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1     **Decoding water-rock interaction and volatile input at**  
2     **La Soufriere volcano (Guadeloupe) using time-series**  
3     **major and trace element analyses in gas condensates**

4  
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13    **Abstract**

14    The geochemical behavior of major and trace elements in fumarolic gas condensate samples  
15    collected between April 2017 and January 2021 was investigated at La Soufriere hydrothermal  
16    volcano. Samples collected from Cratère Sud and Napoleon Nord fumaroles (temperature  
17    varying from 93.9 to 108.4 °C) offer a unique opportunity to reveal the physicochemical  
18    processes that affect the deeper magmatic and shallow hydrothermal systems feeding  
19    fumaroles. Gas condensate samples exhibit abundant solid particles that suggest strong water-  
20    rock interaction and erosive processes in fumarolic conduits at La Soufriere. These particles  
21    were incorporated during sampling, except for rare Si-rich spherules that appeared to have  
22    precipitated during storage time. Gas condensate samples displayed abundant concentrations  
23    of S, halogens (Cl, Br, I), metals/metalloids (B, Ni, Cu, Zn, As, Mo, Ag, Cd, Sb, Pb, and Bi),  
24    as well as enhanced concentrations of rock-related lithophile and siderophile elements. The  
25    relative abundance of major and trace elements in gas condensates suggests the permanent  
26    contribution of volatile-rich magmatic fluids and strong water-rock interaction processes.

27 Based on elemental correlations and the physical properties of chemical elements, it is  
28 postulated that most of them are discharged in the aerosol phase, except for the halogens and  
29 S, which can be found in the gaseous phase in low-temperature fumarolic emissions. Metals  
30 and metalloids (Sb, Bi, Zn, Mo, Ni, Ag, Cd, As, and Pb) enriched in gas condensates were  
31 transported within tiny aqueous droplets, while rock-related elements (including REEs) were  
32 transported in the aerosol phase. Trace element enrichments in La Soufriere's condensates are  
33 comparable with those found in worldwide magmatic-hydrothermal systems such as Kawaj  
34 Ijen (Indonesia), Lastarria (Chile), and White Island (New Zealand) volcanoes. The size of the  
35 hydrothermal system and the degree of water-rock interaction are thought to be important  
36 parameters in controlling the abundance of major and trace elements in low-temperature  
37 fumarolic discharge.

### 38 **Highlights**

39 The chemical composition of gas condensates is investigated  
40 Major and trace elements are mostly released in the aerosol phase  
41 Sulfur and halogens can be emitted in the gaseous phase  
42 Volatile-rich magmatic input and water-rock interaction processes are assessed  
43 Significant amounts of Sb, Bi, and Zn are discharged from La Soufriere fumaroles

### 44 **Keywords**

45 Trace elements; hydrothermal systems; La Soufriere volcano; water-rock interaction; aerosols

## 46 **1. Introduction**

47 Volcanic emissions represent the most important natural sources of gases and particles into the  
48 atmosphere during quiescent degassing and eruptive periods. Indeed, volcanic emissions  
49 contribute to the natural atmospheric cycles of many gas species and trace elements (e.g.,  
50 Aiuppa et al. 2003; Calabrese et al. 2011). Besides the major (H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, HCl, HF)  
51 and minor (N<sub>2</sub>, rare gases, CO, CH<sub>4</sub>, H<sub>2</sub>) components, it has been well known since the early  
52 work by Zoller et al. (1974) that volcanic gases and aerosols are considerably enriched in many  
53 trace elements including alkalis, alkali-earth elements, transition elements, and heavy metals

54 relative to host rocks. Such trace element enrichments are ubiquitously observed in gaseous  
55 emanations from volcanoes worldwide, provided when the magma temperature is high enough  
56 to ensure their volatilization (e.g., Le Guern 1988; Symonds et al. 1994; Delmelle and Stix  
57 2000, and references therein). Trace elements are directly volatilized from a magmatic source  
58 or removed from wall rocks due to erosive processes, and are then emitted in the gas and aerosol  
59 phases. A fraction of the trace elements is trapped in the fumarolic mouth at the surface to form  
60 sublimates and incrustations due to the sharp temperature decrease and reaction with  
61 surrounding rocks. Work on volcanogenic trace elements has increased markedly during the  
62 last two decades, focusing on the understanding of deep ore-forming fluids (e.g., Scher et al.  
63 2013; Keith et al. 2018), speciation and transport (e.g., Aiuppa et al. 2003; Moune et al. 2010),  
64 mineral forming processes (e.g., Yudovskaya et al. 2008; Sainlot et al. 2020), geochemical  
65 cycling of volcanogenic elements (e.g., Pyle and Mather 2003; Kagoshima et al. 2015), and  
66 atmospheric, environmental, and health issues (e.g., Varrica et al. 2014; Edmonds et al. 2015;  
67 Ilyinskaya et al. 2017; Stefánsson et al. 2017).

68 Volcanic trace elements are commonly studied via filter samples, sublimates, and incrustations  
69 (e.g., Allard et al. 2000; Gauthier et al. 2016; Zelenski et al. 2013; Sainlot et al. 2020; Inostroza  
70 et al. 2020). However, the use of condensation techniques has been limited and occasionally  
71 subject to inaccuracy problems due to the recurrent presence of colloidal sulfur which can  
72 remove chalcophile elements from the solution (e.g., Fischer et al. 1998; Shevko et al. 2018).  
73 Nevertheless, this technique has been proven to be appropriate to estimate trace element  
74 concentrations (e.g., Taran et al. 1995; Fischer et al. 1998; Zelenski et al. 2014). Condensation  
75 techniques have been restricted to a few volcanic sites with frequent high-temperature  
76 fumarolic emissions, mainly focused on trace element volatility and thermochemical modeling  
77 of fluid-rock interactions (e.g., Symonds et al. 1990, 1996; Taran et al. 1995; Africano and  
78 Bernard 2000; Zelenski et al. 2013, 2014; Kalacheva et al. 2016). However, low-temperature  
79 hydrothermal-dominated systems remain poorly studied, likely due to secondary processes  
80 (i.e., precipitation and dissolution of mineral phases, the input of meteoric water, and  
81 "contamination" by leaching of host-rock components) occurring within the hydrothermal  
82 system (Stoiber and rose 1970; Symonds et al. 1990; Taran et al. 1995) that could modify or  
83 hide the magmatic signature.

84 The concentration of trace elements in fumarolic emissions mainly depends on outlet gas  
85 temperature, chemical composition of fumarolic gases, and magma composition (Symonds et

86 al. 1990, 1992, 1996; Africano and Bernard 2000; Moune et al. 2010; Edmonds et al. 2018). It  
87 has been postulated that high-temperature and Cl-rich fumarolic emissions present higher  
88 concentrations of trace elements compared with low-temperature hydrothermal-dominated  
89 fumaroles due to the higher vapor pressure of metal-bearing species as temperature increases  
90 and the fact that Cl is a common ligand (Gauthier et al. 2016; Scholtysik and Canil 2020;  
91 Mandon et al. 2020). However, despite several works on medium- to high-temperature  
92 fumarolic emissions, little attention has been paid to major and trace element concentrations in  
93 low-temperature (~100°C) fumaroles. Consequently, deep (magmatic) and shallow  
94 (hydrothermal) physicochemical processes controlling the abundance of these elements and  
95 their transport modes remain poorly understood for steam-rich fumarolic gases.

96 Here we present results for gas condensate samples collected monthly between April 2017 and  
97 January 2021 at La Soufriere de Guadeloupe (hereafter La Soufriere) in the Lesser Antilles. La  
98 Soufriere is a hydrothermal-dominated volcanic system that suffered recent phreatic explosions  
99 (e.g., Le Guern et al. 1980; Komorowski 2005) and is one of the most active and dangerous  
100 volcanoes in the Lesser Antilles Arc. It currently presents permanent fumarolic activity  
101 associated with low-temperature (from 94 up to 111 °C in the investigated period) and steam-  
102 rich (commonly >95 mol%) emissions. Thus, this volcano provides a suitable environment to  
103 improve our understanding of the different parameters involved in the behavior of trace  
104 elements in volcanic condensates. In this study, major and trace element data obtained from  
105 gas condensate samples at La Soufrière's fumaroles are used to i) characterize, physically and  
106 chemically, the fumarolic degassing in terms of volatile versus non-volatile contribution of  
107 trace elements in condensates given their relative volatility, and ii) constrain the factors that  
108 control the abundance of major and trace elements. Our findings have particular relevance for  
109 understanding the transport of chemical elements in low-temperature hydrothermal emissions.

## 110 **2. Geological Background**

111 La Soufriere is an andesitic composite volcano situated in the Lesser Antilles volcanic arc  
112 (16.0446°N, 61.6642°W, 1467 m.a.s.l.; Fig. 1a), which has been formed by the subduction of  
113 the Atlantic plate below the Caribbean one. La Soufriere has been built up over the last 11500  
114 years BP (Komorowski 2005; Boudon et al. 2008), experiencing recurrent magmatic and non-  
115 magmatic eruptions. The last magmatic eruption occurred in 1530 AD and was triggered by an  
116 andesitic magma intrusion at a shallow level, which caused a partial collapse of the SW flank,  
117 and was followed by a sub-plinian eruptive phase culminating in the growth of the current

118 summit dome (Boudon et al. 2008; Komorowski et al. 2008). Subsequent volcano-stratigraphic  
119 studies have revealed a more recent magmatic eruption in 1657 AD (Metcalf et al. 2021),  
120 while recurrent phreatic explosions were recorded in 1797-98, 1836-37, 1956, and 1976-77  
121 (e.g., Legendre 2012; Hincks et al. 2014). From 1992, after a decade of post-eruptive  
122 quiescence, La Soufrière entered a new phase of fumarolic and seismic unrest, whose evolution  
123 has been described in detail in previous works (Komorowski 2005; Allard et al. 2014;  
124 Villemant et al. 2014; Rosas-Carbajal et al. 2016; Tamburello et al. 2019; Moretti et al. 2020a;  
125 Jessop et al. 2021; Metcalfe et al. 2021).

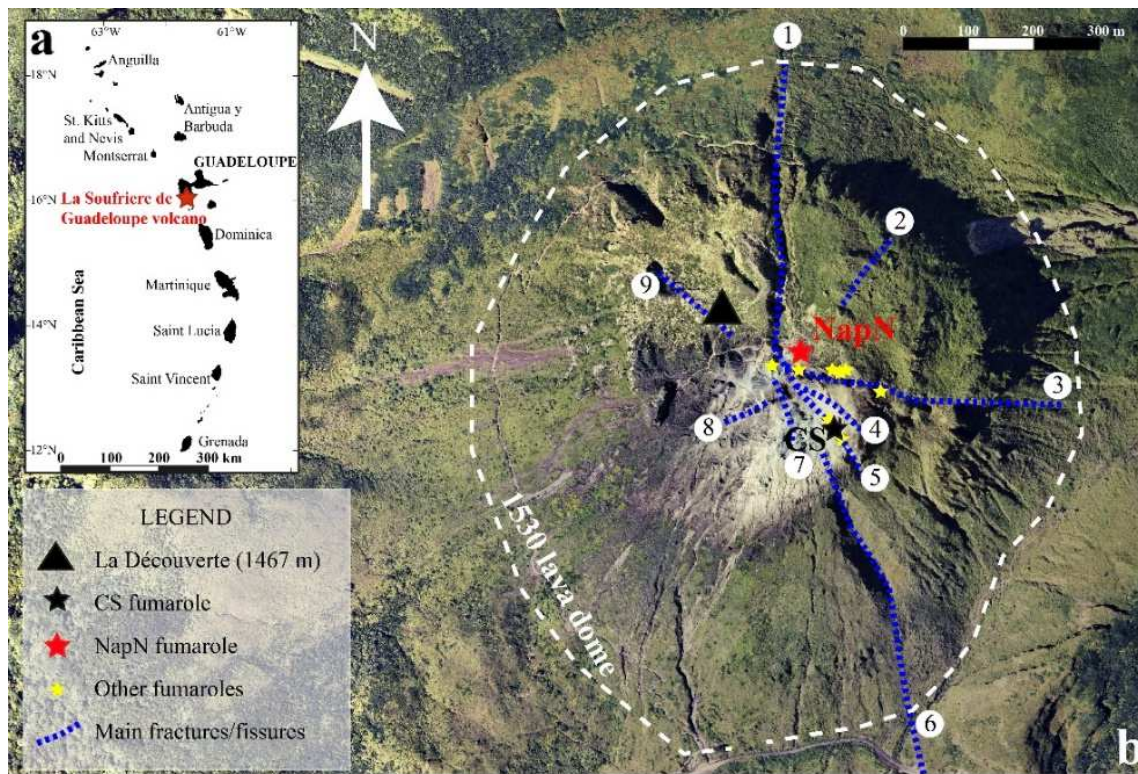
126 Hydrothermal activity at La Soufrière is caused by the input of heat and gases coming from an  
127 andesitic magma chamber (located at a depth of 6-7 km below the summit) into shallow  
128 aquifers mainly fed by meteoric waters (Boudon et al. 2008; Villemant et al. 2014; Pichavant  
129 et al. 2018). Deep magmatic gases likely rise through fractures and fissures until they cool,  
130 condense, and interact with water hosted in reservoir rocks several hundreds of meters below  
131 the summit (Rosas-Carbajal et al. 2016). Previous studies on the chemical composition of  
132 fumarolic gases suggest that they are emitted from a hydrothermal-dominated system with  
133 shallow magmatic influence (Brombach et al. 2000; Villemant et al. 2014; Tamburello et al.  
134 2019; Moretti et al. 2020a,b; Moune et al. 2022). At the surface, fluids are emitted from radial  
135 faults and fractures cutting the dome, such as Cratère Sud (CS; the site of the main fumarolic  
136 emissions) and 8 Juillet 1976 fractures (Fig. 1b), and open pits caused by past eruptions (for  
137 example Gouffre 56). The hot area surrounding fumarolic manifestations and fractures  
138 (particularly around Napoleon Nord and Gouffre 56; Fig. 1b) is progressively expanding,  
139 which has led to an increasing budget of heat flux and soil degassing (Jessop et al. 2021) and  
140 has contributed to the progressive degradation of vegetation. Other signs of strong  
141 hydrothermal activity are the low-deep (<2.5 km below the summit) seismic activity (reaching  
142 up to 3000 very low-magnitude volcano-tectonic events in November 2020; OVSG-IPGP  
143 2020), the nearly radial pattern of the Global Navigation Satellite System (GNSS) displacement  
144 vectors on the dome and the radial opening (3-7 mm/year) of dome fractures at most  
145 hydrothermalized sites (Moretti et al. 2020a). As a result of all these elements, La Soufrière  
146 has a permanent status of increased vigilance (alert level is Yellow, the second on a scale of  
147 four), further reinforced after the 2018 episode of accelerated unrest (Moretti et al. 2020a).

148 Cratère Sud (CS) and Napoleon Nord (NapN) are the only fumaroles accessible for direct  
149 sampling at the summit. They are regularly sampled by the Observatoire Volcanologique and

150 Sismologique de la Guadeloupe (OVSG-IPGP). CS is hosted along the Cratère Sud fault and  
151 is formed of three main vents, Cratère Sud Nord, Cratère Sud Central, and Cratère Sud Sud  
152 (CSN, CSC, and CSS, respectively). Although they have shown, sporadic variable behavior  
153 since 1992, the chemical composition of fumarolic gases and outlet gas temperatures have  
154 remained very similar, if not the same, at the CSN and CSC vents since 2016 (Moretti et al.  
155 2020; Moune et al. 2022), while CSS has not yet been surveyed by in situ techniques. The  
156 temperature at CS has fluctuated between 95 (the temperature of the saturated steam vapor at  
157 the summit atmospheric pressure) and 110 °C, but it reached 140 °C in 1999-2000 (Villemant  
158 et al. 2014). At NapN, a fumarole that emerged in 2014 in the hot expanding area, the  
159 temperature remained virtually stable at 95 °C (Moretti et al. 2020a). According to Moretti et  
160 al. (2020a), temperature increases are primarily associated with the input of deep magmatic  
161 gases into the hydrothermal system, whereas temperature drops and the restoring of the  
162 saturated steam temperature may be favored by interaction with very shallow groundwater and  
163 then be influenced by external forces such as heavy rain (average of 5 m/year in the 2017-2020  
164 period; OVSG-IPGP bulletins) or wetter seasons (Moune et al. 2022). CS is characterized by  
165 jet-type fumarolic emissions, abundant deposition of native sulfur, and sporadic ejection of  
166 solid fragments, while NapN has weaker fumarolic emissions and restricted native sulfur  
167 deposition.

168 Periodic chemical analyses using soda bottles demonstrated that fumarolic gases are mixtures  
169 of steam, CO<sub>2</sub>, and H<sub>2</sub>S (concentrations of 96-98, 1.5-4.0, and 0.3-0.7 mol%, respectively), in  
170 addition to minor concentrations (<0.03 mol%) of N<sub>2</sub>, CH<sub>4</sub>, He, and CO (Brombach et al. 2000;  
171 Moretti et al. 2020a). Such concentrations have remained stable since 2017, except for the  
172 March-June 2018 period where CO<sub>2</sub>, gaseous sulfur species, CO, and He reached maximum  
173 concentrations associated with the arrival of deep anomalous "magmatic" gases and hotter  
174 fluids that perturbed the hydrothermal system (Moretti et al. 2020a; Moune et al. 2022). The  
175 chemical composition of fumarolic gases is controlled by variable scrubbing processes within  
176 hydrothermal aquifers, which efficiently removes SO<sub>2</sub> and H<sub>2</sub>S (Allard et al. 2014; Tamburello  
177 et al. 2019; Moretti et al. 2020a; Moune et al. 2022) to form native sulfur and sulfate/sulfide  
178 mineral assemblages (e.g., Giggenbach 1987; Symonds et al. 2001). Based on relative  
179 concentrations of CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> measured in 2016-2020, previous studies (Tamburello et  
180 al. 2019; Moune et al. 2022) showed that at La Soufriere volcano, CS has a more magmatic-  
181 hydrothermal signature than NapN, responding quickly to any changes occurring in magmatic  
182 and hydrothermal sources. These studies suggested that NapN has been affected by major

183 scrubbing effects due to a localized cold, shallow aquifer that buffers fumarolic emissions both  
184 thermally and chemically (Tamburello et al. 2019).



185  
186 **Figure 1** a) Location of Guadeloupe island and La Soufriere volcano in the Lesser Antilles  
187 volcanic arc. b) Location of fumarolic emissions (yellow stars) and main fissures/fractures  
188 (blue dashed lines) within the 1530 lava dome. Positions of CS and NapN sites are shown as  
189 black and red stars, respectively, while the enclosed area shows the lava dome position. (1)  
190 Nord fracture, (2) Nord-Est fracture, (3) 8 Juillet 1976 fracture and Breislack fault, (4) Lacroix  
191 fracture, (5) Cratère Sud fracture, (6) 30 Août 1976 fracture and Faille de la Ty, (7) Gouffre  
192 Peyssonel, (8) Dolomieu fracture, (9) Nord-Ouest fracture

### 193 3. Sampling and analytical methods

194 Gas condensate (hereafter named condensates) samples were obtained using a 50 cm-long  
195 fiberglass tube used to channel flow from the fumarole, connected to a Pyrex-Dewar glass  
196 elbow. Sample collection followed the "normal" and "direct" procedures proposed by Chevrier  
197 and Le Guern (1982). The "normal" method connected a Pyrex-Dewar glass to a Pyrex coil  
198 condenser cooled with freshwater. The "direct" method replaced the coil condenser with a 20  
199 cm-silicon tube. The "normal" method was used at the CS fumarole, while the "direct" method  
200 was generally used at NapN (Table 1). In-situ chemical analysis for chlorine performed on



201 samples collected simultaneously by the "direct" and "normal" methods showed no significant  
202 variations (e.g., Chevrier and Le Guern 1982). The outlet gas temperature was recorded at the  
203 end of the procedure. Subsequently, the sample was stored in polyethylene bottles and  
204 transported to the OVSG-IPGP laboratory for chemical analysis.

205 Ion chromatography (IC; Dionex Aquion™, Thermo Scientific) analyses were conducted at  
206 the OVSG-IPGP chemistry laboratory, usually within a week of the sampling to determine the  
207 concentration of chloride and sulfate in unfiltered samples. 100 µL of sample diluted by 100  
208 were used for IC analyses, while the remaining solution was hermetically stored at ambient  
209 temperature in a dry, cool place until used for analysis of trace elements. Measurements were  
210 achieved following internal analysis protocols and regular calibration routines. The analytical  
211 error was  $\leq 5\%$ . Then, 2 to 10 mL of condensates were filtered using syringes and 0.20 µm  
212 pore-size sterile cellulose filters (VWR, number 514-0061), and transported to the laboratories  
213 at the IPGP (Paris, France) in acidified (with 0.05 mL of HNO<sub>3</sub>, 67-69%, Fisher Chemical,  
214 A467-250) polyethylene bottles. These samples were analyzed by Inductively Coupled Plasma  
215 Mass Spectrometry (ICP-MS; Agilent 7900) to obtain the concentrations of major and trace  
216 elements. Furthermore, rock samples with minor hydrothermal alteration (23CF and SOU-J4)  
217 from the 1530 lava dome and scoria fallout deposits collected by Boudon et al. (2008) and  
218 Metcalfe et al. (2021), respectively, were selected and analyzed once again in this study for  
219 major and trace elements using the ICP-MS technique. Internal standards for condensate  
220 samples (e.g., Sc, In, Re), international standards (e.g., BEN, BIR-1, BHVO-2, BCR-2, ATHO-  
221 1, LIP, RGM-1) for rock analyses, and blank solutions were used to control possible error  
222 sources and validate results. The analytical error for condensate and rock analyses was  
223 generally  $< 10\%$ .

224 Nine samples that contained noticeable black and white/yellow particles were filtered using  
225 0.45 µm pore-size nitrocellulose filters (Millipore, CAS 9004-70-0) and then analyzed by  
226 Scanning Electron Microscope (SEM, Quanta 250) in the C3-Mag laboratory at the Université  
227 des Antilles (Pointe-à-Pitre, Guadeloupe). First, the sample was shaken, and then 5-8 mL were  
228 poured into a funnel-shaped plastic container where the liquid phase drained and particles were  
229 trapped on the nitrocellulose filter. The filters with particles were then dried for 24 hours at 50  
230 °C. Before analysis, filters were cut into ~8x8 mm squares and mounted on carbon tape-  
231 covered aluminum holders. High-resolution imaging was retrieved using the back-scattered  
232 electron (BSE) mode, while semi-quantitative chemical analyses were performed in the EDS

233 mode using an acceleration voltage of 15 kV, beam current of 5 nA, 15-40 s dwell time, and  
 234 10 mm working distance. Acquisition of high-resolution images and data processing were  
 235 carried out using the INCAEnergy<sup>®</sup> software.

## 236 4. Results

### 237 4.1 Microscopic observations in condensates

238 Condensate samples displayed from a range from a few to abundant small particles, solid  
 239 precipitates in the inner walls of polyethylene bottles, and clear to cloudy appearance (Table  
 240 1). As shown in Table 1, particles were common in the condensates; they were observed in 53  
 241 of the 55 samples studied. Samples with black and white, or just white particles, were  
 242 predominant, while a few samples displayed only black particles. CS samples showed a larger  
 243 number of particles and a much cloudier aspect than NapN samples. In general terms, samples  
 244 with a moderate to abundant number of particles had a cloudy to milky aspect, while samples  
 245 with a limited presence of particles had a predominantly clear aspect. It is important to note  
 246 that samples collected before April 2019 for CS and before July 2019 for NapN displayed a  
 247 predominantly clear aspect with minor to moderate amounts of particles, while cloudy to milky  
 248 samples predominated from mid-2019 in both CS and NapN samples.

249 **Table 1** Color, abundance, and appearance of condensates. Samples with solid crusts in the  
 250 inner parts of bottles and samples selected for SEM-EDS analyses were highlighted. Sample  
 251 appearance reflects the degree of turbidity of the sample, the sample being "clear" with no  
 252 turbidity (colorless, like water), "slightly cloudy" for those samples with noticeable turbidity,  
 253 and "milky" for those samples with significant turbidity (like milk). B&W: black and white  
 254 particles. N/A: Not applicable/Not analyzed.

Sample	Date	Site	Presence of particles	Color	Abundance	Appearance	Solid precipitates	Submitted to microscopic analyses?
C1	11/04/2017	CSC	yes	B&W	abundant	slightly cloudy	no	N/A
C2	08/06/2017	CSC	yes	B&W	few particles	slightly cloudy	no	N/A
C3	25/07/2017	CSC	yes	white	few particles	clear	yes	N/A
C4	24/11/2017	CSC	no	N/A	N/A	clear	no	N/A
C5	24/11/2017	CSC	yes	black	few particles	clear	no	N/A
C6	31/01/2018	CSC	yes	white	few particles	clear	no	N/A
C7	19/04/2018	CSC	yes	white	abundant	clear	yes	N/A
C8	02/05/2018	CSN	yes	white	few particles	clear	no	N/A
C9	02/06/2018	CSC	yes	B&W	few particles	clear	no	N/A
C10	30/07/2018	CSC	yes	white	few particles	clear	no	N/A
C11	11/09/2018	CSC	yes	white	abundant	slightly cloudy	yes	N/A
C12	24/10/2018	CSC	yes	B&W	few particles	slightly cloudy	no	N/A
C13	22/11/2018	CSC	yes	white	middle	slightly cloudy	no	yes

C14	19/12/2018	CSC	yes	white	middle	clear	yes	yes
C15	22/01/2019	CSC	yes	B&W	middle	clear	no	N/A
C16	22/03/2019	CSC	yes	B&W	middle	clear	yes	N/A
C17	30/04/2019	CSC	yes	B&W	few particles	clear	no	N/A
C18	11/06/2019	CSC	yes	B&W	abundant	slightly cloudy	yes	yes
C19	14/07/2019	CSC	yes	white	abundant	slightly cloudy	no	yes
C20	03/09/2019	CSC	yes	B&W	abundant	slightly cloudy	yes	N/A
C21	01/10/2019	CSC	yes	N/A	N/A	slightly cloudy	no	N/A
C22	08/10/2019	CSN	yes	B&W	middle	clear	no	N/A
C23	05/12/2019	CSN	yes	B&W	middle	slightly cloudy	yes	N/A
C24	27/02/2020	CSC	yes	white	few particles	clear	yes	N/A
C25	10/04/2020	CSC	yes	white	few particles	slightly cloudy	yes	N/A
C26	15/05/2020	CSC	yes	white	abundant	slightly cloudy	yes	N/A
C27	18/06/2020	CSC	yes	white	abundant	slightly cloudy	no	N/A
C28	05/08/2020	CSC	yes	B&W	abundant	slightly cloudy	no	N/A
C29	08/10/2020	CSC	yes	B&W	middle	clear	no	N/A
C30	08/10/2020	CSC	yes	B&W	middle	slightly cloudy	yes	N/A
C31	23/11/2020	CSC	yes	white	abundant	milky	yes	N/A
C32	23/11/2020	CSC	yes	B&W	abundant	slightly cloudy	no	N/A
C33	08/12/2020	CSC	yes	B&W	middle	milky	no	yes
C34	16/01/2021	CSC	yes	white	middle	milky	yes	N/A
C35	16/01/2021	CSC	yes	white	abundant	milky	yes	N/A
C36	11/04/2017	NapN	yes	B&W	few particles	clear	no	yes
C37	08/06/2017	NapN	yes	B&W	few particles	clear	no	N/A
C38	25/07/2017	NapN	yes	black	middle	clear	no	N/A
C39	30/07/2018	NapN	no	N/A	N/A	clear	no	N/A
C40	24/10/2018	NapN	yes	white	few particles	clear	no	N/A
C41	19/12/2018	NapN	yes	white	few particles	clear	no	N/A
C42	22/01/2019	NapN	yes	white	few particles	clear	no	N/A
C43	19/02/2019	NapN	yes	B&W	middle	clear	no	N/A
C44	22/03/2019	NapN	yes	B&W	middle	clear	no	N/A
C45	11/06/2019	NapN	yes	white	middle	clear	no	yes
C46	14/07/2019	NapN	yes	B&W	few particles	clear	no	N/A
C47	03/09/2019	NapN	yes	B&W	middle	slightly cloudy	no	yes
C48	01/10/2019	NapN	yes	white	abundant	slightly cloudy	no	yes
C49	08/10/2019	NapN	yes	B&W	few particles	clear	no	N/A
C50	05/12/2019	NapN	yes	B&W	few particles	clear	no	N/A
C51	27/02/2020	NapN	yes	B&W	few particles	slightly cloudy	no	N/A
C52	10/04/2020	NapN	yes	black	few particles	slightly cloudy	no	N/A
C53	05/08/2020	NapN	yes	B&W	abundant	slightly cloudy	no	N/A
C54	08/10/2020	NapN	yes	B&W	few particles	clear	no	N/A
C55	08/12/2020	NapN	yes	B&W	few particles	slightly cloudy	yes	N/A

255 N/A: Not applicable/Not analyzed

## 256 4.2 Microscopic SEM-EDS observations

257 After filtration of nine condensate solutions, 177 EDS analyses (Supplementary Material 1)  
258 and SEM-BSE observations (Fig. 2) were performed, and they allowed us to identify four  
259 distinct types of solid particles (Fig 4, Table 2):

- 260 1) Rock particles. Subrounded- to angular-shaped particles whose size varied from a few  
261 micrometers up to ~140  $\mu\text{m}$ . These particles were Si-rich, with significant  
262 concentrations of rock-related elements (i.e., K, Mg, Ca, Ti, Fe; Fig. 2a). These  
263 fragments were the most abundant and common in condensates, especially at NapN

264 (Fig. 3). They were eroded from the fumarolic conduit, as proven by previous works  
265 focused on volcanic aerosols (e.g., Aiuppa et al. 2003; Martin et al. 2008).

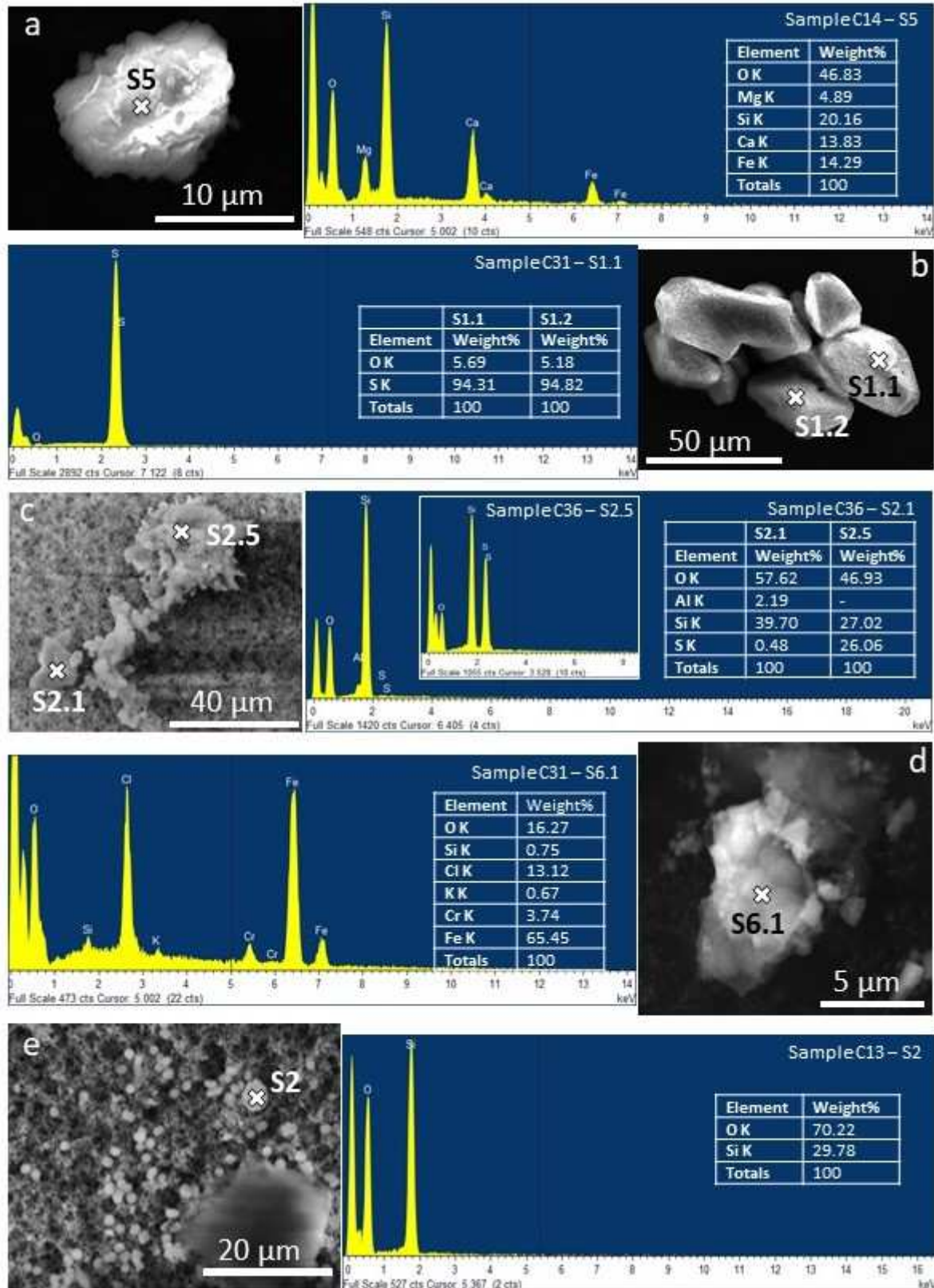
266 2) S-bearing particles. Subrounded to subangular particles of  $\leq 110$   $\mu\text{m}$  diameter  
267 containing significant amounts of S (Fig. 2b). The highest S concentrations (up to 100  
268 wt.%) were ascribed to the presence of amorphous and crystalline native sulfur (Fig.  
269 2b), while lower values were attributed to the presence of sulfates (Supplementary  
270 Material 1). These particles predominated in CS condensates (Fig. 3), while only three  
271 were found in NapN samples. The origin of solid S-particles could be ascribed to sulfur  
272 precipitation during the condensation process (Fischer et al. 1998) and/or emission in  
273 the aerosol phase (e.g., Moune et al. 2010; Calabrese and D'Alessandro 2015), the latter  
274 being trapped during the condensation process.

275 3) Cl-bearing particles. Subrounded- to subangular-shaped particles of  $< 50$   $\mu\text{m}$  in  
276 diameter (Fig. 2d) and occasionally translucent in appearance. These particles had  
277 significant concentrations of Cl (by up to 37.8 wt.%), together with Na, K, Ca, and Fe.  
278 In general terms, all Cl-containing SEM-EDS spectrums were considered within this  
279 group, except for those point analyses which displayed a low Cl concentration ( $< 4$   
280 wt.%) and significant concentrations ( $> 10$  wt.%) of Si. Nine Cl-bearing particles were  
281 found at CS, while only two were found at NapN. These particles were commonly  
282 found in the aerosol phase within volcanic plumes (e.g., Obenholzner et al. 2003;  
283 Moune et al. 2010; Mandon et al. 2019).

284 4) Si-rich spherules. Small ( $< 10$   $\mu\text{m}$ ) rounded particles formed by Si and O. These  
285 particles appeared in both NapN and CS samples (Fig. 2e). However, only four-point  
286 analyses (Supplementary Material 1) enabled them to be identified due to their small  
287 size. Therefore, the number of Si-rich particles could be greatly underestimated. The  
288 origin of Si-rich microspherules in volcanic systems has been commonly associated  
289 with bubbles bursting at the magma air interface (Martin et al. 2008) or leaching of  
290 glass fragments by acidic gases (e.g., Spadaro et al. 2002; Moune et al. 2007). However,  
291 given the low temperature of fumarolic emissions at La Soufriere, Si-rich particles  
292 appear to be related to A-opal precipitation which occurs commonly in geothermal  
293 systems (Garcia-Valles et al. 2008; Peng and Jones 2012).

294 **Table 2** Summary of the physicochemical characteristics of the solid particles identified within  
295 condensate samples. Detailed information is presented in Supplementary Material 1.

<b>Fragment Type</b>	<b>Rock particles</b>	<b>S-bearing particles</b>	<b>Cl-bearing particles</b>	<b>Si-rich particles</b>
<b>Occurrence</b>	Common	Occasional	Occasional	Rare
<b>Morphology</b>	Subrounded to angular. Usually, they formed agglutinates	Subrounded to subangular. Presence of agglutinates of sulfur in CS	Subrounded to subangular	Spherical/ Rounded
<b>Size</b>	<140 $\mu\text{m}$	<110 $\mu\text{m}$	<50 $\mu\text{m}$	<10 $\mu\text{m}$
<b>Chemical composition</b>	Main: Si, O Minor: Fe, Ti, Ca, Zr, Al, K, Ca	Main: S, O Minor: Si	Main: O, Cl, Na, K Minor: Si, S, Ca	Main: Si, O
<b>Mineral phases</b>	-	Native sulfur Na-Ca sulfates	Possible halite Fe-Chlorides	Amorphous silica

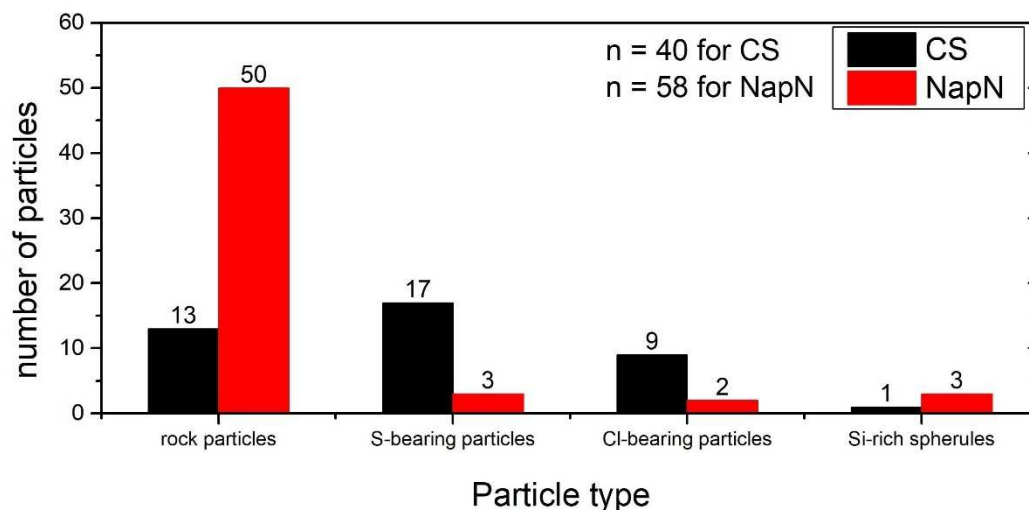


296

297 **Figure 2** Physicochemical characteristics of the solid particles found in condensates: a) rock  
 298 particles that contained variable concentrations of rock-forming elements (i.e., K, Mg, Ca, Ti,  
 299 Fe); b) rhombic native sulfur particles; c) agglutinate of Si particles with variable

300 concentrations of rock-forming elements and sulfur; d) Cl-bearing particle with alkaline, earth-  
301 alkaline, and Fe as main ligand elements; e) small round/spheroidal particles that contained Si  
302 and O. Sample codes were listed in Table 1. White crosses represent EDS analyses, whose  
303 spectrums (S) are included in Supplementary Material 1. Tables within spectrums display  
304 normalized wt.% values.

305 Rock particles were dominant in condensates, followed by S-bearing and Cl-bearing  
306 compounds (Fig. 3). Conversely, Si-rich spherules were less common. However, three sources  
307 of uncertainty could bias the particle count: i) only a modest fraction of samples (9 out of 55  
308 samples) were studied by the SEM-EDS technique, ii) for each sample, not all particles were  
309 analyzed, either due to their similar appearance, their small size that produced significant  
310 background noise, or a working/measuring strategy that was focused on the identification of  
311 particles that displayed different signal intensities, iii) presence of agglutinates (Fig. 2c)  
312 composed of rock- and S-bearing particles that were considered as single fragments.  
313 Consequently, the particle count (Fig. 3) was underrated and should not be taken as strictly  
314 significant to provide sample statistics. However, independent of the possible biased particle  
315 count, two clear tendencies can be distinguished in Fig. 3: 1) the amount of rock particles is  
316 greater at NapN than CS, and 2) S- and Cl-bearing particles are predominant at CS. We can  
317 thus anticipate that the tendencies suggest a significant erosive contribution in NapN  
318 condensates during the study period.



319  
320 **Figure 3** Histograms of the amount and type of particles within condensate samples. A total of  
321 98 particles were identified based on 177 SEM-EDS analyses (Supplementary Material 1,  
322 column "Z") and considered for this plot. However, this number of particles is an was

323 underestimate given that not all of them were analyzed (see text to further details). Black and  
324 red bars represent CS and NapN samples, respectively.

### 325 **4.3 Physicochemical characteristics of condensates**

326 Outlet gas temperature of analyzed samples, pH, and concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  of  
327 condensates collected from CS and NapN fumaroles are presented in Table 3. The outlet gas  
328 temperatures at CS varied from 95 to 108.4 °C, with maximum values in April 2018, November  
329 2019, and January 2021 samples (Fig. 4b). Over the same period, NapN temperatures remained  
330 within the narrow range of  $94.4 \pm 0.9$  °C (Fig. 4b). In the same way as for the outlet gas  
331 temperature, CS samples also recorded greater pH variations (ranging from 0.92 to 4.52) than  
332 NapN samples (between 2.70 and 3.41). These pH variations (Fig. 4a) agreed with those found  
333 in worldwide volcanoes (values from ~0 to 4.5; Gemmell 1987, Taran et al. 1995; Africano  
334 and Bernard 2000; Chaplygin et al. 2016) and coincided with pH values (between 1.1 and 5)  
335 obtained during the 1976 phreatic explosions at La Soufriere (Chevrier and Le Guern 1982).  
336 The lowest pH values (~1) at CS were comparable with those condensates measured in high-  
337 temperature magmatic systems as Kudryavy (Russia) or San Cristobal (Nicaragua) volcanoes  
338 (Gemmell 1987; Taran et al. 1995).

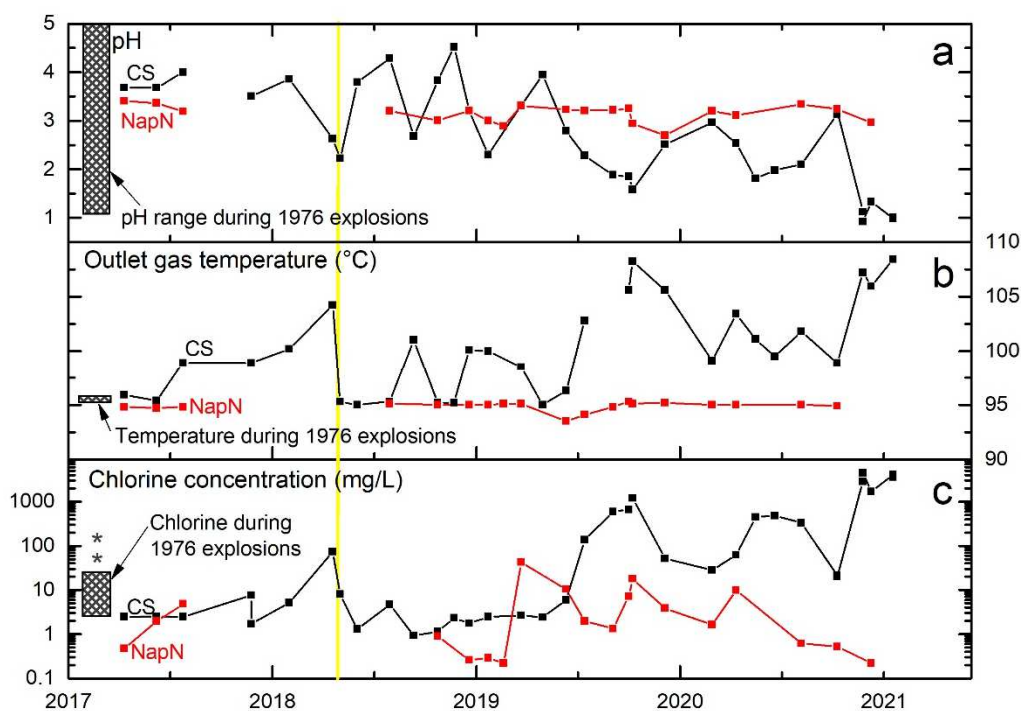
339 The concentration of  $\text{Cl}^-$  in CS and NapN (Table 3) was within the range of 0.9 to 4798 mg/L  
340 and 0.2 to 42.4 mg/L, respectively. Cl contents showed a roughly positive correlation with  
341 outlet gas temperature in the case of CS and a negative correlation with pH (Fig. 4). Sulfate  
342 concentrations for CS and NapN ranged from 2.0 to 573.9 mg/L and 2.2 to 80.8 mg/L,  
343 respectively. No correlation was found between sulfate concentrations (Table 3) and the  
344 amount of particles or sample aspect (Table 1), suggesting that the variable presence of  
345 particles is more related to mechanical processes (i.e., vent erosion) than to the chemical  
346 composition of condensates. Chlorine concentrations measured in CS and NapN agree with  
347 those condensates collected during the 1976 phreatic explosions at Col de l'Echelle (Chevrier  
348 and Le Guern 1982). However, samples collected since July 2019 at CS have exhibited a  
349 notable increase in  $\text{Cl}^-$  concentration, the highest recorded at La Soufriere fumaroles (Fig. 4c,  
350 Table 3). On the other hand, sulfate contents showed variable concentrations (Table 3), but  
351 they did not correlate with the outlet gas temperature nor the pH of condensates.

352 **Table 3** Fumarolic site, pH, outlet gas temperature (in °C) of analyzed samples, condensation  
353 procedure, and concentrations (mg/L) of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in condensate samples.



	Date	Site	pH	Temp °C	Method	Cl <sup>-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L
C1	11/04/2017	CSC	3.68	95.9	Normal	2.4	18.2
C2	08/06/2017	CSC	3.68	95.4	Normal	2.5	19.0
C3	25/07/2017	CSC	4.00	98.9	Normal	2.5	8.4
C4	24/11/2017	CSC	N/A	98.9	Normal	7.6	22.0
C5	24/11/2017	CSC	3.50	98.9	Normal	1.7	9.5
C6	31/01/2018	CSC	3.86	100.2	Normal	5.1	23.9
C7	19/04/2018	CSC	2.63	104.2	Normal	73.9	5.9
C8	02/05/2018	CSN	2.22	95.3	Normal	8.0	138.6
C9	02/06/2018	CSC	3.79	95	Normal	1.3	4.2
C10	30/07/2018	CSC	4.29	95.3	Normal	4.7	17.4
C11	11/09/2018	CSC	2.68	101	Normal	0.9	14.9
C12	24/10/2018	CSC	3.83	95.2	Normal	1.1	2.0
C13	22/11/2018	CSC	4.52	95.2	Normal	2.3	10.9
C14	19/12/2018	CSC	3.21	100.1	Normal	1.8	26.1
C15	22/01/2019	CSC	2.30	100	Normal	2.5	563.6
C16	22/03/2019	CSC	3.32	98.5	Normal	2.7	4.0
C17	30/04/2019	CSC	3.95	95	Normal	2.4	38.7
C18	11/06/2019	CSC	2.79	96.3	Normal	6.0	573.9
C19	14/07/2019	CSC	2.28	102.8	Normal	135.8	15.1
C20	03/09/2019	CSC	1.88	>99.8	Normal	593.5	22.3
C21	01/10/2019	CSC	1.85	105.6	Normal	663.0	3.9
C22	08/10/2019	CSN	1.58	108.2	Normal	1206.0	30.0
C23	05/12/2019	CSN	2.51	105.6	Normal	51.2	2.9
C24	27/02/2020	CSC	2.96	99.1	Normal	28.3	227.4
C25	10/04/2020	CSC	2.53	103.4	Normal	62.6	4.6
C26	15/05/2020	CSC	1.81	101.1	Normal	449.1	5.1
C27	18/06/2020	CSC	1.98	99.5	Normal	483.3	8.8
C28	05/08/2020	CSC	2.10	101.8	Normal	332.0	8.1
C29	08/10/2020	CSC	3.13	98.9	Normal	21.3	2.3
C30	08/10/2020	CSC	3.21	98.9	Normal	20.3	5.3
C31	23/11/2020	CSC	1.12	107.2	Normal	2858.2	10.1
C32	23/11/2020	CSC	0.92	107.2	Normal	4505.0	14.1
C33	08/12/2020	CSC	1.33	106	Normal	1690.5	9.1
C34	16/01/2021	CSC	0.98	108.4	Normal	4129.5	23.6
C35	16/01/2021	CSC	1.00	108.4	normal	3562.0	46.0
C36	11/04/2017	NapN	3.41	94.8	Direct	0.5	2.2
C37	08/06/2017	NapN	3.36	94.7	Direct	2.0	6.5
C38	25/07/2017	NapN	3.19	94.8	Direct	4.8	49.1
C39	30/07/2018	NapN	3.2	95.1	N/A	N/A	N/A
C40	24/10/2018	NapN	3.01	95	N/A	0.9	2.5
C41	19/12/2018	NapN	3.21	95	Direct	0.3	9.1
C42	22/01/2019	NapN	3.00	95	Direct	0.3	6.4
C43	19/02/2019	NapN	2.89	95.1	Direct	0.2	3.6
C44	22/03/2019	NapN	3.31	95.1	Direct	42.4	3.9
C45	11/06/2019	NapN	3.23	93.5	Direct	10.4	67.1
C46	14/07/2019	NapN	3.21	94.1	Direct	2.0	3.7
C47	03/09/2019	NapN	3.22	94.8	Direct	1.3	20.6
C48	01/10/2019	NapN	3.25	95.3	Normal	7.2	14.9
C49	08/10/2019	NapN	2.94	95.1	Normal	17.9	37.1
C50	05/12/2019	NapN	2.70	95.2	Direct	3.9	80.8
C51	27/02/2020	NapN	3.20	95	Direct	1.6	30.4
C52	10/04/2020	NapN	3.11	95	Direct	10.0	8.6
C53	05/08/2020	NapN	3.34	95	Direct	0.6	6.7
C54	08/10/2020	NapN	3.24	94.9	Direct	0.5	9.7
C55	08/12/2020	NapN	2.96	N/A	Direct	0.2	13.8

354 N/A: Not applicable/Not analyzed



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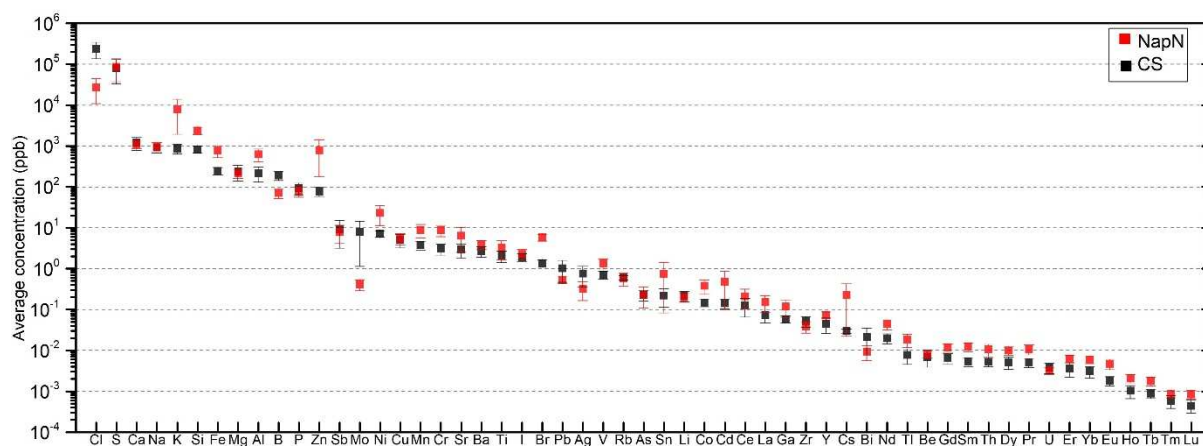
356 **Figure 4** Physicochemical variations in a) pH, b) outlet gas temperature, and c) chlorine  
 357 concentration in CS (black lines) and NapN (red lines) samples during the study period. Dashed  
 358 areas show pH, outlet gas temperature, and Cl concentrations obtained for samples collected  
 359 during the July-August 1976 explosions at Col de l'Echelle (Chevrier and Le Guern 1982).  
 360 Asterisks in panel (c) show two outlier chlorine concentrations measured for the 1976  
 361 eruptions. The yellow line shows the earthquake of  $M_L$  4.1 on April 27, 2018, which was felt  
 362 by the population.

#### 363 4.4 Trace element concentrations in condensate samples

364 Corrected concentrations (in ppb) of major and trace elements for representative samples are  
 365 presented in Table 4, while complete data including analytical dilution factors, blank  
 366 corrections, and %RSD (Relative Standard Deviation) values are provided in Supplementary  
 367 Material 2. Chemical element concentrations displayed great dispersion, as demonstrated by  
 368 significant percentile variation coefficients (49 and 393%) in both CS and NapN, likely  
 369 attributed to variations in outlet gas temperatures, steam fluxes, or the variable chemical  
 370 composition of fumarolic emissions. Of the studied chemical elements, 41.6% exhibit median  
 371 RSD <10%, while 81% showed median RSD values <50%. The lowest %RSD was associated  
 372 with abundant chemical elements (Cl and S), some alkali and earth-alkali elements (Mg, K, Ca,  
 373 Rb, Sr, Cs, Ba), transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y) and other metal and

374 metalloid elements (B, Al, Si, Sb). Various lithophile (Li, Na, Ti, Br, Zr, U, and Rare Earth  
375 Elements; REEs), chalcophile (Ag, Cd, Sn), and siderophile (Mo, Sn) elements had slightly  
376 higher median %RSD (between 10 and 50%), while As and I had medium-high %RSD (median  
377 around 50%). Be, Tl, Bi, and Th reached the highest median %RSD (usually >100%), mainly  
378 due to their very low (generally <0.1 ppb) concentrations.

379 Condensates were mainly composed of Si, S, and Cl, representing 23-99.9% and 50-99.8% of  
380 the total concentration of condensates in CS and NapN samples, respectively. Therefore, trace  
381 elements occasionally represented a small fraction in analyzed samples. Sulfur, Cl, and rock-  
382 forming elements (such as Na, Mg, Al, Si, or Ca) had high concentrations in condensates (Table  
383 4), with values of between  $10^1$  and  $10^7$  ppb. Metal and metalloid elements (i.e., Cr, Co, Ni, Zn,  
384 As, Ag, Cd) had concentrations ranging from  $10^{-1}$  to  $10^2$  ppb, apart from Fe and Zn, which  
385 reached concentrations in the order of  $10^3$ - $10^4$  ppb, like rock-related elements. REEs generally  
386 showed concentrations <1 ppb (Table 4). By comparing condensate samples collected on the  
387 same date at CS and NapN (Fig. 5), the average concentrations at NapN samples were often  
388 higher than those of CS samples, except for Li, B, Cl, Zr, Mo, Ag, Sb, Pb, Bi, and U. This  
389 pattern could result from the minor proportion of condensed steam in NapN compared to CS  
390 (75 mol% versus 96 mol% of steam, respectively, e.g., Tamburello et al. 2019; Moretti et al.  
391 2020a), thus yielding lower degrees of dilution of collected samples and therefore higher  
392 concentrations of elements (e.g., Gemmell 1987). Gas/steam ratios from CS presented in  
393 Moretti et al. (2020), OVSG monthly reports ([http://www.ipgp.fr/fr/ovsg/bulletins-mensuels-](http://www.ipgp.fr/fr/ovsg/bulletins-mensuels-de-lovsg)  
394 [de-lovsg](http://www.ipgp.fr/fr/ovsg/bulletins-mensuels-de-lovsg)), and Brombach et al. (2000) showed slight variations (ranging from 0.018 to 0.058,  
395 with an average of 0.032) between 2017 and 2021, while they reached a maximum value  
396 (0.099) in June 2018 when degassing was markedly perturbed (e.g., Moretti et al. 2020a). Also,  
397 the proportion of steam found in CS using Giggenbach ampoules (96-97 mol%; Moretti et al.  
398 2020a) agrees with MultiGas data (96 mol%) measured by Tamburello et al. (2019) in 2016.  
399 Regrettably, there is no published data from Giggenbach ampoules at NapN. Therefore,  
400 previously collected data from CS show that the proportion of steam remained constant during  
401 this study period. Similarly, based on the behavior of CS, it is believed that NapN maintained  
402 a constant proportion of steam during the study period.



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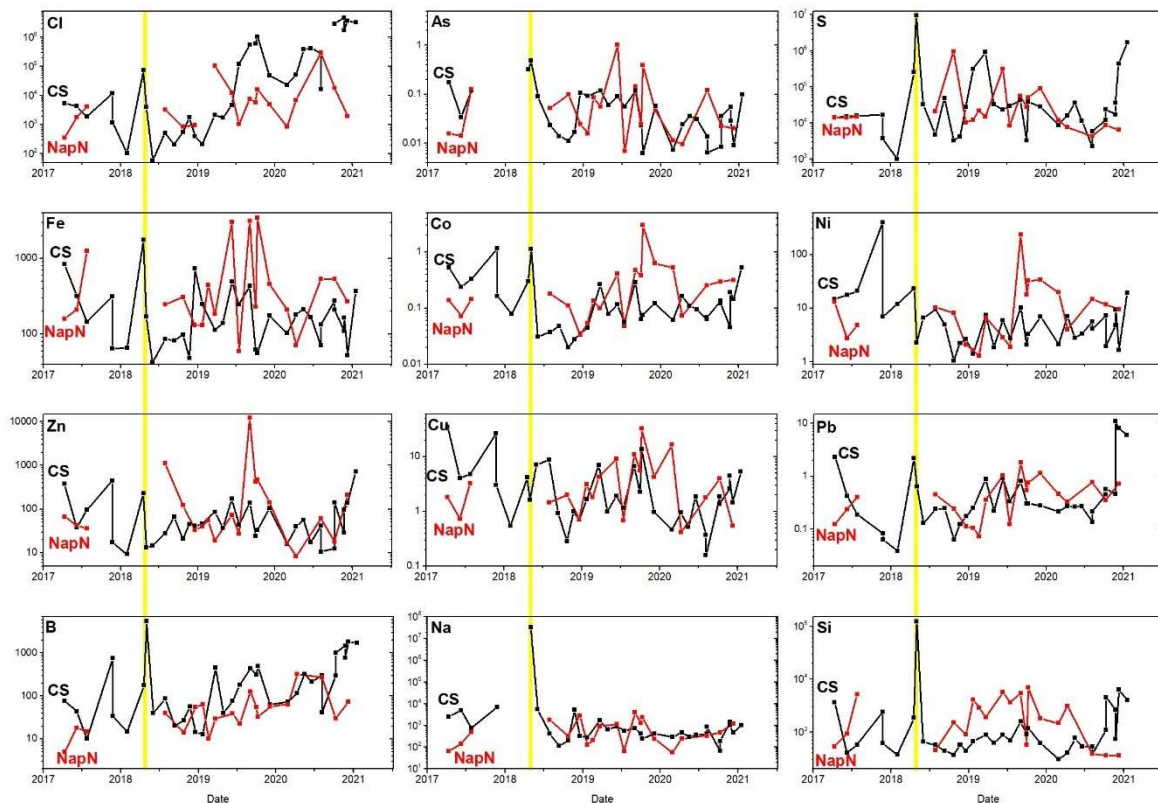
404 **Figure 5** Average concentration (in ppb) of condensates collected on the same dates from CS  
 405 (black squares) and NapN (red squares) fumaroles. For example, concentrations of samples  
 406 collected between mid-2017 and mid-2018 were not considered, given that NapN was not  
 407 sampled in that period. Bars represent the standard error of the mean.

408 Notable chemical variations were depicted at CS and NapN (Fig. 6), even for the most abundant  
 409 elements with high confidence (with low %RSD). Concentrations above baseline values of  
 410 several chemical elements (e.g., S, Si, Na, B) were observed in the CS sample collected in May  
 411 2018 and associated with the volcanic unrest described by Moretti et al. (2020a), with values  
 412 up to four orders of magnitude above average (for instance, S and Na; Fig. 6; Table 4).  
 413 Similarly, CS samples frequently showed greater concentrations at the end of 2020 and the  
 414 beginning of 2021. It is important to note that B and Cl concentrations at CS (Fig. 6) showed a  
 415 generally incremental pattern over the study period. Conversely, chemical elements at NapN  
 416 tended to reach higher concentrations during the second half of 2019. The uniformly disparate  
 417 behavior between CS and NapN suggested variable physicochemical processes that affected  
 418 the feeding source of these emissions.

419 **Table 4** Concentration (in ppb) of major and trace elements in representative condensates  
 420 collected between April 2017 and January 2021 from CS and NapN fumaroles. Complete data  
 421 and Weigh Ash Fraction percentages (%WAF; See Appendix B for further details) are  
 422 presented in Supplementary Material 2. <blk: below detection limit.

Sample	C-3	C-8	C-18	C-35	C-38	C-46	C-55	WAF%	WAF%
Date	25/07/2017	02/05/2018	11/06/2019	16/01/2021	25/07/2017	14/07/2019	08/12/2020	average	average
Fumarole	CS	CS	CS	CS	NapN	NapN	NapN	CSC	NapN
Li	0.170	4.243	0.366	0.284	0.623	0.056	0.143	23.4	36.2
Be	0.0065	0.0471	0.0003	0.0168	0.0123	0.0028	0.0019	39.3	56.4
B	10.24	5593.84	77.14	1721.76	15.04	23.01	72.87	0.08	0.70

Na	757.48	32393671	932.48	1038.46	501.93	65.09	1230.81	100	100
Mg	93.67	4.61	85.34	245.52	474.78	39.55	127.21	100	100
Al	175.67	3807.70	186.90	192.12	2532.46	28.18	119.73	100	100
Si	573.84	122398.81	876.39	3962.99	5111.39	3670.77	356.54	100	100
P	214.83	1792.21	94.96	21.69	314.17	<blk	22.38	100	100
S	15822	9534766	23229	1693274	14955	8484	6399	0.004	0.009
Cl	1869.1	4101.6	4842.1	3276623.2	4167.2	1053.4	1987.5	1.3	1.4
K	2161.2	3516.2	3951.3	359.4	3014.1	811.0	859.3	100	100
Ca	475.9	741.7	994.9	1617.2	1997.0	199.6	755.8	100	100
Ti	10.40	33.07	0.66	3.56	0.84	0.34	0.35	100	100
V	2.55	1.26	0.81	1.36	0.92	0.20	0.27	60.9	62.7
Cr	0.54	3.92	2.24	4.30	0.53	3.50	3.29	100	100
Mn	11.87	2.56	4.89	4.36	13.01	0.65	6.86	100	100
Fe	143.96	169.56	489.47	366.49	1248.10	59.30	269.10	100	100
Co	0.33	1.12	0.12	0.53	0.14	0.05	0.32	45.9	48.6
Ni	20.95	2.27	5.92	19.47	4.84	1.89	9.49	0.9	1.7
Cu	4.77	1.63	1.90	5.39	3.25	0.68	0.55	9.3	13.6
Zn	95.94	13.38	171.89	721.02	36.66	27.64	212.85	0.4	0.6
Ga	0.118	0.486	0.090	0.098	0.127	0.007	0.020	71.7	82.3
As	0.147	3.054	0.183	2.150	<blk	0.042	<blk	2.6	21.3
Br	2.16	4.27	2.09	2.75	21.87	1.04	1.66	0.4	0.2
Rb	0.18	3.14	0.38	0.95	0.44	0.03	1.14	100	100
Sr	1.24	54.42	2.55	2.52	6.65	0.30	1.54	100	100
Y	0.019	0.048	0.035	0.063	0.128	0.008	0.051	100	100
Zr	0.02	32.16	0.03	0.55	0.01	<blk	<blk	100	100
Mo	5.48	57.29	0.07	0.22	0.06	0.05	<blk	1.3	4.9
Ag	0.132	0.016	6.348	0.108	0.020	1.225	<blk	4.5	8.6
Cd	0.114	0.056	0.310	0.254	0.066	0.008	0.355	0.9	1.5
Sn	0.007	0.154	0.017	0.623	0.007	<blk	0.003	20.9	57.3
Sb	3.46	3.84	<blk	7.41	2.55	3.27	3.40	0.19	0.06
I	<blk	130.63	1.42	21.15	<blk	1.08	<blk	2.6	11.5
Cs	0.04	3.41	0.02	0.02	0.07	0.00	0.01	100	100
Ba	4.33	11.76	3.75	5.42	17.13	0.62	1.19	100	100
La	0.04960	0.00460	0.05447	0.05619	0.88457	0.00552	0.06143	100	100
Ce	0.03884	0.03948	0.09101	0.08580	0.61679	0.00165	0.08392	100	100
Pr	0.00155	0.00392	0.00633	0.00745	0.03037	0.00050	0.00395	100	100
Nd	0.00767	0.01448	0.02504	0.03357	0.11957	0.00184	0.01961	100	100
Sm	0.00165	0.02524	0.00743	0.01080	0.02706	0.00041	0.00925	100	100
Eu	0.00161	0.00383	0.00184	0.00271	0.01866	0.00019	0.00162	100	100
Gd	0.01433	0.00065	0.00632	0.01185	0.02493	<blk	0.00520	100	100
Tb	0.00033	0.00107	0.00111	0.00126	0.00409	0.00022	0.00132	100	100
Dy	0.00208	0.00293	0.00576	0.00619	0.02252	0.00058	0.00731	100	100
Ho	0.00034	0.00911	0.00126	0.00113	0.00424	0.00000	0.00096	100	100
Er	0.00089	0.00301	0.00301	0.00399	0.01238	0.00017	0.00470	100	100
Tm	0.00033	0.00115	0.00051	0.00076	0.00167	0.00018	0.00064	100	100
Yb	0.00116	0.00739	0.00391	0.00458	0.01159	0.00103	0.00471	100	100
Lu	0.00012	0.00180	0.00042	0.00028	0.00183	0.00006	0.00052	100	100
Tl	<blk	0.07	0.01	<blk	<blk	<blk	<blk	9.0	6.3
Pb	0.19	0.64	0.92	6.11	0.41	0.12	0.72	2.0	4.6
Bi	0.0023	0.0579	0.0131	0.0288	0.0021	0.0052	0.0013	0.1	0.7
Th	0.0053	<blk	0.0016	<blk	0.0056	<blk	<blk	100	100
U	0.0009	0.0927	0.0033	0.0061	0.0039	0.0002	0.0019	100	100



424

425 **Figure 6** Long-term variations in the concentration of representative chemical elements during  
 426 the period from May 2017 to January 2021. Samples from CS and NapN have a distinct and  
 427 constant dilution factor during the study period. The yellow line shows the earthquake ( $M_L$  4.1)  
 428 on April 27, 2018. Black and red lines represent CS and NapN fumaroles, respectively.

## 429 5. Discussion

### 430 5.1 Representativity of samples

431 IC and ICP-MS techniques are frequently used to characterize the chemical composition of a  
 432 wide variety of solid or liquid samples. While the IC technique offers fast and practical  
 433 measurements of major ions dissolved in liquid samples, the ICP-MS technique offers accurate  
 434 and precise measurements for chemical elements in trace and ultra-trace (<1 ppm)  
 435 concentrations. In this work, chlorine and sulfur contents (in the form of sulfates in the case of  
 436 IC technique) were measured by both IC and ICP-MS methods, allowing the results to be  
 437 compared and their representativeness evaluated. Despite a few outliers, there was a good  
 438 general agreement between the two techniques for chlorine concentration determination for  
 439 both CS and NapN samples (Fig. 7a). On the other hand, the sulfur contents in CS and NapN  
 440 samples showed a large dispersion, with no a clear correlation between the two techniques (Fig.

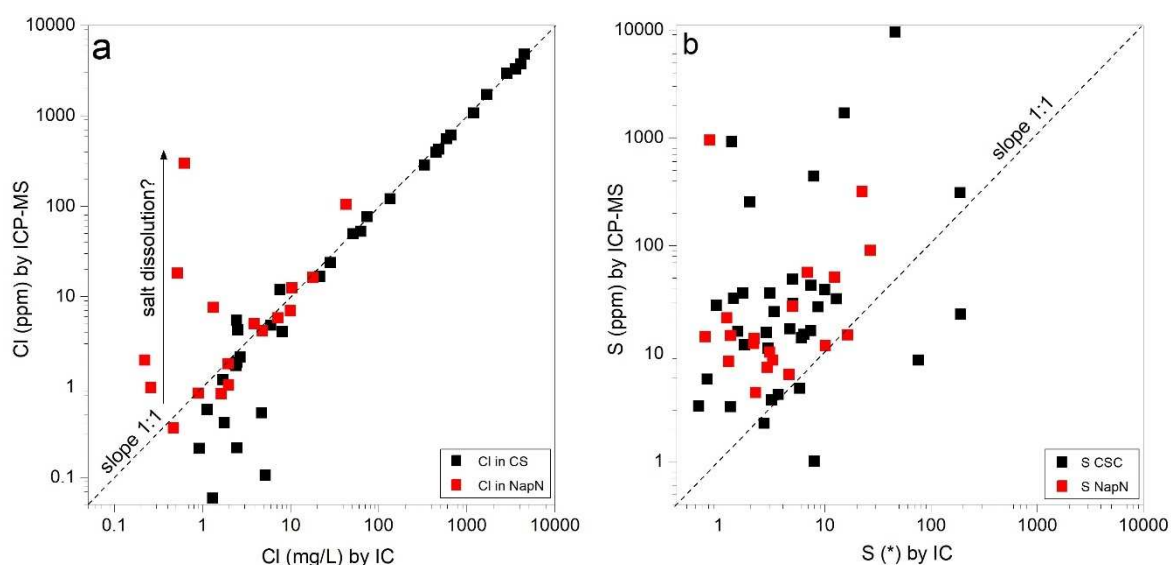
441 7b). It is well known that suppressed or enhanced signals could be obtained in ICP-MS analyses  
442 on high ionic strength solutions due to the precipitation of salts on the nebulizer or the presence  
443 of high concentrations of matrix elements such as H<sub>2</sub>SO<sub>4</sub> (Fischer et al. 1998; Nelms 2005).  
444 Fig. 7 shows that the large inconsistencies between the two methods were beyond the analytical  
445 error of each technique. Greater chlorine and sulfur concentrations in ICP-MS than IC analyses  
446 suggest the presence of other Cl<sup>-</sup> and S-compounds that were not analyzed by the IC technique.  
447 This mismatch was common in the case of sulfur (Fig. 7b), where species such as SO<sub>3</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>  
448 , S<sup>2-</sup> can be found (Africano and Bernard 2000). Based on these assumptions, discrepancies in  
449 S content by both techniques could be explained by the presence of unknown S-species, in  
450 agreement with typically higher S concentrations measured by ICP-MS than IC (Fig. 7b).

451 The presence of solid particles (Fig. 3) could modify the original chemical composition of  
452 condensate samples since re-equilibration processes related to dissolution and/or precipitation  
453 of solid phases could occur within the acid solution, especially in those samples stored for a  
454 longer time (up to four years) and with lower pH. Indeed, dissolution processes could explain  
455 the higher Cl and S concentrations measured by the ICP-MS technique (Fig. 7). Dissolution of  
456 Cl-bearing particles is feasible given the hydrophilic behavior of Cl (Africano and Bernard  
457 2000), which could explain the small number of Cl-bearing particles detected on SEM analyses  
458 (Fig. 3). Similarly, dissolution processes could efficiently remove lithophile and siderophile  
459 elements by leaching of rock particles (Taran et al. 1995; Symonds et al. 1996). Therefore,  
460 dissolution of Cl-bearing and rock particles should increase the concentration of siderophile  
461 and lithophile elements in samples. On the other hand, the dissolution of S compounds is not  
462 expected since it can only occur in the presence of hot aqua regia.

463 Precipitation of S-bearing compounds has been previously documented for condensate samples  
464 (Fischer et al. 1998). Sulfur precipitation in aqueous solutions typically occurs when SO<sub>4</sub><sup>2-</sup>  
465 concentrations are above ~1000 mg/L (e.g., Fischer et al. 1998), while precipitation of sulfur  
466 and sulfate minerals (e.g., gypsum, anhydrite, barite) from highly charged acid waters in crater  
467 lakes (natural analog of condensates) has been documented when SO<sub>4</sub><sup>2-</sup> concentrations are  
468 above 10,000 mg/L (e.g., Agosto et al. 2016; Inguaggiato et al. 2018, Mandon et al. 2020).  
469 Such SO<sub>4</sub><sup>2-</sup> concentrations are higher than those found in La Soufriere's condensates (≤574  
470 mg/L, Table 3), therefore we infer negligible sulfur precipitation in the latter. Consequently,  
471 sulfur crusts found inside polyethylene bottles could be due to the decantation of suspended  
472 matter instead of precipitation processes. Therefore, trace element sequestration from the

473 aqueous solution was discarded, as documented in previous works focusing on sulfur  
474 precipitates (e.g., Fischer et al. 1998). In the case of amorphous silica precipitates, significant  
475 amounts of lithophile elements, in addition to Fe, As, and Sb, could be removed from the  
476 solution (Reyes et al. 2002; Sanchez-Yañez et al. 2017). However, such chemical elements  
477 were not identified during the analysis of A-opal spherules.

478 Although dilution and precipitation processes affecting S- and Cl-bearing particles cannot be  
479 ruled out, it is believed that secondary re-equilibration processes only affected Si-particles.  
480 Moreover, the time-dependent test (Appendix A) demonstrated negligible exchange processes  
481 during a 67-day storage time (Fig. A1), although they did not take into account more extended  
482 periods nor trace elements which might have disguised clues about their behavior during longer  
483 storage times. Data dispersion associated with Cl and S contents mainly corresponded to i)  
484 analytical uncertainties when concentrations were below 10 ppm for Cl, and ii) presence of  
485 unanalyzed and unknown S-species, besides solid sulfur microparticles that caused interference  
486 with the measurement of sulfate concentrations (e.g., Fig. A1). Such analytical uncertainties  
487 become significant when concentrations are closer to the instrumental detection limits (e.g.,  
488 0.1 and 1 ppm for Cl and S in ICP-MS measurements, respectively) as depicted for Cl  
489 concentrations in Fig. 7a. Consequently, the data from the ICP-MS technique seems to be more  
490 reliable because i) analyses were done on filtered samples which minimized the noise caused  
491 by the presence of particles, and ii) ICP-MS carried out direct measurements of the total  
492 concentration for Cl and S. Therefore, data from this technique were used for computations in  
493 the following section.





495 **Figure 7** Comparison between the concentration of (a) Cl and (b) S from both CS and NapN  
496 fumaroles, determined by ion chromatography (IC) and Inductively Coupled Plasma Mass  
497 Spectrometry (ICP-MS) techniques. It is important to note that IC analyses were performed  
498 within a week of sampling, while ICP-MS were carried out from a few months to up to four  
499 years after sampling. Black and red symbols represent CS and NapN samples, respectively.  
500 Dashed lines show the 1:1 ratio. S(\*) corresponds to the molar concentration of sulfur in SO<sub>4</sub>  
501 alone.

## 502 **5.2 Trace element volatility**

503 Volcanic exhalations release volatile species and aerosols (e.g., Taran et al. 1995; Aiuppa et al.  
504 2003; Mather et al. 2003), both mostly trapped during the condensation process. In general  
505 terms, erosion of host rock and hydrothermally altered fragments scavenged from the conduit  
506 walls has been ascribed as the primary process that contributes solid particles to condensate  
507 samples (e.g., Mather et al. 2003). Similarly, the transport of small aqueous particles (i.e., tiny  
508 droplets containing major and trace elements) becomes considerable in low-temperature steam-  
509 rich fumarolic emissions (e.g., Pokrovski et al. 2013; Censi et al. 2017). The erosive  
510 contribution can be accounted for based on the concentration of rock-related refractory  
511 elements (Gauthier and Le Cloarec 1998; Aiuppa et al. 2003; Gauthier et al. 2016). At La  
512 Soufriere, chondrite-normalized values (Fig. B.1) proved that REEs have been removed from  
513 host rocks, while typical rock-related elements (i.e., Al, Ti, Mn, Ca, Fe, Sr, Si, Zr, Na, K, P,  
514 Mg, Cr, Rb, Y, Cs, Ba, U, Th) are equally considered as a product of water-rock interaction  
515 within the hydrothermal system (Appendix B). Consequently, this work considers that Al, Ti,  
516 Mn, Ca, Fe, Sr, Si, Zr, Na, K, P, Mg, Cr, Rb, Y, Cs, Ba, REEs, U, and Th were transported as  
517 solids or within aqueous microparticles since they have a non-volatile behavior in the low-  
518 temperature emissions at La Soufriere volcano. Rock-related elements (including REEs) were  
519 removed following the weigh ash fraction approach (e.g., Aiuppa et al. 2003) presented in  
520 Appendix B.

### 521 **5.2.1 Calculation of enrichment factors**

522 The relative volatility of trace elements has traditionally been estimated using the enrichment  
523 factor (EF; Duce et al. 1975; Mroz and Zoeller 1975), which measures the extent of enrichment  
524 (or depletion) of an element X in the condensate ( $X_{\text{cond}}$ ) compared to whole rocks (e.g.,  
525 Symonds et al. 1990; Africano and Bernard 2000; Zelenski et al. 2013, 2014; Chaplygin et al.  
526 2015, 2016; Aguilera et al. 2016; Taran et al. 2018) following Eq. 1:

527 
$$EF = (X/Y)_{\text{cond}} / (X/Y)_{\text{rock}} \quad (\text{Eq. 1})$$

528 Where X is the element of interest and Y is the reference element in both the condensate (*cond*)  
529 and host rock (*rock*). The choice of the reference element is critical; normally, a trace element  
530 of low-moderate volatility present in low abundance levels in lavas is selected (Moune et al.  
531 2010; Gauthier et al. 2016). Magnesium was used for normalization in previous studies on  
532 condensate samples obtained from volcanic systems at magmatic temperatures (Symonds et al.  
533 1990; Zelesni et al. 2013, 2014; Chaplygin et al. 2016; Taran et al. 2018). However, in the  
534 presence of active hydrothermal systems and low-temperature fumarolic emissions, Mg cannot  
535 be used as a reference element since it is related more to the leaching of host rocks than deep  
536 magmatic degassing. Therefore, cobalt was chosen as the reference element due to its low  
537 volatility and mobility in low-temperature hydrothermal systems (e.g., Scher et al. 2013) and  
538 low concentration in condensates (Table 4) and host rocks (Table 5). In addition, the re-  
539 equilibration processes during storage time for Co is considered as being insignificant since, to  
540 our knowledge, Co does not form secondary minerals, and its leaching from host rocks is  
541 limited (e.g., Scher et al. 2013). Co was also chosen because it presented low RSD percentages  
542 (Supplementary Material 2) and a large amount of data were available in our database for EF  
543 computations.

544 Co-based EFs are presented in Supplementary Material 3, and average values for CS and NapN  
545 computed with ash-corrected concentrations (Appendix B; Supplementary Material 3) are  
546 plotted in Fig. 8a. Theoretically, elements with EFs >1 were emitted mainly in a volatile form,  
547 while elements with EFs ≤1 were emitted in the solid phase (Zelenski et al. 2013). However,  
548 this paper considers that elements with EFs >1 were also transported as aqueous particles for a  
549 better understanding. Average log EF values ranged from -1 for Ga in NapN to 4.6 for S in CS.  
550 Sulfur, Sb, B, Cl, Bi, Br, Zn, Mo, Ni, Ag, Cd, As, I, and Pb showed a high to moderate volatile  
551 behavior, whereas Tl, Cu, Sn, Li, Be, Co, V, and Ga showed a poorly volatile behavior (Fig.  
552 8a). In general terms, EFs for highly to moderately volatile elements were 9.2% (average)  
553 higher in CS than NapN, suggesting slightly higher volatility in CS samples likely due to CS  
554 having higher outlet gas temperatures (Fig. 4b) and fewer thermal and chemical scrubbing  
555 processes than NapN (e.g., Tamburello et al. 2019). Superior scrubbing at NapN would also be  
556 responsible for the decreased EFs of more soluble elements such as B, Cl, I, and As, as well as  
557 Bi, Mo, Pb, Tl, Li, and Ga. On the contrary, Br and Sn showed slightly higher EFs in NapN  
558 compared to CS. Despite such minor discrepancies, both fumarolic sites showed a similar

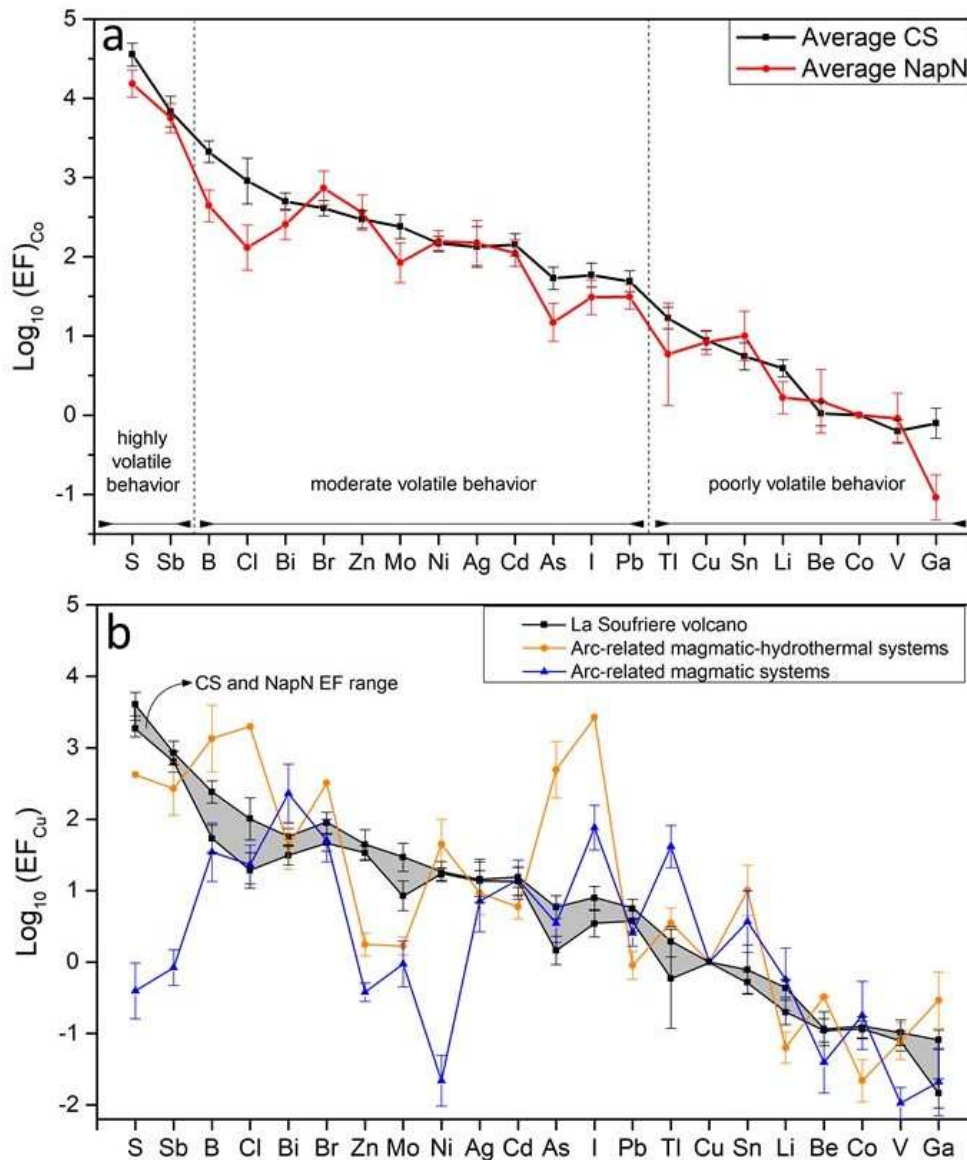
559 decreasing volatility pattern from S to Ga, implying a similar transport mode of each element  
 560 in CS and NapN.

561 S and Sb had the highest volatile behavior in La Soufriere fumaroles (Fig. 8a) with the highest  
 562 average EFs (log EFs between 3.8 and 4.6), followed by B, which reached an average log EF  
 563 of 3.3 and 2.7 in CS and NapN, respectively. Sulfur is a common constituent of volcanic  
 564 exhalations, and their high EFs agree with the presence of S-bearing particles in condensates  
 565 and S-rich fumarolic deposits around fumaroles. Likewise, it was supposed that most of the  
 566 sulfur collected in condensates was released as H<sub>2</sub>S (emission rates up to 3.5 ton/day in CSC;  
 567 Allard et al. 2014; Tamburello et al. 2019; Moune et al. 2022) and, to a lesser extent as SO<sub>2</sub>.  
 568 Nevertheless, H<sub>2</sub>S is difficult to condense given its low solubility, whereas SO<sub>2</sub> is a minor  
 569 constituent at La Soufriere fumaroles despite its greater solubility. Therefore, EFs for sulfur  
 570 must be deeply underestimated given these condensation issues. Then, Sb and B had not been  
 571 previously reported in La Soufriere samples, though their higher EFs agreed with an expected  
 572 volatile behavior in low and high-temperature volcanic emissions (Symonds et al. 1990; Taran  
 573 et al. 2018; Mandon et al. 2020). Chlorine, Bi, Br, Zn, Mo, Ni, Ag, Cd, As, I, and Pb (in  
 574 decreasing order of volatility) showed moderate to low volatility with log EF values ranging  
 575 from ~1.5 to ~3.

576 **Table 5** Concentration (in ppm) of reference host rocks used to compute weight ash fractions  
 577 (WAF; Appendix B) and enrichment factors (EF; Supplementary Material 3). Samples 23CF  
 578 and SOU-J4 were selected due to their minimal hydrothermal alteration, and they correspond  
 579 to an andesite from the 1530 AD lava dome and a scoria fallout deposit from the 1657 eruption,  
 580 respectively. These samples had been previously analyzed for major and certain trace elements  
 581 by Boudon et al. (2008) and Metcalfe et al. (2021).

	23CF	SOU- J4	Average		23CF	SOU J4	Average
Li	7.84	11.02	9.43	La	6.60	7.64	7.12
Be	0.56	0.69	0.62	Ce	15.75	17.98	16.86
B	21.35	24.77	23.06	Pr	2.01	2.31	2.16
S	241.00	N/A	241.00	Nd	9.80	10.52	10.16
Cl	8166	8250.1	8208.1	Sm	2.99	3.01	3.00
V	203.23	166.83	185.03	Eu	0.86	0.88	0.87
Co	24.55	20.37	22.46	Gd	3.10	3.28	3.19
Ni	18.19	9.74	13.96	Tb	0.58	0.58	0.58
Cu	81.25	44.56	62.91	Dy	3.60	3.77	3.68
Zn	62.12	57.52	59.82	Ho	0.80	0.77	0.78

Ga	16.00	15.93	15.97	Er	2.18	2.33	2.26
As	0.05	2.02	1.04	Tm	0.38	0.39	0.39
Br	1.62	0.69	1.15	Yb	2.30	2.49	2.40
Mo	0.65	0.75	0.70	Lu	0.38	0.37	0.37
Ag	0.07	0.06	0.06	Tl	0.067	0.16	0.11
Cd	0.15	0.08	0.11	Pb	2.34	2.82	2.58
Sn	0.90	2.05	1.48	Bi	0.0034	N/A	0.0034
Sb	0.07	0.13	0.10	Th	2.02	2.39	2.21
I	13.70	12.71	13.21	U	0.56	0.70	0.63



582

583 **Figure 8** Calculated enrichment factors (EF) for trace elements degassed at La Soufriere  
 584 volcano and comparison with other worldwide subduction-related volcanoes. a) Average Co-  
 585 based EFs for CS and NapN samples. b) Cu-based EFs estimated for comparison between La  
 586 Soufriere (grey area) and other arc-related volcanoes with trace element data in condensate

587 samples only. Magmatic-hydrothermal systems included Kawaj Ijen, Lastarria, and White  
588 Island volcanoes (Van Hinsberg et al. 2015; Aguilera et al. 2016; Mandon et al. 2020), while  
589 magmatic systems included Augustine, Kudryavy, Tolbachik, and Pallas volcanoes (Symonds  
590 et al. 1990; Taran et al. 1995, 2018; Chaplygin et al. 2016). EFs were recalculated  
591 (Supplementary Material 3) using Cu instead of Co or another lithophile element (e.g., Be, Mg)  
592 because Cu showed lower volatility at La Soufriere volcano (Fig. 8a) and usually presents poor  
593 to moderate volatility in volcanoes worldwide (e.g., Edmonds et al. 2018). Additionally, Cu  
594 was the trace element most commonly found in measurable concentrations at all the sites  
595 selected for comparison. Reference host rock concentrations for Augustine were taken from  
596 andesitic-to-dacitic ash fall deposits (Lepel et al. 1978; Rose et al. 1988; Kodosky and  
597 Keskinen 1990), and from basaltic-andesitic fall deposits for Kawaj Ijen (Handley et al. 2007;  
598 van Hinsberg et al. 2010). Volcanoes with average outlet gas temperatures greater than 450 °C  
599 were considered as magmatic systems, while volcanoes with lower temperatures (average  
600 discharge temperatures of 176, 328, and 408 °C for White Island, Lastarria, and Kawaj Ijen  
601 volcanoes, respectively; Supplementary Material 3) were classed as magmatic-hydrothermal  
602 systems (e.g., Aiuppa et al. 2017). Dashed vertical lines divide highly, moderate, and poorly  
603 volatile elements where the slope threshold was above 15%.

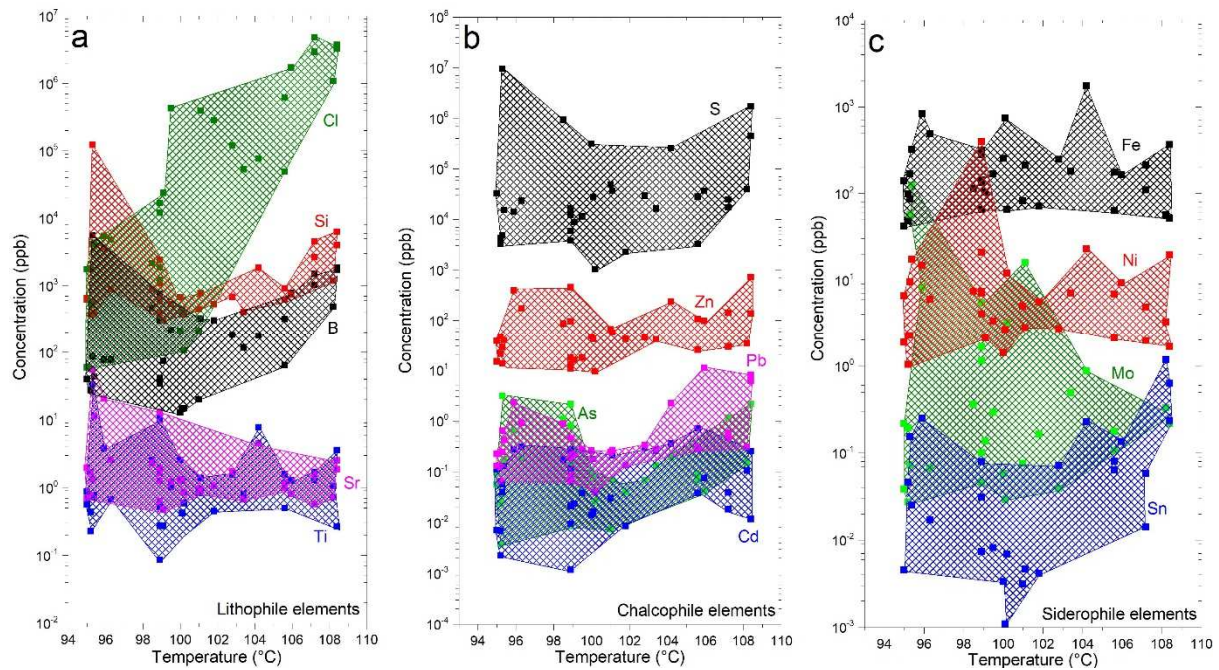
### 604 **5.2.2 Comparison with other volcanoes**

605 Comparison of average EFs at La Soufriere and average EFs from other worldwide subduction-  
606 related volcanoes (Fig. 8b) enabled us to identify the different volatility behaviors of the trace  
607 elements collected using the same sampling technique. Despite some discrepancies, trace  
608 elements showed a general decrease in EF from the most (S) to the least (Ga) volatile element  
609 (Fig. 8b). EF patterns at La Soufriere are close to those of magmatic-hydrothermal systems, for  
610 which elements such as S, Sb, Bi, Ni, Ag, Cd, Pb, Tl, and Cu presented similar EFs, and  
611 therefore a similar behavior in terms of volatility. However, significant discrepancies were seen  
612 in B, Cl, As, Br, I, and Sn, which showed increased EFs in magmatic-hydrothermal volcanoes  
613 compared to La Soufriere volcano. Such discrepancies could be associated with the greater  
614 solubility of these elements where large hydrothermal reservoirs developed, such as at La  
615 Soufriere volcano, contrasting with magmatic-hydrothermal volcanoes characterized by less  
616 developed hydrothermal systems (e.g., Lastarria volcano; Aguilera et al. 2012). On the other  
617 hand, significantly higher EFs of S, Sb, Zn, Mo, Cd, and Pb were observed at La Soufriere  
618 relative to high-temperature magmatic systems. This could be ascribed to i) the greater  
619 volatility of these elements in emissions at lower outlet gas temperatures (<200°C; Quisefit et

620 al. 1989; Pokrovski et al. 2013; Mandon et al. 2020), ii) the greater volatility of Cu in magmatic  
621 systems that artificially lowered EFs from Eq. (1), or iii) the greater concentration of these  
622 elements in host rocks from magmatic subduction-related volcanoes relative to condensate  
623 samples (Supplementary material 3). Given the same geological context (i.e., subduction  
624 volcanoes), variations in the volatility of trace elements between La Soufriere and the other  
625 systems could likely be produced by different gas outlet temperatures and variable chemical  
626 composition fluid discharge as a result of variable fluid-rock interaction and scrubbing  
627 processes.

### 628 ***5.2.3 Temperature control, transport, and speciation of trace elements***

629 Periodic sampling carried out at the CS fumarole made it possible to investigate the behavior  
630 of lithophile, chalcophile, and siderophile elements against a background of varying  
631 temperature and chemical composition of the fumarolic emissions. In general, the  
632 concentration of chemical elements remained relatively stable as the temperature increased  
633 (Fig. 9). However, Cl displayed a faintly positive correlation with the outlet gas temperature,  
634 although with only a very low determination coefficient ( $r^2$  of 0.50; Supplementary Material  
635 4). Pb and Sn reached their maximum concentrations for temperatures above 106 °C (Fig. 9b,  
636 c), but these maxima concentrations did not follow any trend. Hence, it appears that the outlet  
637 gas temperature has a negligible effect on the chemical composition of the gas phase. A similar  
638 behavior was observed in magmatic systems (temperatures of between 585 and 940 °C for  
639 Kudryavy volcano; Taran et al. 1995; Symonds et al. 1996), where a slight increment in the  
640 concentration and volatility of certain species (e.g., Cl, I, Pb, As) as temperature increased was  
641 noted. At La Soufriere volcano, low outlet gas temperatures and the low-temperature range  
642 during the study period make it difficult to discuss the influence of temperature on the  
643 concentration of condensates in detail.



644

645 **Figure 9** Trace element concentrations of representative a) lithophile, b) chalcophile, and c)  
 646 siderophile elements in condensates versus outlet gas temperature at CS fumarole. Only  
 647 chemical elements with some degree of correlation with temperature (i.e., Cl from  
 648 Supplementary Material 4) and greater volatility behavior were plotted.

649 The transport and speciation of trace elements is usually accounted for using determination  
 650 coefficients (hereafter expressed as  $r^2$ ) from linear correlations between common ligands (i.e.,  
 651 S, Cl, and Br) and selected major and trace elements (e.g., Crowe et al. 1987; Moune et al.  
 652 2006, 2010). Computed  $r^2$  values (Supplementary Material 4) for NapN and CS were generally  
 653 low (average  $r^2 < 0.37$ ), using Cl, Br, and S as ligand elements. However, NapN fumarole had  
 654  $r^2$  values above 0.7 between Fe and some rock-forming elements such as Mg, Ca, and U, and  
 655 both NapN and CS exhibited  $r^2$  values  $> 0.5$  between Fe and non-mobile trace elements,  
 656 including REEs. These higher correlation coefficients suggest that either at the source or during  
 657 transport, major and trace lithophile elements followed similar physicochemical processes  
 658 within the hydrothermal reservoir or fumarolic conduits. Leaching from host rocks and  
 659 subsequent transport to the surface as aqueous particles could explain the relationship between  
 660 Fe and lithophile elements in La Soufriere condensates. A deep magmatic source of lithophile  
 661 elements was discarded since they only show volatile behavior at high-temperature ( $> 400$  °C)  
 662 fumarolic emissions where lithophile elements are directly deposited from the gas phase (e.g.,  
 663 Taran et al. 2001; Africano et al. 2002; Henley and Seward 2018). Slightly higher  
 664 determination coefficients between Fe and lithophile elements at NapN compared to CS

665 (Supplementary Material 4) are ascribed to the incipient chemical dissolution of less  
666 hydrothermally altered host rocks deduced from the lower resistivity of rocks in the northern  
667 area of the dome where NapN is located (Rosas-Carbajal et al. 2016). The markedly larger  
668 amount of rock particles at NapN (Fig. 3) also supports the occurrence of erosive processes  
669 driven by high water-rock ratios within the fumarolic conduit. Low determination coefficients  
670 for halogens and sulfur suggest the enhanced transport of major and trace elements as solid and  
671 aqueous particles rather than halogen- and S-containing gaseous species, as typically occurs in  
672 magmatic and magmatic-hydrothermal volcanoes (e.g., Moune et al. 2010; Mandon et al. 2019;  
673 Scholtysik and Canil 2020). Consequently, the metals and metalloids plotted in Fig. 8a were  
674 mostly transported within tiny aqueous particles, following their low vapor/liquid partition  
675 coefficients at low temperatures and high boiling points which prevents their conversion to the  
676 gaseous phase in fumaroles at ~100 °C (e.g., Pokrovski et al. 2013). It is concluded that the  
677 enhanced transport of solid and aqueous particles is a specific characteristic of La Soufriere  
678 and suggests that this is a feature characterizing water-dominated fumarolic emissions in  
679 volcanic-hydrothermal systems.

## 680 **6. Conclusions**

681 This work provides the chemical composition of major and trace elements in condensate  
682 samples collected between April 2017 and January 2021 from two fumaroles (CS and NapN)  
683 at La Soufriere volcano, and is the first record of long-term trace element analyses in low-  
684 temperature (93.5 to 108.4 °C) fumarolic emissions. Despite low outlet gas temperatures,  
685 condensates contained significant amounts of siderophile, chalcophile, and lithophile elements.  
686 Such a broad contribution reflects the scavenging of chemical elements from magmatic and  
687 hydrothermal reservoirs. Furthermore, we found a faint positive correlation between Cl  
688 concentration, acidity of condensates, and outlet gas temperature at CS fumarole. At the same  
689 time, the low concentration of S in condensates from these emissions appeared to be  
690 underestimated given the problematic condensation of H<sub>2</sub>S, which requires the use of other  
691 specialized techniques (e.g., alkaline traps) to obtain reliable S concentrations.

692 Compared to andesitic host rocks, condensates were enriched in S, Sb, B, Cl, Bi, Br, Zn, Mo,  
693 Ni, Ag, Cd, As, I, and Pb. Based on their physical properties (e.g., boiling temperature), it is  
694 believed that halogens and S were emitted as components of the gaseous phase. However,  
695 enrichments of Sb, Bi, Zn, Mo, Ni, Ag, Cd, As, and Pb were better explained through efficient  
696 transportation by tiny aqueous droplets, given their lower affinity with the vapor phase in low-



697 temperature emissions. Rock-related elements (including REEs) were present as solid particles,  
698 as shown by SEM analyses, as well as aqueous particles given their enhanced concentrations  
699 in filtered ( $<0.20\mu\text{m}$ ) condensates.

700 Cu-based EFs suggest that the behavior of trace elements at La Soufriere volcano is comparable  
701 with other worldwide arc-related magmatic-hydrothermal systems such as Lastarria (Chile),  
702 Kawaj Ijen (Indonesia), and White-Island (New Zealand) volcanoes. However, some  
703 differences were noticed: i) a greater amount of rock-related elements in La Soufriere  
704 condensates, and ii) higher abundance of typically soluble species (mainly halogens) in  
705 magmatic-hydrothermal systems (i.e., volcanoes with magmatic influence but less developed  
706 hydrothermal systems) related to La Soufriere. The abundance of major and trace elements is  
707 likely controlled by the extent of the hydrothermal aquifer(s) (basically the water/rock ratio),  
708 their acidity and the pressure-temperature conditions that favor water-rock interaction in  
709 hydrothermal reservoirs. Our study demonstrates that the transport of chemical elements in  
710 low-temperature fumaroles is governed by the aerosol phase (except for noble gases,  $\text{N}_2$ ,  
711 halogens, and related elements), and their abundances are linked with physicochemical  
712 processes taking place in hydrothermal reservoirs.

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### 740 **Data Availability**

741 Appendix A, B, and Supplementary Material xxxx can be found at XXXXXXXXXXXXXXXX

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