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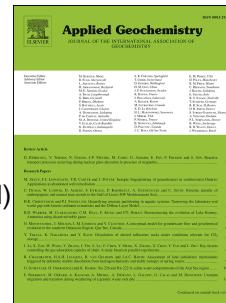
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1 An integrated geochemical spatial and temporal survey of thermal springs to 2 characterize the geothermal resource of a volcano (Piton des Neiges, Réunion 3 Island)

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14 Highlights

15 The heat source of hydrothermal waters is one of the volcanic rift zones.

16 There are two independent hydrothermal reservoirs on the northern and southern sides of the
17 volcano.

18 Recharge of the two hydrothermal systems is plurennial and mostly fed by cyclones.

19 Geothermometry yields water-rock interaction temperatures of up to $141 \pm 15^\circ\text{C}$.

20 The southern side of the volcano is the most promising target for future exploitation.

21 Coupling spatial and temporal geochemical information is useful for the geochemical exploration of
22 hidden geothermal systems.

23 Abstract

24 Geothermal exploration can be challenging in the absence of obvious surface indicators of a high
25 enthalpy geothermal resource such as geysers, fumaroles or thermal springs with temperatures near
26 100°C . This is the case at the Piton des Neiges volcano (Réunion Island), which displays evidence of
27 hydrothermal activity mostly as thermal springs with temperatures not exceeding 50°C , affected by
28 mixing and reequilibration, and emerging in a complex geological framework, resulting from the
29 polygenic history of this dormant volcano. Yet, these thermal springs keep a partial record of the
30 reservoir geochemistry. Here, we propose an exploration method to set this thermal signature apart
31 from the contribution of other processes and trace back the equilibrium conditions, enabling us to
32 locate thermal fluid circulations, and evaluate their temperature and availability. We report its
33 application at Piton des Neiges volcano. We led an extensive geochemical survey which nearly doubled
34 the number of thermal springs reported on the volcano and dramatically extended the existing
35 geochemical database in space and time. In tandem, we also monitored $\delta^{18}\text{O}$ and δD values in
36 rainwaters and thermal springs over two years to compare their temporal variations.

37 Our surveys show that the repartition of thermal springs is controlled by only one of the volcanic rift
38 zones (the N30°E axis), which is thus identified as the heat source of hydrothermal circulations. This
39 N30°E rift zone is also a preferential pathway for the degassing of mantellic CO₂. In addition, the
40 composition of thermal waters is influenced by syenite intrusions along the rim of the caldera, acting
41 as drains for the uprise of hydrothermal waters. O, H and Sr isotopic signatures of springs show that
42 the geothermal resource of Piton des Neiges is in fact made of two independent and unconnected
43 hydrothermal systems on the northern and southern circular depressions of the volcano (the cirques
44 of Salazie and Cilaos, respectively). Their recharge is meteoric, multi-year, and mostly achieved by
45 cyclonic events. Thermal waters experience reequilibration during their ascent and various degrees of
46 CO₂ input or degassing. Last equilibrium temperatures of water/rock interaction, estimated by
47 multicomponent geothermometry, reach up to 125 ± 6°C in the cirque of Salazie, and up to 141 ± 15°C
48 in the cirque of Cilaos, with possibility for hotter waters before reequilibration. Taken together, our
49 results suggest that the most promising target for future exploration is located in the cirque of Cilaos,
50 along the caldera rim, and in proximity of syenite intrusions.

51 With a thorough prospecting of thermal springs, a comprehensive geochemical study and a
52 geochemical monitoring of the different water reservoirs, we improved our understanding of the
53 geothermal resource and identified future exploration targets at Piton des Neiges volcano.

54 Keywords

55 Geothermal ; Exploration ; Geochemistry ; Piton des Neiges ; Volcano ; Thermal springs

56 Introduction

57 Geothermal energy is a renewable energy source with little emission of carbon dioxide to the
58 atmosphere and thus well suited to climate change mitigation. However, geothermal exploration can
59 be challenging in the absence of obvious surface indicators of a high enthalpy geothermal resource
60 such as geysers, fumaroles or thermal springs with temperatures near 100°C. Yet, these “hidden”
61 systems can represent the majority of the geothermal potential resource (e.g. in the U.S.A., Williams
62 et al., 2009). In order to address this issue, several methods are in development to assess their
63 geothermal potential such as statistical analysis (e.g. in Hawaii, Lautze et al., 2017b, 2017a), machine
64 learning (e.g. in the U.S.A., Vesselinov et al., 2021), or 3D magnetotelluric surveys (e.g. in La Palma,
65 Canaries, Di Paolo et al., 2020). Most of the time, these systems still display some evidence of
66 hydrothermal activity, often in the form of non-boiling thermal waters, which can represent a
67 supplementary exploration tool. This type of manifestation is especially common on mature and
68 polygenic volcanoes, for example as groundwaters with thermal anomalies in the islands of Maui and
69 Lanai, Hawaii (Lautze et al., 2017a), or as thermal springs on the Taburiente volcano in La Palma,
70 Canaries (Troll and Carracedo, 2016) and in Quaternary and Tertiary formations of western Iceland
71 (Arnórsson, 1995). However, polygenic volcanoes are by essence made of multiple eruptive periods,
72 quiescent phases and destabilization episodes. This history results in complex internal architectures,
73 which affect the geometry of thermal water circulation as well as the location, depth, and nature of
74 the heat sources and the permeability of rocks (e.g. at Mount Meager in British Columbia, Grasby et
75 al., 2019), making the use of thermal springs for geothermal exploration challenging.

76 Réunion Island is a good example of a polygenic volcanic island offering potential for geothermal
77 energy, but where exploitation is hampered by a lack of geological knowledge on the hydrothermal
78 systems (see review by Dezayes et al., 2022). Piton des Neiges volcano displays evidence of
79 hydrothermal activity, in the form of thermal springs (up to 48°C), fumarole deposits, and CO₂ – He –

80 Rn anomalies (Marty et al., 1993; Rançon and Rocher, 1985; Sanjuan et al., 2001). This volcano also
81 hosts several geophysical indicators in favor of a geothermal resource (Dezayes et al., 2022). Moreover,
82 two exploratory boreholes revealed the existence of elevated temperature gradients (180°C/km and
83 82°C/km) on this dormant volcano. All these lines of evidence confirm the presence of a heat source
84 and of hot water circulation, which may be suitable for the development of geothermal energy on the
85 island. However, exploratory drillings made so far did not reach zones of sufficient permeability to
86 allow an exploitation of hot water (Augé et al., 1989; Demange et al., 1989). More geological
87 information is needed to locate fluid circulations in this dormant volcano, assess the resource
88 represented by its hydrothermal system, and define the most promising targets for future exploration.

89 In a previous paper, we proposed a conceptual model for the Piton des Neiges hydrothermal system
90 in a first study (Bénard et al., 2020). Based on the chemical and isotopic composition of 17 thermal
91 springs, we determined the different mineralization processes responsible for their geochemical
92 profiles. We found that thermal waters are of meteoric origin, subject to CO₂ dissolution from a
93 degassing magma, to water-rock interaction with either basalts or differentiated rocks which increase
94 their total mineral content, and some samples also showed a contamination from elements originating
95 from seawater. With the knowledge of the processes involved in the mineralization of thermal waters,
96 the aim of the present work is to characterize the geothermal resource and estimate its temperature.
97 For this purpose, we led an extended field prospection and sampling, which includes waters displaying
98 field evidence of a thermal component and rocks from different geological units. We used
99 physiochemical parameters, major element concentrations, and CO₂ partial pressure (PCO₂)
100 computations to highlight the zones displaying the most promising geothermal resource. In order to
101 better understand the hydrogeological characteristics of the aquifer systems with which thermal
102 waters are mixed, we studied the spatial distribution of Cl, δ¹⁸O and δD in waters and that of ⁸⁷Sr/⁸⁶Sr
103 in waters and rocks. To refine our understanding of aquifer recharge, we monitored the monthly
104 isotopic composition (δ¹⁸O, δD) of rain and thermal springs over two years. We then applied the most
105 up-to-date thermodynamic-based geothermometry tools (Cioni and Marini, 2020; Spycher and
106 Finsterle, 2016) to reconstruct the temperature history of the geothermal fluids. This work leads to a
107 considerably improved model of hydrothermal circulation at Piton des Neiges, which may be used to
108 target zones where the geothermal resource is most likely present and to plan the next steps of
109 geothermal exploration. Our methodology of geochemical investigation may be exported to any other
110 volcano with thermal springs mixing with superficial waters.

111 1. Geological and hydrogeological settings

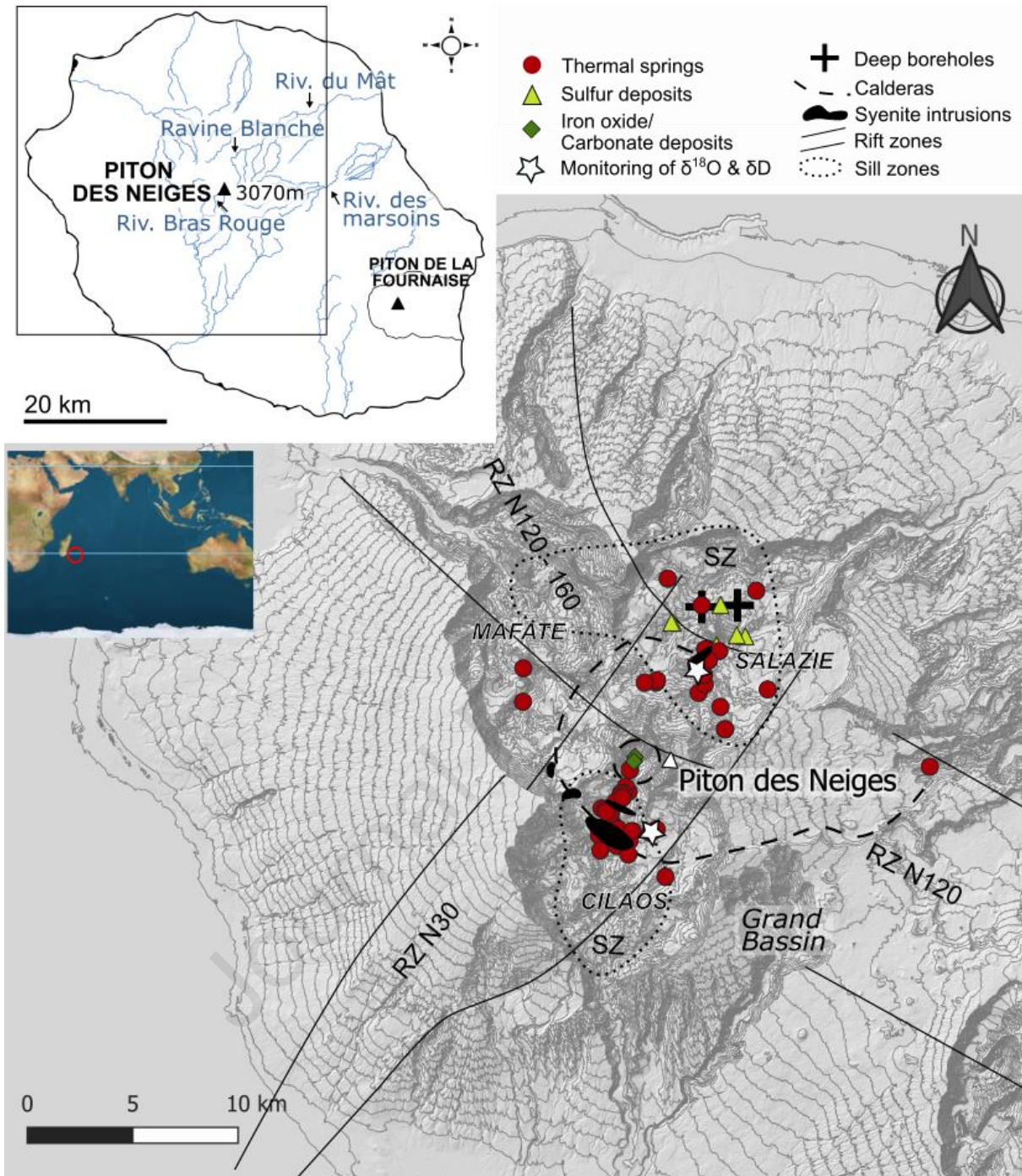
112 Réunion Island was formed by two main volcanoes: Piton des Neiges and Piton de la Fournaise. Piton
113 des Neiges, presently dormant, is the oldest and the largest edifice. Piton de la Fournaise, still active,
114 grows on the south-eastern flank of Piton des Neiges. Estimated to have emerged at 3 Ma ago, Piton
115 des Neiges has a polygenic history of at least five eruptive periods separated by quiescence and erosion
116 intervals. The shield building stage of this volcano has produced transitional basic magmas until 430
117 ka (Kluska, 1997; McDougall, 1971). After a 80 ka period of rest, the volcano entered into a
118 degenerative stage 350 ka ago and produced alkali differentiated magmas ever since (Gillot and
119 Nativel, 1982; Kluska, 1997). The last known eruption of Piton des Neiges dates back to 27 ka (see
120 review by Famin et al., 2022). This last period of quiescence, and the heavy rainfalls under tropical
121 climate, have favored erosion of the volcanic edifice, now incised by three cirques (subcircular
122 depressions), Salazie to the north, Mafate to the northwest, and Cilaos to the south (Figure 1). These
123 deep cirques have dissected the inner structure of the volcano, erasing most of the surface evidence
124 of calderas. Based on patchy observations of faults, offset lava layers, pyroclastic deposits or radial
125 dykes, two calderas have been proposed (Figure 1): a large one running through the three cirques

126 formed during the differentiated stage (210 – 180 ka), and a smaller one in the summit area of Piton
127 des Neiges formed during its last activity (Chevalier, 1979; Rocher, 1988).

128 Erosion has exposed the hypovolcanic complex, made of dense gabbroic plutons and basaltic, trachytic
129 and syenitic planar intrusions. Planar intrusions are organized into two rift zones N30°E and N110-
130 160°E, and two sill zones between 800 and 1300 m above sea level (Chaput et al., 2017, 2014). The
131 two deep boreholes SGTH-1 (201 m) and SLZ1 (2108 m) drilled for geothermal exploration in the 1980s
132 (Chovelon, 1986; Gérard and Stieltjes, 1979) intersect a pluri-kilometric gabbroic intrusive complex,
133 associated with the shield building stage of Piton des Neiges. The high geothermal gradients
134 (respectively of 180°C/km and 82°C/km) obtained in these boreholes show that heat issued from
135 volcanic activity is still being transmitted into the massif. However, both boreholes were dry and the
136 nature of the heat source (either the gabbro pluton or the planar intrusions) remains unknown. Syenite
137 intrusions, which consist in 30 – 100 m thick dykes in the cirques of Salazie and Cilaos, are of particular
138 interest for this study. Ages of less than 150 ka, they represent major dyke structures of the terminal
139 volcanic activity (Famin et al., 2022), located within the N30°E rift zone, and interpreted to delineate
140 the largest caldera (Chevalier, 1979; Rocher, 1988). Additionally, many thermal springs are observed
141 in these intrusions or in their immediate vicinity. All these criteria suggest that syenite intrusions
142 represent a candidate heat source for the hydrothermal system, or at least act as conduits for hot fluid
143 flow (Bénard et al., 2020; Frissant et al., 2003; Sanjuan et al., 2001).

144 Fluid circulation in the edifice is complexified by its long history of construction, destruction, intrusive
145 activity and secondary mineral precipitation. Indeed, the hypovolcanic complex of Piton des Neiges is
146 affected by several phases of low-grade metamorphism and hydrothermal alteration (Chevalier, 1979;
147 Rançon, 1985), resulting in a porosity clogging by secondary precipitation of phrenite-pumpellyite
148 facies minerals in rocks of the shield-building stage, followed by carbonate precipitation in
149 differentiated rocks as well as in mafic rocks (Famin et al., 2016). The ensued low hydraulic
150 conductivity, associated with the geological barriers formed by planar intrusions, limit the escape of
151 freshwater toward the sea and its downward infiltration in the lowermost, oldest and most
152 impermeable rock units (Join et al., 2005). Thermal waters, accordingly, is mostly fed by meteoric water
153 (Bénard et al., 2020). The tropical climate of Réunion Island consists in a dry season (April-November),
154 and a wet season (December-March) that delivers huge precipitation rates (annual mean of ~2500 mm
155 in the cirques). Most of these wet season rainfalls occur as cyclones or tropical storms (five events per
156 year in average for the period 1981 – 2010; Jumaux et al., 2011).

157 Despite the present-day inactivity of Piton des Neiges, there is still evidence of magmatic degassing
158 from a deep mantle source on a regional scale (Boudoire et al., 2017). Magmatic carbon dissolves in
159 large quantities in the hydrothermal system (Bénard et al., 2020; Marty et al., 1993; Trull et al., 1993).
160 Fumarolic sulfur deposits are also observed, but it is unknown whether they are fossil or still active
161 (Lopoukhine and Stieltjes, 1978; Rançon and Rocher, 1985).



162

163 Figure 1: Localization of the field indicators of hydrothermal activity in Piton des Neiges: thermal springs, iron oxide
 164 deposits, carbonate deposits and sulfur deposits from previous studies (Aunay et al., 2013; Belle, 2014; Bénard et
 165 al., 2020; Frissant et al., 2003; Iundt et al., 1992; Lopoukhine and Stieltjes, 1978; Louvat and Allègre, 1997;
 166 Sanjuan et al., 2001), the main rift zones (RZ) and sill zones (SZ) of Piton des Neiges (Chaput et al., 2017), the
 167 two supposed calderas (Chevalier, 1979; Rocher, 1988), the two deep boreholes drilled for geothermal exploration
 168 in the 1980s (Chovelon, 1986; Gérard and Stieltjes, 1979), the two monitoring sites of $\delta^{18}\text{O}$ and δD in springs and
 169 rain. Relief contours at 100 m intervals from RGE ALTI® - IGN.

170 2. Material and Methods

171 2.1. Fieldwork and sampling

172 We led an extensive prospection on the field to identify all indicators of hydrothermal activity and
173 measure and sample new thermal springs. Springs were considered as an indicator of
174 hydrothermal activity whenever they displayed at least two of the following criteria:

- 175 - Presence of iron oxide/carbonate/sulfide deposits,
- 176 - A higher temperature ($\geq 5^{\circ}\text{C}$) compared to nearby river water at the time of sampling,
- 177 - A higher electrical conductivity (EC) ($\geq 200 \mu\text{S}/\text{cm}$) compared to nearby river water at the time
178 of sampling,
- 179 - A lower pH (≤ 1) compared to nearby river water at the time of sampling.

180 Temperature, EC, and pH were measured at the outlet and EC was normalized at 25°C .

181 In total, our spatial and temporal sampling campaign yielded a set of 130 water samples. The first
182 spring samples were taken during an exploratory phase in June 2015, hereafter referred to as “the first
183 phase”. All the others spring samples were taken over a long period lasting from December 2015 to
184 May 2019, hereafter referred to as “the second phase”.

185 Thermal springs were sampled to be analyzed for major elements, Al, Sr, and Br concentrations and
186 $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. Thermal springs displaying particularly interesting or
187 intriguing features were sampled several times. The three large rivers Bras Rouge in Cilaos, Rivière du
188 Mât and Ravine Blanche in Salazie were also sampled at the highest possible altitude for analysis of
189 $\delta^{18}\text{O}$ and δD isotopic ratios in order to give reference points for river waters, respectively at 2050, 1830
190 and 1739 m. We also sampled several rocks from the late activity of Piton des Neiges – and thus the
191 most likely to produce heat – in order to compare their strontium isotopic signature to that of thermal
192 springs.

193 For all the samples, water was filtered at $0.2 \mu\text{m}$ on site. Bottles were rinsed three times with filtered
194 water before sampling. Bottle caps were sealed with parafilm. For the analysis of major and trace
195 elements, and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios, water samples were collected in LDPE bottles. Water samples
196 for analysis of major cations, Al, Sr, and Br concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios were acidified
197 with acid (HNO_3 0.3N) on site. However, for the samples of the second phase, there was too little acid
198 to prevent calcite precipitation in the bottles, which resulted in erroneous values for the
199 concentrations of Ca and Sr for 17 samples, which were displayed in Bénard et al., (2020). For the
200 purpose of this study, we added back acid to unused samples from the second phase and re-analyzed
201 them for cations and trace elements. For $\delta^{18}\text{O}$ and δD analyses, water was sampled 15 mL amber glass
202 or HDPE bottles with no headspace. During the second phase, water samples were also collected for
203 analysis of total dissolved inorganic carbon content (TDIC) and $\delta^{13}\text{C}$ in Labco 12 mL Exetainer vials with
204 no headspace.

205 Additionally, we monitored rainwater and thermal springs time fluctuations on two sites from April
206 2017 to May 2019. On a monthly basis, we collected water from two thermal springs in each cirque
207 (Trou Blanc Amont – TBA – in Salazie and Irénée – IRN – in Cilaos, Figure 1) and from rainwater
208 collectors installed nearby these two springs (at elevations 910 m and 1120 m respectively) for analysis
209 of $\delta^{18}\text{O}$ and δD isotopic ratios. Springs IRN and TBA were also analyzed for major and trace elements.
210 These two springs were selected because of (i) their unambiguous hydrothermal signature (Bénard et
211 al., 2020), (ii) their relatively easy access, and (iii) the possibility of installing rainwater collectors
212 nearby. For the two rain collectors, rainwater was collected in a PEHD container through a funnel and
213 trapped under a layer of liquid paraffin to prevent water evaporation. Each month, one sample was
214 taken out of the total volume of water collected in a 15 mL bottle, made of amber glass with a cone-
215 shaped cap or of HDPE with no headspace. As for thermal springs, water was filtered at $0.2 \mu\text{m}$ on site,

216 bottles were rinsed three times with filtered water before sampling and bottle caps were sealed with
217 parafilm.

218 All the samples were stored at a temperature of 6°C before shipment.

219 2.2. Analysis

220 For the water samples of the first sampling phase, alkalinity, major/trace elements and $\delta^{18}\text{O}$, δD and
221 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios' analyses were performed at the Bureau de Recherches Géologiques et
222 Minières (BRGM) in Orléans (France). For the water samples of the second sampling phase, total
223 dissolved inorganic carbon (TDIC) and major elements analyses were performed at the Institut de
224 Physique du Globe de Paris (IPGP). $\delta^{18}\text{O}$ and δD of thermal springs and precipitations were analyzed at
225 the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Saclay. Sr concentrations and
226 isotopic ratios analyses on rocks were performed by the Service d'Analyse des Roches et des Minéraux
227 (SARM-CRPG) in Nancy.

228 Major anions concentrations were determined by ion exchange chromatography (ICS1100
229 Thermofisher, column Ionpac thermo AS14 and precolumn Ionpac thermo AG14, column AS14 and
230 precolumn AG14). Major cations concentrations were determined using inductively coupled plasma
231 atomic emission spectrometry (ICP-AES, iCAP6200 Thermofisher). For the Ca and Sr concentrations of
232 the 17 samples for which the previous analysis was inaccurate, we performed a new analysis using
233 inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900). Al, Sr, and Br concentrations
234 were determined by ICP-MS for the two phases. Precision for major cations and anions concentrations
235 is $< 5\%$ (except HCO_3 , $< 10\%$, see below), and $< 20\%$ for trace elements. Uncertainties were calculated
236 using the standard deviation on measurement replicates and the uncertainty on the internal standard
237 concentration.

238 For the water samples of the first phase, alkalinity was determined using potentiometric titration,
239 giving HCO_3 concentrations with a quantification limit of 10 mg/L. For the water samples of the second
240 phase TDIC and carbon isotope ratios $\delta^{13}\text{C}$ analyses were made by gas chromatography and isotope
241 ratio mass spectrometry (GC-IRMS), after releasing TDIC as CO_2 by H_3PO_4 acidification (Assayag et al.,
242 2006). For this phase, HCO_3 concentrations were computed using the temperature dependent acid
243 dissociation constants from Mook and Koene, (1975), knowing the TDIC, temperature and pH of
244 waters. However, this analysis method gave poor estimates of dissolved carbonate concentrations for
245 the thermal springs with a high TDIC as 35 samples from the second phase yielded ionic balances $>$
246 5% . For these 35 samples, HCO_3 concentrations had to be corrected and were estimated by setting
247 the ionic balance to 0%. $\delta^{13}\text{C}$ are expressed in per mil (‰) with respect to the PDB standard, with a
248 precision of 0.1‰.

249 For the water samples of the first phase, $\delta^{18}\text{O}$ and δD of thermal spring and rivers were obtained by
250 gas chromatography coupled to isotope ratio mass spectrometry (GC-IRMS), after equilibration with
251 H_2 for hydrogen and CO_2 for oxygen, leading to an accuracy of 0.1‰ in $\delta^{18}\text{O}$ and 0.8‰ in δD . For the
252 water samples of the second phase, $\delta^{18}\text{O}$ and δD were obtained using the CO_2 - H_2O equilibration
253 method on a Finnigan Mat 252 and the WS-CRDS infrared laser method respectively. $\delta^{18}\text{O}$ and δD are
254 expressed in ‰ with respect to the VSMOW standard. The accuracies are of $\pm 0.05\%$ and $\pm 0.7\%$ for
255 $\delta^{18}\text{O}$ and δD , respectively.

256 For the water samples of the first phase, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined by mass spectrometry using
257 a triple multidynamic acquisition and a single W filament. For the water samples of the second phase,

258 strontium isotopic ratios $^{87}\text{Sr}/^{86}\text{Sr}$ were determined by multi-collector mass spectrometry (TIMS).
259 Precisions are between 0.000006 and 0.000018.

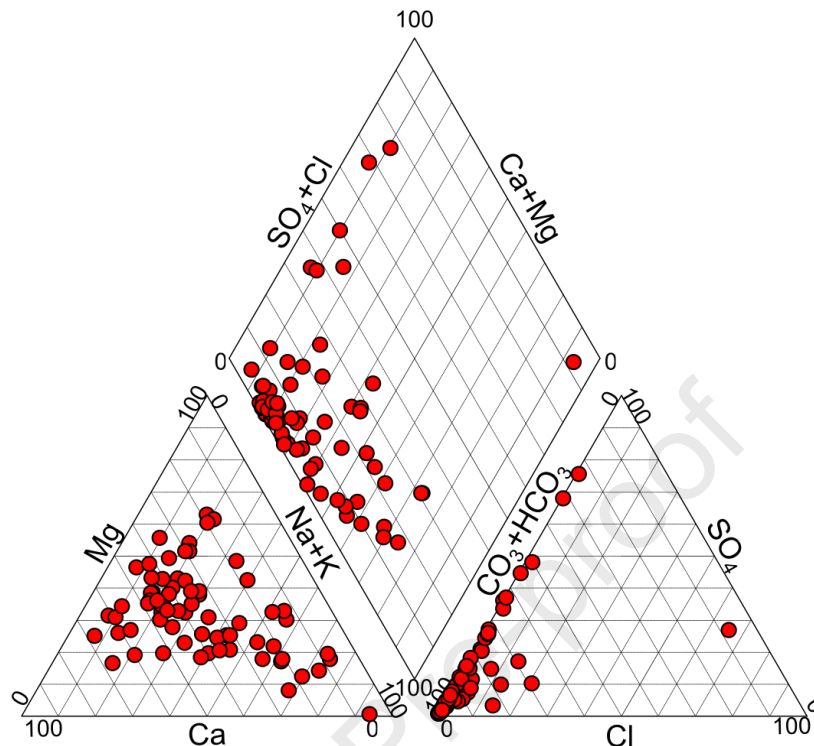
260 Strontium isotopic ratios in rocks were determined by the Service d'Analyse des Roches et des
261 Minéraux (SARM) of the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy,
262 France. About 100 to 200 mg of sample were weighed in a 15 ml Savillex and digested using a solution
263 of 14M HNO_3 (4 mL). The whole mixture was heated on a hot plate at 115°C for 24 - 48 h, evaporated
264 to dryness and dissolved in 6M HCl and heated again for 24 h. After complete dissolution and
265 subsequent evaporation, the residue was diluted in 2 mL of 2 M HNO_3 . Sr, Rb and REE were separated
266 using the Sr spec and Tru Spec resins (Pin et al., 1994). The Sr cuts were loaded onto Re filaments and
267 analyzed by TIMS Triton Plus (Thermo electron) in static multicollection. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were
268 normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. Repeated analysis of the NBS 987 standard yielded an average
269 of 0.710255 ± 0.000017 .

270 3. Results

271 Our field prospection highlighted 118 new surface indicators of hydrothermal activity to the already
272 71 reported in previous studies (Aunay et al., 2013; Belle, 2014; Bénard et al., 2020; Frissant et al.,
273 2003; lundt et al., 1992; Lopoukhine and Stieltjes, 1978; Louvat and Allègre, 1997; Manès, n.d.; Marty
274 et al., 1993; Poul, 1966; Rocher, 1988; Sanjuan et al., 2001). Their coordinates and description and the
275 physiochemical parameters of the springs are given in Supplementary Material. We observed and
276 measured 28 out of the 71 indicators from previous studies, and found that 9 more have since
277 disappeared in landslides. Out of the total 189 field indicators, 28 are dry iron oxide/carbonate/sulfide
278 dry deposits and 161 are thermal springs. Thermal springs temperatures range from 9.8 to 48°C,
279 electrical conductivities range from 194 to 3370 $\mu\text{S}/\text{cm}$ and pH range from 5.3 to 9.4. Mean values are
280 $1050 \pm 512 \mu\text{S}/\text{cm}$ for electrical conductivity, 6.9 ± 0.7 for pH and $20.8 \pm 4.6^\circ\text{C}$ for temperature. These
281 wide ranges of physiochemical parameters reflect the variability of the contribution of the
282 hydrothermal component to the geochemistry of the springs.

283 Major elements and Al, Sr, and Br concentrations were analyzed on 38 thermal springs (Table 1. For
284 our study, we included analyses of thermal springs from previous studies (Aunay et al., 2013; Belle,
285 2014; Frissant et al., 2003; lundt et al., 1992; Lopoukhine and Stieltjes, 1978; Louvat and Allègre, 1997;
286 Sanjuan et al., 2001). For a comprehensive compilation of this literature data, see appendix A and B in
287 Bénard et al., (2020). On a Piper diagram, most springs gather at the HCO_3 end in the anion triangle
288 plot, and only a few springs tend toward the SO_4 or Cl ends (Figure 2). Therefore, most thermal springs

289 of Piton des Neiges can be considered bicarbonate waters. In the cation plot, some springs show a
 290 trend towards the Na+K pole in the cation plot but most plot in the middle.



291

292 Figure 2: Piper diagram of thermal springs of Piton des Neiges. The composition of each thermal spring is the mean
 293 of all the available data from this study and the literature.

294 Springs for which several analyses are available over the years show very little variation of their
 295 geochemical composition. Their relative proportions of major elements display little variation over
 296 time (1 s.d. of Na + K, Ca + Mg, SO₄+Cl, HCO₃ mole fractions ≤ 8 %) with the exception of TR and OLIVbis.

297 The results of δ¹³C, δ¹⁸O and δD analyses in thermal springs are presented in Table 1. δ¹³C values range
 298 between -14.8 and 5.2 ‰. When considering the mean value of each spring, δ¹⁸O and δD values for all
 299 thermal springs range from -8.58 to -5.4 ‰ and from -58.8 to -23.5 ‰, respectively. Additionally,
 300 surface water samples measured in rivers (Rivière Bras Rouge rBRO), Rivière du Mât (rRMA) and Ravine
 301 Blanche (rRBL) yielded δ¹⁸O and δD values of -7.18 and -44.4 ‰, -7.97 and -51.3 ‰, and -7.26 and -
 302 46.1 ‰, respectively. These values are in the upper range of those measured in thermal springs.

303 Results of monthly monitoring of δ¹⁸O and δD in rainwaters and thermal springs in the cirques of
 304 Salazie and Cilaos are presented in Table 2. Over the sampled period, the δ¹⁸O and δD of the thermal
 305 springs TBA and IRN show almost no variation (δ¹⁸O=-6.81 ± 0.16 ‰ and δD=-40.2 ± 0.5 ‰ for TBA;
 306 δ¹⁸O=-8.08 ± 0.06 ‰ and δD=-51.2 ± 0.23 ‰ for IRN). In contrast, rainwaters exhibit a wide range of
 307 δ¹⁸O and δD values, from -7.22 to -1.49 ‰ and -47.3 to +3.2 ‰ for Salazie, respectively, and from -
 308 9.68 to -1.31 ‰ and -66.3 to +4.4 ‰ for Cilaos, respectively.

309 Analyses of strontium isotopic ratios are presented in Table 1 for thermal springs and Table 3 for rocks.
 310 The ⁸⁷Sr/⁸⁶Sr ratios of Piton des Neiges thermal springs (0.704129 to 0.704364) are in the range of rocks
 311 values from Salazie and Cilaos (0.704041 to 0.704504, Table 3). Our new analyses of trachyte and
 312 syenite rocks display low ⁸⁷Sr/⁸⁶Sr ratios (0.704156 to 0.704215), in agreement with literature data
 313 available for these types of rocks (0.704153 to 0.704268, mean 0.704181, Nauret et al., 2019;
 314 Smietana, 2011).

315 Table 1: Physicochemical parameters, major elements concentrations, $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in thermal springs of Piton des Neiges.

Spring	Location	Date dd/mm/yyyy	Electrical Conductivity ($\mu\text{S}/\text{cm}$)	pH	Temperature ($^{\circ}\text{C}$)	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	K (mmol/L)	HCO_3 (mmol/L)	SO_4 (mmol/L)	Cl (mmol/L)	SiO_2 (mmol/L)	Br ($\mu\text{mol}/\text{L}$)	Al ($\mu\text{mol}/\text{L}$)	Sr ($\mu\text{mol}/\text{L}$)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}$ (‰ PDB)
AGS*	Salazie	17/06/2015	1746	6.5	21.1	6.75	3.49	1.65	0.1	14.52	4.11	0.03	1.28		0.0					
BACH*	Salazie	15/06/2015	1260	6.9	25.6	2.85	2.58	3.94	0.12	14.38	0.14	0.07	1.33		0.1		-6.7	-41.6	0.704317	1.4
BB*	Cilaos	05/05/2017	1699	6.7	25.1	3.96**	3.29	5.89	0.11	15.48**	2.32	0.39	1.99	0.43	0.8	5.4	-8.06	-53.1	0.704139	-1.4
BB6	Cilaos	30/11/2017	1332	6.5	22.8	2.41	3.15	4.35	0.07	13.52	0.36	0.1	1.32	0.07	b.d.l.	2	-7.47	-49.7	0.704129	-2
BB7	Cilaos	30/11/2017	652	6.9	19.8	1.12	0.84	2.85	0.03	4.51	1.16	0.1	0.8	0.08	b.d.l.	0.8	-7.58	-50.6		-14.2
BBLEU1	Cilaos	29/06/2017	524	7.7	18.6	0.91	0.63	2.77	0.03	6.13	0.09	0.05	0.46	0.05	1.0	3.9	-8.08	-53.4	0.704203	-6.1
BC	St-Benoît	15/12/2015	3270	6.5	23	4.08	13.31	7.86	0.45	42.98		0.12	2.1	0.10	b.d.l.	1.3	-7.62	-43.4	0.704196	-3.2
BE	Cilaos	26/10/2017	1257		19.8	2.17	4.3	1.83	0.15		0.03	0.1	1.77	0.06	b.d.l.	5.9	-8.15	-55.1	0.704167	-1.3
BR14	Cilaos	06/03/2016	1630	6.2	42.4	2.22	2.38	10.68	0.32	19.52**		0.68	2.35	0.95	0.2	11	-8.19	-51.9	0.704156	-1.5
BR14	Cilaos	21/11/2015	1684	6.1	39.1	2.65	2.69	12.03	0.33	21.97**		1.07	2.39	0.57	0.1	13.1	-8.44	-52.5	0.704172	-0.2
BR14*	Cilaos	08/09/2017	1764	6.8	37.2	2.17**	2.54	12.36	0.35	19.10**	0.91	1.21	2.49	0.97	b.d.l.	12.6	-8.53	-53.7	0.704179	-0.8
BR16*	Cilaos	30/07/2016	2530	6.8	25.9	2.52**	2.39	18.35	0.86	24.93**		3.22	2.02	2.70	b.d.l.	8	-8.41	-52	0.704165	1.8
BR16*	Cilaos	29/10/2017	3370	6.5	29.1	2.70**	3.14	25.01	0.99	31.61**	0.48	5.13	2.58	4.02	b.d.l.	11.1	-8.67	-53.3	0.704162	0.6
BR21*	Cilaos	23/08/2016	1256	6.2	25.1	1.64**	0.58	9.8	0.1	12.98**	0.5	0.36	0.56	0.38	b.d.l.	17.6	-8.07	-51.7	0.704249	3
BR6	Cilaos	26/08/2017	1221	6.1	25.3	3.42	1.15	2.93	0.09	10.16	0.44	0.1	0.93	0.09	b.d.l.	10.9	-7.35	-46	0.704212	-1.5
BR9	Cilaos	20/03/2016	1149	6.0	26.5	2.53	3.06	2.6	0.12	13.85**		0.05	1.64	0.05	b.d.l.	10.5	-7.96	-53.1	0.704175	0.1
DUP*	Salazie	15/06/2015	714	8.1	23.3	1.39	1.25	2.78	0.08	7.23	0.39	0.06	0.96		b.d.l.		-6.5	-38.4	0.704224	3.4
EDN*	Salazie	16/05/2015	1855	6.4	25.5	3.17	6.17	3.99	0.22	23	0.12	0.05	2.34		0.0		-6.5	-38.7	0.704237	3
FSJ2	Salazie	14/07/2017	864	7.1	15.8	2	1.25	2.35	0.07	8.70**	0.07	0.08	1.36	0.08	b.d.l.	7.8	-5.96	-34.4	0.704240	-2.6
G3	Cilaos	20/03/2016	1416	6.2	22.4	3.34	4.27	2.66	0.13	17.97**		0.05	2	0.13	b.d.l.	18.1	-8.23	-51.9	0.704183	0.2
GDS*	Salazie	17/06/2015	1234	7.7	18.7	4.74	2.23	1.31	0.07	8.79	3.34	0.03	0.79	0.14	0.0		-5.9	-33.1	0.704330	1.7
IRN*	Cilaos	29/11/2017	2570	6.7		4.00**	4.19	15.13	0.19	29.48**	1.04	0.15	2.51	0.10	b.d.l.	19.8	-8.14	-51.1		
IRN*	Cilaos	05/05/2017	2510	6.5	35.1	**	4.16	15.01	0.21		1.01	0.17	2.32	0.11	b.d.l.	12.2	-8.05	-51		-1.2
IRN*	Cilaos	15/06/2017	2500	6.4	36	3.99**	4.08	14.79	0.2	28.98**	1.01	0.15	2.36	0.17	b.d.l.	19.7	-8.1	-51.2		-0.9
IRN*	Cilaos	26/10/2017	2570	6.4	34.3	4.05**	4.26	15.33	0.2	29.92**	1.04	0.15	2.43	0.11	b.d.l.	20	-8.06	-51		-0.5
IRN*	Cilaos	25/09/2017	2560	6.6	36.2	4.00**	4.15	15.05	0.2	29.36**	1.02	0.16	2.42	0.10	b.d.l.	19.4	-7.89	-50.9	0.704168	-0.5
IRN*	Cilaos	30/08/2017	2560	6.4	36.2	4.08**	4.17	15.46	0.22	28.97	1.04	0.21	2.41		b.d.l.	20	-8.04	-50.9		-0.4
MAN*	Salazie	16/06/2015	1395	6.6	30.6	3.3	2.69	4.39	0.2	16.57	0.11	0.07	1.76		0.0		-7.2	-43.4	0.704277	1.6
MAN	Salazie	19/08/2016	1520	6.7	30.4	3.6	2.84	4.45	0.21	17.16**	0.14	0.11	1.53	0.08	b.d.l.	9.7	-7.19	-42.5	0.704273	1.2
MANa	Salazie	19/08/2016	274	6.2	14.9	0.42	0.51	0.61	0.14	2.51**	0.03	0.05	0.65	0.04	b.d.l.	0.6	-8.58	-54.8	0.704240	1.5
MANc	Salazie	19/08/2016	687	5.9	17.5	1.27	1.5	1.79	0.24	7.39**	0.06	0.06	1.12	0.06	b.d.l.	2.6	-8.54	-53.8	0.704258	5.2
MANES	Cilaos	29/11/2017	2310	6.5	29.6	3.75	3.99	13.14	0.19	26.77**	0.9	0.26	2.21	0.12	b.d.l.	17.7	-8	-51.3		-0.9
MANES	Cilaos	26/10/2017	2340	6.0	30.3	3.55	3.99	13.02	0.2	23.82**	0.9	0.16		0.09		18.1	-8.06	-51.4		-1.4
MANES	Cilaos	25/09/2017	2310	6.6	30.8	3.78	3.99	13.18	0.2	27.00**	0.89	0.15		0.08		18.1	-7.98	-51		-1.3
MANES	Cilaos	30/08/2017	2320	6.4	30.7	3.72	3.93	12.94	0.2	26.52**	0.88	0.16		0.08		17.6	-8.02	-51.4		-0.8
MANES*	Cilaos	15/06/2017	2310	6.4	29.8	3.72**	3.86	13.02	0.2	26.52**	0.86	0.16		0.16		17.7	-8.04	-51.5		-1.2
MANES	Cilaos	05/05/2017	2300	6.4	30.5	3.66	3.99	13.23	0.19	26.75**	0.9	0.18				17.3	-8.03	-51.3		0
MVP1	Salazie	12/05/2017	476	7.9	21	1.56	0.88	0.48	0.04	2.69	1.29	0.11	0.59	0.22	0.8	4	-5.84	-35.2	0.704330	-12.9
OLIVbis	Salazie	22/11/2017	551	8.1	22.3		0.87	1.62	0.04	5.05**	0.45	0.11	0.5	0.08	b.d.l.		-6.01	-37.1	0.704364	-12.3
OLIVbis	Salazie	30/01/2018	735	7.8	22.3	1.92	1.23	1.59	0.04	2.39**	1.37	0.13			b.d.l.	7.1			0.704347	-12.1
PEND	Cilaos	29/11/2017	618	7.1	22.9	0.89	0.98	2.86	0.14	5.41**	0.6	0.13	0.94	0.11	b.d.l.	0.5	-8.18	-58.8	0.704212	-14.8

Spring	Location	Date dd/mm/yyyy	Electrical Conductivity ($\mu\text{S/cm}$)	pH	Temperature ($^{\circ}\text{C}$)	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	K (mmol/L)	HCO_3 (mmol/L)	SO_4 (mmol/L)	Cl (mmol/L)	SiO_2 (mmol/L)	Br ($\mu\text{mol/L}$)	Al ($\mu\text{mol/L}$)	Sr ($\mu\text{mol/L}$)	$\delta^{18}\text{O}$ (‰ VMOW)	δD (‰ VMOW)	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}$ (‰ PDB)
RB1*	Salazie	15/10/2016	929	6.0	19.8	2.30**	1.83	1.21	0.19	9.44**	0.08	0.05	1.62	0.09	b.d.l.	4.5	-6.5	-37.1	0.704308	-1.9
RB2	Salazie	15/10/2016	1030	6.1	19.8	3.11	1.94	1.25	0.15	11.26**	0.1	0.05	1.53	0.08	b.d.l.	6.7	-6.37	-36.6	0.704309	-1.9
RBGR1	Cilaos	30/06/2017	1334	6.6	19	1.78	4.17	2.86	0.03	14.1**	0.3	0.09	1.63	0.04	b.d.l.	0.6	-6.9	-45.9	0.704176	-4.3
RBR3	Cilaos	23/08/2016	379	7.5	12.1	0.96	0.74	0.83	0.06	3.9	0.27	0.02	0.52	0.02	b.d.l.	3.6	-8.01	-50.4	0.704181	2.8
RBR5	Cilaos	23/08/2016	634	7.8	14	1.8	1.34	1.21	0.06	4.16	1.69	0.05	0.44	0.02	b.d.l.	11.6	-7.76	-48.1	0.704185	-0.2
RBR8	Cilaos	23/08/2016	1145	7.4	13.5	4.72	1.76	0.97	0.06	4.61	4.94	0.07	0.28	0.02	b.d.l.	21.9	-7.97	-50.2	0.704169	0.9
RM22	Salazie	17/05/2017	660	7.4	23.3	1.32	2.14	0.64	0.1	6.74	0.45	0.08	1.24	0.09	0.5	3	-5.98	-36.5	0.704216	-7.5
RR1*	Cilaos	30/07/2016	1586	6.2	32.5	2.29**	1.41	10.3	0.3	14.72**	0.91	1.47	1.77	1.25	b.d.l.	9.2	-8.48	-56.3	0.704167	2.6
TB*	Salazie	22/11/2017	1410	6.3	34.4	2.14**	1.03	9.35	0.29	14.08**	0.57	0.75	1.09	0.63	b.d.l.	7.6	-6.42	-38.7	0.704194	-1.7
TBA*	Salazie	15/06/2015	1718	6.3	26.6	4	2.46	7.07	0.16	16.95	0.97	0.1	2.08		0.0					
TBA	Salazie	11/05/2017	1651	7.0	26.4		2.5	6.96	0.16	14.74	1.85	0.11	2.07		b.d.l.		-6.59	-39.9	0.704265	0.3
TR*	Salazie	21/07/2017	379	7.3	20.8	0.71**	0.78	0.73	0.04	1.51**	1.08	0.07	0.54	0.11	0.9	1.9	-6.69	-41.1	0.704333	-8
TR*	Salazie	30/01/2018	1016	7.5	20.8		2.71	1.05	0.06		5.07	0.09	0.6		1.2				0.704308	-6.4
VERO	Cilaos	29/11/2017	1980	6.2	29.7	3.2	3.37	10.69	0.16	22.39**	0.74	0.14	2.03	0.10	b.d.l.	15.6	-7.97	-51.3		-2
VERO	Cilaos	26/10/2017	1994	6.1	29.5	3.13	3.47	10.93	0.16	21.74	0.74	0.12		0.10		15.4	-8	-51.5		-2.1
VERO	Cilaos	25/09/2017	1988	6.4	29.9	3.16	3.4	10.69	0.25	22.38**	0.72	0.25				15.3	-7.96	-51.4		-2.2
VERO*	Cilaos	15/06/2017	1938	6.2	29.5	3.16**	3.33	10.56	0.16	20.79	0.68	0.14		0.04		15.3	-7.96	-51.6		-2.2
VERO*	Cilaos	30/08/2017	1986	6.2	29.7	3.12**	3.36	10.65	0.16	22.21**	0.72	0.13		0.06		15.2	-7.96	-51.2		-2.2
VERO	Cilaos	05/05/2017	1888	6.4	29.3	3.01	3.16	10.21	0.18	19.52	0.67	0.14		0.05		14.7	-7.93	-51.3		-2.3

316 *Bénard et al., (2020) ; **corrected values (re-analyzed Ca concentrations and HCO_3 concentrations estimated from ionic balance)

317 Table 2: monitoring of $\delta^{18}\text{O}$ and δD values (‰ VSMOW) from rainwaters and thermal springs (TBA and IRN) in the
 318 cirques of Salazie and Cilaos. Rainwater samples correspond to a cumulate of rainfalls collected over about 4 weeks.
 319 Spring samples were taken when rainwaters were collected. Rainfall amount (mm) is deduced from the collected
 320 rain volume, except when information is missing (no data or overflow indicated by an *). In the latter case, we
 321 used the rainfall data from the closest METEOFRACTICE meteorological station accessible at their online data
 322 repository publitheque.meteo.fr (we accounted for a proportionality coefficient to adjust for the systematic
 323 difference between METEOFRACTICE and our rainfall data).

Location	Sampling period (Rain)/ Sampling date (Spring, end of period) Dates in dd/mm/yy	Rain				Spring (TBA in Salazie, IRN in Cilaos)	
		$\delta^{18}\text{O}$ (‰)	δD (‰)	Volume (L)	Rainfall (mm) corrected	$\delta^{18}\text{O}$ (‰)	δD (‰)
Salazie	07/04/17-11/05/17	-4.06	-16.8	5.2	67.5	-6.59	-39.9
	11/05/17-14/06/17	-3.11	-9.8	1.6	20.0	-6.72	-40.4
	14/06/17-21/07/17	-2.70	-5.2	0.7	9.0	-6.79	-40.3
	21/07/17-25/08/17	-2.07	1.8	1.2	14.9	-6.83	-40.0
	25/08/17-21/09/17	-3.77	-15.7	0.9	11.0	-6.92	-41.1
	21/09/17-19/10/17	-1.86	1.5	1.0	13.4	-6.97	-40.7
	19/10/17-22/11/17	-2.89	-8.7	2.6	34.1	-6.97	-40.8
	22/11/17-20/12/17	-1.49	3.2	0.0*	8.6	-7.05	-40.5
	20/12/17-30/01/18	-7.22	-47.3	20.0*	298.4	-6.53	-39.0
	30/01/18-31/05/18	-6.90	-42.8	20.0*	506.2	-6.60	-39.7
	31/05/18-17/07/18	-2.47	-1.3	2.0	25.8	-6.74	-39.6
	17/07/18-18/10/18	-2.24	-1.8	2.9	36.8	-6.88	-40.5
	18/10/18-07/11/18	-2.58	-10.0	1.4	18.1	-6.96	-40.1
	08/11/18-21/01/19	-5.61	-32.3	11.1	143.3	-6.81	-40.3
	21/01/19-12/02/19	-5.19	-29.0	1.6	20.7	-6.83	-40.5
	12/02/19-13/03/19	-3.61	-15.5	1.9	23.9	-6.89	-40.3
	13/03/19-17/04/19	-4.73	-25.3	2.4	31.0	-6.96	-40.4
17/04/19-28/05/19	-2.66	-4.4	1.5	19.4	-7.03	-40.5	
Cilaos	30/03/17-05/05/17	-4.40	-18.4	0.0*	53.7	-8.05	-51.0
	05/05/17-15/06/17	-3.61	-18.2	1.0	12.3	-8.10	-51.2
	15/06/17-28/07/17	-2.67	-4.6	0.7	9.0	-8.09	-51.2
	28/07/17-30/08/17	-2.70	-5.1	1.0	12.9	-8.04	-50.9
	30/08/17-25/09/17	-2.76	-2.8	0.8	9.7	-7.89	-50.9
	25/09/17-26/10/17	-1.31	4.4	0.3	3.2	-8.06	-51.0
	26/10/17-29/11/17	-3.16	-11.7	1.8	23.6	-8.14	-51.1
	29/11/17-21/12/17	-2.74	-7.2	0*	10.1	-8.09	-51.3
	21/12/17-06/02/18	-8.34	-57.8	20.0*	304.4	-8.05	-51.5
	06/02/18-21/05/18	-9.68	-66.3	20.0*	430.9	-8.10	-51.6
	21/05/18-15/10/18	-2.25	-1.9	2.6	32.9	-8.10	-50.9
	15/10/18-08/11/18	-4.97	-25.3	2.2	27.8	-8.11	-51.1
	08/11/18-05/12/18	-3.70	-17.3	2.0	25.2	-8.13	-51.4
	05/12/18-22/01/19	-5.69	-34.8	3.9	50.4	-8.12	-51.6
	22/01/19-13/02/19	-5.20	-25.8	2.0	25.8	-8.11	-51.2
	13/02/19-14/03/19	-3.59	-15.8	0.9	11.6	-8.11	-51.2
	14/03/19-18/04/19	-4.86	-26.6	1.6	20.7	-8.12	-50.8
18/04/19-29/05/19	-3.24	-8.3	0.6	7.1	-8.17	-50.9	

324 Table 3: $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of rocks from the cirques of Salazie and Cilaos.

Sample	Rock type	Source of data	Location	X (RGR92 /UTM40S)	Y (RGR92 /UTM40S)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	Error (2 σ)	Stage	
BR14	Syenite	This study	Cilaos			40.0	0.704184	0.000006	Differentiated	
CHAP	Syenite		Cilaos			149	0.704215	0.000023	Differentiated	
RN18-5	Syenite		Salazie			634	0.704182	0.000015	Differentiated	
BAF1-6	Trachyte		Summit			498	0.704156	0.000010	Differentiated	
PdNMS21	Aphyric Basalt	Smietana, 2011	Cilaos	340237	7648804	393.8	0.704153	0.000004	Shield	
PdNMS21	Aphyric Basalt		Cilaos	340237	7648804	289.2	0.704153	0.000004	Shield	
CB16290513	Gabbro	Berthod, 2016	Salazie	343698	7670796		0.704220	0.000010	Shield	
CB2150914	Gabbro		Salazie	343808	7669712	54.8	0.704166	0.000009	Shield	
CB2260513	Gabbro		Salazie	344106	7670815	288.4	0.704258	0.000007	Shield	
CB3230914	Syenite		Salazie	343534	7670756	331.6	0.704190	0.000008	Differentiated	
CB3A260513	Gabbro		Salazie	344120	7670828	245.7	0.704255	0.000010	Shield	
SAB 1	Syenite	Nauret et al., 2019	Salazie	341515	7669423	245.0	0.704155	0.000008	Differentiated	
SAL 1	Basalt		Salazie	344105	7670824	542.6	0.704283	0.000022	Shield	
SAL 102	Oceanite		Salazie	344238	7670893	497.5	0.704041	0.000008	Shield	
SAL 106	Gabbro		Salazie	344194	7670885	558.5	0.704290	0.000008	Shield	
SAL 110	Gabbro		Salazie	343667	7670778	472.5	0.704256	0.000008	Shield	
SAL 153	Oceanite		Salazie	342913	7674274	228.9	0.704085	0.000007	Shield	
SAL 18	Gabbro		Salazie	344180	7670872	512.7	0.704290	0.000012	Shield	
SAL 200	Trachy-Basalt		Salazie	343775	7669845	573.9	0.704158	0.000007	Differentiated	
SAL 200 (duplicate)	Trachy-Basalt		Salazie	343775	7669845		0.704159	0.000007	Differentiated	
SAL 201	Trachy-Basalt		Salazie	343895	7669717	376.8	0.704268	0.000006	Differentiated	
SAL 203	Trachy-Basalt		Salazie	343317	7670409	487.4	0.704167	0.000007	Differentiated	
SAL 206	Dunite		Salazie	344492	7668744	23.9	0.704277	0.000011	Shield	
SAL 48	Basalt		Salazie	343567	7670290	512.4	0.704223	0.000008	Shield	
SAL 51	Basalt		Salazie	343482	7670368	357.1	0.704223	0.000010	Shield	
SAL 88	Trachyte		Salazie	344734	7670476	531.1	0.704169	0.000008	Differentiated	
SAL 88 (duplicate)	Trachyte		Salazie	344734	7670476		0.704185	0.000009	Differentiated	
RUN 027-2006	Olivine basalt		Cilaos				89.0	0.704154	0.000008	Shield
RUN 029-2006	Olivine basalt		Cilaos				73.5	0.704144	0.000010	Shield
RUN 040-2006	Benmoreite		Salazie				89.0	0.704504	0.000015	Differentiated
ANTN	Benmoreite		Summit				176	0.704176	0.000014	Differentiated
RN18-9	Trachyte	Summit				256	0.704153	0.000010	Differentiated	

325

326 4. Discussion

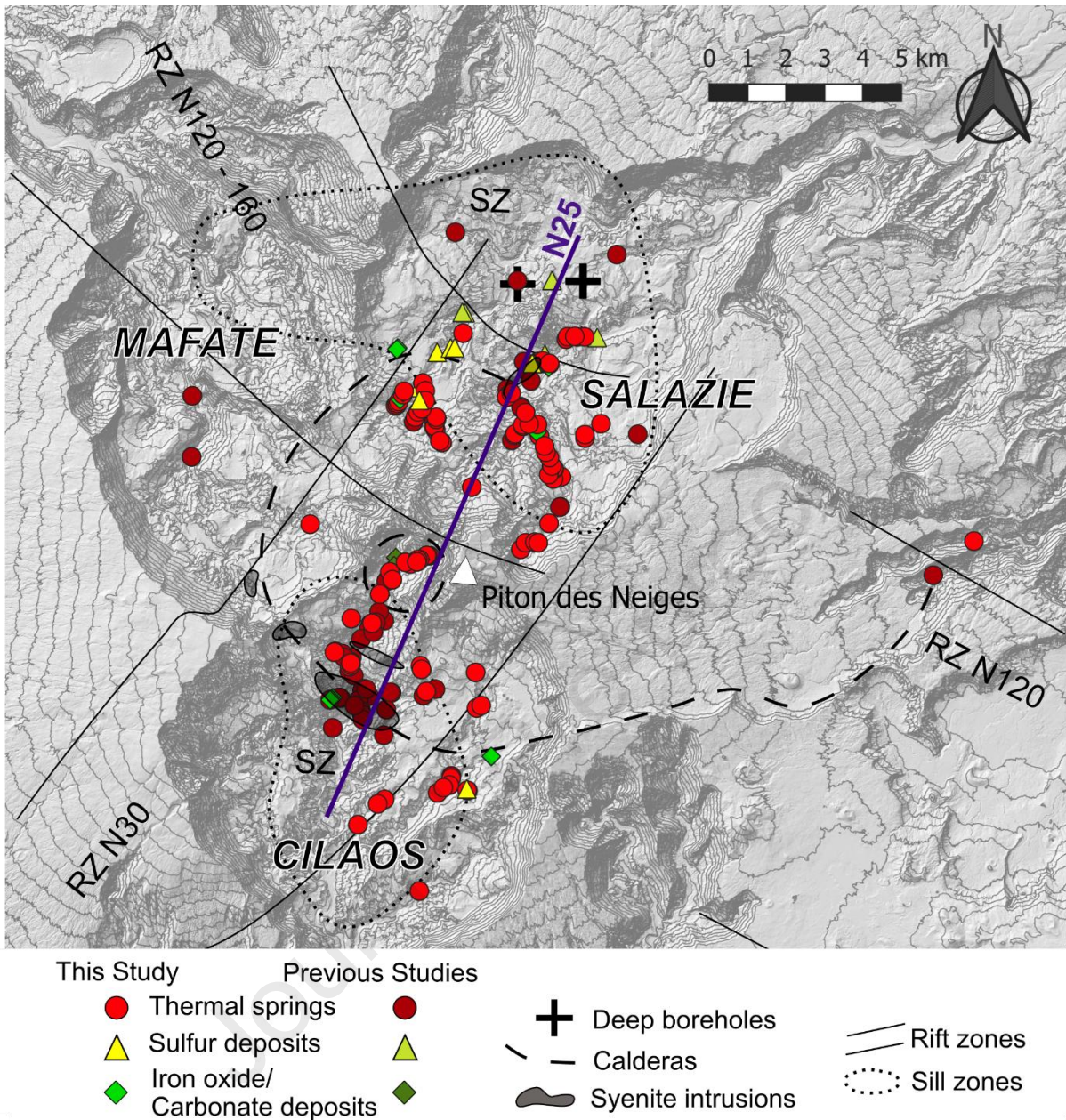
327 4.1. Spatial distribution of hydrothermal features

328 In this section, we study the spatial distribution of several geochemical features related to
329 hydrothermal activity: the occurrence of field indicators of hydrothermal activity, the temperature and
330 electrical conductivity at the outlets of springs and their CO₂ partial pressure. This spatial distribution
331 is then superimposed to the main geological features to decipher if they may constitute heat sources
332 or drains for the thermal fluids.

333 4.1.1. *Field indicators of hydrothermal activity*

334 Thermal springs and dry deposits of iron oxide/carbonate/sulfide, which are indicators of
335 hydrothermal activity, are observed in the three cirques (Figure 3) with two springs reaching farther
336 east in Saint-Benoît. The majority of them are found in the cirques of Salazie and Cilaos, with a greater

337 abundance in the upper slopes of the cirques beneath the summit of Piton des Neiges. A first important
338 result of our field prospection is that hydrothermal indicators largely extend outside the proposed
339 caldera, suggesting that the hydrothermal system is not directly fed by this major volcanic structure
340 nor limited by it. Secondly, most of these indicators are spread along a \sim N25° axis, coinciding with the
341 N30° rift zone defined by Chaput et al., (2017, 2014). This N25° spatial repartition is not biased by
342 prospecting, as rivers from the northeastern part of Salazie, from the western part of Cilaos, from
343 Mafate, from the two branches of the Grand Bassin depression, and from the Marsouins basin were
344 surveyed and found to be devoid of thermal springs. Based on a study of outcropping planar intrusions,
345 Chaput et al., (2017) showed that the N30°E rift zone is composed of mafic and differentiated dykes,
346 implying a more recent activity than the N110-160° rift zone composed only of mafic intrusions. Our
347 study confirms that the N30° rift zone is the most recently active volcano-tectonic lineament in the
348 edifice, sufficiently young to provide heat for a shallow hydrothermal system. Thirdly, dry deposits
349 (sulfides, oxides or carbonates) are mostly found at the external parts of the area containing
350 hydrothermal indicators, and principally at the northern and southern extremities of this \sim N25°-
351 elongated zone. This suggests that dry hydrothermal indicators correspond to the external limits of the
352 hydrothermal system. Interestingly, the two boreholes drilled in Salazie are located in this zone of dry
353 hydrothermal indicators, possibly outside the hydrothermal system, which may explain why these two
354 boreholes found heat but no water yield.



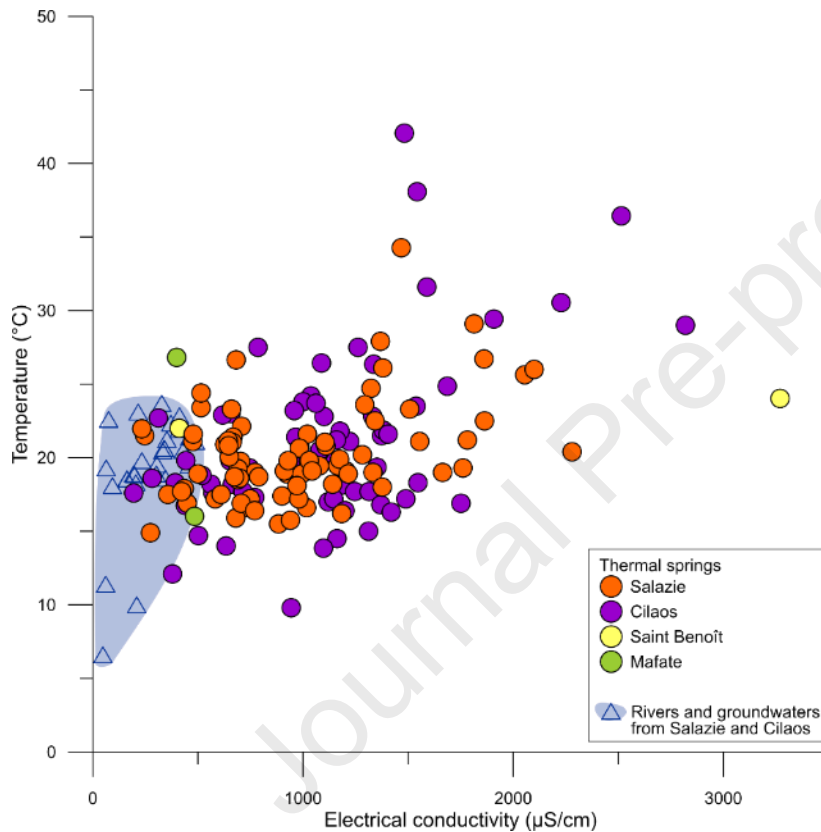
355

356 Figure 3: Map of the field indicators of hydrothermal activity at Piton des Neiges volcano from this study (bright
 357 shades) and previous studies (darker shades, Aunay et al., 2013; Belle, 2014; Frissant et al., 2003; Iundt et al.,
 358 1992; Lopoukhine and Stieltjes, 1978; Louvat and Allègre, 1997; Sanjuan et al., 2001). These indicators include
 359 thermal springs and sulfur, iron oxide, or carbonate dry deposits. Most of the indicators are spread along a $\sim N25^\circ$
 360 axis, coinciding with the $N30^\circ$ rift zone.

361 4.1.2. Temperature and electrical conductivity

362 High temperatures and elevated amounts of total dissolved solids (proxied by EC) at the outlet of
 363 thermal springs are indicators of hydrothermal activity. These physicochemical parameters can be
 364 modified during fluid upflow from the geothermal reservoir to the surface by mixing with shallow cold
 365 waters, by further interaction with the surrounding rocks, or by cooling and deposition of secondary
 366 minerals. Thermal springs display various degrees of enrichment in dissolved solids and warming
 367 compared to rivers and groundwaters of Salazie and Cilaos (Figure 4), reflecting varying contributions
 368 of a hydrothermal component. Those displaying higher values for outlet temperature and/or EC
 369 indicate a closer reservoir, a faster transfer from the reservoir to the surface, a higher intensity of

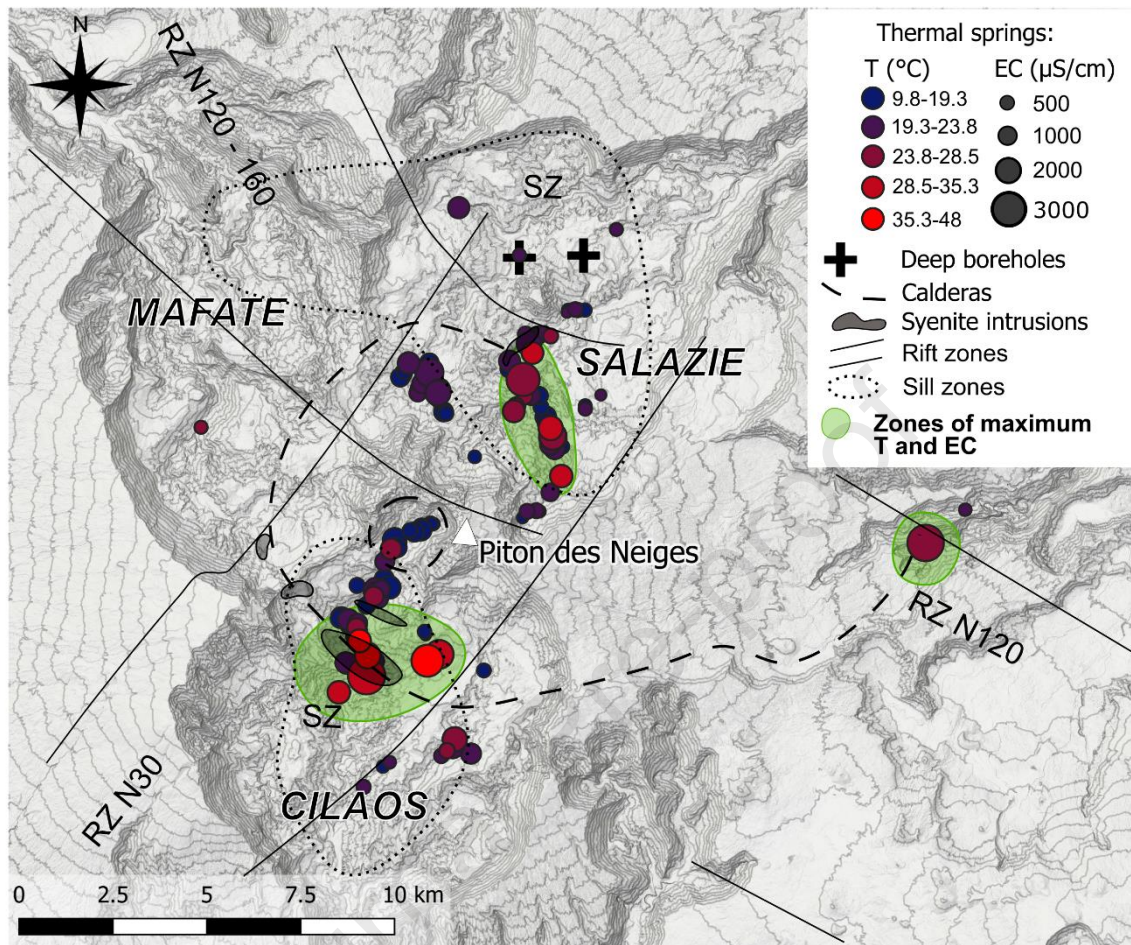
370 water/rock interaction, or a lower dilution by cold waters. These physicochemical parameters are thus
 371 of paramount importance in geothermal exploration to locate zones of fastest circulation and/or of
 372 highest fluid temperature. The thermal springs of Piton des Neiges are represented according to their
 373 outlet temperature and EC in Figure 5. This figure shows that the hottest and most mineralized springs
 374 are not only located along the N30°E rift zone, but also in immediate vicinity of syenite intrusions
 375 and/or along the proposed rim of the caldera. Previous work suggested that syenite intrusions, thought
 376 to delineate the caldera, play at least a role of drain transferring thermal waters from the reservoir to
 377 the surface, and possibly even constitute the heat source and/or the reservoir itself (e.g. Frissant et
 378 al., 2003; Sanjuan et al., 2001). Our study strengthens these conclusions, as they remain valid even
 379 with our larger dataset.



380

381 Figure 4: Mean temperature (°C) and electrical conductivities (µS/cm) of thermal springs from Piton de Neiges (this
 382 study, Aunay et al., 2013; Belle, 2014; Frissant et al., 2003; Iundt et al., 1992; Lopoukhine and Stieltjes, 1978;

383 Louvat and Allègre, 1997; Marty et al., 1993; Poul, 1966; Sanjuan et al., 2001) and rivers and groundwaters of
 384 Salazie and Cilaos (this study, Belle, 2014; Louvat and Allègre, 1997).



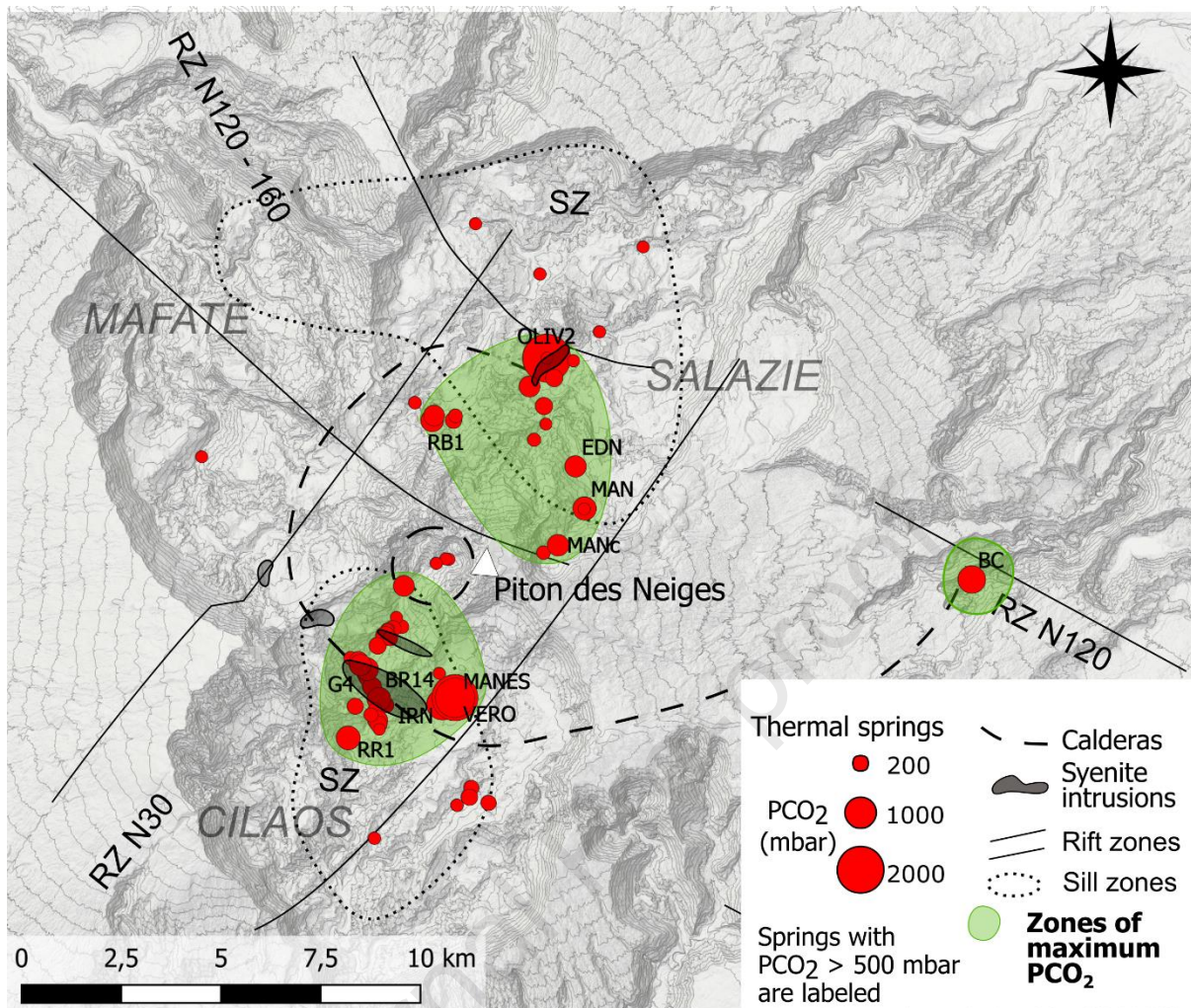
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386 Figure 5: Spatial distribution of temperature (represented by a color scale) and electrical conductivity (EC in $\mu\text{S}/\text{cm}$,
 387 represented by symbol size) in the thermal springs of Piton des Neiges. Green fields represent zones of highest
 388 temperatures and EC, and hence of most promising geothermal resource according to these parameters. Volcano-
 389 tectonic structures (rift zones, sill zones, syenite intrusions, and calderas) are also represented.

390 4.1.3. Magmatic CO_2

391 All the thermal springs of Piton des Neiges analyzed in previous studies display evidence of interaction
 392 with magmatic CO_2 , which essentially comes from mantle degassing associated with the Réunion
 393 hotspot (Bénard et al., 2020). The $\delta^{13}\text{C}$ signature of this mantellic CO_2 has been estimated from gas
 394 and fumarole samples of Piton de la Fournaise, the active volcano of La Réunion, and is comprised
 395 between -0.5 and -8 ‰ (Boudoire et al., 2018; Marty et al., 1993; Trull et al., 1993). Bénard et al.,
 396 (2020) showed that higher values may be measured in thermal springs due to loss of gaseous CO_2 from
 397 waters which results in isotopic fractionation. Lower values may also be expected due to mixing with
 398 a biogenic carbon source with $\delta^{13}\text{C} \leq -20$ ‰ (Liuzzo et al., 2015). The newly measured values of $\delta^{13}\text{C}$
 399 in thermal springs (from -14.8 to 5.15 ‰) from this study are consistent with the previous observations.
 400 Only four springs (BB7, MVP1, OLIVbis, PEND) display $\delta^{13}\text{C}$ values lower than -8 ‰, indicating a slight
 401 biogenic contribution. Therefore, magma degassing is the main carbon source in thermal springs and
 402 consequently, CO_2 can be used to highlight magmatic processes.

403 Consequently, we use the spatial distribution of the carbon content to locate zones of maximum CO₂
404 degassing, which may be interpreted as preferential pathways in the edifice for the rise of deep fluids.
405 For each thermal spring, we computed the mean partial pressure of CO₂ (PCO₂, Table 4) at the outlet,
406 from the water compositions displayed in Table 1 and using the “Diagrammes” software (created by
407 R. Simler, Université d’Avignon et pays du Vaucluse, <http://www.lha.univ-avignon.fr/LHA-Logiciels.htm>) from PhreeqC, USGS®, with the WATEQ4F thermodynamic database (Ball and
408 Nordstrom, 1991). Most of the gas being already lost at the spring outlet (Bénard et al., 2020; Marty
409 et al., 1993; Sanjuan et al., 2001), PCO₂ cannot be considered as entirely representative of the total
410 carbonate species’ concentrations at depth. However, the preservation of a high PCO₂ in thermal
411 springs is an indicator of an initial elevated CO₂ input and/or a shorter pathway from depth to surface.
412 In Figure 6, we displayed the spatial distribution of PCO₂ along with geological features. It is worth
413 noting that the thermal springs with the highest PCO₂ are not necessarily those with a high outlet
414 temperature or EC, showing that CO₂ input is disconnected from the heat source. Nevertheless, as for
415 temperature and EC, the most enriched springs (PCO₂ > 500 mbar) are those located in the N30°E rift
416 zone and in the vicinity of syenite intrusions and/or along the proposed rim of the caldera, except for
417 spring BC. The thermal spring BC, also displaying a high PCO₂, is located west of these structures, on
418 the rift zone N120°E running throughout the island between Piton de la Fournaise and Piton des
419 Neiges. CO₂ anomalies in soils have been observed along this rift zone (Boudoire et al., 2017). This
420 spatial repartition suggests that the N30°E and N120°E rift zones and syenite intrusions and the larger
421 caldera represent preferential pathways for the rise of CO₂ into the hydrothermal system.
422



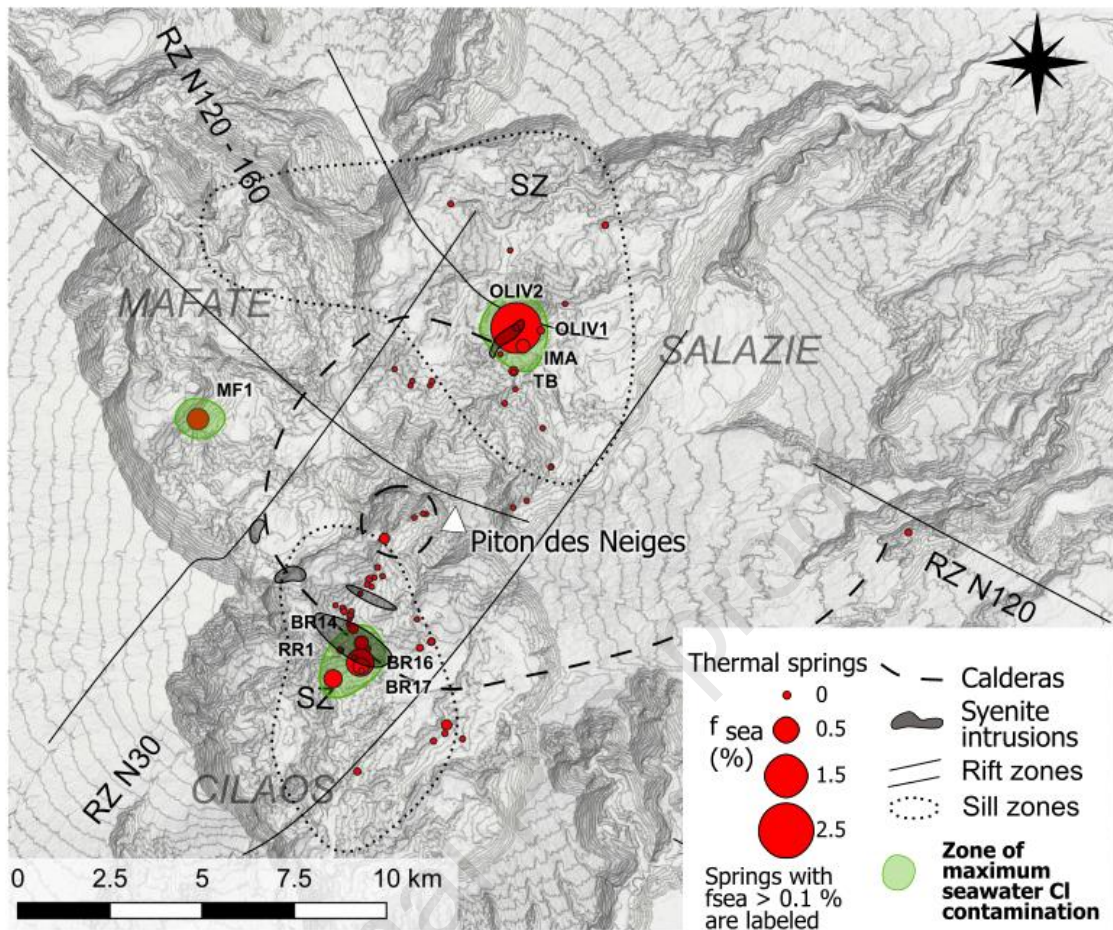
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424 Figure 6: Spatial distribution of the mean partial pressure of CO₂ (PCO₂, in mbar) at the outlet of thermal springs
 425 from Piton des Neiges, relative to volcano-tectonic structures (rift zones, sill zones, syenite intrusions, calderas).
 426 Green fields represent zones of higher PCO₂, which are interpreted as zones of preferential mantle degassing.
 427 Volcano-tectonic structures (rift zones, sill zones, syenite intrusions, and calderas) are also represented.

428 4.2. Hydrogeological features

429 4.2.1. *Contamination by elements originating from seawater*

430 From the study of the $\delta^{37}\text{Cl}$ signature of thermal springs, Bénard et al., (2020) showed that two main
 431 end-members contribute to their Cl budget: seawater and freshwater recharge. This is confirmed by
 432 the Cl/Br concentration ratios obtained from this study which correspond to that of seawater (Figure
 433 7). This seawater contamination likely does not originate from a current connection to the sea, as
 434 saltwater intrusion is limited to coastal areas in La Réunion (Dumont et al., 2018). It could however
 435 come from a trapped ancient reservoir or from seawater residual brines from when the area was still
 436 connected to the sea, as observed in other volcanic islands (Herrera and Custodio, 2014). Whatever its
 437 origin, this seawater Cl source is located at a depth of at least that of the seawater table.



461

462 Figure 8: Spatial distribution of seawater contamination (in mol%) in the thermal springs of Piton des Neiges relative
 463 to volcano-tectonic structures (rift zones, sill zones, syenite intrusions, and calderas). Green fields represent zones
 464 of highest seawater contamination, interpreted as the deepest drains for the ascent of hydrothermal fluids. Volcano-
 465 tectonic structures (rift zones, sill zones, syenite intrusions, and calderas) are also represented.

466

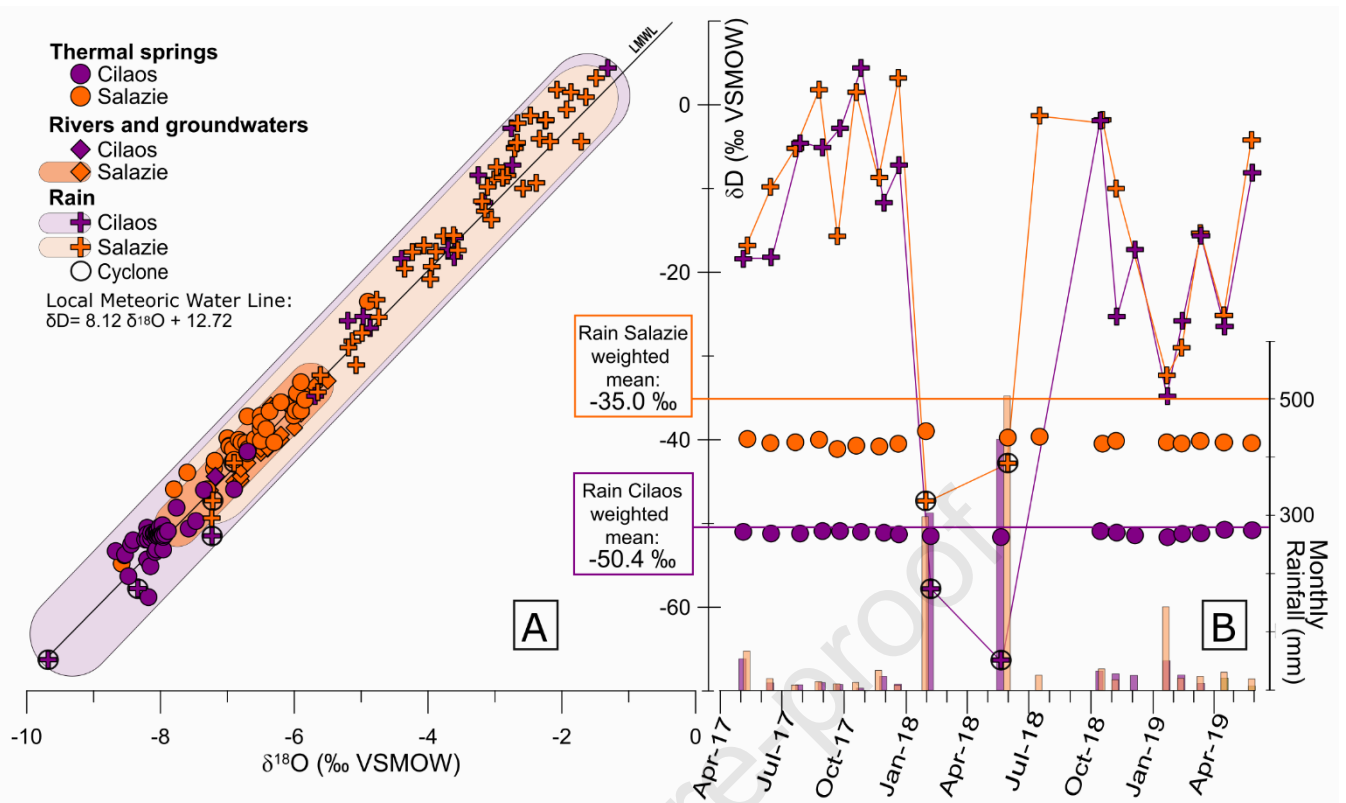
467 Table 4: Mean values of partial pressure of CO₂ at spring outlet (PCO₂, in mbar), molar proportion of seawater
 468 contamination (f_{sea}, in mol%), δ¹⁸O and δD (in ‰ VSMOW) for each thermal spring.

Thermal spring	Mean PCO ₂ (mbar)	Mean f _{sea} (mol%)	Mean δ ¹⁸ O (‰)	Mean δD (‰)	Thermal spring	Mean PCO ₂ (mbar)	Mean f _{sea} (mol%)	Mean δ ¹⁸ O (‰)	Mean δD (‰)
AGS	237	0.00			G2	101	0.00		
BACH	70	0.00	-6.70	-39.4	G3	381	0.00	-8.23	-51.9
BB	162	0.05	-8.13	-53.7	G4	537	0.00		
BB6	249	0.00	-7.47	-49.7	GDS	95	0.18	-5.40	-28.3
BB7	33	0.00	-7.58	-50.6	IMA	259	0.01		
BBLEU1	7	0.00	-8.08	-53.4	IRN	1075	0.00	-8.07	-51.1
BC	865	0.01	-7.62	-43.4	MAN	628	0.00	-7.24	-43.6
BE	213	0.00	-8.15	-55.1	MAN G	12	0.00	-7.00	-39.8
BR1	97	0.00			MANa	90	0.00	-8.58	-54.8
BR10	387	0.00			MANc	530	0.01	-8.54	-53.8
BR11	16	0.00			MANES	1900	0.39	-8.04	-51.7
BR12	382	0.04	-8.20	-50.5	MF1	0	0.00		
BR13	6	0.00			MVP1	2	0.23	-5.84	-35.2
BR14	641	0.13	-8.33	-52.5	OLIV1	28	2.34	-6.50	-40.1
BR15	72	0.01			OLIV2	2583	0.00	-7.80	-45.9
BR16	440	0.68	-8.54	-52.7	OLIVbis	4	0.00	-6.01	-37.1
BR17	273	0.21			PC	17	0.01		
BR18	3	0.00			PEND	23	0.00	-8.18	-58.8
BR2	4	0.00			PISSA	154	0.00	-6.70	-41.4
BR21	487	0.05	-8.07	-51.7	RB1	588	0.00	-6.50	-37.1
BR27	265	0.01			RB2	484	0.00	-6.37	-36.6
BR3	220	0.00			RBGR1	174	0.00	-6.90	-45.9
BR4	120	0.00			RBR3	6	0.00	-8.01	-50.4
BR5	66	0.01			RBR5	4	0.00	-7.76	-48.1
BR6	404	0.00	-7.35	-46.0	RBR8	8	0.00	-7.97	-50.2
BR7	279	0.00			RFOUQ	496	0.00	-6.50	-37.9
BR8	67	0.00			RM22	16	0.25	-5.98	-36.5
BR9	603	0.00	-7.96	-53.1	RR1	656	0.01	-8.48	-56.3
DUP	3	0.00	-6.50	-38.4	sRMAT	14	0.00	-5.90	-36.5
EDN	517	0.00	-6.50	-38.7	sRMAT2	46	0.04	-6.20	-35.5
FJ1	93	0.00			sRMAT3	43	0.12		
FJ2	224	0.00			TB	305	0.00	-6.42	-38.7
FJ3	106	0.00			TBA	291	0.00	-6.83	-40.5
FSJ2	35	0.00	-5.96	-34.4	TR	7	0.01	-6.50	-40.7
G1	108	0.00			VERO	1530		-7.98	-51.4

469

470 4.2.2. Recharge

471 Mean values of δ¹⁸O and δD for each thermal spring computed from our new and previous data (Table
 472 4) plot close to the local meteoric water line (Figure 9.A). This δ¹⁸O and δD signature indicates that the
 473 hydrothermal system is supplied by rain infiltration, as already evidenced by Bénard et al., (2020). With
 474 our new data, however, δ¹⁸O and δD reveal a dichotomy between the thermal springs of Salazie and
 475 Cilaos. δ¹⁸O and δD are less negative in the cirque of Salazie (from -7.80 to -4.9 ‰ and from -45.9 to -
 476 23.5 ‰, respectively) than in Cilaos (from -8.67 to -6.70 ‰ and from -58.8 to -41.4 ‰, respectively),
 477 except for the two springs at the extreme south of the cirque of Salazie MANa (-8.6 and -54.8 ‰) and
 478 MANc (-8.5 and -53.8 ‰, respectively) that show very negative values compatible with the Cilaos
 479 group.



480

481 Figure 9: A. Mean $\delta^{18}\text{O}$ and δD isotopic ratios of thermal springs (this study, Aunay et al., 2013; Belle, 2014; Sanjuan
 482 et al., 2001) compared to that of river waters, groundwaters (this study, Belle, 2014; Louvat and Allègre, 1997) and
 483 rainwaters (this study, Belle, 2014; Grunberger, 1989; IAEA/WMO, 2019) from Salazie and Cilaos. Rainwaters from
 484 cyclones are circled in black. B. Comparative monitoring of the δD isotopic ratios (‰ VSMOW) of thermal springs
 485 and rain in Salazie and Cilaos, relative to rainfall heights (mm).

486 In order to understand this difference, we compared the $\delta^{18}\text{O}$ and δD values of thermal springs to that
 487 of rivers, groundwater and rain in both cirques (Figure 9.A) and monitored $\delta^{18}\text{O}$ and δD for two years
 488 in thermal springs IRN in Cilaos and TBA in Salazie and in rainfall at both sites (Figure 9.B). In Salazie,
 489 the distribution of $\delta^{18}\text{O}$ and δD values of thermal springs is very similar to that of rivers and
 490 groundwaters ($\delta^{18}\text{O}$ from -8.0 to -5.5 ‰ and δD from -46.1 to -33.0 ‰), indicating a similar recharge.
 491 In Cilaos, the only river sample available (rBRO, from this study) displays $\delta^{18}\text{O}$ and δD values (-7.18 and
 492 -44.4 ‰, respectively) in the range of that of thermal springs from Salazie and Cilaos, and that of rivers
 493 and groundwaters from Salazie. Additional data would thus be necessary to discuss $\delta^{18}\text{O}$ and δD values
 494 of rivers and groundwaters compared to thermal springs in the cirque of Cilaos. The range of $\delta^{18}\text{O}$ and
 495 δD isotopic ratios in rains is similar in Salazie and Cilaos expect for 2 data points with lower values in
 496 Cilaos corresponding to samples from cyclones (Figure 9).

497 We considered recharge by computing the volume-weighted mean $\delta^{18}\text{O}$ and δD isotopic ratios of rains
 498 over two years for each cirque (2017-2019), using our monthly monitoring data at both sites (Table 2).
 499 The weighted mean $\delta^{18}\text{O}$ and δD isotopic ratios in rainwater is much higher in the cirque of Salazie
 500 ($\delta^{18}\text{O}$ = -5.94 ‰ and δD = -35 ‰, Figure 9) than in Cilaos ($\delta^{18}\text{O}$ = -7.70 ‰ and δD = -50.4 ‰). A similar
 501 difference is also observed in the chronicles of rain analyses over the period 1985-1986 between
 502 Salazie ($\delta^{18}\text{O}$ = -6.50 ‰ and δD = -37.6 ‰) and Cilaos (weighted mean $\delta^{18}\text{O}$ = -7.23 ‰ and δD = -51.5 ‰,
 503 Grunberger, 1989). This difference is mostly visible during cyclones (Figure 9.B), which appear to
 504 constitute a low $\delta^{18}\text{O}$ and δD end-member with different values for Salazie and Cilaos. The $\delta^{18}\text{O}$ and
 505 δD dichotomy in thermal springs may thus be explained by a difference in the isotopic signature of the
 506 recharge by cyclones between the two cirques. We tentatively explain this contrast by the isotopic air

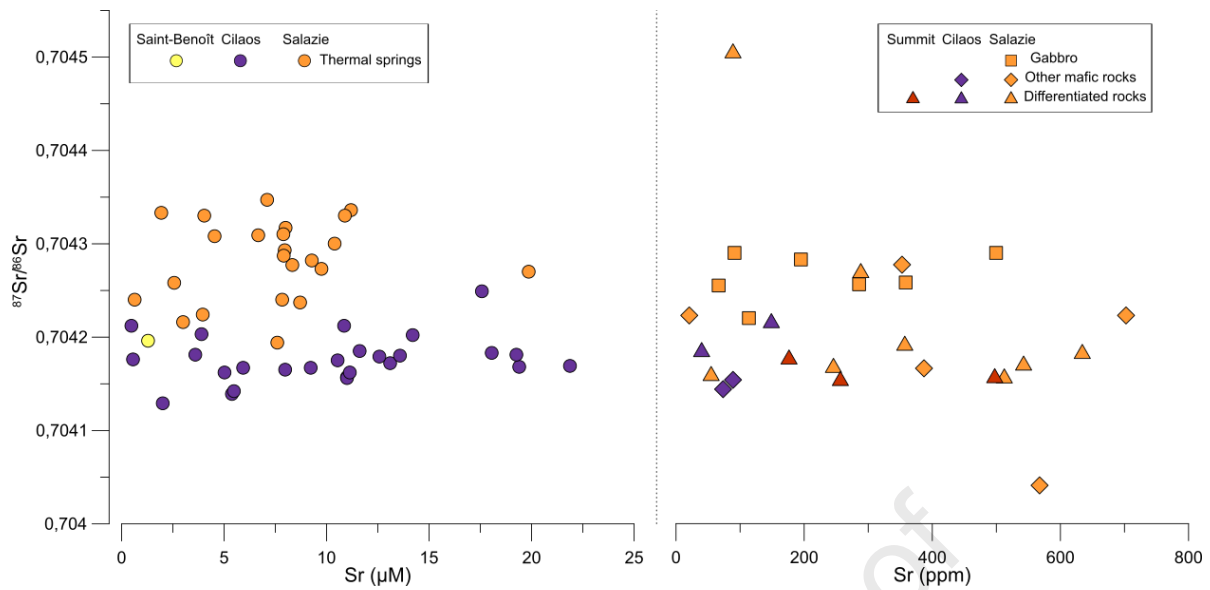
507 masses distillation at their passage over Piton des Neiges summit, from the windward slopes in Salazie
508 to the leeward slopes in Cilaos. This strongly suggests that the Salazie and Cilaos hydrothermal
509 reservoirs are not connected.

510 In comparison with rains, the two monitored thermal springs display very limited temporal $\delta^{18}\text{O}$ and
511 δD variations (Figure 9.B). The Cilaos spring (IRN) is not only very stable (from -50.9 to -51.2 ‰, mean
512 -51.0 ‰ for δD), but also very close to the volume-weighted mean $\delta^{18}\text{O}$ and δD isotopic ratios of rains
513 in this cirque (-50.4 ‰ for δD , Figure 9.B). This stability holds over a ~20 year period with a δD value
514 of -51.3 ‰ measured at IRN in 2000 by Sanjuan et al., (2001). $\delta^{18}\text{O}$ and δD values of the Salazie thermal
515 spring (TBA) are also very stable over the two-year period (e.g. from -38.7 to -41.1 ‰, mean -40.2 ‰
516 for δD), and their mean is relatively close to the volume-weighted mean $\delta^{18}\text{O}$ and δD isotopic ratios of
517 rains in this cirque (-35 ‰ for δD , Figure 9.B). This comparison of time series shows that thermal springs
518 at these two sites are neither influenced by the seasonal variations of rains nor by mixing with shallow
519 cold waters. The recharge, mostly influenced by important inputs of cyclonic water, is buffered by
520 multi-year infiltration. This suggests that the Salazie and Cilaos hydrothermal reservoirs, although
521 disconnected from each other, are sufficiently large and/or deep to be protected from superficial
522 perturbations.

523 4.2.3. *Host rock*

524 In this section, we compared the $^{87}\text{Sr}/^{86}\text{Sr}$ in rocks and thermal waters to identify the geological units
525 hosting the hydrothermal system. As with the $\delta^{18}\text{O}$ and δD isotopic ratios, we observe that $^{87}\text{Sr}/^{86}\text{Sr}$
526 ratios are higher in the thermal springs of Salazie (0.704194 to 0.704364, mean 0.704276 ± 0.000047)
527 than in those of Cilaos (0.704129 to 0.704249, mean 0.704180 ± 0.000026), irrespective of Sr
528 concentrations (Table 1, Figure 10), as already mentioned by Sanjuan et al., (2001). Because there is
529 no fractionation between Sr isotopes during water-rock interaction, the strontium isotopic ratio is
530 preserved when Sr is leached from the rock by thermal waters. This dichotomy thus reflects a
531 difference between the two cirques in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rocks interacting with thermal fluids.

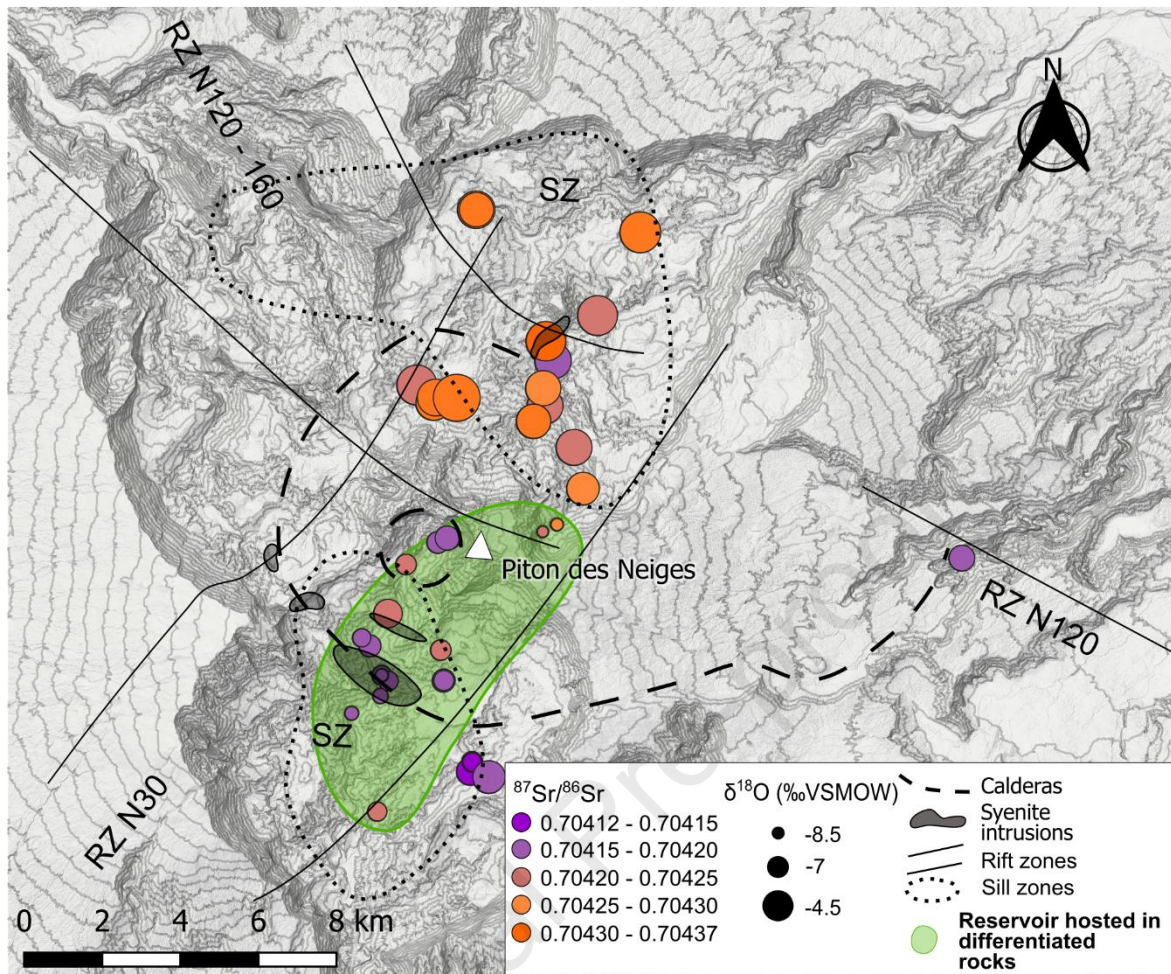
532 All rocks from Salazie and Cilaos (Table 3, Figure 10) fall in the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of thermal
533 springs (from 0.704086 to 0.704290), except for two outliers in Salazie (0.704041 and 0.704504).
534 However, our new analyses show that syenite intrusions, trachyte dykes and other differentiated
535 products fall in the lower range of this $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic diversity (from 0.704153 to 0.704269, mean
536 0.704181), whether they come from Salazie, Cilaos, or from the summit. The comparison of rock and
537 thermal spring $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic signatures thus strongly suggests that the hydrothermal fluids of Cilaos
538 interact with differentiated rocks at low $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios whereas those from Salazie interact
539 with more mafic rocks at higher $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. Differentiated intrusions belong to the latest
540 volcanic activity of Piton des Neiges (150 to 27 ka), and thus represent the likeliest heat sources in the
541 edifice.



542

543 Figure 10: Strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in thermal springs ($\mu\text{mol/L}$) and rocks (ppm) from
 544 the cirques of Salazie and Cilaos.

545 Consequently, the contrasted $^{87}\text{Sr}/^{86}\text{Sr}$ values of thermal springs of Salazie and Cilaos implies that the
 546 hydrothermal fluids interact with different rocks on the two sides of the summit. When combined with
 547 the contrasted $\delta^{18}\text{O}$ and δD signatures of thermal springs (Figure 11) which show that meteoric
 548 recharge is independent in the two cirques, we can deduce that the hydrothermal system is made of
 549 two reservoirs that do not mix with each other. The Cilaos reservoir, which shows more evidence of
 550 interaction with trachytes and syenites than the Salazie reservoir, is thus possibly closer to a heat
 551 source related to the terminal activity of Piton des Neiges, and is therefore more promising from a
 552 geothermal perspective.



553

554 Figure 11: Spatial distribution of $\delta^{18}\text{O}$ (‰ VSMOW in symbol size) and $^{87}\text{Sr}/^{86}\text{Sr}$ (in color scale) in the thermal
 555 springs of Piton des Neiges. The green field represents the zone of lowest $^{87}\text{Sr}/^{86}\text{Sr}$ indicating an interaction of
 556 thermal waters with differentiated rocks, which may represent heat sources for the hydrothermal system. Volcano-
 557 tectonic structures (rift zones, sill zones, syenite intrusions, and calderas) are also represented.

558 4.3. Equilibration and geothermometry

559 The next step in the geochemical characterization of the resource is to provide a quantitative estimate
 560 of the temperatures at which thermal waters and rocks interact. In a previous study, Sanjuan et al.,
 561 (2001) proposed a reservoir temperature reaching 120-130°C, based on empirical and semi-empirical
 562 geothermometers applied to the set of thermal springs known at that time. We now dispose of a wider
 563 set of analyses of thermal springs. We chose to start our geothermometry study by selecting the
 564 thermal springs most likely to have retained their reservoir characteristics. We then applied
 565 multicomponent geothermometry and fluid reconstruction with a thermodynamic approach on this
 566 selected subset of thermal springs to get an estimate of the reservoir conditions. The approach is
 567 summarized below and detailed in Appendix B.

568 We compared outlet temperatures to the results of geothermometers for rapidly adjusting
 569 equilibriums at low temperatures, such as K-Mg and amorphous silica systems (Fournier, 1977;
 570 Fournier and Potter, 1979; Giggenbach, 1988), to assess the equilibrium state of thermal waters. The
 571 closer the outlet temperature is to the temperatures obtained with these geothermometers, the more
 572 re-equilibrated the waters are. We also used the values of the outlet temperatures as indicators of the
 573 speed of transfer between the reservoir at depth and the surface. The higher the outlet temperatures

574 are, the faster the transfer and thus, the closer to reservoir conditions the waters are likely to be. Our
 575 results show that the silica system is re-equilibrated for all springs, hence, equilibrium with silica will
 576 have to be estimated for reservoir conditions in geothermometry computations. For the K-Mg systems
 577 however, some springs are not fully re-equilibrated and may have retained some of their reservoir
 578 characteristics. For geothermometry computation, we chose to select the five thermal springs that
 579 displayed a $> 20^{\circ}\text{C}$ difference between their outlet temperatures and temperatures obtained with the
 580 K-Mg geothermometer, as well as outlet temperatures higher than 25°C : BR16, BR17, RR1, TB and
 581 OLIV2. Additionally, we selected thermal springs BR14 and BR12, whose K-Mg system are re-
 582 equilibrated, but have the highest outlet temperatures (48.0 and 42.4°C , respectively). This selection
 583 of analyses, based on outlet temperatures and geochemistry, corresponds to thermal springs found in
 584 immediate vicinity of the syenite intrusions. This supports that syenite intrusions play the role as heat
 585 sources and/or as drains channeling hydrothermal waters.

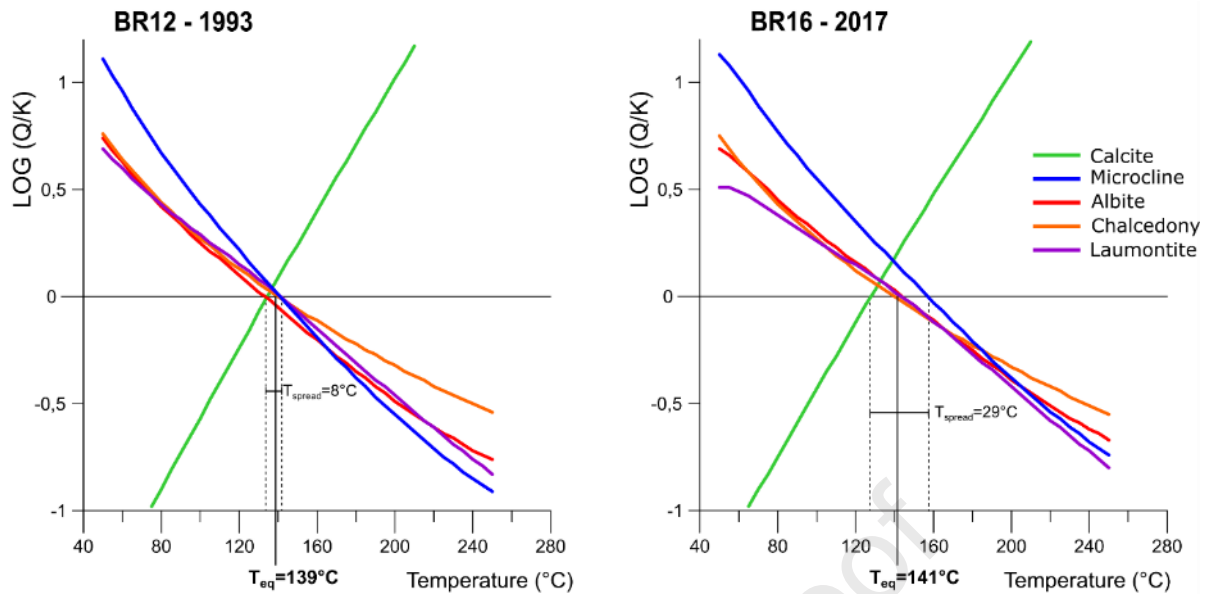
586 On these seven selected thermal springs, we performed multicomponent geothermometry using the
 587 software iGeoT (Spycher and Finsterle, 2016), which couples the parameter estimation software
 588 iTOUGH2 (Finsterle, 2007) with GeoT (Spycher et al., 2016). The principle is to find a temperature that
 589 satisfies equilibrium between waters of a known composition and chosen reservoir minerals using
 590 iterations of mass-balance/mass-action equations. Based on our previously acquired knowledge of the
 591 hydrothermal system, we also modelled CO_2 loss and silica re-equilibration in our computations. For
 592 thermal springs with several samples available (BR12, BR14, BR16, TB), the samples with the highest
 593 equilibrium temperatures obtained with iGeoT are the less diluted, and hence those that we consider
 594 as the most representative of reservoir conditions. The equilibrium temperatures obtained for this
 595 selection of thermal springs are presented in Table 5. The uncertainties correspond to the T_{spread}
 596 indicator of the iGeoT software, which gives the spread of $\log(Q/K)$ values for the selected minerals on
 597 the temperature axis. Two examples of temperature estimations with iGeoT are shown in Figure 12
 598 for the two highest temperatures obtained (springs BR12 and BR16).

599 Because the Na, K, and Ca activity ratios and the fugacity of CO_2 obtained with the model are all critical
 600 parameters in the computation of the equilibrium temperatures, it is important to compare the results
 601 of multi-equilibrium geothermometry with other geothermometers and geoindicators, such as those
 602 from Fournier and Truesdell (1973), Giggenbach, (1984), and Cioni and Marini, (2020). The details of
 603 this analysis are in section B.3 of the Supplementary material. We found that multi-equilibrium
 604 geothermometry results are in discrepancy with the other geothermometers only for one sample of
 605 spring BR14 and for three samples of spring BR16. In these samples, the equilibrium is likely disturbed
 606 by an excess amount of CO_2 entering the system, which forces us to reject the temperatures deduced
 607 from these analyses in our interpretation. For all the other samples, multi-equilibrium temperatures
 608 and compositions obtained with iGeoT are in general consistency with other geothermometers and
 609 geoindicators.

610 Table 5: Equilibrium temperatures obtained with geothermometry for selected analyses of thermal springs.

Thermal spring	BR12	BR14	BR16	BR17	RR1	OLIV2	TB
Location	Cirque of Cilaos					Cirque of Salazie	
Equilibrium temperature ($^{\circ}\text{C}$)	139	136	141	124	135	93	125
Uncertainty (T_{spread} , $^{\circ}\text{C}$)	8	13	29	20	19	27	12
Confidence	Good	Medium	Medium	Good	Good	Good	Good

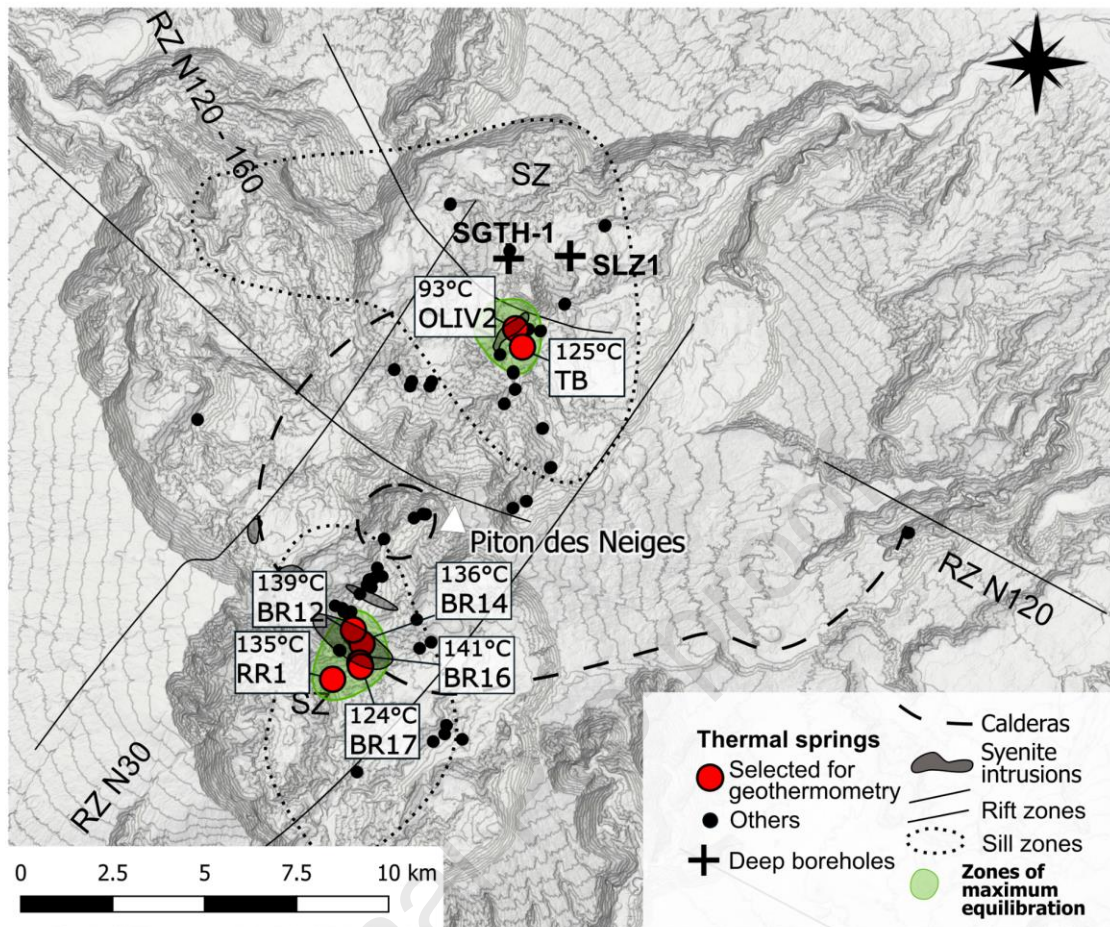
611



612

613 Figure 12: Examples of iGeoT computations on samples BR12 from Louvat and Allègre, (1997) and
 614 B nard et al., (2020), represented as saturation indices ($\log(Q/K)$) of reservoir minerals versus temperatures. Q is
 615 the computed ion activity product with iGeoT and K the thermodynamic equilibrium constant of each mineral. The
 616 clustering of $\log(Q/K)$ curves near zero gives the reservoir temperature (T_{eq}), weighted to take into account the
 617 root-mean square, the standard deviation, the mean, and the scaled $\log(Q/K)$ absolute values. The uncertainty is
 618 the spread of $\log(Q/K)$ values (T_{spread}) for all minerals on the temperature axis.

619 Our multi-equilibrium geothermometry approach yields equilibrium temperatures from $93 \pm 14^\circ\text{C}$ to
 620 $125 \pm 6^\circ\text{C}$ (weighted mean $120 \pm 5^\circ\text{C}$) for the two selected springs in the cirque of Salazie, and from
 621 $124 \pm 10^\circ\text{C}$ to $141 \pm 15^\circ\text{C}$ (weighted mean $137 \pm 3^\circ\text{C}$) for the five springs in Cilaos (Table 5). These results
 622 are in general agreement with other geothermometers applied here and in Sanjuan et al., (2001,
 623 section B.3 of the Supplementary material). This consistency of multiple geothermometers suggests
 624 that the selected hydrothermal waters have reached equilibrium in their interaction with rock at the
 625 obtained temperatures. These springs are the ones most likely to have retained reservoir
 626 characteristics due to a fast transfer between the deep reservoir and the surface. It is important to
 627 note that this equilibrium is only the last one that the hydrothermal waters may have experienced,
 628 and that higher temperature equilibria may have occurred. In consequence, our results should be
 629 considered as minimum temperatures for the two independent hydrothermal systems of Salazie and
 630 Cilaos. Keeping this in mind, more thermal springs have reached equilibrium in Cilaos than in Salazie
 631 (5 against 2), and the Cilaos hydrothermal system appears to have reached slightly higher minimum
 632 temperatures than that of Salazie (Figure 13). In terms of geothermal resource, minimum equilibrium
 633 temperatures are thus more favorable in the cirque of Cilaos than in Salazie.



634

635 Figure 13: Spatial distribution of the thermal springs showing the best evidence of preserved high-temperature
 636 equilibrium, and their multi-equilibrium temperature computed using iGeoT. relative to volcano-tectonic structures
 637 (rift zones, sill zones, calderas). The green field represents the zone of highest equilibrium temperature of water-
 638 rock interaction as defined in text. Volcano-tectonic structures (rift zones, sill zones, syenite intrusions, and
 639 calderas) are also represented.

640 4.4. Geothermal resource

641 Our work has led us to identify zones where the geothermal resource appears to be the most promising
 642 according to different criteria:

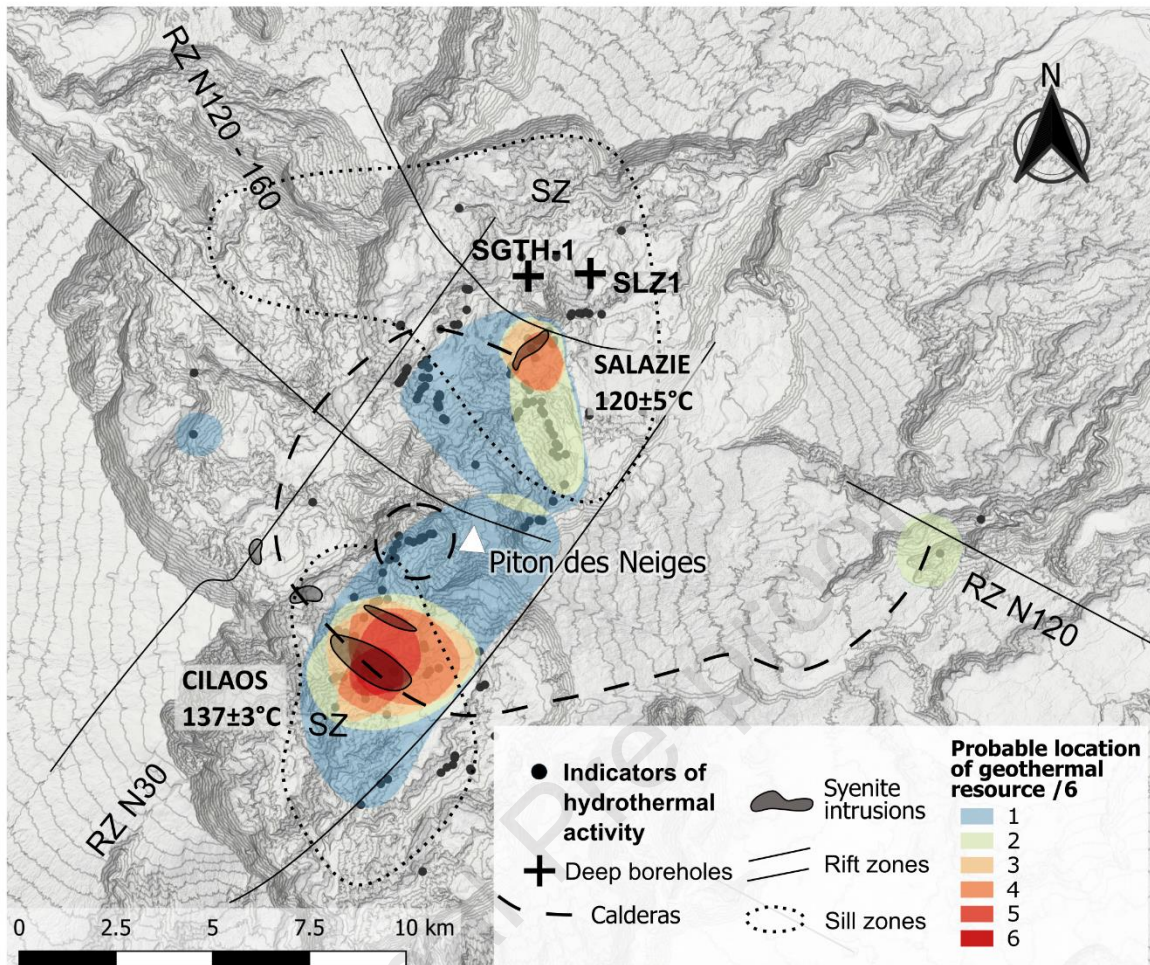
- 643 - 1. Maximum temperature and electrical conductivity in thermal springs,
- 644 - 2. Maximum degassing of CO₂,
- 645 - 3. Maximum contamination by seawater Cl, indicating that the hydrothermal system there is
 646 deeply rooted,
- 647 - 4. Compartmented reservoir which is hosted in late stage differentiated rocks that could be a
 648 heat source,
- 649 - 5. Most preserved equilibrium between thermal springs and the reservoir host rocks,
- 650 - 6. Minimum reservoir temperature of 130°C.

651 Figure 14 is a summary map superimposing all these six zones and thus giving the most probable
 652 location of the geothermal resource. Two most promising zones are highlighted, one in the cirque of
 653 Cilaos and the second is in the cirque of Salazie. This supports the observations made from the study

654 of the recharge and host rocks that there are two unconnected hydrothermal systems. These two
655 promising zones are located in the immediate surroundings of syenite intrusions, themselves located
656 at the junction of the N30°E rift zone and the supposed caldera of Piton des Neiges. This spatial
657 repartition clearly indicates that the differentiated magmas intruded in the N30°E rift zone during the
658 last activity of Piton des Neiges (150 – 27 ka, Famin et al., 2022), and to which the syenites belong,
659 represent the likeliest heat source of the two hydrothermal systems. The caldera structures and the
660 syenite intrusions could also represent preferential pathways for the ascent of hydrothermal fluids,
661 from a depth corresponding at least to the seawater level according to the slight contamination of
662 some springs by elements originating from seawater. The two hydrothermal systems appear large
663 and/or isolated enough to maintain a stable geochemical composition over several years.

664 The Cilaos zone is a more promising geothermal resource than the Salazie zone. This is partly due to
665 the higher average temperature obtained for the Cilaos reservoir ($137 \pm 3^\circ\text{C}$) compared to the Salazie
666 reservoir ($125 \pm 5^\circ\text{C}$). Additionally, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of thermal springs from Cilaos, contrary to those
667 from Salazie, indicate that the thermal waters are interact with differentiated rocks that probably
668 constitute the heat source.

669 It is worth noting that in both cirques, the reservoir temperature estimates are below the limit of a
670 conventional energy-producing geothermal exploitation, which requires water at 150°C at the head of
671 the geothermal well (Moore and Simmons, 2013). We recall, however, that our estimates are minimum
672 temperatures of water-rock interaction, for hydrothermal waters that reach the surface. It is thus likely
673 that hotter hydrothermal waters exist at depth in the edifice, but either do not reach the surface or
674 are re-equilibrated at low temperature during their ascent.



675

676 Figure 14: Superimposition of zones of: high temperature and electrical conductivity, high partial pressure of CO_2 ,
 677 high seawater contribution relative other thermal springs (meaning that waters circulated deep), strontium isotopic
 678 ratios corresponding to interaction with rocks from the late stage geological units, occurrence of thermal springs
 679 equilibrated with their reservoir host rock, and equilibrium temperatures of water-rock interaction of thermal springs
 680 superior to 130°C . The colors scale (/6) reflects how many zones are superimposed. The larger the number of
 681 superimposed zones, the most probable it is that there is a geothermal resource.

682 Conclusion

683 Our vast exploration campaign and our extended dataset in space and time of major, trace elements
 684 analyses and $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of thermal springs, rainwaters and rocks, allows us
 685 to significantly precise the location of the geothermal resource of Piton des Neiges volcano, to estimate
 686 a minimum temperature and to characterize its recharge. We show that the density of hydrothermal
 687 indicators, including thermal springs and dry sulfur, iron oxide, and carbonate deposits, is dramatically
 688 higher in the cirques of Salazie and Cilaos, along a $\text{N}30^\circ\text{E}$ axis corresponding to one of the volcanic rift
 689 zones of the edifice. Dry deposits, particularly abundant on the northern extremity of this axis, may
 690 represent the northern limit of hydrothermal activity. This may explain why previous investigation
 691 boreholes located north of Salazie encountered heat but no sufficient water yield.

692 Contrasted $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures in and Salazie and Cilaos thermal springs show that Piton
 693 des Neiges hosts in fact two unconnected hydrothermal reservoirs, with independent meteoric
 694 recharges and different water-rock interactions. For these two reservoirs, the most promising
 695 geothermal resource is centered on syenite intrusions from the late stage magmatic activity. These

696 structures appear to be the likeliest heat source of hydrothermal activity, but also a preferential
 697 pathway for the upward circulation of hot fluids. Thermal springs in the vicinity of these zones keep a
 698 constant stable isotopic composition despite annual variations in rains. The recharge is multi-year,
 699 mostly due to cyclones and tropical storms. This buffering capacity indicates large aquifer volumes
 700 compared to annual infiltrations. The two hydrothermal aquifers display a slight seawater
 701 contamination, which suggest that hot fluids rise from depths equal to or greater than sea level. Multi-
 702 equilibrium geothermometry of selected thermal springs allow us to estimate a minimum temperature
 703 of $125 \pm 5^\circ\text{C}$ for the Salazie hydrothermal system, and a slightly higher minimum temperature of 137
 704 $\pm 3^\circ\text{C}$ for Cilaos.

705 Our spatial and temporal investigation of geochemical parameters in thermal springs lead us to
 706 considerably refine the characterization of the geothermal resource compared to previous studies. In
 707 particular, intersections of major volcano-tectonic structures such as the N30°E rift zones, the trace of
 708 the supposed caldera and syenites intrusions represent preferential targets for future investigations,
 709 which should prioritize the cirque of Cilaos.

710 Our spatial and temporal visualization of the geochemical information is thus well suited for
 711 geothermal exploration for geothermal systems with thermal springs strongly affected by mixing and
 712 re-equilibration. This geochemical exploration methodology is applicable to any volcano as long as the
 713 hydrothermal system leaks to the surface.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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