 2020). However, they are
 566 characterized by volatility close to zero at the temperatures found in La Soufrière volcano (up to 111 °C)
 567 and concentrates in dense and high-temperature brines within the hydrothermal system (Pokrovski et al.
 568 2013). This highlights the important role of water in the transport of metals and metalloids, whose
 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

578 Any trace element emission rate $F(X)$ can be calculated by multiplying gas-normalized ratios in filter
579 packs by the corresponding gas emission rates (Mather et al. 2004). Typically, SO_2 is the normalization gas
580 species chosen for this calculation because it has an unambiguously magmatic signature, significant
581 concentrations in volcanic plumes, and a wide range of available techniques to measure its concentration.
582 However, SO_2 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
584 species to estimate La Soufrière's volatile fluxes released from the magma chamber. Their study
585 demonstrated that at La Soufrière, H_2S 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 $F(H_2S)$, the H_2S 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
593 one G56 samples, using H_2S emission rates of 1.50-2.83 and 0.34 t/d, respectively (Table 4). Heavy metal
594 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
595 samples presenting higher emission rates than the G56 one (Fig. 9) with the exception of Fe, which
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 ~1 g/d, especially in the sample collected in March 2021.
598 Fe, Zn, Ni, and Sb emission rates are comparable to Hg rates of 2.19 g/d measured at CS in 2006 by
599 Bagnato et al. (2009). Emission rates of Sn, Cu, As, Se, Tl, Pb, Ni, Bi, Te, Co, and Mo generally remained
600 below 0.1 g/d. By comparing CS and G56 fumaroles, it can be shown that Fe, Sn, As, Se, and Co presented
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.

604 These emission rates represent the first data obtained from low-temperature steam-rich volcanic emissions
605 and provide valuable information about the efficiency of trace element scavenging by hydrothermal
606 processes. These emission rates must however be considered as minimum values given possible leaching
607 affecting PTFE filters during sampling in the presence of humid climatic conditions and partial deposition
608 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/m^3) 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
 614 $\text{kg m}^{-2} \text{y}^{-1}$ into kg/d using the areal factor of $35 \pm 5 \text{ m}^2$, which corresponds to the average plume cross-
 615 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}	H_A	H_A	H_A	H_A	-
Date	16/03/2021	04/06/2021	15/06/2021	25/08/2021	19/07/2021	-
F(H₂S)	1.50	2.83	2.83	1.57	0.34	-
H₂S	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
Co	7.3×10^{-3}	7.7×10^{-4}	2.0×10^{-3}	1.3×10^{-3}	2.7×10^{-4}	1.0×10^{-5}
Mo	4.8×10^{-2}	4.8×10^{-4}	nd	7.4×10^{-4}	nd	1.1×10^{-5}

617 Nd: not determined/not calculated

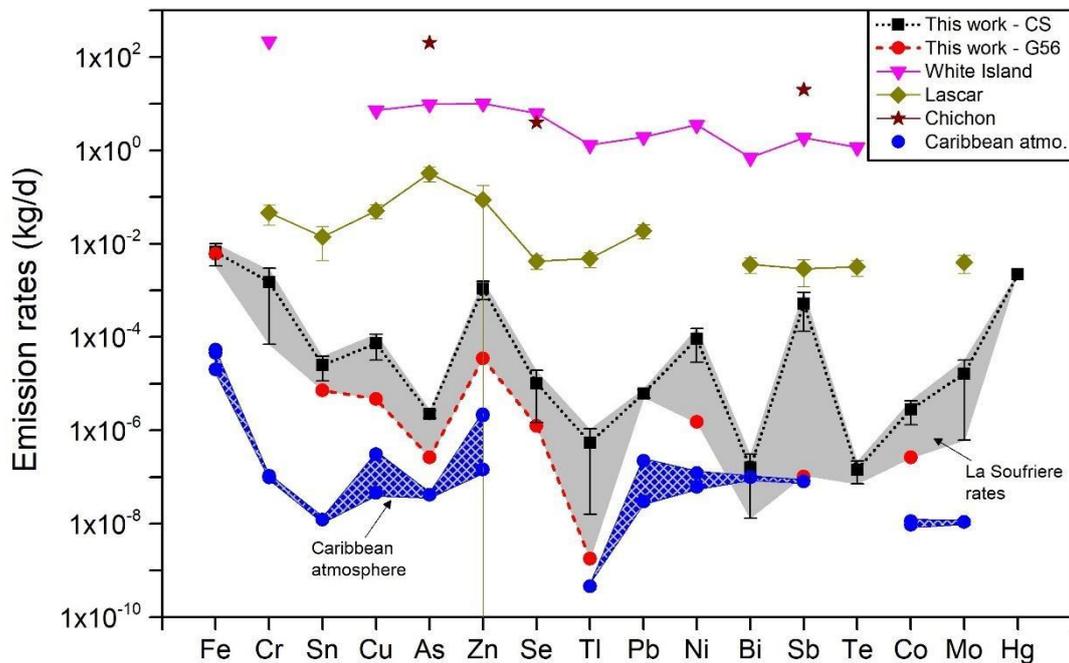
618 Comparing La Soufrière emission rates with other quiescently degassing subduction-related volcanoes
 619 permits a better understanding of the heavy metal contribution at this volcano and low-temperature
 620 hydrothermal emissions. Figure 9 shows that La Soufrière's emissions rates are the lowest 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
 624 ranging from 0.004 to 220 kg/d (Phelan Kotra et al. 1983; Menard et al. 2014; Mandon et al. 2019).
 625 Emission rates of <15 g/d at La Soufrière (Table 5) represent a modest contribution compared to global
 626 heavy metal emission rates in actively degassing volcanoes. Such differences can be explained based on
 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

631 Chichon or White Island (Global Volcanism Program 2022), and also at open vent volcanoes such as
632 Masaya and Ambrym. We suggest that low emission rates of heavy metals observed at La Soufrière and
633 Lascar can be attributed to the depth of the magma chamber, which in both is located at >6 km below the
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,
638 while La Soufrière is impacted by huge inputs of rainwater (up to 10 m per year; Dessert et al. 2015). Such
639 an input favors widespread hydrothermal emissions at La Soufrière, supported by the predominance of H₂S
640 instead of SO₂, including numerous cold and thermal emissions on volcano flanks. On the other hand,
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.
643 1997; Global Volcanism Program 2013). Consequently, it is believed that low heavy metal emissions rates
644 at La Soufrière and other low-temperature volcanic emissions are strongly influenced by the location of the
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
649 volcanic emissions from La Soufrière represent an important pollution source in the Caribbean
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
655 anthropogenic influence in Cuba. However, Fe and Zn fluxes (Supplementary Material 3), which are
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.

659 Atmospheric fluxes have been converted into kg/d using the areal factor of $35 \pm 5 \text{ m}^2$, which corresponds to
660 the average plume cross-section considering a flattened plume of 3-4 m high and 10 m wide, following the
661 observations made by Allard et al. (2014), Gaudin et al. (2016), Jessop et al. (2021) and Moune et al.
662 (2022). Successively, normalized fluxes ranged between 4.6×10^{-10} and 4.0×10^{-5} kg/d (Fig. 9). These
663 atmospheric fluxes are up to four times lower (e.g., Cr, Sb, Sn, Mo) than La Soufrière fluxes, especially in
664 the case of the CS fumarole, which is considered as the primary heavy metal source at this volcano.
665 Notably, atmospheric and volcanic fluxes of Bi displayed closer values, while the G56 fumarole has
666 average fluxes equal to or slightly higher than atmospheric fluxes. Consequently, modest heavy metal
667 emissions from La Soufrière can be regarded as a source of pollution in Guadeloupe, although their impact

668 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

672 **Figure 9** Heavy metal emission rates (kg/d) compared with other subduction-related and quiescently
 673 degassing volcanoes with evidence of hydrothermal activity, such as White Island (Mandon et al. 2019),
 674 Lascar (Menard et al. 2014), and El Chichon (Phelan Kotra et al. 1983) volcanoes. The gray area
 675 represents emission rates at La Soufrière, and the black dotted and red dashed lines are average emission
 676 rates from CS and G56 fumaroles, respectively. The blue dashed area represents the average trace element
 677 deposition fluxes in the Caribbean atmosphere according to published bibliographic data (Chester et al.
 678 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
 681 Cratere Sud, Napoleon Nord, and Gouffre 56 fumaroles, three of the most important degassing sites in La
 682 Soufrière de Guadeloupe volcano. The sampling was challenging because of harsh weather conditions on
 683 the volcano summit and the nature (steamy- and H₂S-rich) of fumarolic emissions, forcing the adaptation
 684 of traditional sampling procedures. Given these distinctive characteristics, aerosol filters developed
 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.

688 Microscopic and chemical analyses identified major and trace elements transported within gas and aerosol
689 phases. Remarkably, volcanic plumes at La Soufrière contain significant concentrations of lithophile or
690 rock-related elements from water-rock interaction processes in the hydrothermal system, in addition to
691 significant concentrations of chalcophiles related to a deeper magmatic source. Moreover, La Soufrière is
692 an important source of potentially toxic heavy metals such as Sb, Bi, Cr, As, Ni, Pb, and Tl. Given low
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
698 fumaroles. Modest emissions rates (up to 15 g/d) are ascribed to the combination of two physicochemical
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

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

731 CONFLICTS OF INTEREST

732 The authors declare there are no conflicts of interest.

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