

Sulfur, selenium and tellurium fractionation during magma crystallization and degassing: constraints from southwest Indian Ocean volcanism (La Réunion Island and Fani Maoré volcano, Mayotte)

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2	degassing: constraints from Southwest Indian Ocean volcanism (La Réunion
3	Island and Mayotte Fani Maoré eruption)
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24 Abstract

25 Selenium (Se) and tellurium (Te) are oxygen group elements that share chemical properties 26 with sulfur, but also show subtle differences that are useful to constrain magma genesis and 27 source. Using high-precision isotope dilution measurements, this study characterizes the 28 behavior of Se and Te, relatively to S, during the degassing and crystallization of cogenetic magmas from the southwest Indian Ocean. The study of subaerial and submarine lavas from 29 30 La Réunion Island first shows that, unlike S and Te, Se is not significantly lost during the rapid, final ascent of less differentiated magmas (MgO > 6wt%). This is because Se is retained as 31 32 selenide in primary melts despite relatively oxidized conditions. Conversely, selenium 33 degassing occurs during magma crystallization below 6 wt% MgO, at a similar rate as sulfur, 34 yielding small S/Se fractionation in the residual magma. Sulfide fractionation, which begins 35 between 5 and 4 wt% MgO, has minor effect on Se compared to Cu. Tellurium is extensively 36 outgassed from La Réunion subaerial lavas but shows a very specific behavior in submarine 37 lavas where it is retained and even accumulate near 6 wt% MgO. The very different behaviors 38 of Se and Te during magma degassing yields extremely large Se/Te variations between 39 subaerial (up to 225) and submarine (down to 1) lavas from La Réunion. The Fani Maoré 40 eruption that occurred between 2018 and 2021 offshore the island of Mayotte (Comoros 41 Archipelago) also provided the opportunity to study chalcogens degassing during the 42 emplacement of submarine lavas. The study of a pillow lava showing a radial textural zonation 43 typical of degassing-crystallization during cooling reveals that S, Se and other moderately 44 volatile elements (Mo, W, Cs) are the most depleted at intermediate depth within the pillow 45 where pipe vesicles occur, suggesting these elements escape with major volatiles. Conversely, 46 Te is depleted in the whole interior of the pillow, suggesting Te escapes through other means. 47 Assessment of pillow degassing during emplacement yields a 6.5% loss of the initial S content, 48 7.2% for Te, but only 1.6% for Se confirming the lower volatility of Se during lava 49 emplacement. Chalcogens degassing is accompanied with significant loss of W (8.9%), Mo (5.1%) and Cs (5.1%) from Fani Maoré lavas. Based on these values, the 6.5 km³ Fani Maoré 50 eruption released 1.1 – 1.5 x 10⁶ tons of S, 2300 – 2700 tons of Mo, 970 – 1130 tons of W, 194 51 52 - 339 tons of Cs, 13.3 - 16 tons of Se and 4.5 - 11.8 tons of Te during emplacement. The 53 unusually elevated S/Se ratios (16929 — 22130) of Fani Maoré lavas requires a mantle source extensively fertilized by sulfide melts, whereas the reconstructed S – Se – Te composition of 54

- La Réunion plume source is consistent with the preservation of chondritic S/Se and Se/Teratios.
- 57
- 58 Keywords : selenium, tellurium, magma degassing, magma differentiation, La Réunion,
- 59 Mayotte, Fani Maoré eruption

60 1. Introduction

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62 Selenium (Se) and tellurium (Te) are group 16 elements sharing chemical and physical properties with the element sulfur. In particular S²⁻, Se²⁻ and Te²⁻ have very similar ionic radii 63 (Shannon et al., 1976) allowing extensive substitution in reducing conditions. These elements 64 65 are the object of a growing interest because Se and Te are useful elements to constrain models 66 of Earth accretion and differentiation (Wang and Becker, 2013), upper mantle processes such partial melting and refertilization of the lithosphere (Lorand and Allard, 2010; König et al., 67 68 2012), while Se plays an important role in biogeochemical cycle (Sharma et al., 2015). 69 Selenium and tellurium are highly volatile elements but also tend to substitute for sulfur in 70 immiscible sulfide liquids. This dual nature led to different views regarding the fate Se and Te 71 during magma genesis an eruption. On the one hand, studies of mantle rocks, ultramafic 72 cumulates and lavas show that Se and Te are trapped in dense sulfides that accumulate in the 73 deep roots of volcanoes (Hertogen et al., 1980; Lissner et al., 2014; Collins et al., 2012; Yierpan 74 et al., 2019). On the other hand, studies of more-or-less degassed lavas (Yierpan et al., 2021) 75 and volcanic gas products (Greenland and Aruscavage; 1986; Zelenski et al., 2021; Rosca et al., 76 2021) show that Se and Te extensively partition into the vapor phase and are delivered to the 77 outer layers of the Earth. At the heart of this debate is the timing of sulfide saturation relative 78 to magma degassing, and the degree to which Se and Te partition into sulfide melts relative 79 to the gas phase. Edmonds et al. (2018) suggest that sulfide saturation control the metal 80 signature of volcanic gas, and its variations in arc and hotspot settings. Conversely, Zelenski et al. (2021) suggest that the trace element budget of volcanic gas is mainly determined by the 81 82 near-surface partitioning of elements between gas and silicate melt.

This paper investigates the S – Se – Te signature of La Réunion hotspot magmatic system to 83 84 constrain the nature of the hotspot source, and the role of sulfide saturation versus degassing on the composition of the erupted lavas. Our approach is based on the study of cogenetic 85 86 rocks including plutonic rocks and lavas showing a wide range of degassing (submarine and 87 subaerial) and crystallization (basalt to trachyte) extents, as well as contrasted cooling rates (lava flow and glassy tephra). We also compare the S-Se-Te signature of the low-pressure 88 89 Réunion magmas to the signature of the high-pressure sulfide saturated magmas that were 90 emitted during the 2018-2021 Fani Maoré eruption offshore the Mayotte Island (Berthod et al., 2021, 2022). The results show that the residual abundances of S, Se and Te in lavas are 91

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92 dominantly controlled by degassing processes, unlike less volatile Cu, which records the93 deeper processes of sulfide saturation.

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95 2. Geological setting

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The island of La Réunion (Indian Ocean) is the present location of the hotspot that created the 97 98 Deccan traps ca. 66 Ma ago (Fig. 1a). The oldest submarine activity is dated at 3.8 Ma 99 (Smietana, 2011), but the edifice most likely started to grow ca. 5 Myr ago (Bonneville et., 100 1988). The emergent part of the island comprises a quiescent volcano (Piton des Neiges) in 101 the NW and a basaltic shield volcano (Piton de la Fournaise) in the SE (Fig. 1b). Piton des Neiges 102 produced olivine basalts between 2.1 and 0.43 Ma ago, and increasingly differentiated lavas 103 (hawaiite, benmoreite, mugearite and trachyte) until its final activity ca. 27 ka ago (Upton and 104 Wadsworth, 1972; Gillot and Nativel, 1982; Famin et al., 2022). Piton de la Fournaise has been 105 regularly active since at least 400-450 ka (Gillot and Nativel, 1989; Merle et al., 2010) and is 106 still presently in its shield building stage. This volcano, one of the most regularly active of the 107 planet, is well known for producing olivine basalts with little compositional variability 108 (Albarède et al., 1997; Vlastelic et al., 2018).

109 Mayotte is one of the four islands of the Comoros Archipelago located between Africa and 110 Madagascar (Fig. 1a). The origin of Comoros volcanism is debated and could either be related 111 to a mantle plume or to lihosphere deformation (Hajash and Armstrong, 1972; Emerick and 112 Duncan, 1982; Class et al., 2005; Nougier et al., 1986; Famin et al., 2020; Feuillet et al., 2021; Thinon et al., 2022). The Fani Maoré submarine eruption occurred between 2018 and 2021, 113 114 50 km east of Mayotte, along the East-Mayotte submarine Volcanic Chain, on a 3300 m-deep seafloor (Fig. 1c). The eruption produced 6.5 km³ of homogeneous basanitic magmas during 115 116 three main eruption phases related to different magma paths (Berthod et al., 2021, 2022; 117 Chauvel et al. 2024).

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- 119 3. Samples
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La Réunion sample set, summarized in Table 1 and displayed in Figure 1b, is composed of: (1) twelve co-genetic samples from the Piton des Neiges differentiation suite, including three olivine-basalts, two hawaiites, two benmoreites and five trachytes. These samples covered all 124 four magmatic stages of Piton des Neiges (Upton and Wadsworth, 1972; Gillot and Nativel, 125 1982) and were previously selected and studied by Famin et al. (2016), Nauret et al. (2019), 126 and Berthod et al. (2020) to cover the four magmatic stages of Piton des Neiges volcano. All 127 these samples were collected on land, some emplaced as lava flows and others as sheet 128 intrusions; (2) three plutonic rocks with wehrlitic composition (33 - 41.5 wt% MgO)129 interpreted as magma chamber cumulates (Barrat and Bachèlery, 2019; Berthod et al., 2020); 130 (3) nine lava samples from the recent (2007-2020) activity of Piton de la Fournaise volcano 131 studied by Vlastelic et al. (2013), including eight basalts with a homogeneous MgO content 132 (6.4 to 8 wt%), and one olivine-rich lava (29.2 wt% MgO). These samples were selected to 133 cover a wide range of textures and cooling rates (crystallized lava, quenched lava, scoria, 134 pumice, Pele's hairs). (4) Ten submarine lavas, including four samples related to the early 135 history of Piton des Neiges, and six lavas related to the submarine volcanism that occurred in 136 the southeast of the island prior to Piton de la Fournaise. These samples have MgO content 137 between 5.1 and 13 wt% (Smietana et al., 2010; Smietana, 2011).

138 The Fani Maoré samples selected for this study are all fresh submarine lavas studied by 139 Berthod et al. (2021, 2022) and Chauvel et al. (2024). The samples were dredged during 140 MAYOBS (Rinnert et al., 2019) and GEOFLAMME cruises (Rinnert et al., 2021). Dredge 141 locations are reported in Table 1 and displayed in Figure 1c. Samples include: (1) eight evolved 142 basanites covering the three main phases of the 2018-2020 submarine eruption (Table 1). 143 Except for one sample with 9.9 wt% MgO, the eight samples display small compositional 144 variations (3.8 \leq MgO \leq 4.8 wt%) ascribed to magma differentiation in a large (\geq 10 km³) 145 reservoir located within the lithospheric mantle (Berthod et al., 2021). Bulk porosity decreases 146 from 30 – 45% during phase 1 to 5 – 20% during phase 3 (Verdurme et al., 2024). Sulfides droplets occur in all these samples and are most abundant in the third phase samples (Berthod 147 148 et al., 2022). (2) Nine samples regularly drilled from the glassy margin to the center of a pillow 149 lava (Fig. 2) erupted during the third phase of the 2018-2021 eruption (sample GFL-DR20-0101 150 in Berthod et al., 2022, with MgO of 4.45 wt%).

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152 4. Analytical methods

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154 Selenium and tellurium concentrations were analyzed by isotope dilution (ID) hydride 155 generation (HG) quadrupole inductively coupled plasma mass spectrometry (ICP-MS) 156 following a method modified from Yierpan et al. (2018). We first prepared ⁷⁷Se enriched (44.773 ppb Se with 94.38% ⁷⁷Se) and ¹²⁵Te enriched (5.214 ppb Te with 95.52% ¹²⁵Te) spike 157 solutions from solid sources obtained from Oak Ridge National Laboratory, USA. The 158 159 concentrations of the spike solutions were calibrated by isotope dilution against solutions prepared by diluting a 10 μ g/g certified standards from Inorganic Venture. The spikes 160 concentrations were obtained by averaging the measurements of three spike-standard 161 162 mixtures prepared around the spike/standard optimal ratio. For sample analysis, 200 mg of 163 rock powders were weighted in 15 ml Teflon vials. Immediately after, we added between 250 and 500 mg of ⁷⁷Se enriched spike and between 150 and 300 mg of ¹²⁵Te enriched spike. The 164 165 silicates were digested by adding successively 1 ml of 14M HNO₃ and 6 ml of 29M HF and 166 placing the vials on a hotplate at 90°C for 24 hours. The samples were evaporated at 70°C to 167 avoid major Se and Te volatilization (Vlastélic and Piro, 2022). The dry residues were taken in 168 3 ml of 6M HCl, heated at 90°C for 24H, and evaporated at 70°C. This step of HCl conversion 169 was repeated once. The two-step chemistry from Yierpan et al. (2018) was used to purify Se 170 and Te. The column separation was calibrated by dissolving 320 mg of a La Réunion basalt 171 doped with 500 ng of Se and Te. After HCl conversion, the sample residues were dissolved in 172 3 ml of 4M HCl, centrifuged for 5 min, before being loaded on anionic columns (polypropylene 173 Biorad filled with 5 ml AG1-X8 100-200 mesh). Most elements and Se were eluted by adding 174 successively 3 x 1 ml and 4 ml of 4M HCl, while Te was retained probably as chloro-complex. 175 Iron was eluted with 2 x 5 ml of 2M HCl – 5M HF and 2 x 3 ml of 0.4M HCl. Tellurium, with 176 minor amount of remaining Pb, was eluted with 6 ml of 0.4M HCl. After evaporation at 65°C, 177 the major element – Se fraction was dissolved in 4 ml of 0.1M HNO₃ and centrifugated before 178 being loaded on cationic columns (polypropylene Biorad filled with 5 ml AG50-X8 200-400 179 mesh). Selenium was eluted by adding successively 2 x 1 and 3ml of 0.1M HNO₃. The collected Se fraction is not highly pure but is sufficiently depleted in Fe and other transition metals for 180 181 efficient hydride generation during subsequent ICPMS analysis.

After evaporation at 85°C the fractions of Se (0.14 – 135 ng) and Te (0.04 – 24 ng) recovered from samples were taken in 6 and 3 ml of HNO₃ 1M, respectively. The resulting solutions with 0.02- 23 ppb Se and 0.013 – 8 ppb Te were mixed online with 0.3 M NaBH₄–0.1 M NaOH in a hydride generation system (HGX-200 from Teledyne Cetac Technologies). The H₂Te and H₂Se vapors were entrained by two Ar flows (carrier flow of 0.42 L/min and make up flow of 0.82 L/min) to an Agilent 7500 ICPMS. To improve ICPMS sensitivity, we used two primary pumps

increasing the vacuum of the interface. ⁷⁸Se/⁷⁷Se was measured using the reaction cell (He 188 mode) to lower polyatomic interferences from the Ar carrier gas (e.g., ⁴⁰Ar³⁸Ar⁺, ³⁶Ar⁴⁰Ar¹H⁺, 189 ³⁸Ar₂¹H⁺), while ¹²⁶Te/¹²⁵Te was measured in "no-gas" mode. Each measurement included 190 typically 100 scans, with 200 ms acquisition on each mass, and lasted 1 minute. The HNO₃ 1M 191 192 solution used to dissolve samples was repeatedly measured for background correction. 193 Instrumental mass fractionation was corrected by measuring a 5 ppb Se isotopic standard 194 (NIST SRM 3149) and a 1 ppb Te isotopic standard (NIST SRM 3156) at the beginning and/or at the end of each measurement session. Signals of ca. 130 000 CPS/ppb ⁷⁸Se and 500 000 195 CPS/ppb ¹²⁶Te were measured on the NISTs. 196

Sulfur concentration was measured by isotope dilution using a ³⁴S enriched spike (262 ppm S, 197 with 99.79% ³⁴S). The spike, initially in the form of native sulfur, was dissolved in 14M HNO₃ 198 199 and calibrated against IAEA-S-1 sulfur isotope reference material. For sample analysis, 50 mg 200 of rock powders were weighted in 15 ml Teflon vials, spiked and digested with 1 ml of 14M 201 HNO₃ and 6 ml of 29M HF at 90°C for 24 hours. After evaporation, the fluoride residue was 202 reduced by addition and evaporation of a few drops of 14M HNO₃. Unlike in the procedure 203 applied by Wang and Becker (2013), sulfur was not separated because of important S release 204 (>1 µg) from the cationic resin. Instead, the residue was taken in 5 ml of H₂O, centrifugated, 205 and ³²S/³⁴S of the supernatant was directly analyzed on an Element XR ICP-MS in high mass-206 resolution mode (m/ Δ m of 10 000). To check the accuracy of S isotope compositions, the 207 ³²S/³⁴S ratios of a subset of samples from Fani Maoré were also measured as oxides (³²S¹⁶O/³⁴S¹⁶O), using the oxygen reactive mode of an Agilent 8900 triple quadrupole ICPMS. 208 209 Instrumental mass fractionation was corrected by running IAEA-S-1 sulfur isotope reference 210 material. Sample concentration (C_{Sample}) was calculated according to Eq. 1:

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212
$$C_{Sample} = C_{Spike} \times \frac{m_{Spike}}{m_{Sample}} \times \frac{Ab_{Spike}^B}{Ab_{Sample}^B} \times \frac{R_{Spike}-R_{mes}}{R_{mes}-R_{Sample}}$$
(1)

213

Where C_{spike} is the spike concentration, m_{spike} and m_{sample} are the spike and sample masses, R_{spike}, R_{sample} and R_{mes} are the isotopic ratios of the spike, the sample and the measured sample-spike mixture, respectively. R_{sample} being not measured, we use the natural abundances of Se ant Te isotopes of the NIST standards. Ab^B is the isotopic abundance of the denominator isotope. The precision of isotopic ratios measured by ICPMS are on the order of 1-3 %. The precision of the concentrations obtained by isotope dilution is inferred from the
error magnification (M), defined as (Eq. 2) :

221

$$M = \frac{\Delta C_{Sample}}{C_{Sample}} / \frac{\Delta R_{mes}}{R_{mes}} = \frac{R_{mes}.(R_{Spike} - R_{Sample})}{(R_{Spike} - R_{mes}).(R_{mes} - R_{Sample})}$$
(2)

223

Error magnification ranges between 1.03 and 1.3 for most samples and reaches 2-3 for the 224 most depleted (olivine-rich basalt) or enriched (Réunion pumice and Pele's hairs) samples. 225 226 Average procedural blanks are 0.8 ng S, 0.2 ng Se and 0.05 ng Te. The concentrations of the 227 four reference basalts measured during this study (BHVO-2, BCR-2, BEN and BIR-1, Table 2) 228 fall within the range of the recommended values reported in the GeoRem database (Jochum 229 et al. 2005). However, our S value of BIR-1 (4.4 ppm) is much lower than the information value 230 of 70 ppm. Réunion samples that were not previously analyzed for major and trace elements 231 were analyzed conventionally at LMV by ICP-AES (major elements) and ICPMS (trace 232 elements) using the methods described in Gurioli et al. (2018) and Vlastélic et al. (2013), 233 respectively. The only difference is that the plutonic rocks were dissolved using NH₄-HF₂ 234 instead of HF-HNO₃ for ICPMS analysis to ensure complete dissolution.

235

236 5. Results

237

The concentrations of S, Se and Te of La Réunion and Fani Maoré samples are reported in
 Table 2. Major element and trace element data are reported in supplementary Table S1.

240

241 5.1. S – Se – Te budget of La Reunion plutonic rocks

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The Piton des Neiges wehrlites (SAL206 and CB150914) have 264-358 ppm S, 19-36 ppb Se and 2.7-3.1 ppb Te. They show S/Se ratios (9985-16966) higher than La Réunion lavas and mantle peridotites (S/Se<8000) but preserve similar Se/Te ratios (6.1 - 13.2) (Fig. 3). The Piton de la Fournaise wehrlite (CHI-7) has 12.7 ppm S, 9.96 ppb Se and 2.56 ppb Te and plot within the compositional field of mantle peridotites (Fig. 3) (Lorand and Alard, 2010; Wang and Becker, 2013). The S/Se (1275) and Se/Te (3.9) ratios of this sample are significantly lower than in carbonaceous chondrites. 250

251 5.2. Differentiation of La Réunion and Mayotte magmas

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Major element and trace element variations during the differentiation of La Réunion and Mayotte magmas are shown in Figure 4. The Réunion samples show four evolution steps, described in Fig. 4 caption, which are consistent with the sequence of low-pressure crystallization of La Réunion magmas (e.g., Villemant et al. 2009; Pichavant et al. 2016). Compared to La Reunion lavas, Fani Maoré lavas are characterized by lower Sc and V, in keeping with high-pressure fractionation of clinopyroxene (Berthod et al., 2021) (Fig. 4e,f). Fani Maoré lavas also have higher Th at given MgO (Fig. 4h).

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261 5.3. Evolution of S, Se and Te in La Réunion magmas

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263 La Réunion lavas are extensively depleted in sulfur (5 - 884 ppm S) compared to primitive 264 melts with up to 1800 ppm S (Bureau et al., 1998; Vigouroux et al., 2009; Di Muro et al., 2016) 265 (Fig. 5a). The least degassed submarine lavas from step 1 with 416 – 632 ppm S have already 266 lost between 65 and 77% S, while submarine lava from step 2 (119 – 146 ppm) have lost 92 % 267 of S mostly through degassing because the magmas are not yet sulfide saturated (Fig. 5a). In 268 subaerial conditions, lavas from step 1 (30 – 266 ppm S) have 36 to 95% less S than their 269 submarine counterpart, while lavas from steps 3 and 4 are even more depleted with 5 – 168 270 ppm S. Generally, sulfur concentration shows some scattering in subaerial lavas, and there is 271 only a rough trend of decreasing S with decreasing MgO.

272

In submarine environment, selenium displays a similar behavior as sulfur with relatively 273 274 uniform concentrations (74 – 131 ppb Se) in lavas from step 1 and lower concentrations (34 – 275 51 ppb Se) in lavas from step 2 (Fig. 5b). Unlike sulfur, the selenium contents of subaerial (121 276 \pm 21 ppb, n=10) and submarine lavas (104 \pm 16 ppb, n=8) from step 1 are similar. The absence 277 of subaerial degassing of Se results in a smooth trend of decreasing Se with decreasing MgO 278 in subaerial samples from Piton des Neiges, with less than 3 ppb Se in the most differentiated 279 samples (Fig. 5b). Most lavas plot within a narrow range of S/Se (2300 – 5000), close to the 280 chondritic value (2750 \pm 200), except for subaerial lavas with 4 – 8 wt% MgO where S/Se 281 decreases down to 400 due to degassing loss of S (Fig. 5d). The Cu/Se ratio is relatively uniform

(605 – 1234) in subaerial and submarine lavas from step 1, but markedly increases up to 3010
in the submarine lavas from stage 2 (Fig. 5e). This increase must reflect Se degassing because
Cu remains elevated during step 2 (Fig. 4d). The Cu/Se ratio then drops to 89 during step 3
and early step 4 due to sulfide saturation. During late step 4 (<2.5 wt% MgO), Cu/Se increases
again up to 9029 due to extensive Se degassing.

287

288 Tellurium shows more complex variations (Fig. 5c). The tellurium concentrations of submarine 289 lavas first decrease from 12.4 to 3.7 ppb as MgO decreases from 13 to 7.6 wt%, before 290 increasing abruptly until the end of step 1 (6 wt% MgO) where Te reaches 62 ppb. Then, Te 291 concentrations decrease again during stage 2, while remaining elevated (23 – 33 ppb). 292 Samples collected on land show a very different behavior, with a marked decrease of Te at 293 the end of step 1, from 2.95 to 0.38 ppb. Only sample SAL 51 seems to plot on the submarine 294 trends, possibly because this dyke sample emplaced under elevated pressure. An event of Te 295 increase above 1 ppb occurs during step 3, or early step 4, before the final decrease of Te 296 down to 0.2 ppb. The large variations of Se/Te (1 - 225) between 5 and 8 wt% MgO (Fig. 5f) 297 are mostly due to the large variations of Te between Te-depleted subaerial and Te-enriched 298 submarine lavas (Fig. 5c), while Se remains relatively uniform (Fig. 5b).

299

300 Noteworthy, a few samples with biased compositions plot outside the frame of Fig. 5 or are 301 highlighted: (1) The picritic sample (070408-1b) with 29.2% wt% MgO has low S (24 ppm), Se 302 (59 ppb) and Te (0.69 ppb) contents due to the occurrence of olivine crystals highly depleted 303 in S, Se and Te. Yet this sample has Se/Te (86) within the range of subaerial basalts. (2) 304 Compared to other subaerial samples with identical MgO content, the Pele's hairs sample (200409-6) has 80 times more Te (120 ppb) and 5 times more Se (677 ppb), but similar S 305 306 concentration (196 ppm), yielding very low S/Se (290) and low Se/Te (5.7) ratios (Fig. 5 d, f). 307 (3) Some of the trachytes from Piton des Neiges (SAL 201 and SAL 203) hosting hydrothermal 308 pyrite have anomalously elevated S (730 – 884 ppm), and to a lesser extent Se (76 – 206 ppb) 309 and Te (1.3 – 2.5 ppb) contents. The occurrence of pyrite increases S/Se up to 9600 (Fig. 5d) 310 but does not seem to drastically fractionate the Se/Te ratios of these samples (58 – 83).

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312 5.4. S – Se – Te signature of 2018-2021 Fani Maoré submarine lavas

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All Fani Maoré lavas are enriched in sulfur (1342 – 1711 ppm) compared to La Réunion lavas (Fig. 5a), consistently with the occurrence of droplets of iron sulfide (Berthod et al., 2021). Within the narrow S range, we note a trend of increasing S concentration during the 2018-2021 eruption with 1342 – 1413 ppm during phase 1 (July 2018 - May 2019), 1386 – 1509 ppm during phase 2 (May 2019 - August 2019), and 1712 ppm during phase 3b (October 2020 -January 2021). The S content (1430 ppm) of the magnesian sample DR11-0704 is consistent with other samples produced during phase 2.

- 321 Unlike sulfur, the selenium concentration of Fani Maoré lavas (66 – 81 ppb) is only slightly 322 higher than La Réunion subaerial and submarine lavas (38 – 51 ppb) with similar MgO 323 content, excluding samples hosting pyrite (Fig. 5 b). Consequently, Fani Maoré lavas display 324 very elevated S/Se ratios (16929 – 22130) (Fig. 5 d), which increase slightly with decreasing 325 MgO. The tellurium concentrations (4.4 - 13.6 ppb) (Fig. 5 c), and Se/Te ratios (5.1 - 15.6)326 (Fig. 5 f) of Fani Maoré lavas are within the range of La Réunion submarine lavas. The two 327 most evolved Fani Maoré samples (MgO <3.9 wt%) have distinctly higher Te contents (9.5 — 328 13.6 ppb) and lower Se/Te ratios (5.1 - 7.2).
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330 5.5. S – Se – Te degassing within the Fani Maoré pillow lava

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332 The studied GFL-DR20-0101 pillow lava presents five concentric layers with distinctive 333 textures (Fig. 2): In the core of the pillow (layer 1), only rare small rounded (<1 mm) vesicles 334 occur. The overlying thick layer 2 shows the occurrence of 1-3 cm pipe vesicles with radial 335 distribution. The number of pipes markedly increases in layer 3. However, closer to the surface 336 where the extent of crystallization decreases, neither vesicles nor degassing pipes occur in the layers 4, 5 and 6. Layer 5 stands out from layer 4 due to the occurrence of glass, while the 337 338 pillow rim (layer 6) is fully glassy. This textural structure is very similar to that described by 339 Berthod et al. (2022) for a pillow lava erupted earlier during the eruption. More generally, this 340 degassing-crystallization structure is typical of pillows lavas (e.g., Philpotts and Lewis, 1987; 341 Merle et al., 2005).

Variations of S, Se and Te concentrations, and S/Se and Se/Te ratios from pillow rim to pillow
core are reported in Figure 6. Sulfur and Se display similar variations, with the base of layer 2
being depleted in S (1518 – 1593 ppm) and Se (76.8 – 77.0 ppb) compared to pillow core (1671
– 1794 ppm S and 82.6-83.5 ppb Se) and external layers (1751– 1881 ppm S and 82.1-83.6 ppb

Se). Sulfur loss (13%) being more important than Se loss (7%), S/Se is lower in layer 2 (19706 - 20738) compared to pillow core (20235 - 21496) and external layers (21243 - 22641). Tellurium displays a different zonation pattern, with low and homogeneous concentrations (4.5 - 4.9 ppb) in the internal layers 1 and 2, and markedly higher concentrations (5.7 - 6.0ppb) in the external layers 3-6. Consequently, the Se/Te ratio is lower in the external layers (13.8 - 14.7) compared to the internal layers (16.3 - 17.2).

Concentration profiles are also reported for elements showing remarkable variations across the pillow. Like S and Se, Mo and W are markedly depleted (20 – 30%) in the intermediate layer 2 compared to pillow core and rim. Unlike lighter alkali, Cs is also depleted (12%) in the outer part of layer 2. Antinomy is enriched in the outermost layer of the pillow.

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357 6. Discussion

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359 6.1. Processes controlling selenium retention in and degassing from magmas

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361 The drop of sulfur solubility in oxidized melts below 100 MPa (Lesne et al., 2011; Di Muro et 362 al., 2016) explains why sulfur outgassing from submarine lavas increases with decreasing 363 water depth and is extensive in shallow or subaerial lavas. No experimental work has 364 characterized selenium degassing during magma decompression, but several studies of 365 oceanic basalts noted that, unlike sulfur, selenium is retained in seafloor lavas emplaced over 366 a wide depth range (Jenner et al., 2010; Lissner et al., 2014; Yierpan et al. 2019, 2021; Kurzawa 367 et al., 2019). This work shows that moderately differentiated (MgO> 6%) subaerial lavas from 368 La Réunion Island also preserve the same Se content as their submarine counterpart (Fig. 5b), while S is extensively lost (Fig. 5a). Jenner et al. (2010) suggested that selenium must be 369 370 stabilized in silicate melts as Se²⁻, in the same manner as sulfur is stabilized as S²⁻. The 371 stabilization mechanism involves substitution of S²⁻ and Se²⁻ for O²⁻ in the silicate liquid (Wykes 372 et al., 2015). The low volatility of Se during final magma ascent and decompression may be 373 related to the selenide-selenate transition occurring at an oxygen activity > 10³ higher than 374 the sulfide-sulfate transition. In the relatively oxidized redox conditions of undegassed basaltic 375 magmas (near the nickel nickel-oxide buffer, Moussallam et al. 2016; Pichavant et al., 2016) a 376 large fraction of sulfur occurs as sulfate not stabilized in the silicate melt and thus available 377 for degassing, while selenium still occurs as selenides retained in the silicate melt structure.

During magma differentiation, Se loss starts during step 2, where clinopyroxene and 378 379 plagioclase join olivine as major fractionating phases, and is extensive during step 4 where 380 sulfide is stable (Fig. 5). This can be explained either by (1) Se degassing and/or (2) the 381 fractionation of a sulfide phase in which Se partition. Note that selenide saturation has hardly 382 any chance to form because Selenium Content at Selenide Saturation (SeCSeS >1000 ppm) is 383 much higher than the total Se budget of magmas (Se < 0.5 ppm) (Wykes et al., 2015). The drop 384 of Se concentration in the most differentiated subaerial lavas from La Réunion Island (Se < 5 385 ppb for MgO < 2 wt%) contrasts with the subtle Se decrease reported for evolved submarine 386 lavas from convergent margins (Jenner et al., 2015; Kurzawa et al. 2019), where Se remains 387 above 70 ppb even in the most evolved samples. For La Réunion samples, the drop of Se below 388 4 wt% MgO correlates with a factor of 100 increase of Cu/Se (Fig. 5), from 89 to 9020. Selenium 389 being more volatile than Cu, but less compatible in sulfide, the Cu/Se ratio reflects the 390 contribution of Se degassing (high Cu/Se) relative to sulfide saturation (low Cu/Se). This 391 observation indicates that Se exhaustion in the most evolved Réunion lavas results from 392 extensive degassing, either during shallow magma storage or during eruption.

393

394 The question then arises as to how and why Se volatilizes during magma differentiation, while 395 it does not during magma decompression. The critical decrease of Se between 6.0 and 0.5% wt 396 MgO (Fig. 5b) despite the important decrease of the melt fraction (a factor of 6 based on Th 397 increase, Fig. 4h) requires a major drop of Se solubility. Selenium must remain in the form of 398 Se²⁻ in a differentiating melt that becomes increasingly reduced due to SO₂ degassing 399 (Moussallam et al. 2016). If Se²⁻ substitutes for O²⁻ in the melt, it is hypothesized that the Se-400 (Si, Al) bonds are weaker than the original O—(Si, Al) bonds and are preferentially broken 401 during crystal nucleation and growth, releasing Se. Kinetic might also play a major role 402 because magma storage and differentiation occur over long timescales compared to magma 403 ascent, which inevitably facilitates the diffusion and loss of volatile elements. For instance, it 404 took about 300 ka for Piton des Neiges olivine basalts to evolve into trachyte (Upton and 405 Wadsworth, 1972; Gillot and Nativel, 1982), whereas Piton de la Fournaise magmas can 406 ascend from crustal reservoirs to the surface in a matter of days (Battaglia et al., 2005). 407 Between these two end-member cases, variable Se loss is expected in the current steady-state 408 regime of Piton de la Fournaise, where magma undergo static degassing during its storage at 409 different depths before being by rapidly extruded. Interestingly, S/Se is little fractionated in the most differentiated subaerial lavas (MgO< 4 wt%). This suggests that in the reducing conditions of differentiated magmas, sulfur dominantly occurs as S²⁻ and follows the same degassing processes as Se. However, detailed inspection of the data (Fig. 5) reveals a slight decrease of S/Se in the most differentiated samples (step 4), in keeping with the high S/Se of cumulative rocks (Fig. 3) where sulfides accumulate (Upton et al., 2000).

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416 6.2. Tellurium specific behavior

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418 As for sulfur, tellurium is extensively lost from subaerial lava, with nearly no overlap between 419 Te-depleted subaerial lavas and Te-enriched submarine enriched lavas: in the Réunion-420 Mayotte data set, 18 out of the 20 subaerial samples have less than 3.5 ppb Te, whereas all 421 the submarine lavas (20) have more than 3.5 ppb Te. This feature is also generally seen in the 422 global OIB data set (Yi, 2000; Forrest et al., 2017, Yierpan et al., 2021), although some well-423 documented subaerial basalts from Hawaii (BHVO2 from Kilauea with 14.2 ppb Te) or Iceland 424 (BIR-1 from Iceland with 5.8 ppb Te) have similar Te content as their submarine counterparts (Yierpan et al., 2018). Like S and Se, Te²⁻ solubilizes in silicate melt by replacing O²⁻ (Renggli et 425 426 al, 2022). The telluride – tellurate transition being close to the sulfide – sulfate transition along 427 the oxygen fugacity scale (McPhail et al., 1995), only a fraction of Te occurs as soluble Te²⁻ in 428 the redox conditions of basaltic magmas. Thus, Te exsolution and volatilization at atmospheric 429 pressure might thus result from partial oxidation, as for sulfur.

430 During the crystallization sequence of La Réunion magmas, major degassing-induced loss of 431 Te (from 2.9 to 0.38 ppb) occurs in subaerial lavas between MgO of 8.2 and 5 wt%. 432 Remarkably, over the same MgO range where Te is extensively lost from subaerial lavas, the Te content of submarine lavas rises from 3.7 to 62 ppb Te, exceeding the highest 433 434 concentrations reported so far in submarine basalts (29.2 ppb Te in one sample from Loihi 435 seamount, Hawaii, Yi et al., 2000)). Such enrichment cannot be explained by crystallization 436 alone because the concentration of highly incompatible elements, like Th, increases by no 437 more than 50%. Another possibility is that the most elevated Te concentrations of submarine 438 basalts result from sample contamination with seawater derived Fe-Mn oxides, in which Te is 439 enriched more than any other elements relative to Earth crust (Hein et al., 2003). However, 440 we consider this possibility as unlikely because (i) the whole rock powders analyzed were 441 made from the interior of the pillow lavas (Smietana, 2011), and (ii) elements highly enriched 442 in Fe-Mn crusts, such as Mn and Co, do not show anomalous concentrations in the Te-enriched 443 sampled. Instead, the anomalous Te increase correlates with a marked increases of the 444 metalloids As (from 1 to 13.8 ppm) and Sb (from 0.1 to 1 ppm), suggesting that Te is mobilized 445 and enriched by degassing processes. We also note that, despite very different volcanic and 446 petrologic contexts, Te concentration also anomalously increase in the most differentiated 447 lavas from the Fani Maoré eruption (Fig. 5c), hence pointing to a general process. We 448 hypothesize that Te enrichment at some steps of magma evolution could result from Te 449 exsolution from deep melts, transfer and accumulation in magmas stored at shallower depth, 450 in a similar manner as CO₂ fluxing (Blundy et al., 2010). Such process is supported by the lower 451 solubility of Te in silicate melts compared to S and Se (Helmy et al., 2020). Alternatively, Te 452 accumulation could occur after eruption at the surface of thick lavas flows that undergo 453 internal differentiation and degassing. Such process has been shown to occur for Li, B and Cs 454 (Kuritani and Nakamura, 2006), and is not inconsistent with the fact that the surface of 455 submarine lavas flow is preferentially sampled during dredging. In both cases, extensive 456 degassing of Te in subaerial setting is expected to prevent Te accumulation in the lavas.

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458 6.3. Assessment of S – Se – Te degassing during the emplacement of Fani Maoré submarine 459 lavas

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461 Pillow lava degassing is a complex process due to the opposite effects of rim quenching and 462 progressive crystallization of is interior. Previous studies reported differences in S, Se and Te 463 concentrations between pillow interiors and glassy rims (Lissner 2014; Forrest et al. 2017). 464 They noted that sulfur concentration is generally lower in pillow interiors, and that the 465 difference between rim and interior is less systematic for Se, and especially for Te. The 466 compositional profile reported here for a sample from the Fani Maoré eruption provides a 467 more detailed view on pillow degassing, revealing that only the intermediate layer of the 468 pillow hosting pipes vesicles is extensively outgassed in S and Se. Pipes vesicles are the textural 469 remnants of the internal degassing of pillow lavas. They are though to form by exsolution of 470 gas from crystallizing magma onto bubbles attached to the advancing solidification front 471 (Philpotts and Lewis, 1987). Merle et al. (2005) estimated that at least 25 vol% crystallization 472 is necessary to produce a crystal framework required for generating the segregation 473 structures in pillows. In the studied differentiated Fani Maoré sample (MgO of 4.45 wt%), pipe

vesicles are not rooted deep in the pillow, which explains the degassing of the intermediate
layer mainly. Unlike S and Se, Te is depleted in both layers 1 and 2, showing a zonation (Fig. 6)
unrelated to the pipe vesicles. This suggests that Te does not behaves as major volatile
species. To explain Te degassing of layer 1 in the absence of degassing pipes, it is hypothesized
that Te is less soluble than major volatile species in silicate melts and is lost earlier by diffusion.
In support of this possibility, Te is less soluble than S and Se in silicate melts saturated in
sulfide, selenide and telluride (Helmy et al., 2020).

The compositional profile reported on Fig. 6 allows an assessment of pillow degassing during emplacement and cooling. The sample was divided into nine shells (s) corresponding to the nine analyzes. The boundary between each shell was set at equal distance between neighboring drill holes (Fig. 2). The volume of each shell (V_s) was calculated assuming a spherical geometry. The density (ρ) of the pillow was assumed to be uniform ($\rho_s=\rho_{tot}$). At the scale of the pillow, the mass fraction of element lost by degassing (ϵ) is calculated according to (Eq. 3):

- 488
- 489

$$\varepsilon_x = 1 - \frac{\sum_{s=1}^{s=9} [X]_s \times V_s \times \rho_s}{[X]_{max} \times V_{tot} \times \rho_{tot}}$$

490

491 Where [X]_s is the element concentration in shell s, and [X]_{max} is the highest concentration 492 measured in the pillow thought to be close to the pre-eruptive value. Values of ϵ are 6.5% for 493 S, 7.2% for Te, but only 1.6% for Se confirming the lower volatility of Se during lava 494 emplacement. Chalcogens degassing is accompanied with significant loss of W (ε = 8.9%), Mo 495 (ε =5.1%) and Cs (ε = 5.1%), which appear to be much more volatile than during subaerial 496 eruptions where ε is lower than 0.15% for those elements (Rubin et al., 1997). W and Mo are 497 highly refractory elements, but their oxides are known to volatilize readily at 1000°C and 1 498 atmosphere pressure in the presence of water vapor (Millner and Neugebauer, 1949), and this 499 effect is expected to increase with pressure. Thus, water exsolution from the pillow seems to 500 have played a role in mobilizing refractory elements. Between 2018 and 2020, the Fani Maoré submarine eruption produced 6.5 km³ of lava with an average vesicularity of 27% (i.e., 4.8 km³ 501 502 of dense rock) (Berthod et al., 2021). Using a dense rock density of 2500 kg/m3 (Verdurme et 503 al., 2024) and the highest element concentrations of the three eruptive phases as reference, 504 it is estimated from the ε values that the Fani Maoré eruption released 1.1 – 1.5 x 10⁶ tons of S, 2300 – 2700 tons of Mo, 970 – 1130 tons of W, 194 – 339 tons of Cs, 13.3 – 16 tons of Se
and 4.5 – 11.8 tons of Te. By comparison the Se amount released in the ocean by the Fani
Maoré eruption between 2018 and 2021 corresponds to 1% of the degassing fluxes of midocean ridges (Rubin et al., 1997).

509

510 6.4. Brief constraints on magma sources

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512 The elevated S/Se ratios of the two Piton des Neiges wehrlites confirm previous field and 513 petrological evidences (Berthod et al., 2020) that the samples formed at the bottom of a magma chamber where they accumulated dense sulfides (Fig. 3). Conversely, the S – Se – Te 514 515 signature of Piton de la Fournaise wehrlite (CHI-7) is consistent with a mantle origin. Its low 516 S/Se and Se/Te ratios relative to the Bulk Silicate Earth (BSE) (Fig. 3), together with its 517 depletion in incompatible elements (Table S1), indicate that this sample is a mantle residue 518 after melt extraction. To reconstruct the possible composition of the parental fertile peridotite, the CHI-7 melting residue is mixed with the extracted melts, best represented by 519 520 the erupted lavas. The resulting mixing curve intercept the BSE composition (Fig. 3), raising 521 the possibility that the La Réunion plume source preserved the same S/Se and Se/Te ratios as 522 the BSE and CI chondrites. This agrees with previous inferences from Highly Siderophile 523 Elements (Peters et al., 2016) and U-Th-Pb isotope systematics (Vlastélic et al., 2006) that the 524 Réunion plume samples a less differentiated mantle domain.

525 All Fani Maoré lavas including the magnesian sample (MAY04-DR11-0704) display S/Se ratios 526 (16929 — 22130) that are much higher than in worldwide MORB and OIB (S/Se < 10000). The 527 S/Se ratios of Fani Maoré lavas are also higher than the most fertile mantle peridotites (S/Se~8000) (Wang and Becker, 2013) and the two cumulative rocks from La Réunion (S/Se 528 529 10000<S/Se<14000), which are known to be enriched in sinking sulfur liquids (Upton et al., 530 2000). Fani Maoré's S – Se signature is hardly explained by magma generation processes and must reflect a source property. The most likely explanation is that the Fani Maoré lavas derive 531 from the melting of a lithospheric mantle extensively refertilized by sulfide melts. This is not 532 533 inconsistent with previous inferences that the Fani Maoré volcano, like the island of Mayotte, 534 formed by melting of a carbonated mantle source enriched in Ba and volatiles (Chauvel et al. 535 2024; Pelleter et al. 2014). Lithosphere refertilization is a common process driven by repeated

- 536 melt intrusions, but in the case of the Fani Maoré volcano, it might have reached an unusual
- 537 extent and caused this exceptionally large-volume eruption.
- 538

539 7. Conclusions

540

541 This work obtained the following results:

542 (1) Unlike sulfur, selenium degassing is not significant during the final (30 – 0.1 MPa), 543 presumably rapid ascent of moderately differentiated (MgO > 6wt%) magmas from La 544 Réunion. Conversely, selenium degassing occurs during magma differentiation below 6 wt% 545 MgO, at a similar rate as sulfur, yielding small S/Se fractionation in the residual magma. The 546 long timescales require to markedly differentiate La Réunion magmas certainly facilitates the 547 diffusion and loss of less volatile selenium. Variable Se loss is expected in the intermediate 548 situations involving both static degassing during more or less prolonged magma storage 549 followed by rapid extrusion of magma.

(2) During the evolution of La Réunion magma reservoir, the onset of sulfide saturation occurs
between ~5 and ~4 wt% MgO, while olivine just left the liquidus, and Ti-magnetite has not yet
appeared. Sulfide fractionation controls Cu/Se variations over this narrow MgO range, while
degassing dominates outside.

(3) As sulfur, tellurium is extensively lost from La Réunion subaerial lavas, whereas submarine
lavas tend to retain Te and possibility accumulate Te near 6% MgO. The contrasted behavior
of Se and Te yields extremely large Se/Te variations between subaerial (up to 225) and
submarine (down to 1.0) lavas.

(4) A pillow lava emplaced during the Fani Maoré eruption offshore Mayotte shows degassingdriven radial compositional zonation. Degassing of S, Se and other moderately volatile elements (Mo, W, Cs) is the most important at intermediate depth within the pillow where pipe vesicle occur, suggesting they escape with major volatiles. Conversely, Te is depleted in the whole interior of the pillow, suggesting Te degassing through other means.

563 (5) Assessment of pillow degassing during emplacement yields losses of 6.5% for S, 7.2% for 564 Te, but only 1.6% for Se confirming the lower volatility of Se during lava emplacement. 565 Chalcogens degassing is accompanied with significant loss of W (8.9%), Mo (5.1%) and Cs 566 (5.1%). Based on these values, the 6.5 km³ Fani Maoré eruption released $1.1 - 1.5 \times 10^6$ tons

- 567 of S, 2300 2700 tons of Mo, 970 1130 tons of W, 194 339 tons of Cs, 13.3 16 tons of Se
- 568 and 4.5 11.8 tons of Te during emplacement.
- 569 (6) The reconstructed S Se Te composition of La Réunion plume source is consistent with
- 570 the preservation of chondritic S/Se and Se/Te ratios, in agreement with previous suggestions
- 571 that the Réunion plume samples a less differentiated mantle domain.
- 572 (7) The unusually elevated S/Se ratios (16929 22130) of Fani Maoré lavas suggests that the
- 573 mantle source of this exceptional eruption has been extensively fertilized by sulfide melts.

574

575 Figure captions

576

577 Figure 1. Location maps. (a) Relief map of the southwest Indian Ocean showing the locations 578 of La Réunion and Mayotte islands. (b) Relief map of La Réunion Island showing the location 579 of the Piton des Neiges and Piton de la Fournaise volcanoes, and the location of subaerial and 580 submarine samples analyzed in this study. Closed triangles: Piton des Neiges lavas; closed 581 circles: Piton de la Fournaise lavas; closed hexagons: cumulates ; closed diamond: peridotite, 582 open circles: submarine lavas. (c) Relief map of Mayotte Island, showing the locations of the 583 samples from the Fani Maoré submarine eruption (open diamonds) that occurred between 584 2018 and 2021 50 km east of Mayotte island, along the East-Mayotte submarine Volcanic 585 Chain. All maps done with GeoMapApp (https://www.geomapapp.org/).

586

Figure 2. Cross section of GFL-DR20-0101 pillow lava emplaced during phase 3 of the Fani Maoré eruption. Drill holes are shown and numbered from pillow interior (DR20-1) to pillow rim (DR20-12). Pillow surface (DR20-Sp) is the thin external glassy layer not shown here (layer 6). The five main textural unit (1-5) described in text are shown. Because the external layers 4 and 5 are thinner than other layers, between 3 and 4 smaller drill holes were made and mixed within each layer.

593

594 Figure 3. Composition of La Réunion plutonic rocks reported in (a) S/Se and (b) Se/Te versus 595 Al₂O₃ plots. The compositional field of mantle peridotites, and the composition of 596 carbonaceous chondrites (CI) and Bulk Silicate Earth (BSE) are shown (Lorand and Alard, 2010; 597 König et al., 2012; Wang and Becker, 2013). Closed hexagons: cumulates; closed diamond: 598 peridotite. Analytical error is smaller than symbols size. Data are from Table 2 (S, Se and Te 599 concentrations) and supplementary Table S1 (Al₂O₃ concentrations). The dashed line is a 600 mixing curve calculated by mixing CHI-7 peridotite with the less degassed submarine DR6-2 601 lava sample, which is representative of the most common composition of La Réunion 602 volcanism.

603

Figure 4. Major-trace elements versus MgO plot showing the composition of La Réunion and
Fani Maoré lavas. Vertical thin lines indicate major changes in the crystallization assemblage.
The crystallization sequences of La Réunion magma involves four steps (Villemant et al. 2009;

607 Pichavant et al. 2016) : (1) primary melts (MgO \geq 9%) first crystallize olivine and spinel causing 608 an important decrease of Ni and Cr; (2) Clinopyroxene and plagioclase appear at the liquidus 609 at MgO⁻⁶ wt% as recorded by the onset of Sc, V and Ca/Al decrease. (3) Between ⁻⁵ and ⁻⁴ 610 wt% MgO, the increase of Fe and Ti indicate that olivine is no longer a liquidus phase, while 611 Ti-magnetite has not yet appeared. The abrupt drop of Cu (from 97 to 18 ppm) indicates that the onset of sulfide saturation occurs at this step. This corresponds to the first phase of sulfide 612 613 formation which is triggered by S becoming saturated in magmas (Collins et al. 2012). (4) 614 Below ~4 wt% MgO, the decrease of Fe, Ti, Ca/Al, Sc and Cu, and the increase of Th are 615 consistent with precipitation of clinopyroxene, plagioclase, magnetite and sulfides. This 616 second phase of sulfide saturation is related to the crystallization of titanomagnetite which 617 reduces the sulfur content at sulfide melt saturation (Jenner et al., 2010; Collins et al. 2012). 618 The crystallization assemblage of Fani Maoré samples (80% Cpx – 20 % Ol) is from Berthod et 619 al. (2021). Symbols are as in previous figures. Data are from Table 2 (S, Se and Te 620 concentrations) and supplementary Table S1 (major and trace element concentrations from 621 La Réunion samples). Fani Maoré data are from Berthod et al. (2022) (major elements) and 622 Chauvel et al. (2024) (trace elements). Fani Maoré trace element data not given in Chauvel et 623 al. (2024) were taken from Berthod et al. (2022).

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Figure 5. Chalcogen contents (S, Se, Te) and ratios (S/Se, Cu/Se, Se/Te) plotted against MgO content of lavas. Vertical thin lines indicate major changes in the mineral assemblage crystallizing (see figure 4). The composition of La Réunion and Fani Maoré lavas are reported using the same symbols as in previous figures. Analytical error is smaller than symbols size. Data are from Table 2 (S, Se and Te concentrations) and supplementary Table S1 (MgO and Cu concentrations from La Réunion samples). Fani Maoré data are from Chauvel et al. (2024) (Cu) and Berthod et al. (2022) (MgO and Cu).

632

633 Figure 6.

Radial compositional zonation of GFL-DR20-0101 pillow lava emplaced during the third and
last phase (October 2020 - January 2021) of the Fani Maoré eruption (Berthod et al., 2020).
Vertical dashed lines separate the major textural units shown in figure 2 and described in text.
Error bars are indicated or smaller than symbols size. Data are from Table 2 and
supplementary Table S1.

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Table 1: Sa	Table 1: Samples type and location								
Site	Volcano	Sample	Composition	Sample type	Location / eruption phase	Lat. °S	Long. °E	Elevation (m)	
Reunion	PdN subaerial	CB2150914	Wehrlite	Cumulate	LM	-21.07	55.50	876	
		SAL 206	Wehrlite	Cumulate	Phase I	-21.08	55.50	1077	
		BSUZ 2	SSB	Lava flow	Phase I	-21.00	55.42	500	
		SAL 51	SSB	Dyke in breccia	Phase I	-21.06	55.49	830	
		SAL 48	SSB	Dyke in breccia	Phase I	-21.06	55.49	830	
		RUN 008-2006	Hawaiite	Lava flow	Phase III	-21.12	55.27	220	
		RUN 038-2006	Benmoreite	Lava flow	Phase IV	-21.09	55.55	1505	
		RUN 048-2006	Benmoreite	Lava flow	Phase IV	-21.07	55.38	2020	
		SAB 1	Trachyte	Dyke	Phase IV	-21.07	55.47	1710	
		SAL 88	Trachyte	Sill in breccia	Phase IV	-21.06	55.51	858	
		SAL 200	Trachyte	Sill in breccia	Phase IV	-21.07	55.50	820	
		SAL 203	Trachyte*	Sill in breccia	Phase IV	-21.06	55.49	880	
		SAL 201	Trachyte*	Sill in breccia	Phase IV	-21.07	55.50	890	
	PdF subaerial	CHI-7	Wehrlite	Peridotite	Piton Chisny	-21.24	55.67	2363	
		REU 070402-1b	SSB	Lava flow	April 2007 eruption	-21.28	55.77	580	
		REU 070403-b	SSB	Lava flow	April 2007 eruption	-21.28	55.77	580	
		REU 070404-b	SSB	Lava flow	April 2007 eruption	-21.28	55.77	580	
		REU 070408-1b	Olivine-rich basalt	Lava flow	April 2007 eruption	-21.28	55.77	580	
		REU 150731-7	SSB	Golden pumice	July 2015 eruption	-21.22	55.71	2139	
		REU 180413-1	SSB	Lava crust	April 2018 eruption	-21.21	55.72	1920	
		REU 180403	SSB	Scoria	April 2018 eruption	-21.21	55.72	1920	
		REU 180713-1	SSB	Lava, water guenched	July 2018 eruption	-21.23	55.70	2230	
		REU 200409-6	SSB	Pele hairs	April 2020 eruption	-21.23	55.66	2269	
	PdN submarine	ERO2 DR6-2	SSB	Pillow lava	Etang Salé Ridge, 2.48 Ma	-21.35	55.24	-2000	
		ERO2 DR7-4B	SSB	Pillow lava	Etang Salé Ridge	-21.35	55.24	-1780	
		ERO2 DR7-3	SSB	Pillow lava	Etang Salé Ridge	-21.35	55.24	-1780	
		ERO2 DR7-5	SSB	Pillow lava	Etang Salé Ridge	-21.35	55.24	-1780	
	PdF submarine	ERO2 DR2-6	SSB	Pillow lava	North of PdF NE Rift Zone, 3.34 Ma	-21.09	55.86	-1700	
		GSR2-DR11-47	Mg-rich basalt	Pillow lava	North of PdF NE Rift Zone, 3.77 Ma	-21.09	55.86	-1850	
		ERO2 DR8-7	Mg-rich basalt	Pillow lava	South of PdF NE Rift Zone, 0.439 Ma	-21.20	55.91	-1443	
		ERO2 DR8-1	Mg-rich basalt	Pillow lava	South of PdF NE Rift Zone, 0.439 Ma	-21.20	55.91	-1443	
		ERO2 DR8-6	Mg-rich basalt	Pillow lava	South of PdF NE Rift Zone, 0.439 Ma	-21.20	55.91	-1443	
		ERO2 DR8-8	Mg-rich basalt	Pillow lava	South of PdF NE Rift Zone, 0.439 Ma	-21.20	55.91	-1443	
Mayotte	Fani Maoré	MAY01-DR01-05	Evolved basanite	Pillow lava	Phase 1 (July 2018 - May 2019)	-12.91	45.72	-2935	
,		MAY02-DR08-01ALF	Evolved basanite	Pillow lava	Phase 2 (May 2019 - August 2019)	-12.94	45.71	-3061	
		MAY02-DR08-0102MB	Evolved basanite	Pillow lava	Phase 2 (May 2019 - August 2019)	-12.94	45.71	-3061	
		MAY04-DR10-07	Evolved basanite	Pillow lava	Phase 1 (July 2018 - May 2019)	-12.92	45.72	-3035	
		MAY04-DR11-0704-2	Evolved basanite	Pillow lava	Phase 2 (May 2019 - August 2019)	-12.92	45.69	-3239	
		MAY04-DR12-0301	Evolved basanite	Pillow lava	Phase 1 (July 2018 - May 2019)	-12.88	45.72	-3222	
		MAY04-DR11-0704	Evolved basanite	Pillow lava	Phase 2 (May 2019 - August 2019)	-12.92	45.69	-3239	
		GFL-DR20-0101	Evolved basanite	Pillow lava	Phase 3b (October 2020 - January 2021)	-12.87	45.67	-3179	

SSB : Steady State Basalts. Most common basalts at La Réunion Island, with composition transitionnal between tholeiites and alkali basalts

PdN : Piton des Neiges. PdF : Piton de la Fournaise.

* With hydrothermal pyrite

Table 2: S, Se and Te concentrations of La Réunion and Mayotte samples													
Site	Volcano	Sample		MgO (wt%)	[S] ppm		SD	[Se] ppb		SD	[Te] ppb		SD
		BHVO-2			185	±	7 (n=10)	170	±	11 (n=20)	14.52	±	0.77 (n=14)
		BCR-2			341	±	1 (n=2)	79.6	±	0.8 (r=3)	2.84	±	0.07 (r=3)
		BE-N			336	±	5 (r=1)	71.7	±	0.9 (r=1)	1.06	±	0.01 (r=2)
		BIR-1			4.43	±	0.04 (r=3)	16.1	±	0.04 (r=2)	5.90	±	0.06 (r=1)
La Réunion	PdN subserial	CB2150014		33.0	358	+	1 0	35.0	+	1 2	2 72	+	0.04
La Reuliion	i un subacitai	SAL 206		41 5	264	÷	2.9	10.0	÷	1.2	2.72	÷	0.05
		JAL 200		41.5	204	- -	2.8	71.0		0.0	0.20		0.03
		502 Z		6.7	257	- -	0.2	122		2.4	0.50		0.02
		SAL SI		0.7	257	±	2.5	152	±	4.2	0.70	±	0.07
		SAL 48		8.2	141	±	1.1	93.4	±	3.3	2.95	±	0.04
		RUN 008-2006		4.4	20	±	0.5	57.9	±	1.5	0.25	±	0.02
		RUN 038-2006		1.4	10	±	0.2	3.0	±	0.2	0.46	±	0.02
		RUN 048-2006		2.4	40	±	0.3	11.0	±	0.4	1.00	±	0.03
		SAB 1		0.4	4.9	±	0.1	2.0	±	0.2	0.27	±	0.01
		SAL 88		0.6	-			0.7	±	0.1	0.19	±	0.02
		SAL 200		2.3	168	±	1.2	23.0	±	0.9	0.64	±	0.03
		SAL 203		2.8	730	±	5.4	75.8	±	2.5	1.30	±	0.02
		SAL 201		4.4	884	±	11	206	±	5.0	2.47	±	0.03
	PdF subaerial	CHI-7		33.4	13	±	0.1	10.0	±	0.4	2.56	±	0.12
		070402-1b		7.3	101	±	1.6	124	±	2.7	2.16	±	0.21
		070403-b		7.5	266	±	1.8	130	±	2.9	1.54	±	0.15
		070404-b		7.3	102	±	1.2	134	±	2.7	1.07	±	0.11
		070408-1b		29.2	24	±	0.3	59.3	±	1.0	0.69	±	0.09
		150731-7		6.4	245	±	3.1	131	±	2.7	0.74	±	0.01
		180413-1		6.9	199	±	2.5	134	±	2.9	0.87	±	0.09
		180403		6.9	210	±	2.8	133	±	2.2	1.53	±	0.17
		180713-1		6.9	147	±	0.6	127	±	2.7	0.56	±	0.05
		200409-6		8.0	196	+	0.8	677	+	10	120	+	6
		200103-0		0.0	150	-	0.0	0,,	-	10	120	-	Ū
	PdN submarine	DR6-2		7.6	416	±	1.7	96.7	±	2.4	3.73	±	0.23
		DR7-4B		5.1	119	±	0.7	51.0	±	2.1	22.8	±	0.79
		DR7-3		6.2	437	±	4.3	112	±	2.9	61.6	±	4.88
		DR7-5		5.5	146	±	0.8	33.8	±	1.1	33.0	±	0.63
	PdF submarine	DR2-6		6.7	165	+	10	74 3	+	18	9 54	+	0.52
	i di submanne	GSR2-DR11-47		10.5	564	+	3.0	116	+	5.4	1 17	+	0.21
		DR8-7		10.9	632	+	7.5	125	+	2.6	6.95	+	0.07
				10.9	551	+	7.5	123		2.0	12.4		0.07
				13.1	502	- -	3.8	112		2.4	2 71	±	0.55
				9.0	302	±	4.0	20.9	±	5.1	5.71	±	0.02
		DR0-0		12.0	455	Ξ	4.9	69.9	Ξ	1.0	0.04	Ξ	0.20
Mayotte	Fani Maoré	MAY01-DR01-0	5	4.77	1342	±	32	76.7	±	1.1	6.15	±	0.06
		MAY02-DR08-0	1ALF	3.77	1509	±	40	68.2	±	1.1	9.53	±	0.07
		MAY02-DR08-0	102MB	3.79	1454	±	32	69.4	±	1.0	13.6	±	0.10
		MAY04-DR10-0	7	4.18	1413	±	41	72.8	±	1.0	6.26	±	0.05
		MAY04-DR11-0	704-2	3.97	1386	±	32	66.5	±	1.2	4.43	±	0.06
		MAY04-DR12-0	301	4.52	1367	±	39	80.7	±	1.3	5.71	±	0.06
		MAY04-DR11-0	704	9.89	1430	±	25	67.3	±	1.1	5.48	±	0.06
		GFL-DR20-0101	Bulk	4 45	1711			81 5			5 22		
		drilling	distance to nillow rim		1/11			01.0			5.25		
		DR20-1	21.3 cm		179/	+	30	83 5	+	2.1	<u> 1 90</u>	+	0.05
		DR20-3	17.5 cm		1671	+	26	87 F	+	2.0	4.05	+	0.06
		DR20-5	13.5 cm		15071	÷ +	47	02.0 76 0	÷ +	17	4.73	∸ +	0.06
		DR20-7	95 cm		1510	+	37	70.8 7 T	∸ +	2.0	4.70	÷ +	0.05
		DR20-9	5.5 cm		1675	÷ +	34	77.U Q1 4	÷ +	1.6	+.+/ / Q7	∸ +	0.05
		DR20-10	3.5 cm		1760	+	<u></u>	01.4 02 7	∸ +	1.0	4.0/ E 7F	÷ +	0.06
		DR20-10	2.5 cm		1751	÷ +	35	03.2	- +	1.7	5.75	÷ +	0.06
		DR20-11	2 cm		1001	т т	35	02.1	- -	1.4	5.94		0.00
		DB30 80			1001	Ţ	20	03.0	<u>ت</u> ب	1.0	0.04 E CE		0.08
		DN20-3P	0 cm		1001	Ξ	30	05.1	Ţ	1.0	5.05	<u>+</u>	0.07

n: dissolution & chemistry duplicate r : analysis replicate (same solution)

SD : sample SD is calculated by propagating errors on isotopic ratios (see text)

MgO data are from the supplementary table S1 (La Reunion) and from Berthod et al. (2022) PdN : Piton des Neiges. PdF : Piton de la Fournaise.



F1



DR20-Sp



La Réunion

- (1) OI + Spl
- (2) OI + Cpx + Plg + Spl
- (3) Cpx + Plg + Sulf
- (4) Cpx + Plg + Mnt + Sulf
- Fani Maoré eruption (Mayotte)
- (2-3) 80% Cpx + 20% OI + Sulf
- La Réunion submarine lavas
 Piton de la Fournaise lavas
- Piton des Neiges lavas
- ♦ Fani Maoré submarine eruption



La Réunion (1) Ol + Spl

(2) OI + Cpx + Plg + Spl

(4) Cpx + Plg + Mnt + Sulf

(3) Cpx + Plg + Sulf

Fani Maoré eruption (Mayotte) (2-3) 80% Cpx + 20% OI + Sulf

Piton de la Fournaise lavas

Ο

- P.H. PdF Pele's Hairs
- Piton des Neiges lavas
- Piton des Neiges lavas with pyrite

La Reunion submarine lavas

 \diamond Mayotte submarine lavas

