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## ► To cite this version:

Carolina Rosca, Ivan Vlastélic, Maria Isabel Varas-Reus, Stephan König. Isotopic constraints on selenium degassing from basaltic magma and near-surface capture by fumarolic deposits: Implications for Se redistribution onto the Earth's surface. *Chemical Geology*, 2022, 596, pp.120796. 10.1016/j.chemgeo.2022.120796 . hal-03619382

**HAL Id: hal-03619382**

**<https://uca.hal.science/hal-03619382>**

Submitted on 14 Oct 2022

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1 Isotopic constraints on selenium degassing from basaltic magma and near-surface  
2 capture by fumarolic deposits: Implications for Se redistribution onto the Earth's surface

3

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14

## 15 **Abstract**

16 Volcanic emanations from cooling basaltic lava represent a diffuse and relatively poorly  
17 constrained source of metallic and non-metallic compounds to the Earth's surface. These  
18 compounds become incorporated in fumarolic minerals and redeposit at the surface of  
19 lava flows before entering the environmental cycle. The semi-volatile and chalcophile  
20 element selenium (Se) can be either vital or toxic to animals and humans. Thus,  
21 understanding the pathways of Se capture and relative concentrations in fumaroles is  
22 imperative for estimating their contributions to soils and aquifers in volcanically active  
23 regions, with implications for animal and human health. In this study, we report Se  
24 concentrations and Se stable isotope composition in a sample suite comprising degassed  
25 and undegassed basalts and various fumarolic deposits (thenardite, Na-K sulfate,  
26 gypsum, fluoride, and native sulfur) fed from degassing lava flows at Piton de la Fournaise  
27 volcano, Réunion Island. Erupted basaltic lavas ( $136 - 58 \text{ ng}\cdot\text{g}^{-1} \text{ Se}$ ) lost up to more than  
28 half of their pre-eruptive Se due to subaerial degassing and retained a heavier isotope  
29 composition ( $\delta^{82/76}\text{Se} = 0.11 \pm 0.17 \text{ ‰}$ , 2s.d.) compared to undegassed volcanic glass ( $138$   
30  $\text{ ng}\cdot\text{g}^{-1} \text{ Se}$  and  $\delta^{82/76}\text{Se} = -0.19 \pm 0.04 \text{ ‰}$ , 2s.e.). Fumarolic deposits that formed over a  
31 temperature range of  $\sim 800\text{-}100^\circ\text{C}$  and captured Se from the degassing lava show higher  
32 to very high Se concentrations ranging from  $0.54 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  to  $1578 \text{ }\mu\text{g}\cdot\text{g}^{-1}$  and significant Se  
33 isotope fractionation ( $\delta^{82/76}\text{Se} = +0.6$  to  $-2.08 \text{ ‰}$ ). We propose two separate models that  
34 can explain the relative concentration and Se isotope composition of the deposits: 1) A  
35 compound oxidation state-dependent Se incorporation into the various fumarolic minerals,  
36 or 2) Temperature-dependent Rayleigh condensation from a cooling gas triggered by  
37 compound saturation. The Rayleigh condensation model can entirely explain the Se  
38 concentration and isotope composition of the fumaroles and predicts that up to 80 % of  
39 the Se released from the lava is likely to be captured by precipitation to form solid phases  
40 within the lava pile, most dramatically in the coldest deposits below the sublimation  
41 temperature of  $\text{SeO}_2$  ( $< 315^\circ\text{C}$ ). In contrast, mineral-dependent isotope pathways cannot  
42 fully explain our data, including the lighter Se isotope compositions in the more oxidized  
43 compounds compared to more reduced ones. Such a mineralogical effect cannot be  
44 excluded but further investigations and experimental studies are required in order to  
45 scrutinize and invoke its role. Finally, the environmental impact of these degassing-  
46 induced secondary products will be dependent on the relative compound water solubilities

47 resulting in either Se mobilization towards aquifers or accumulation onto developing soils  
48 and plants. Such studies could prove useful for developing risk assessments in  
49 volcanically active regions on our planet, and for reaching a better understanding of the  
50 global continent-ocean Se isotope budget and signature.

51

52 **Key words:** low-temperature volcanic emissions, fumaroles; selenium, Se isotopes; Piton  
53 de la Fournaise; Réunion island

54

## 55 **1. Introduction**

56 Selenium (Se, atomic number 34) is a chalcophile, semi-volatile and redox-sensitive non-  
57 metal that naturally occurs in four valence states: -2, 0, +4 and +6 (Johnson and Bullen,  
58 2004) in low- and high-temperature environments on our planet. Over the past decade,  
59 significant progress has been made to understand the behavior of Se in terrestrial  
60 magmatic systems, especially in conjunction with its chalcophile siblings S and Te (e.g.,  
61 Jenner et al., 2010; Lissner et al., 2014; Edmonds and Mather, 2017; Yierpan et al., 2018;  
62 2019; 2020). Selenium concentrations in submarine lavas of various geotectonic settings  
63 (arc lavas, hot-spot influenced magmatism and MORB glasses) suggest a lack of Se  
64 degassing during magmatic differentiation (e.g., Jenner et al., 2010; Jenner et al., 2015;  
65 Lissner et al., 2014; Kurzawa et al., 2019; Yierpan et al., 2021). The observed volatility of  
66 S compared to the negligible volatility of Se at submarine depths enable Se concentrations  
67 and Se/S ratios to be used as estimates for the pre-eruptive S concentrations of mantle  
68 melts (e.g., Jenner et al., 2010; 2015; Reekie et al., 2019). Near surface volcanic activities,  
69 on the other hand, are associated with significant Se enrichment in eruption plumes and  
70 volcanic ashes with respect to the residual volcanic rocks, which points to pronounced  
71 subaerial Se degassing (e.g., Davidson and Powers, 1959; Crowe et al., 1987; Allard et  
72 al., 2000; Toutain et al., 2003; Floor and Román-Ross, 2012). Global volcanic Se  
73 emissions are estimated to be in the range of 100 - 1800 tons per year (e.g., Mosher and  
74 Duce, 1987; Nriagu, 1989; Mather et al., 2004), which translates to 50 - 65 % of the total  
75 atmospheric Se concentration. On average, volcanic Se gas concentrations range  
76 between 0.6 and 3  $\mu\text{g}\cdot\text{g}^{-1}$  in arc settings and between 5 and 40  $\mu\text{g}\cdot\text{g}^{-1}$  in ocean island  
77 settings (e.g., Zelenski et al., 2021). Although the anthropogenic Se emissions are  
78 sometimes calculated to dominate the atmospheric Se budget during more passive  
79 volcanic periods (Wen and Carignan, 2007), exceptions exist at regional scale, such as  
80 the island Sicily with its active stratovolcano Etna. Here, volcanic Se emissions surpass  
81 those from anthropogenic activities and the biosphere, and constitute the main point  
82 source of Se in the entire Mediterranean region (Calabrese et al., 2011). Overall, large  
83 variations in Se emission budget observed not only between contrasting volcanic settings  
84 such as subduction zones vs. OIBs (Edmonds et al., 2018), but also within one group  
85 impede accurate assessments on global volcanic Se gas emissions.

86           Advancements in mass-spectrometry with respect to Se isotope measurements  
87 over the past 10 years allow now the characterization of samples in the  $\text{ng}\cdot\text{g}^{-1}$   
88 concentration range (e.g., Kurzawa et al., 2017; Labidi et al., 2018; Varas-Reus et al.,  
89 2019; Yierpan et al., 2020). In the context of our study, Yierpan et al. (2021) showed that  
90 volcanic glasses formed at the Reykjanes ridge below  $\sim 250$  m water depth maintain a  
91 magmatic Se budget and isotope signature, while degassed basalts derived from  
92 shallower levels exhibit heavier isotope compositions accompanied with lower  
93 concentrations. This points to preferential loss of light Se isotopes in the gas phase.  
94 Supported by a Rayleigh distillation model, the isotope systematics in the study of Yierpan  
95 et al. (2021) strengthen the previous findings of magmatic Se volatilization in reduced form  
96 as SeS,  $\text{H}_2\text{Se}$ , and Se(0) (Zelenski et al., 2021) preferentially mobilizing lighter isotopes.  
97 However, further mechanisms of Se degassing from volcanic activities are scarce and  
98 relatively difficult to quantify. Poorly addressed in the surficial mass-balance are for  
99 example, the *i*) Se release from passive lava-lake degassing, *ii*) emanations during cooling  
100 of lava flows, and *iii*) fumarole activity in between main eruption events.

101           In general, volcanic degassing activities are known to release significant amounts  
102 of chalcophile elements (S, Cu), heavy metals (Tl, Pb, Hg) and metalloids in quantities  
103 that can reach potentially toxic levels to humans (e.g., Rodríguez-Mercado and  
104 Altamirano-Lozano, 2013). While the role of Se as a vital micronutrient, reproductive-,  
105 metabolic- and antiseptic functions are widely accepted (e.g., Khatiwada and Subedi,  
106 2021; Sunde, 2012), it is also well known that a narrow margin of 40 - 400  $\mu\text{g}$  intake per  
107 person per day can cause either Se deficiency or severe toxicity (Rayman, 2000).  
108 Therefore, robust constraints on the magnitude of the various near-surface Se emissions  
109 are required not only for the assessment of a more precise global inventory, but also for  
110 the health safety of the approximately 10 % of the world population living in volcanically  
111 active areas (Small and Naumann, 2001) and who are subjected to direct and continuous  
112 exposure.

113           To contribute to a better understanding of the systematics and magnitudes of  
114 volcanic Se release from cooling lava flows to the immediate environment, we investigate  
115 the Se mass fractions and Se isotope compositions of a unique suite of undegassed and  
116 degassed basaltic rocks, as well as various fumarolic products at one of the most active  
117 volcanoes in the world, Piton de la Fournaise (PdF) (Peltier et al., 2009; Roult et al., 2012),

118 Réunion Island (Fig. 1). The fumarolic precipitates are attributed to the 1977, 2007 and  
119 2009 volcanic eruptions and were formed over large temperature gradients (~800 to ~  
120 100°C) on the respective lava flows, allowing a consideration of the temperature control  
121 in the formation of these products. In detail, the following questions motivated our study:

- 122 1) What is the Se budget of fumarolic products relative to the degassed melts?
- 123 2) What are the physicochemical mechanisms and efficiency of Se transfer from  
124 volcanic gaseous compounds to surface deposits at PdF?
- 125 3) What are the most commonly formed mineralogical phases and what is their  
126 expected environmental impact?

127

## 128 **2. Geological setting and sample description**

129 Piton de la Fournaise is a basaltic shield volcano forming the southeastern part of La  
130 Réunion island located in the Indian Ocean (Fig. 1). Together with Mauritius, it represents  
131 the youngest volcanic activity on the Mascarene basin, attributed to the same mantle hot-  
132 spot that generated the Deccan Traps (Duncan et al., 1989; Lénat et al., 2001). The ca.  
133 2632 m a.s.l. high shield volcano (Liuzzo et al., 2015) is considered one of the most active  
134 intraplate volcanoes in the world today; its periodic activity being sometimes compared to  
135 Kilauea on the Hawai'i Big Island (Di Muro et al., 2014). The magmatism is dominated by  
136 basaltic lava flows with very modest gas release in intracrater fumaroles during dormant  
137 periods. Previous geochemical investigations of lavas and extruded mantle xenoliths from  
138 La Réunion island concluded that the magmatic source has changed relatively little over  
139 time (Albarède et al., 1997; Bosch et al., 2008; Pietruszka et al., 2009; Vlastélic et al.,  
140 2009). Therefore, PdF makes an excellent example for a focused investigation of Se  
141 fumarole degassing and capture following major active phases.

142 For this study, basaltic rocks and accompanying fumarolic deposits were sampled  
143 during several field campaigns between 2007 and 2011 and comprise products from the  
144 eruptions of April 1977, April 2007, and November 2009 (Fig. 1b). The April 2007 eruption  
145 lasted 29 days and produced  $210 \cdot 10^6 \text{ m}^3$  of lava at an average rate of  $84 \text{ m}^3 \cdot \text{s}^{-1}$ . It  
146 represents the most voluminous eruption of the island in at least two centuries  
147 (Staudacher et al., 2009). The November 2009 eruption was a very small event that lasted  
148 several hours and produced  $0.14 \cdot 10^6 \text{ m}^3$  of magma at an average rate of  $5.4 \text{ m}^3 \cdot \text{s}^{-1}$ . Both  
149 eruptions produced magmas with compositions transitional between alkali and tholeiitic

150 basalts, with variable amounts of olivine phenocrysts in April 2007. Pre-eruptive magma  
151 temperatures were estimated based on the MgO thermometer and ranged between 1174-  
152 1196 °C in April 2007 and ca. 1155 °C in November 2009 (Gurioli et al., 2018).

153 Lava samples include poorly phyrific and olivine-rich lavas and a glassy pumice  
154 (REU 091204-3). From these, one of the olivine-rich samples (REU 0704-051) was  
155 quenched in a water bucket. Short-lived fumarole deposits were collected at the outlet of  
156 a 15-m-deep degassing skylight, at an elevation of 100 to 150 m a.s.l., on the thickest part  
157 (ca. 68 m) of the April 2007 lava flow. This vent was repeatedly sampled while its  
158 temperature decreased from ~400 to ~300 °C. The collected deposits were previously  
159 characterized as aphthitalite ((K,Na)<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>), referred here as Na–K sulfates (Fig. 2b),  
160 and thenardite (Na<sub>2</sub>SO<sub>4</sub>). Low-temperature deposits sampled at the surface of the same  
161 lava flow were identified as Ca–Mg–Al–(Fe) hydroxy-fluorides, among which ralstonite  
162 (Na<sub>x</sub>Mg<sub>x</sub>Al<sub>2-x</sub>(F,OH)<sub>6</sub>·H<sub>2</sub>O), MgAlF<sub>5</sub>·1.5H<sub>2</sub>O, or a mixture of both are the most abundant  
163 (see Vlastélic et al., 2013). Also, a low-temperature thenardite crust (0808-292) was  
164 collected on the 2007 lava flow at ca. 100 °C. However, as this sample occurred as an  
165 incrustation it is very likely that it was initially formed at a higher temperature, dissolved  
166 into water and recrystallized at ca 100 °C (Table 1). Gypsum (Ca(SO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O) was sampled  
167 from a lava cave formed as well during the April 2007 eruption. These samples were  
168 deposited on the wall of a lava tunnel in which temperature decreased from 200 °C in  
169 2010 to 120 °C during sampling in 2011 (Fig. 2a). Servadio (2011) estimated that between  
170 2007 and 2011, the temperature of the April 2007 lava flow decreased from 1150 °C to  
171 780 °C (at a depth of 15 m). Following the 2009 volcanic activity, freshly produced  
172 thenardite powder (sample 0912-0411) was sampled in the November 2009 degassing  
173 fractures just after the cessation of the eruption (Fig. 2c). This syn-eruptive deposit formed  
174 just above a lava flow at an estimated temperature of ca. 800 °C, in agreement with the  
175 thenardite stability field (400-900 °C, Stoiber and Rose, 1974). All details are provided in  
176 Table 1. Samples investigated here were subjected to careful microscopic investigations,  
177 trace element compositions and Pb isotope ratios by Vlastélic et al. (2013) and Re-Os  
178 isotope compositions by Gannoun et al. (2015), who provide further details about the  
179 samples.

180

### 181 3. Analytical techniques

182 All measurements were performed following original methods previously established at  
183 the Isotope Geochemistry Laboratory, University of Tübingen (Kurzawa et al., 2017;  
184 Yierpan et al., 2018). In brief, sample powders equivalent to ~30 ng Se and ~3 ng Te were  
185 weighed into conventional Teflon beakers, adding similar amounts of  $^{74}\text{Se}$ - $^{77}\text{Se}$  double-  
186 spike and  $^{125}\text{Te}$  single spike, respectively. The sample-spike mixtures were digested with  
187 a 5:1 (v/v) mixture of concentrated HF to concentrated  $\text{HNO}_3$  in closed beakers on a hot-  
188 plate at 85 °C for 48 hours. Selenium and Te were purified from sample solutions by two-  
189 step ion-exchange chromatography. First, we employed an anion exchange column to  
190 remove Fe and collect purified Te. Secondly, Se was purified using a cation exchange  
191 column to remove the remaining cations.

192 Tellurium concentrations were determined by hydride generator quadrupole ICP-  
193 MS on the iCAP-Qc instrument, and Se isotope abundances and elemental  
194 concentrations were measured by hydride generation multi-collector ICP-MS on the  
195 ThermoFisher Scientific NeptunePlus instrument of the Isotope Geochemistry Laboratory,  
196 University of Tübingen. Typically, currents of 0.8 - 0.9 V were obtained on mass  $^{82}\text{Se}$   
197 during measurements (using an amplifier resistor of  $10^{11} \Omega$ ) for a  $30 \text{ ng} \cdot \text{mL}^{-1}$  Se solution,  
198 with operating parameters similar to those reported by Kurzawa et al. (2017). A signal of  
199 32,000 cps on mass  $^{126}\text{Te}$  was obtained for a Te standard solution of  $0.5 \text{ ng} \cdot \text{mL}^{-1}$ , similar  
200 to operating parameters reported by Yierpan et al. (2018). Selenium and Te  
201 concentrations were determined at similar signal intensities compared to those of  
202 standard solutions.

203 Selenium isotope values are expressed as  $\delta^{82/76}\text{Se}$  in ‰ deviations from the  
204 NIST3149 reference material throughout this study. Measurements of the inter-laboratory  
205 standard solution MH-495 relative to NIST3149 yielded an average  $\delta^{82/76}\text{Se}$  value of  $-3.25$   
206  $\pm 0.07$  ‰ (2s.d.,  $n=25$ ,  $30 \text{ ng} \cdot \text{mL}^{-1}$  solutions), indistinguishable from results of previous  
207 studies (Kurzawa et al., 2017; Labidi et al., 2018; König et al., 2019; König et al., 2021;  
208 Varas-Reus et al., 2019; Yierpan et al., 2019; 2020). External reproducibility on  $\delta^{82/76}\text{Se}$   
209 is conservatively expressed as  $\pm 0.12$  ‰ (2s.d.), based on replicate digests and  
210 measurements of different samples, among which the highly heterogeneous sample  
211 0808293 is the least reproducible ( $0.12$  ‰,  $n=3$ , 2s.d.). All samples were chemically  
212 processed and measured together with international USGS rock reference materials  
213 (Table 1). For 3 times digested basalt BCR-2 we obtained on average  $78.6 \text{ ng} \cdot \text{g}^{-1}$  Se,  $2.62$

214  $\text{ng}\cdot\text{g}^{-1}$  Te, and  $\delta^{82/76}\text{Se}_{\text{NIST3149}} = 0.12 \pm 0.08 \text{‰}$  (2s.d.). These results are indistinguishable  
215 from values obtained previously ( $76 \pm 3 \text{ ng}\cdot\text{g}^{-1}$  Se,  $2.54 \pm 0.08 \text{ ng}\cdot\text{g}^{-1}$  Te and  $\delta^{82/76}\text{Se}_{\text{NIST3149}}$   
216  $= 0.23 \pm 0.13 \text{‰}$ ,  $n=10$ , compilation by Yierpan et al. [2020]). For one digested diabase  
217 W2a, we obtained  $103 \text{ ng}\cdot\text{g}^{-1}$  Se,  $1.78 \text{ ng}\cdot\text{g}^{-1}$  Te, and  $\delta^{82/76}\text{Se}_{\text{NIST3149}} = -0.09 \pm 0.07 \text{‰}$   
218 (2s.e.), indistinguishable from previously obtained  $107 \pm 3 \text{ ng}\cdot\text{g}^{-1}$  Se,  $1.71 \pm 0.07 \text{ ng}\cdot\text{g}^{-1}$  Te  
219 and  $\delta^{82/76}\text{Se}_{\text{NIST3149}} = -0.07 \pm 0.11 \text{‰}$ ,  $n=9$ , (Yierpan et al., 2019). Long-term analytical  
220 reproducibility for both Se and Te concentration determination is  $\sim 3 \%$  r.s.d. (1 s.d.;  $n>100$ ,  
221 Yierpan et al. 2019). All blanks were below detection limit.

222

#### 223 **4. Results**

224 Along with Se elemental data and isotope ratios for basaltic and fumarolic samples (Table  
225 1), we provide Te concentrations for future reference but keep the following description  
226 and discussion focused on Se only. One basaltic glass shows the highest Se content ( $138$   
227  $\text{ng}\cdot\text{g}^{-1}$ ) compared to basalts with a crystalline matrix (poorly phyrlic to olivine-rich) that  
228 range to lower Se contents ( $136$  to  $58 \text{ ng}\cdot\text{g}^{-1}$ ). Fumarolic samples are all enriched in Se  
229 with concentrations ranging from  $0.543$  to  $1578 \mu\text{g}\cdot\text{g}^{-1}$ . In detail, Na-K sulfates show  
230 decreasing Se contents ( $1.55$  to  $0.543 \mu\text{g}\cdot\text{g}^{-1}$ ) with decreasing condensation temperatures  
231 ( $400$  to  $325 \text{ °C}$ ). The low- and high-temperature thenardite samples show respective Se  
232 contents of  $13.6$  and  $1.70 \mu\text{g}\cdot\text{g}^{-1}$ . Gypsum, representing colder deposits ( $200$  to  $120 \text{ °C}$ ),  
233 contain between  $2.58$  to  $11.3 \mu\text{g}\cdot\text{g}^{-1}$  Se, while the Ca–Mg–Al–Fe fluorides and native sulfur  
234 with lowest condensation temperatures ( $\sim 100 \text{ °C}$ ) incorporate the highest Se mass  
235 fraction ( $82.3$  to  $370 \mu\text{g}\cdot\text{g}^{-1}$  and  $1578 \mu\text{g}\cdot\text{g}^{-1}$ , respectively).

236 Basalt Te concentrations range between  $0.12$  and  $0.3 \text{ ng}\cdot\text{g}^{-1}$ , significantly lower  
237 than Atlantic and Pacific MORB values ( $\sim 1.3$  to  $6.2 \text{ ng}\cdot\text{g}^{-1}$ , Yierpan et al., 2019, Yierpan  
238 et al., 2020), and lower than most fumarolic deposits. The latter have highly variable Te  
239 concentrations, with Na-K sulfates displaying the highest Te concentrations by several  
240 orders of magnitude ( $285 - 589 \text{ ng}\cdot\text{g}^{-1}$ ). High-T thenardite has a much higher Te  
241 concentration ( $82 \text{ ng}\cdot\text{g}^{-1}$ ) than the low-T equivalent ( $0.26 \text{ ng}\cdot\text{g}^{-1}$ ), followed by fluorides with  
242 concentrations that range between  $7.8$  and  $0.10 \text{ ng}\cdot\text{g}^{-1}$ , and gypsum samples ( $1.6 - 0.44$   
243  $\text{ng}\cdot\text{g}^{-1}$ ). Tellurium concentrations for native sulfur are below the detection limit of the  
244 method.

245 Selenium concentrations in fumarolic deposits are up to four orders of magnitude  
246 higher than in basaltic lavas. The relative degree of enrichment compared to other trace  
247 elements is quantified by their enrichment factor (EF), defined as per [Eq. 1]:

$$248 \text{EF}_{X/R} = (C_X/C_R)_{\text{gas condensate}} / (C_X/C_R)_{\text{lava}} \quad [\text{Eq. 1}]$$

249  
250  
251 where  $C_x$  is the concentration of element  $x$  and  $C_R$  is the concentration of the refractory  
252 element used for normalization. Following the approach of previous studies (Vlastélic et  
253 al., 2013; Gannoun et al., 2015), Be is used for normalization because of its low volatility  
254 and low abundance in lavas, thereby highlighting the relative enrichment of volatile  
255 elements. The lava sample REU 0704-04 (paroxysmal phase of April 2007) which is most  
256 enriched in a number of volatile trace metals (Bi, Cd, In, Sn) and thus estimated to be  
257 least degassed, is taken as reference for EF calculation (Table 1 and Fig. 2 a, b). Relative  
258 to basaltic glass, all fumarolic deposits are enriched in Se in the order Na–K sulfates <  
259 thenardite (average) < gypsum (average) < Ca–Mg–Al–Fe fluorides << native sulfur. Apart  
260 from the two thenardites (one secondary and one *in situ*), which do not follow a specific  
261 pattern, a clear systematic is observed between the formation temperature of fumarolic  
262 deposits and their EF Se/Be. The coldest deposits (Ca–Mg–Al–Fe fluorides and especially  
263 native sulfur) show the highest Se enrichments, whereas deposits formed well above the  
264 sublimation temperature of  $\text{SeO}_2$  [ $\sim 315$  °C, Devillanova (2007)], are characterized by the  
265 lowest Se enrichments (Na-K sulfates).

266 The  $\delta^{82/76}\text{Se}$  of basaltic glass ( $-0.19 \pm 0.04$  ‰ 2s.e.) is within uncertainty identical  
267 to the average value previously obtained for basaltic glasses from Atlantic and Pacific  
268 MORBs ( $\delta^{82/76}\text{Se} = -0.16 \pm 0.12$  ‰, 2s.d.,  $n=31$ , Yierpan et al., 2019). Analyzed basalts  
269 with a crystalline matrix show significantly higher  $\delta^{82/76}\text{Se}$  ranging from 0.04 to 0.23 ‰  
270 ( $\pm 0.17$  ‰,  $n=4$ , 2s.d.). These compositions are within uncertainty identical to previously  
271 published data for subaerially erupted basaltic reference materials BHVO-2, BCR-2, BE-  
272 N and BIR-1a ( $\delta^{82/76}\text{Se} = 0.15$  to  $0.29 \pm 0.13$  ‰ max., 2s.d. Yierpan et al., 2020).

273 Fumarolic samples extend to both significantly lighter and heavier isotope values  
274 ( $\delta^{82/76}\text{Se} = +0.6$  to  $-2.08$  ‰, Fig. 2d) compared to undegassed volcanic glass. Na–K  
275 sulfates show decreasing  $\delta^{82/76}\text{Se}$  from  $-0.91$  to  $-1.46$  ‰ with decreasing deposition  
276 temperatures from 400 to 325 °C. A difference is also seen between the high-temperature

277 thenardite powder ( $\delta^{82/76}\text{Se} = -0.44 \pm 0.04 \text{ ‰}$ , 2s.e.) and cooler, secondary thenardite  
278 ( $\delta^{82/76}\text{Se} = -0.97 \pm 0.05 \text{ ‰}$ , 2s.e.). Gypsum samples extend the trajectory to the most  
279 negative  $\delta^{82/76}\text{Se}$  values ( $\delta^{82/76}\text{Se} = -1.37$  to  $-2.08 \text{ ‰}$ ). This is followed by an inversion  
280 towards least negative values ( $\delta^{82/76}\text{Se} = -0.55$  to  $-0.94 \text{ ‰}$ , Ca–Mg–Al–Fe fluorides) to  
281 even positive ( $\delta^{82/76}\text{Se} = +0.6 \text{ ‰}$ , native sulfur) in coldest deposits.

282 Altogether, the data show Se-enriched fumarole deposits complementing Se-  
283 depleted basalts. With decreasing fumarole depositional temperatures, a tendency  
284 towards lighter isotopic compositions is first observed. However, this trend stops with the  
285 coldest deposits (fluorides and native sulfur), which display the highest contents and  
286 relative Se enrichments and are accompanied by a significant isotope excursion up to  
287 positive  $\delta^{82/76}\text{Se}$ .

288

## 289 **5. Discussion**

290 Mineralogically distinctive fumarolic products were formed at the surface of cooling  
291 basaltic lava flows following months after the initial effusive eruption. The fumarolic solid  
292 products were formed at the fumarolic gas temperatures measured at the time of  
293 sampling. Except for one secondary thenardite, the fumaroles are associated with variable  
294 formation temperatures ranging from  $\sim 800^\circ\text{C}$  to  $\sim 100^\circ\text{C}$ . In the following, we address first,  
295 the general principles of Se degassing and estimate the emanation factor (degree to which  
296 an element is released from the melt) in different tectonic settings and for PdF volcano in  
297 more detail, to then suggest mechanisms that can explain the formations of the individual  
298 fumarole groups at our study site. Finally, the Se contribution of the fumarolic products to  
299 the immediate environment as well as potential implications for human health are  
300 addressed.

301

### 302 **5.1 Constraints on Se volatility and emanation at Piton de la Fournaise**

303 The degree of volatility of a certain element during a volcanic eruption depends on the  
304 gas-melt partition coefficients, which are in turn influenced by the element speciation,  
305 affinity for ligand formation, sulfur and chlorine content of the system (e.g., Zelenski et al.,  
306 2021). Available studies suggest that Se, as a semi-volatile element (condensation  
307 temperature,  $T_{50} \sim 428^\circ\text{C}$ , Wood et al., 2019), will be preferentially degassed as hydrides  
308 ( $\text{H}_2\text{Se}$ ), free atoms  $\text{Se}(0)$ , as well as  $\text{SeS}$  compounds in equilibrium with  $> \sim 1100^\circ\text{C}$  hot

309 silicate magma (Tetsuro, 1964; Mason et al., 2021). According to these constraints, higher  
310 gas-melt partition coefficients ( $D^{\text{gas-melt}}$ ) are expected in S-rich, reduced hotspot and rift-  
311 related volcanism compared to more oxidized arc volcanism. Indeed, calculations made  
312 by Zelenski et al. (2021) suggest higher Se  $D^{\text{gas-melt}}$  in hot-spot and rift settings (51 - 329,  
313 average of 129) compared to more oxidized arc systems (49 - 56, average of 52).  
314 Exceptions are observed, for example, for the subduction-related magmatism of Stromboli  
315 (1993-1997) and Ambrym (2007-2008), where Se concentrations in their gas plumes  
316 exceeded those of some individual intraplate volcanoes (e.g., Mason et al., 2021). From  
317 the studies of Mason et al. (2021) and Zelenski et al. (2021) it can be deduced that the  
318 principles and factors influencing Se degassing (and likely the calculation of it) at different  
319 geotectonic settings (i.e., hot-spot vs. arc- influenced) require consideration of further  
320 parameters such as the total amount of dissolved gas and lava production rate, as well as  
321 the less monitored low-temperature degassing from effusive eruptions. Strikingly, the  
322 systematics seem more straightforward for elements like Mo, Cu, In, W, Tl, which appear  
323 to be consistently more enriched in basaltic gas plumes of arc-related magmatism (Mason  
324 et al., 2021) and thus, show a clearer relationship to a specific tectonic setting.

325 Selenium isotope data corroborate the mechanisms of subaerial Se degassing  
326 elaborated above. Here we report a preferential loss of lighter isotopes in the degassed  
327 melts ( $\delta^{82/76}\text{Se} = +0.17 \text{ ‰}$ ,  $n = 4$ ) compared to undegassed glass ( $\delta^{82/76}\text{Se} = -0.19 \text{ ‰}$ ,  $n =$   
328  $1$ ), which agrees with a Se volatilization in reduced form. Similar observations have also  
329 been made through experimental studies (Kurzawa et al., 2017) and recent analyses of  
330 variously degassed volcanic samples from the Reykjanes ridge (Yierpan et al., 2021).

331 The emanation coefficient ( $\epsilon$ ) is defined as the mass fraction of Se degassed.  
332 Several strategies have been proposed to calculate  $\epsilon$  using pre-eruptive and post-eruptive  
333 lava compositions, sometimes together with normalizing parameters such as S or Pb (for  
334 a comparison see Lambert et al., 1985; Gauthier and Le Cloarec, 1998; Gauthier et al.,  
335 2000; Wieser et al., 2020). Here we adapt the equation A1 of Gauthier et al. (2000) to  
336 calculate  $\epsilon$ : Se volatilization of a gas in chemical equilibrium with the magma ( $D^{\text{gas-melt}}$ ),  
337 which also includes the theoretically determined, setting-specific fraction of total gas in  
338 the undegassed magma [Eq. 2].

339

340

$$\varepsilon_{Se} = \frac{\Phi D_{Se}^{gas-melt}}{\Phi D_{Se}^{gas-melt} + 1 - \Phi}$$

341

[Eq.2]

342

343 Where  $\Phi$  is the fraction of gas in the undegassed magma, and a  $\varepsilon_{Se}$  value of 1 would  
 344 mean complete volatilization of the element. Applying an average  $\Phi$  of 0.008 in volatile-  
 345 poor hot-spot and rift settings, and a  $\Phi$  of 0.04 for volatile-rich arc settings (i.e., 0.8 % and  
 346 4 % respectively, Bureau et al., 1999; Plank et al., 2013), together with the  $D_{Se}^{gas-melt}$   
 347 presented above, we obtain a  $\varepsilon_{Se}$  in the range of 0.29 to 0.73 for hot-spot and rift settings  
 348 and between 0.67 and 0.70 for arc settings. We can now estimate the  $\varepsilon_{Se}$  at PdF using  
 349 our measured Se concentration data (olivine corrected values in Table 1) and assuming  
 350 a primary melt (PM) composition of  $0.2 \mu\text{g}\cdot\text{g}^{-1}$  Se (Collins et al., 2012). In this case,  $\varepsilon_{Se}$  is  
 351 calculated in the range of 0.31 - 0.53 ( $= [\text{Se}_{PM} - \text{Se}_{lava}] / \text{Se}_{PM}$ ), which agrees with the  
 352 general estimate discussed above. Combining the average lava production rate (ALPR)  
 353 at PdF volcano ( $16\cdot 10^6 \text{ m}^3\cdot\text{a}^{-1}$ , dense rock equivalent, Roult et al., 2012) and the typical  
 354 lava density ( $\rho = 2700 \text{ kg}\cdot\text{m}^{-3}$ ) yields that between 2.7 and 4.6 tons of Se potentially  
 355 volatilize every year at this site ( $= \text{Se}_{PM} \cdot \text{ALPR} \cdot \rho \cdot \varepsilon_{Se}$ ). Deviations from this range are  
 356 expected during larger volcanic eruptions. As such, by using the dense rock equivalent  
 357 volume of degassing melt of  $58\cdot 10^6 \text{ m}^3$  ( $V^{2007}$ ) from Di Muro et al. (2014), yields that the  
 358 high-rate eruption of April 2007 emitted between 10 and 17 tons of gaseous Se ( $= \text{Se}_{PM} \cdot$   
 359  $V^{2007} \cdot \rho \cdot \varepsilon_{Se}$ ). These values are between 100 and 1000 times higher than during the 2009  
 360 activity, which erupted at a lower rate. We conclude that significant amounts of Se escape  
 361 from the Earth's interior during volcanic eruptions as component in aerosols ( $> 1000^\circ$ ) and  
 362 fumarolic products ( $\sim 800 - 100^\circ \text{C}$ ). In this study we assess the mechanism of Se  
 363 emanation and isotope fractionation during basaltic lava cooling which leads to the  
 364 formation of fumaroles.

365

## 366 **5.2 Selenium capture in fumarolic deposits – a mineralogical control?**

367 Fumarole minerals form by condensation through the interaction of hot gases with the cold  
 368 atmosphere or by gas-rock interactions (e.g., Stoiber and Rose, 1974; Getahun et al.,  
 369 1996). Initially degassed Se species are most likely to be reduced, however rapid

370 convergence with the cold atmosphere is expected to trigger a series of oxidative  
371 reactions. During these processes, hydrogen selenide ( $\text{H}_2\text{Se}$ ) can be oxidized to  
372 elemental Se ( $\text{Se}^0$ ),  $\text{SeO}_2$ , and further to  $\text{SeO}_3$ , accompanied by saturation of the  
373 compounds favoring precipitation (Wen and Carignan, 2007). Therefore, Se concentration  
374 and isotopic composition in fumarolic deposits can reflect the ability of gaseous Se species  
375 to enter the various crystal networks of the minerals. Possible mineral-specific reactions  
376 include  $\text{Se}^0$  substitution for  $\text{S}^0$  in native sulfur as the ionic radii and electronegativities of  
377 the two elements are very similar. The same applies for  $\text{Se}^{-2}$  substitution for  $\text{S}^{-2}$  (Shannon,  
378 1976). However, in other oxidation states these parameters change substantially, and  
379  $\text{Se}^{4+}$  substitution for  $\text{S}^{4+}$  is unlikely. Condensation of other compounds like  $\text{SeF}_4$  (102°C  
380 boiling point) might also occur, and although Se partitioning into S-free fluoride minerals  
381 is rather poorly constrained, it must involve chemical reactions either in the gas phase (as  
382  $\text{SeF}_4$  is a volatile compound) or at the surface of the precipitated mineral. In a recent  
383 comprehensive study of fumarole deposits from Fogo volcano, Cape Verde, Silva et al.  
384 (2019) suggested that  $\text{SeF}_{4(g)}$  condensation can be facilitated due to  $\text{Se}^{4+}$  sequestration  
385 into oxygen pyramids.

386 It is thus plausible that the chemical processes (such as oxidation) involving Se  
387 incorporation into thenardite, sulfates and potentially gypsum can be different than those  
388 governing Se capture into fluoride and elemental sulfur minerals. In the following model,  
389 we assume that: *i*) each mineral is in equilibrium with a gas with a constant isotopic  
390 composition but at different temperatures reflecting the formation temperature of that  
391 mineral. Isotopic effects imparted on the gas by a given mineral are assumed to not  
392 influence other minerals, which formed from independent gas aliquots; *ii*) all mineral  
393 phases represent individual mineral end-members in equilibrium with the gas, meaning  
394 that individual fractionation factors ( $\alpha$ ) will be at play. As a starting point, we assume that  
395 *i*) the initial  $\delta^{82/76}\text{Se}$  of the gas is relatively close to the composition of the hottest sample  
396 ( $\sim 800^\circ\text{C}$  thenardite,  $-0.44\text{‰}$ ), and that *ii*) condensation of Se is very small, with no effect  
397 on the Se isotope composition of the gas. The observed isotopic variation in fumaroles is  
398 thus governed primarily by the Se oxidation state in the respective minerals: +6 in sulfates  
399 (including thenardite and gypsum), +4 in fluorides, and 0 in native sulfur.

400 Fig. 3 shows expected or calculated individual linear relationships between the  
401 isotopic composition of the mineral and that of the gas ( $\Delta^{82/76}\text{Se}$ ), in accordance with the

402 general theory of isotopic fractionation between two phases. Namely,  $\Delta^{82/76}\text{Se}$  (Phase A –  
403 Phase B) varies linearly with  $1/T$  at low temperature and  $1/T^2$  at high temperature [Eq. 3]:

404  
405 
$$\Delta^{82/76}\text{Se}_{\text{mineral-gas}} = \delta^{82/76}\text{Se}_{\text{mineral}} - \delta^{82/76}\text{Se}_{\text{gas}} = 1000 \ln \alpha_{\text{mineral-gas}} = A+B / T^2 \quad [\text{Eq. 3}]$$

406  
407 Alternatively, one could address the “mineral-gas” relationship as “oxidized-reduced”  
408 fractions. The  $\Delta^{82/76}\text{Se}_{\text{mineral-gas}}$  variations observed for the mineral group consisting of the  
409 most oxidized Se compounds,  $\text{Se}^{\text{VI}}$  (thenardite, sulfates and gypsum) most likely reflect  
410 the increase of mineral-gas isotope fractionation with decreasing T. Additionally, but not  
411 necessarily, a kinetic effect could also be at play during the formation of the hotter phases.  
412 This hypothesis is suggested based on the observed linear relationship between  $\delta^{82/76}\text{Se}$   
413 and temperature. The combination between significantly higher Se concentrations and Se  
414 present as  $\text{Se}^{\text{IV}}$  in fluorides can in turn be explained through a rapid condensation from  
415 gaseous  $\text{SeO}_2$ . The smaller  $\Delta^{82/76}\text{Se}_{\text{mineral-gas}}$  of fluorides compared to the more oxidized  
416 end-members sulfates and gypsum also points at the dominance of  $\text{SeO}_2$  and likely  $\text{Se}^0$   
417 species in the gas phase (Fig. 3). The latter is required to explain the extremely high Se  
418 concentrations (up to 1.6 wt. %) in native sulfur, where a  $\text{Se}^0 - \text{S}^0$  substitution, and thus  
419 the simplest and most direct reaction likely facilitates the enrichment. In support of this,  
420 the presence of  $\text{Se}^0$  in volcanic gas has been previously observed (Bichler et al., 1995).

421 Altogether, the preferential incorporation of variably oxidized Se species into the  
422 crystal lattice of individual fumarolic minerals could have resulted in the observed isotope  
423 variations. At this stage, we have to emphasize that little work has been done on oxidation  
424 reactions, and mostly in aqueous solutions (e.g., Johnson and Beard, 1999; Johnson,  
425 2004; Wasserman et al., 2021), and none at all exist for gas-phase reactions. The situation  
426 becomes even more uncertain if a potential kinetic effect is coupled to one or several  
427 oxidation reaction(s). Although simple kinetic effects tend to produce light products, some  
428 of the individual oxidation steps within the overall reaction could, if they are able to attain  
429 equilibrium, result in isotopically heavy products. We conclude that *i*) the observed light  
430 Se isotopic composition of the sulfate minerals could reflect a kinetic isotope effect relate  
431 to oxidation, and that *ii*) experimental studies could contribute to a clearer understanding  
432 of the isotope signatures of variably oxidized fumarolic precipitates.

433

### 434 **5.3 Temperature-dependent Rayleigh condensation**

435 The formation of individual fumarole minerals at certain temperatures as the lava and  
436 gases cool down invites us to test the hypothesis of a temperature-dependent  
437 condensation process and potential Se isotope fractionation due to this effect. This model  
438 assumes that instead of the oxidation state, the relative near-surface stability of Se  
439 compounds (as a function of temperature) plays a decisive role in the Se partitioning into  
440 the fumarolic mineral phases. The condensation hypothesis can be independently  
441 evaluated with Se stable isotopes. Although condensation can involve several reactions  
442 between multiphase gas and solid reservoirs, we consider a single isotopic exchange  
443 reaction accounting for the bulk condensation process. The corresponding coefficient of  
444 isotopic fractionation for this reaction, is defined as Eq. 4.

445

$$446 \alpha_{s/g} = ({}^{82/76}\text{Se})_{(s)} / ({}^{82/76}\text{Se})_{(g)} \quad [\text{Eq. 4}]$$

447

448 for both equilibrium and kinetic isotope fractionation where (s) and (g) are for the bulk solid  
449 and bulk gas, respectively. Here, the temperature dependence of Se isotopes suggest  
450 that equilibrium fractionation is the dominant process. This does not exclude the fact that  
451 kinetic fractionation can be temperature dependent too, however gaseous diffusion or  
452 evaporative effects tend to show a lack of temperature dependence (e.g., Schauble 2004).  
453 In a similar manner as for the mineral-dependent model presented above, we assume that  
454 all deposits derive from fractional condensation of the same high-temperature parental  
455 gas, with an isotope composition close to the hottest thenardite ( $\delta^{82/76}\text{Se} = -0.44 \text{‰}$ ). The  
456 general differential equation for a Rayleigh process writes (Criss et al., 1999; Eq. 5):

457

$$458 d\ln({}^{82/76}\text{Se})_g = (\alpha_{s/g} - 1) d\ln f \quad [\text{Eq. 5}]$$

459

460 where  $({}^{82/76}\text{Se})_g$  is the isotope ratio of the gas and  $f$  is the mass fraction of Se remaining  
461 in the gas phase. When  $\alpha_{s/g}$  is constant, the well-known solution of [Eq. 5] is:

462

$$463 ({}^{82/76}\text{Se})_g = ({}^{82/76}\text{Se})_i \cdot f^{(\alpha_{s/g} - 1)} \quad [\text{Eq. 6}]$$

464

465 where ( $^{82/76}\text{Se}$ )<sub>i</sub> is the initial ratio of the gas. According to Eq. 6, both gas and condensate  
 466  $^{82}\text{Se}/^{76}\text{Se}$  ratios will evolve in the same direction during the condensation process,  
 467 continuously increasing if  $\alpha_{s/g} < 1$  and continuously decreasing if  $\alpha_{s/g} > 1$ . Consequently,  
 468 no constant  $\alpha_{s/g}$  matches the  $^{82/76}\text{Se}$  evolution of the deposits. Conversely, increasing the  
 469 magnitude of isotopic fractionation between the solid and gas phases as condensation  
 470 proceeds can reproduce the initial decrease and subsequent increase of  $^{82/76}\text{Se}$ . This is  
 471 shown on the basis of two numerical integrations of Eq. 5 assuming a linear and a non-  
 472 linear relationship between  $f$  and  $\alpha$  as a function of  $T$  (Fig. 4 a and b). For this, we used  
 473 an iterative method where the value of  $f$  is changed incrementally. This means that for  
 474 each value of  $f$  we calculate the relevant value of  $\alpha$  (using the chosen  $\alpha$  vs.  $f$  equation  
 475 given in figure caption), the incremental change  $d\ln(f)$  and, using the differential Eq. 5, the  
 476 incremental change  $d\ln(^{82}\text{Se}/^{76}\text{Se})$ . At each step,  $d\ln(^{82}\text{Se}/^{76}\text{Se})$  is added to the preceding  
 477 value of  $\ln(^{82}\text{Se}/^{76}\text{Se})$ . The calculation is repeated successively from  $f=1$  to  $f=0$  to produce  
 478 the curves shown in Fig. 4. In both scenarios, the initial gas fractionates solid deposits  
 479 enriched in the lighter Se isotope ( $\alpha_{s/g} < 1$ ). The size of isotopic fractionation is very small  
 480 at high temperature but increases as temperature decreases, so that the gas accordingly  
 481 evolves toward higher  $^{82/76}\text{Se}$ , only subtly at first, but more rapidly as condensation  
 482 proceeds. At the point where the gas  $^{82/76}\text{Se}$  rises faster than the difference between the  
 483 two phases ( $\Delta^{82/76}\text{Se} = 1000\ln\alpha_{s/g}$ ), the evolution of the condensates trends reverse (Fig.  
 484 4 a and b). In the absence of constraints on how  $\alpha_{s/g}$  varies with  $f$ , the linear model (Fig.  
 485 4a) predicts that decreasing  $\alpha_{s/g}$  linearly from 0.9995 at  $f=1$  to 0.9940 at  $f=0$  ( $\alpha_{s/g} = 0.0055 \cdot f$   
 486  $+ 0.9940$ ) matches the measured data, and yields the lightest  $^{82/76}\text{Se}$  ratios of gypsum at  
 487 ca. 50 % Se condensation. The second model in Fig. 4b shows that a non-linear decrease  
 488 of  $\alpha$  from 0.9995 at  $f=1$  to 0.9970 at  $f=0$ , following the relationship  $\alpha_{s/g} = 0.0025 \cdot f^5 + 0.9970$   
 489 offers the best fit for the data, yielding the  $\delta^{82/76}\text{Se}$  minimum for the gypsum (-2 ‰) at ca.  
 490 30% Se condensation. The low Se concentrations in the minerals deposited between 800  
 491 and  $\sim 300^\circ\text{C}$  suggest little change in  $f$  over this temperature segment, whereas at lower  $T$ ,  
 492 small changes in  $T$  trigger rapid loss of Se and therefore a greater change in  $f$  and  $\alpha$  as a  
 493 function of  $T$ . We therefore suggest that the non-linear model (Fig. 4b) likely represents a  
 494 better reflection of the reality. Both models explain the trajectory towards positive  $\delta^{82/76}\text{Se}$   
 495 values in the late-stage deposits ( $< 315^\circ\text{C}$ ) where isotopic fractionation between gas and  
 496 solid increases with decreasing temperature. In detail, this temperature dependency is

497 also observed at a smaller scale within the Na-K sulfate samples suite, which shows  
498 decreasing  $\delta^{82/76}\text{Se}$  (from -0.91 to -1.46 ‰) and increasing Se content (from 0.54 to 1.5  
499  $\mu\text{g}\cdot\text{g}^{-1}$ ) as temperatures drop from > 400 to 325°C.

500 The sublimation temperature of  $\text{SeO}_2$  below ~315°C (Tetsuro, 1964) likely plays a  
501 critical role in explaining the highest Se concentrations and thus near-quantitative  
502 precipitation in the coldest products (fluorides and elementary sulfur, Fig. 4). In addition,  
503 the return to less fractionated Se isotopes and even towards positive  $\delta^{82/76}\text{Se}$  may also  
504 be used in favor of a condensation reaction. Further support for this model comes from  
505 the results of an earlier experiment deploying a silica tube emplaced in a crack on the roof  
506 of a lava tunnel of Piton de la Fournaise (see Toutain et al., 1990). This experiment  
507 allowed the investigation of Se condensation merely as a function of temperature as the  
508 amount of oxygen is expected to remain relatively constant along the tube. The data of  
509 Toutain et al. (1990) are plotted together with our fumarole compositions in Fig. 2c and  
510 show an almost logarithmic increase in Se concentration with a gradual decrease in  
511 temperature, namely the highest Se condensation in the coldest products below ~315°C.  
512 Importantly, the chemical compositions of the silica-tube sublimates differ from the natural  
513 fumarolic products investigated in this study, potentially hinting at a rather minor  
514 importance of the resulting mineral phases *per se*. Nevertheless, the SEM images of the  
515 sublimates in the Toutain et al. (1990) study revealed the occurrence of  $\text{SeO}_2$ -rich  
516 minerals such as chalcocite ( $\text{Cu}_2\text{Se}$ ) at the cold end of the silica tube, which  
517 was not found as individual cold (< 315°C) fumarolic deposits in this study.

518

#### 519 **5.4 A brief comparison between the two suggested models**

520 One important criterion of the mineralogical control model, which is based on the oxidation  
521 state of the individual Se compounds, is the assumption that the Se isotope composition  
522 of the gas does not change during cooling. Thus, the amount of Se trapped in fumarole  
523 deposits would need to be extremely small. While these conditions may be met for the  
524 sulfates, thenardite and gypsum as their low Se content suggests little depletion and  
525 fractionation of the gas, the opposite is observed for the colder, significantly more Se  
526 enriched deposits. Also, until further experimental observations and investigations of  
527 natural fumarolic products at other sites are available, the contrasting picture of lighter  
528 isotope composition in the more oxidized mineral species and heavier in the more reduced

529 compounds remains unexplained. The proposed Rayleigh condensation models, on the  
530 other hand, provide a very plausible explanation for the Se isotope signatures of  
531 degassing lava and complementary fumarole deposits as a function of decreasing  
532 temperature ( $\leq 800 - 100$  °C). By analogy, a similar condensation model explains the Zn  
533 isotope data at Merapi volcano (Toutain et al., 2008). It also clarifies the most dramatic  
534 Se concentrations of the deposits formed  $< 315$  °C in agreement with experimental  
535 determination of  $\text{SeO}_2$  sublimation temperature. According to this model, up to 80 % of  
536 Se emanated by the cooling lava will be re-captured onto the Earth's surface by  
537 condensation (Fig. 4). While this model does not rule out mineral-dependent reactions, it  
538 also shows that they are not necessarily required to explain the data. In fact, contrary to  
539 the mineral model, the temperature-dependent model does not leave any unexplained  
540 observations. Based on our investigation, we infer that the effect of non-linear  
541 temperature-dependent condensation is likely the primary cause of the observed Se  
542 fumarolic signature. However, at this point we do not rule out a modest mineralogical  
543 control that does not disturb the observed temperature trend.

544

### 545 **5.5 Environmental relevance of volcanic fumarole precipitates**

546 The environmental significance of the fumaroles is determined by the mobility, i.e.,  
547 solubility and bioavailability or accumulation of the Se-bearing compounds. Further  
548 geochemical processes, i.e., complexation and oxidation, change in pH conditions, are  
549 also expected to influence the Se behavior in developing soils and surrounding aquifers.  
550 Results of experimental studies conducted under controlled conditions have shown that  
551 selenite ( $\text{SeO}_3^{2-}$ ) is more stable in neutral to slightly acidic soils and under less oxic  
552 conditions (e.g., temperate climate), while selenate ( $\text{SeO}_4^{2-}$ ) will be favored by oxic and  
553 alkaline conditions (e.g., tropical climate; Balistrieri and Chao, 1990; Fordyce, 2005;  
554 Wijnja and Schulthess, 2000; Wu et al., 2000; Peak and Sparks, 2002). Selenate is  
555 extremely susceptible to leaching and is considered bioavailable to plants and food crops  
556 to a greater extent than selenite (Bitterli et al., 2010). At the same time,  $\text{SeO}_3^{2-}$  capture  
557 and retention has been observed to occur onto developing soils, especially in the  
558 presence of poorly crystalline Al-Fe phases (e.g., John et al., 1976; Nakamaru et al., 2005,  
559 2006; Nakamaru and Sekine, 2008). Lastly, metal selenides (e.g.,  $\text{ZnSe}_2$ ,  $\text{FeSe}_2$ ,  $\text{NiSe}_2$ )  
560 and elemental Se potentially released to the topsoil from the reduction of selenite in the

561 presence of dissolved organic carbon (Bruggeman et al., 2007) are extremely immobile  
562 and bio-unavailable and can lead to accumulation. In this context, the fumarolic deposits  
563 are expected to have variable primary solubilities, with sulfates, thenardites and gypsum  
564 generally carrying a smaller amount of Se being the most soluble and gypsum being  
565 moderately water-soluble. Fluorides and native sulfur that are extremely enriched in Se  
566 (0.1 to 1.6 wt. %), being the least soluble phases, are expected to accumulate their Se in  
567 soils, potentially leading to higher concentrations in plants and crops.

568         In the months to years following an eruption, the persisting high temperature in the  
569 core of a lava flow will impede the penetration of rainwater through near-surface boiling  
570 and evaporation. However, as soon as the temperature approaches < 100 °C, rainwater  
571 infiltration can leach or even completely dissolve fumarolic deposits in a matter of weeks.  
572 Such a scenario has been observed following the venting of a lava cave formed during  
573 the April 2007 eruption, where the penetration of runoff rainwater dissolved nearly all  
574 gypsum fumarolic deposits (Fig. 5). During such an event, the chemical parameters of the  
575 rainwater (e.g., pH properties) can significantly influence the Se speciation (Fig. 6),  
576 leading to some dramatic re-mobilization events, in extreme scenarios such as those  
577 observed along the flanks of Mt. Etna (Calabrese et al., 2011). Furthermore, sudden  
578 dramatic enrichments can result in unexpected Se concentration increase in the  
579 surrounding aquifers, which can surpass the WHO recommended concentration of 10  
580 mg·L<sup>-1</sup> (John et al., 1976).

581         We encountered several unknowns while attempting to establish a relative mass  
582 balance of environmental Se contribution from the individual fumarolic products. One  
583 major requirement will be to assess the distribution and abundance of the mineral phases,  
584 which can only be achieved through comprehensive mapping. Such an investigation will  
585 rely on a hyperspectral image of the lava flow with individual calibration for the different  
586 minerals. To our knowledge, no such method has yet been designed or published. A  
587 solution will be to tackle the environmental impact through combined investigations of Se  
588 concentrations and isotopic compositions in soils and riverine Se. Furthermore,  
589 distribution comparisons should be made between populated and agricultural areas, as  
590 well as pristine locations to ensure the health safety of the humans living on and with the  
591 volcanic landscape.

592

593 **Conclusions**

594 The long-term activity of the Piton de la Fournaise shield volcano emanates, on average,  
595 between 2.7 and 4.5 tons of gaseous Se per year. Selenium concentrations and isotope  
596 compositions of undegassed and degassed lavas support the preferential Se release in  
597 reduced form, inducing the enrichment of light isotopes in the gas phase. Secondary  
598 fumarolic minerals (consisting of thenardites, sulfates, gypsum, fluorides and native sulfur  
599 at this site) were formed by condensation from gas at the surface of cooling lava flows at  
600 temperatures between ~800°C and ~100°C. Combined Se concentration- and isotope  
601 analyses of individual fumarolic phases allowed us new insights into the mechanisms of  
602 near-surface Se capture. Altogether, the following conclusions are drawn from this study:

- 603 (1) All fumarolic products display significantly higher Se concentrations than degassed  
604 and undegassed lavas pointing at the environmental relevance of this Se source  
605 in volcanic areas.
- 606 (2) Apart from native sulfur, all minerals carry a light Se isotope signature in  
607 accordance with the composition of the gas, and complementing the heavier  
608 isotope composition of the degassed lavas.
- 609 (3) In minerals where Se is likely to be present as oxidized species (thenardite, sulfate,  
610 gypsum) and which were formed at temperatures ~800 to > 315°C, the most  
611 negative  $\delta^{82/76}\text{Se}$  (as low as  $-2.08 \pm 0.06$  ‰) and lower Se concentrations of max.  
612  $13 \mu\text{g}\cdot\text{g}^{-1}$  are detected.
- 613 (4) Mineral species identified to incorporate less oxidized Se compounds (fluorides  
614 and native sulfur) and which are likely precipitated below the sublimation  
615 temperature of  $\text{SeO}_2$  show less negative (fluorides,  $\delta^{82/76}\text{Se} = -0.94$  to  $-0.55$  ‰) to  
616 positive  $\delta^{82/76}\text{Se}$  (native sulfur;  $\delta^{82/76}\text{Se} = 0.6$  ‰ on average) and very high Se  
617 concentrations (0.1 to 1.6 wt. %).
- 618 (5) Se concentrations and isotopic compositions of the fumaroles can be entirely  
619 reconstructed through Rayleigh condensation mechanisms as a function of  
620 decreasing gas temperature, i.e., increasing gaseous compound instability. Based  
621 on isotope data, this model estimates that as much as 80 % of the melt emanated  
622 Se is potentially captured by fumarolic phases. According to this model, no other  
623 processes are needed to explain the observed patterns.

- 624 (6) A phase-dependent fractionation between more oxidized and reduced Se  
625 compounds, could tentatively explain an isotope variation, and particularly the  
626 highest Se concentration in native sulfur, which is most likely to have occurred  
627 through the exchange between gaseous  $\text{Se}_0$  and  $\text{Se}_0$  within the  $\text{S}_0$  solid phase.  
628 Further investigations are needed to shed more light on the isotope fractionation  
629 mechanisms in products formed by a potential effect of kinetically induced  
630 oxidation in gas-solid systems.
- 631 (7) Based on the available data, we conclude that a combination of modest  
632 mineralogical and mostly T-dependent kinetical effects leads to the Se capture in  
633 fumaroles.
- 634 (8) The environmental impact of fumarolic Se will be dependent on the oxidation state  
635 of the compounds, with oxidized species being generally more mobile in aqueous  
636 media than reduced ones. In this context, it is expected that most of the Se  
637 originating from native sulfur and perhaps fluoride fumarolic deposits will  
638 accumulate onto soils and eventually plants, while leaching of sulfates will mobilize  
639 Se towards aquifers. Monitoring the two pools is necessary to understand the  
640 relative fluctuation levels and potential consequences for humans and animals due  
641 to high levels of Se.
- 642 (9) Fumarolic deposits might constitute an important end-member in the oceanic Se  
643 mass-balance and ocean water Se isotope composition and requires careful  
644 consideration in these calculations. Complementary studies of Se concentrations  
645 and isotope ratios in fumarolic products at other volcanically active sites will help  
646 expand our knowledge on the mechanisms of Se recycling from the Earth's interior  
647 back to its surface.

648

## 649 **Acknowledgments**

650 C.R., S.K., and M.I.V.R., acknowledge the ERC Starting Grant project O<sub>2</sub>RIGIN (636808)  
651 to S.K. for funding this research. M.I.V.R. additionally acknowledges funding from the DFG  
652 project VA 1568/1-1. C.R. acknowledges funding from the Excellence Strategy of the State  
653 of BW and University of Tübingen for young postdocs (PRO-ROSCA-2021-11). A.  
654 Finizola, T. Staudacher and J-P. Toutain are thanked for their participation in the fumarole  
655 sampling. Eva Stüeken and one anonymous reviewer are thanked for their constructive

656 comments and suggestions. Ronny Schoenberg is thanked for his continuous support as  
657 head of the Tübingen isotope geochemistry group. Elmar Reitter and Ilka Kleinhanns are  
658 thanked for maintaining the clean laboratory at the highest standards.

659

## 660 **Figure captions**

661 **Fig. 1 a)** Schematic map of the Réunion island located in the SW Indian Ocean (top right  
662 corner), highlighting the location of Piton de la Fournaise caldera; **b)** Map of Piton de la  
663 Fournaise volcano showing the location of the 2007 and 2009 lava flows and the samples  
664 of this study, as well as the native sulfur sample from the eruption of 1977 collected from  
665 deposits on the eastern side of the flank.

666

667 **Fig. 2** Relationships between **a)** EF Se/Be vs. formation temperature; **b)** EF Se/Be vs. Se  
668  $\text{ng}\cdot\text{g}^{-1}$ ; **c)** Se  $\mu\text{g}\cdot\text{g}^{-1}$  vs. formation temperature of the fumarolic deposits of this study  
669 together with silica-tube condensates data of Toutain et al. (1990); **d)** Se isotope  
670 composition vs. formation temperature. Light grey shaded areas represent the  
671 temperature range below the sublimation temperature of  $\text{SeO}_2$  ( $< 315\text{ }^\circ\text{C}$ ). For simplicity,  
672 the average value obtained from two individual digests of the native sulfur is plotted.  
673 Legend to all plots is shown in panel b). Bulk Silicate Earth (BSE)  $\delta^{82/76}\text{Se}$  in panel d) is  
674 from Varas-Reus et al. (2019). Uncertainty bars are smaller than the symbols.

675

676 **Fig. 3** Plot of  $\Delta^{82/76}\text{Se}_{(\text{mineral-gas})}$  versus temperature ( $10^6/T^2$  in K) where  $\Delta^{82/76}\text{Se}_{(\text{mineral-gas})}$   
677  $= \delta^{82/76}\text{Se}_{\text{mineral}} - \delta^{82/76}\text{Se}_{\text{gas}}$ .  $\delta^{82/76}\text{Se}_{\text{gas}}$  is assumed to be constant and identical to the  
678 value of the hottest thenardite ( $-0.44\text{‰}$ ) (dashed line). This representation assumes that  
679 all minerals equilibrate at different temperatures with a gas of constant Se isotope  
680 composition. The formation of sulfates (thenardite, K-Na sulfates and gypsum) over a wide  
681 temperature range allows the T-dependency of  $\Delta^{82/76}\text{Se}$  ( $\text{Se}^{\text{VI}}$ - gas) to be quantified (linear  
682 regression). The temperature control on  $\Delta^{82/76}\text{Se}$  ( $\text{Se}^{\text{IV}}$ - gas) and  $\Delta^{82/76}\text{Se}$  ( $\text{Se}^0$ - gas)  
683 cannot be evaluated because fluoride ( $\text{Se}^{\text{IV}}$ ) and native sulfur ( $\text{S}^0$ ) form only at low  
684 temperatures. Interrupted light grey lines between gas and fluorides as well as gas and  
685 native sulfur represent expected trends. This plot suggests a possible relationship  
686 between  $\Delta^{82/76}\text{Se}_{(\text{mineral-gas})}$  and selenium oxidation state in minerals.

687

688 **Fig. 4.** Evolution of the Se isotope composition of the gas and solid phases calculated  
689 using numerical integrations of Eq. 5. In both models, the initial gas is assumed to have  
690 the same composition as the 800°C thenardite (-0.44 ‰). Model **a)** is based on a linear  
691 relationship between  $f$  and  $\alpha$  as a function of  $T$ . Here,  $\alpha_{s/g}$  varies linearly from 0.9995 at  $f$   
692 = 1 to 0.994 at  $f = 0$  ( $\alpha_{s/g} = 0.0055 \cdot f + 0.994$ ). Model **b)** describes a non-linear relationship  
693 between  $f$  and  $\alpha$ , where  $\alpha_{s/g}$  varies non-linearly from 0.9995 at  $f = 1$  and 0.9970 at  $t = 0$   
694 ( $\alpha_{s/g} = 0.0025 \cdot f^5 + 0.9970$ ). The gas curve (dashed line) is plotted versus the mass fraction  
695 of Se remaining in the gas ( $f$ ). The evolution of the solid phase (solid line) is inferred from  
696  $\alpha_{s/g}$ . Because we cannot accurately estimate the  $\text{Se}/\text{Se}_i$  in the individual fumarolic  
697 minerals, we theoretically indicate their distribution in the models according to their  
698  $\delta^{82/76}\text{Se}$  composition.

699  
700 **Fig. 5 a)** Gypsum (with Cu sulfates) deposits that were sampled from the lava cave  
701 AF1105 (eruption April 2007), and **b)** a close-up photo of the remaining of the same  
702 gypsum deposits following venting of the lava cave and penetration of runoff water which  
703 dissolved and mobilized all gypsum (and by analogy also the incorporated Se). Photos  
704 were taken and kindly provided by A. Finizola (University of Reunion).

705  
706 **Fig. 6** Schematic illustration of the different stages of lava cooling and near-surface  
707 fumarole formation in the context of Se degassing. The indicated temperature is that of  
708 the gas fraction. Unlike S, a large fraction of Se remains soluble in high-temperature lava  
709 flows during the syn-eruptive phase (Stage 1). The largest Se release occurs at lower  
710 temperatures (~315 to 100°C; Stage 3). Exsolution of F during the very late stage of  
711 crystallization promotes Se volatilization as  $\text{SeF}_4$  or  $\text{SeF}_6$ . Dissolution and leaching of  
712 fumaroles through penetrating rainwater mobilize oxidized Se into aquifers. Adsorption  
713 onto Al-Fe phases in young soils accumulates Se. The zoom-in depiction of the cooling  
714 lava shows the progressive formation of fumarolic deposits on top of lava flows, in caves  
715 and within cavities of the solidified lava (microscopic scale). Sulfur deposits are shown in  
716 bright yellow, thenardite in grey, gypsum and fluorides are shown in white-bluish colors.  
717 Note that deviations from these colors are possible depending on the respective  
718 incorporation of trace elements.

719

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941 derived from volcanic gas geochemistry. *Geochimica et Cosmochimica Acta*, 295:  
942 112-134.

943

**Table 1.** Characteristics and geochemical data of the lavas, fumarolic deposits and rock reference materials analyzed in this study

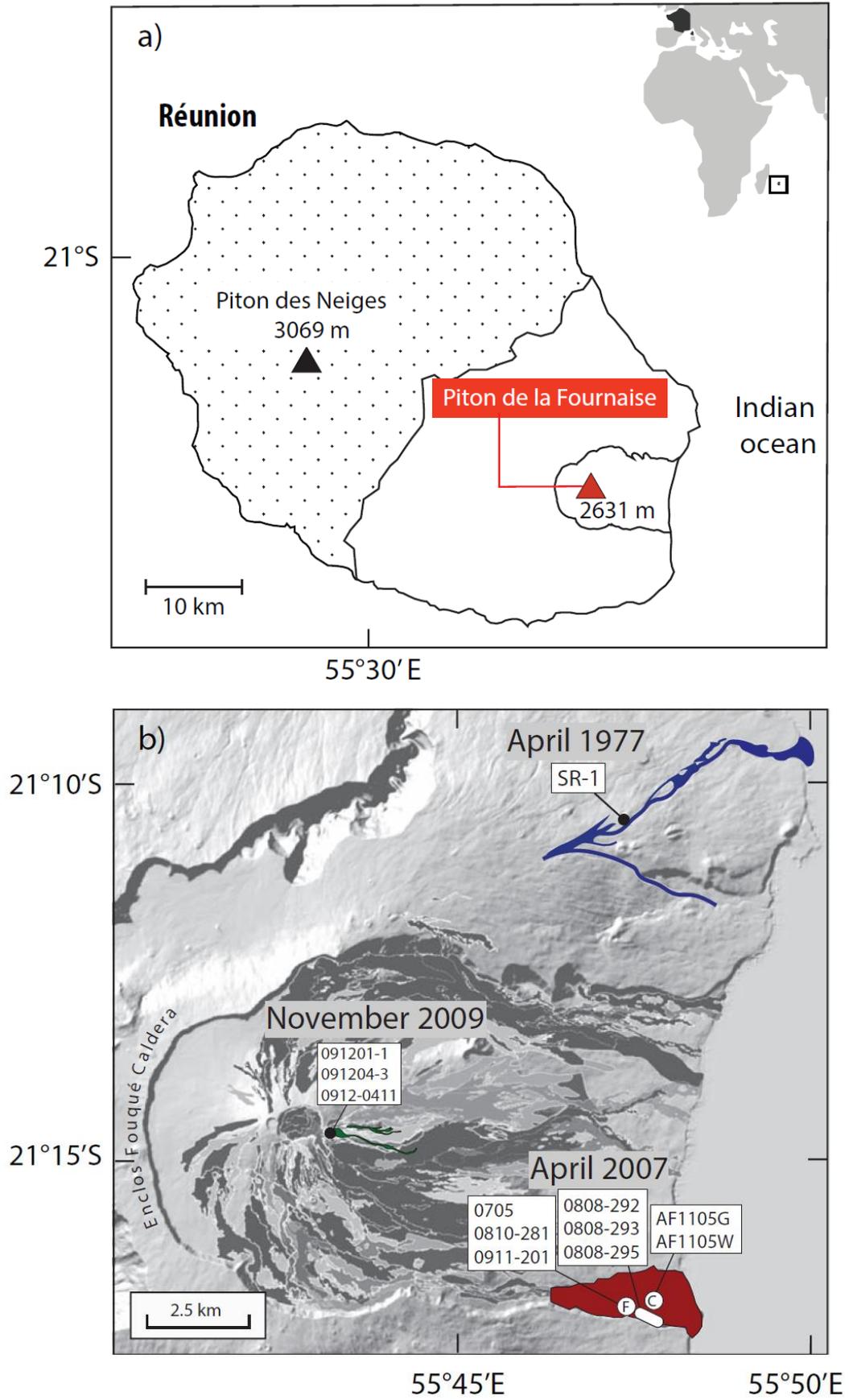
Eruption year	Sample date	Sample name	Coordinates		Material	Formation or condensation Temp. (°C)	Se (ng/g)	Te (ng/g)	$\delta^{82/76}\text{Se}$ (‰)	2 s.e. (‰)	Be (ng/g)	EF <sub>Se/Be</sub>	MgO (wt.%)	Se olivine-corrected*
			Lat. (S)	Long. (E)										
<b>LAVAS</b>														
2007	2007/04	REU 0704-04	21°17'24"	55°47'49"	Basaltic lava	1185	136	0.299	0.12	0.05	930	1.0	7.3	135
2007	2007/04	REU 0704-05-1	21°17'24"	55°47'49"	Basaltic lava	1185	72	0.129	0.04	0.06	570	0.87	21	124
2007	2007/04	REU 0704-08-1	21°17'24"	55°47'49"	Basaltic lava	1185	58	0.252	0.23	0.15	400	1.0	29.2	142
2009	2009/11	REU 0912-01-1	21°14'45.3"	55°43'15.6"	Basaltic lava	1155	94	0.115	0.06	0.07	1030	0.63	7.8	96
2009	2009/11	REU 0912-04-3	21°14'45.3"	55°43'15.6"	Basaltic glass	1155	138	0.277	-0.19	0.04	1050	0.90	8.3	141
<b>FUMAROLIC DEPOSITS</b>														
2009	2009/11	REU 0912-0411	21°14'45.3"	55°43'15.6"	Thenardite	800	1698	82	-0.44	0.04	32	363		
2007	2008/06	REU 0705	21°17'14.8"	55°47'34"	Na-K sulfate	400	1552	453	-0.91	0.04	2760	3.8		
2007	2008/10	REU 0810-281a	21°17'14.8"	55°47'34"	Na-K sulfate	384	807	285	-0.94	0.07	2200	2.5		
2007	2008/10	REU 0810-281b	21°17'14.8"	55°47'34"	Na-K sulfate	384	849	332	-1.03	0.04	2200	2.6		
2007	2009/11	REU 0911-201	21°17'14.8"	55°47'34"	Na-K sulfate	325	543	589	-1.46	0.15	2040	1.8		
2007	2010	AF 1105 G	21°17'17.1"	55°47'46.2"	Gypsum/Cu sulfate	200	2686	1.631	-1.37	0.06	209	88		
2007	2011/05	AF 1105Wa	21°17'17.1"	55°47'46.2"	Gypsum	120	2577	0.437	-1.94	0.12	114	155		
2007	2011/05	AF 1105Wb	21°17'17.1"	55°47'46.2"	Gypsum	120	11298	0.437	-2.08	0.06	114	679		
2007	2008/08	REU 0808-292a	21°17'17.5"	55°47'41.2"	Thenardite	100 <sup>‡</sup>	13617	0.257	-0.97	0.05	140	666		
2007	2008/08	REU 0808-293a	21°17'19.7"	55°47'45.8"	Ca–Mg–Al–Fe fluorides	100	119797	7.79	-0.85	0.03	550	1491		
2007	2008/08	REU 0808-293b	21°17'19.7"	55°47'45.8"	Ca–Mg–Al–Fe fluorides	100	118953	7.79	-0.83	0.04	550	1481		
2007	2008/08	REU 0808-293c	21°17'19.7"	55°47'45.8"	Ca–Mg–Al–Fe fluorides	100	370147	7.79	-0.94	0.07	550	4608		
2007	2008/08	REU 0808-295	21°17'19.8"	55°47'46.1"	Ca–Mg–Al–Fe fluorides	100	82322	0.1	-0.55	0.07	420	1342		
1977	1977/04	SR-1a	21°10'48"	55°46'48"	Native sulfur	100	1.571 x 10 <sup>6</sup>		0.65	0.08	< 5	> 2 x 10 <sup>6</sup>		
1977	1977/04	SR-1b	21°10'48"	55°46'48"	Native sulfur	100	1.584 x 10 <sup>6</sup>		0.55	0.05	< 5	> 2 x 10 <sup>6</sup>		
<b>ROCK REFERENCE MATERIALS</b>														
		BCR-2 a			Basaltic lava		80	2.7	0.08	0.07				
		BCR-2 b			Basaltic lava		78	2.8	0.12	0.13				
		BCR-2 c			Basaltic lava		78	2.3	0.16	0.04				
		W-2a			Diabase		103	1.8	-0.09	0.07				

\*Se (at MgO: 7.5 wt. %) = Se - S · (MgO - 7.5) where S is the slope of the Se vs. MgO correlation in the lavas (S = - 3.863), and assuming an initial Se content of 200 ng·g<sup>-1</sup> (Collins et al., 2012), as well as an initial  $\delta^{82/76}\text{Se}$  of -0.30 ‰.

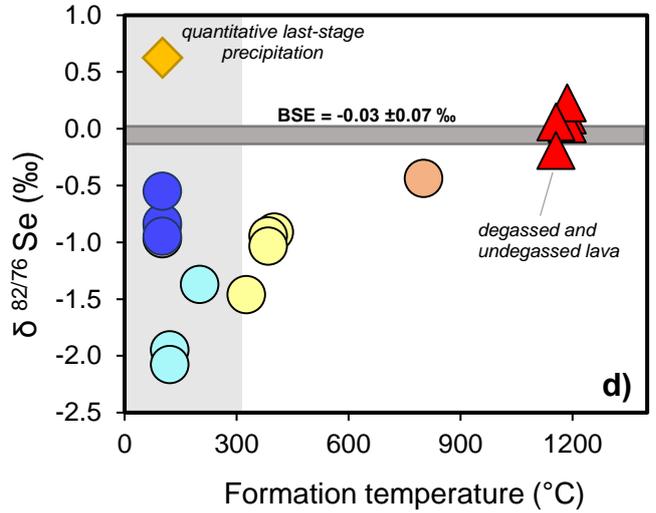
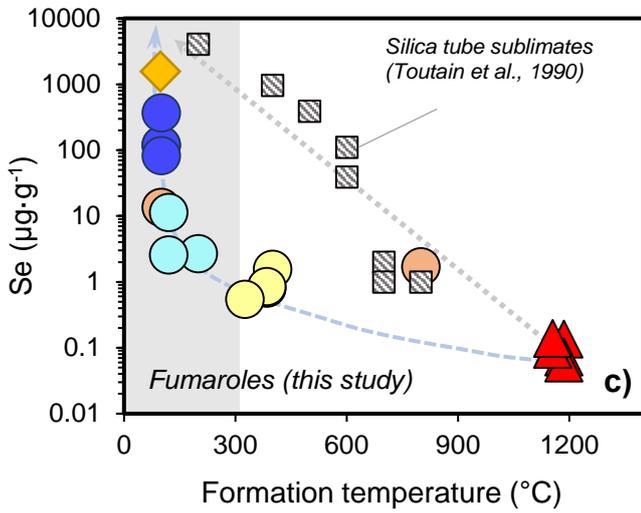
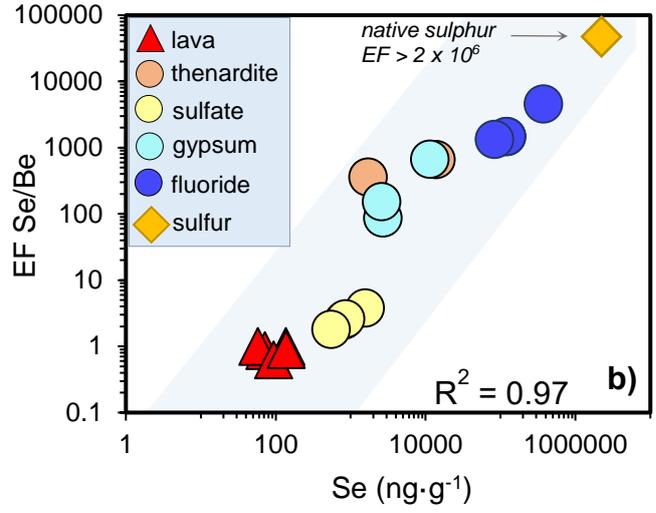
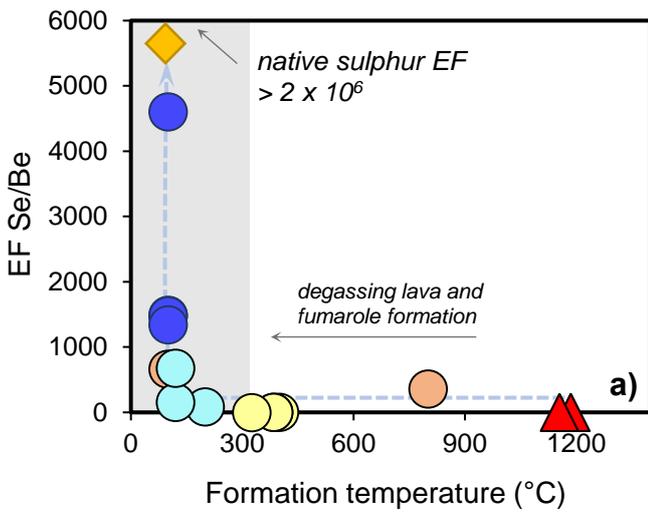
The data presented for native sulfur (SR-1a, and SR-1b) are two replicates based on individual digests.

<sup>‡</sup> Thenardite initially formed at higher temperature but then dissolved in aqueous solution and reprecipitated at ca. 100°C.

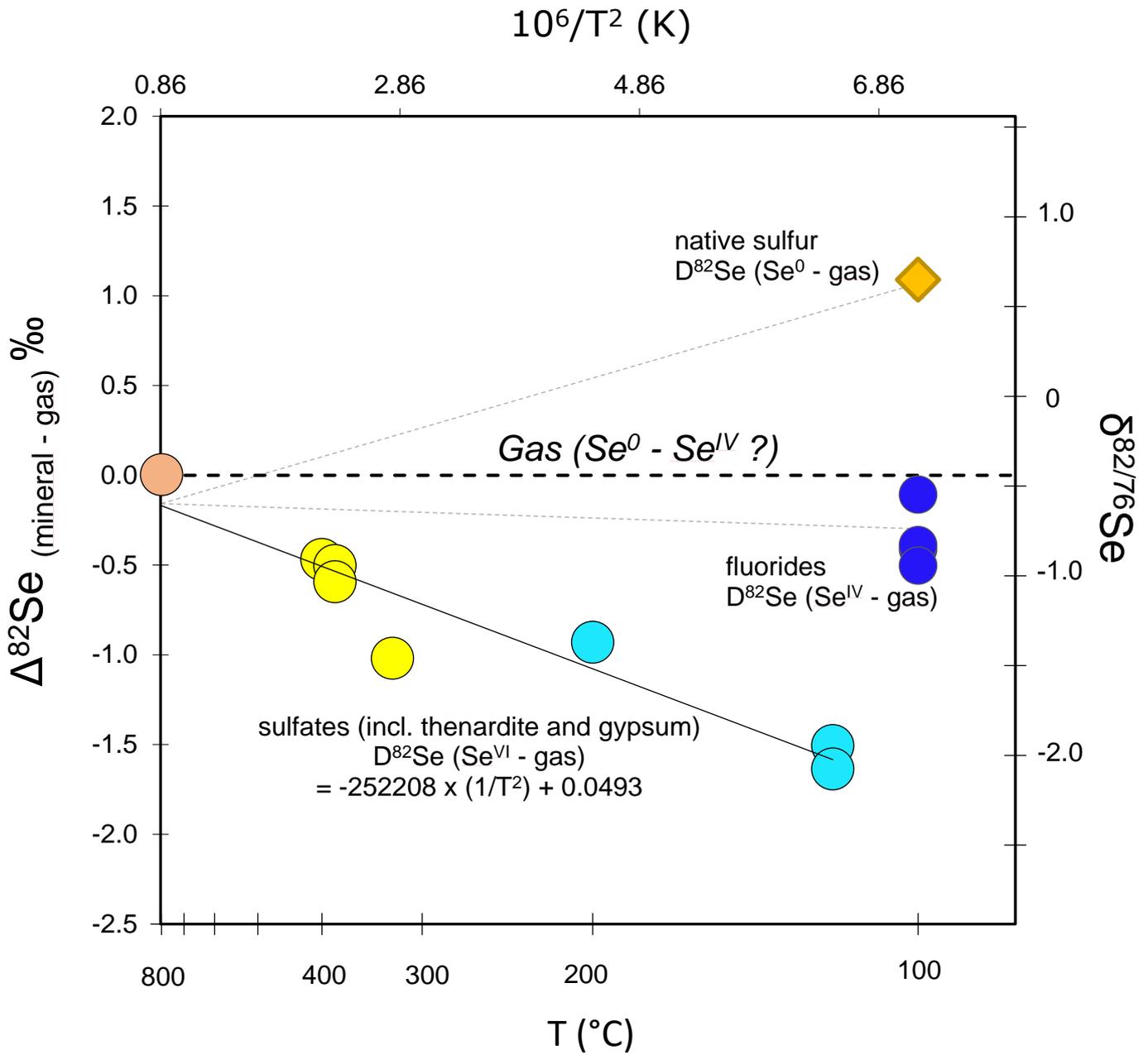
Rosca et al. Fig. 1



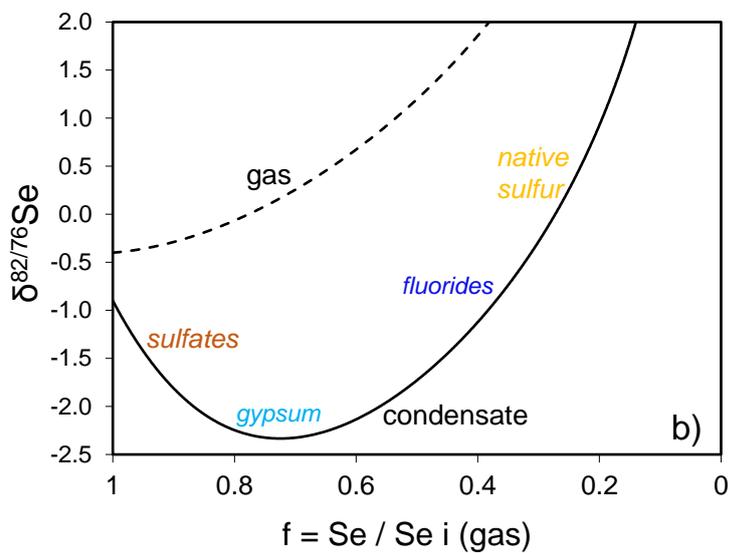
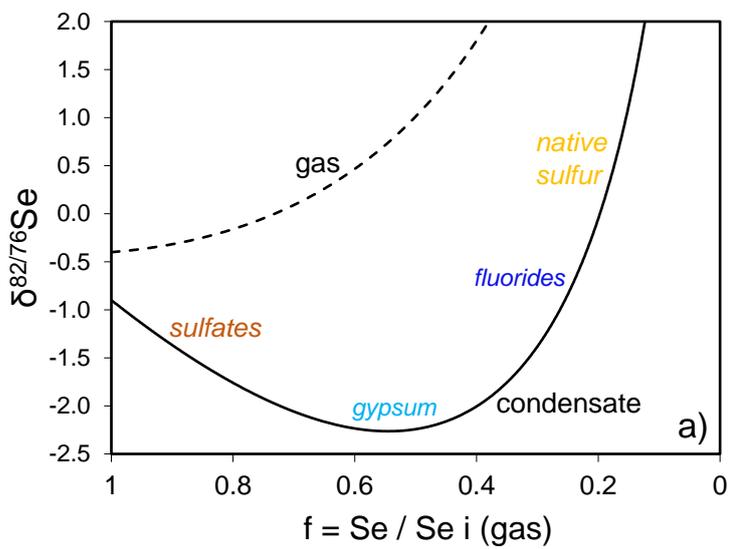
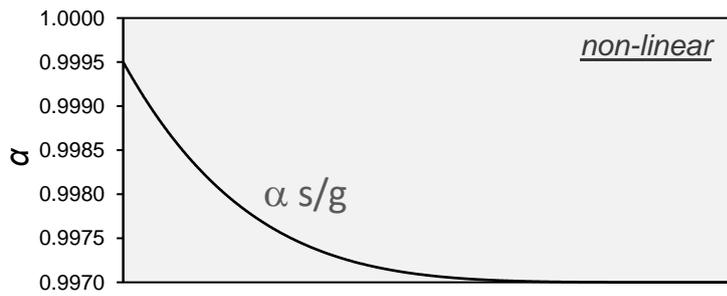
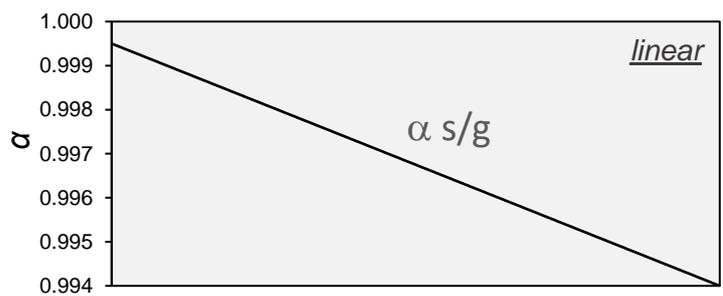
Rosca et al. Fig. 2



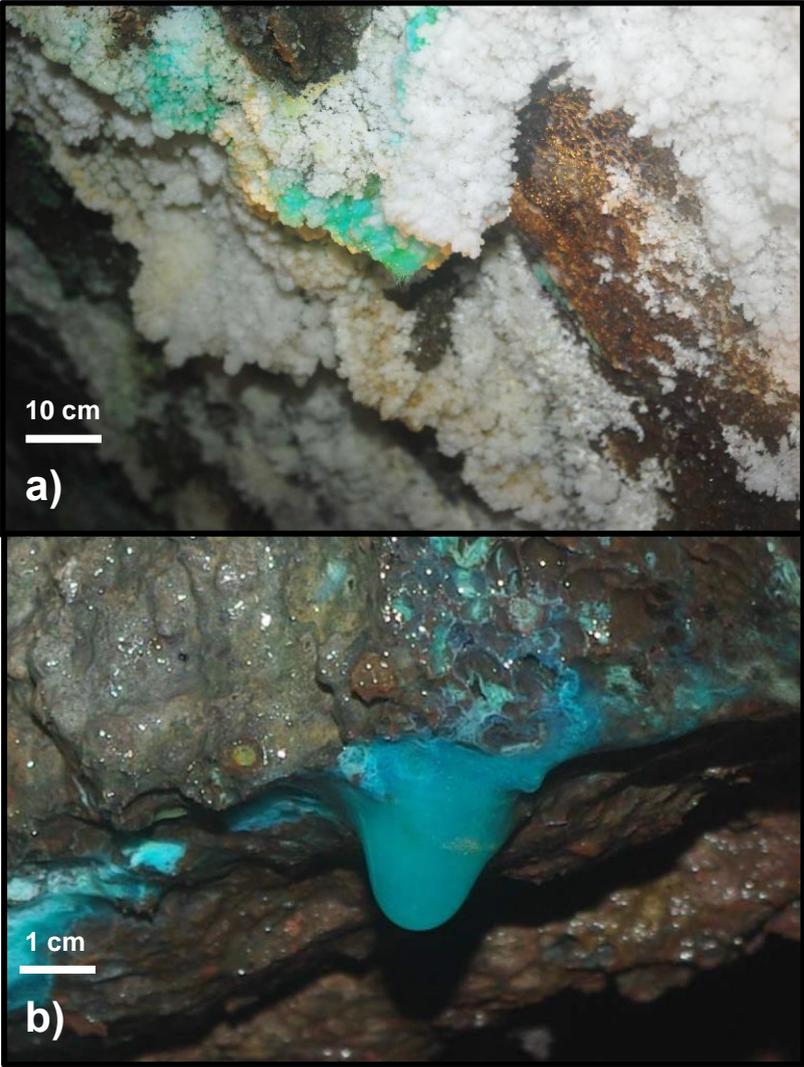
Rosca et al. Fig. 3



Rosca et al. Fig. 4



Rosca et al. Fig. 5



Rosca et al. Fig. 6

