



# **Prolonged trachyte storage and unusual remobilization at Piton de la Fournaise, La Réunion Island, Indian Ocean: Li, O, Sr, Nd, Pb and Th Isotope study**

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**Prolonged trachyte storage and unusual remobilization at Piton de la Fournaise, La Réunion Island, Indian Ocean: Li, O, Sr, Nd, Pb and Th Isotope study**

Running title: Exhuming old trachyte, La Réunion Island

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**Abstract**

La Réunion Island includes two major volcanic systems. About 0.5 Ma ago, Piton des Neiges volcano declined, while Piton de la Fournaise volcano grew on its flank. Since then the Piton de la Fournaise shield volcano has produced homogeneous lavas with chemical compositions transitional between alkali and tholeiitic basalts. In April 2007, the volcano emitted a very small volume of trachytic pumice during its largest historical eruption. We conducted a comprehensive petrological and geochemical study of the pumice to understand the occurrence of such silicic melt in the feeding system of this highly active basaltic volcano. Isotopes of Sr, Nd, Pb and O, together with trace elements, indicate that the trachyte is genetically related to the La Réunion mantle plume and derives from crystallization of a typical basalt. The trachyte chemistry records a long and complex history of differentiation and outgassing. The extensive depletion of moderately volatile elements (F, Cl, B, Cs, Cu, Li) and less volatile uranium are consistent with exsolution of dense fluids at depths of several kilometres. Lithium isotopes point to closed-system degassing during the very late stages of crystallization. U-series isotopes and radiogenic  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  constrain the time elapsed since U loss to between 0.4 and 2.1 Ma. This age is as old or older than Piton de la Fournaise shield edifice. The 2007 trachyte could thus be a liquid remnant of an extinct volcano, such as Piton des Neiges or Les Alizés (Piton de la Fournaise proto-volcano). It could also result from partial melting of an old syenite intrusion or remobilization of interstitial melts not fully solidified. Thermal modelling indicates that the sustained heat flux from hot basaltic magmas rising from the mantle can maintain temperatures above 800°C in the central feeding system, and prevent magmas trapped in this hot core from total solidification.

**Key words:** Trachyte; Magma degassing; Li isotopes; U-series; La Réunion

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3 54 **INTRODUCTION**  
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7 56 Volcanoes from intraplate ocean islands produce basalts during their shield building stage.  
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9 57 More differentiated lavas are typically restricted to the declining and post-shield stages as the  
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11 58 rate of mantle melt supply decreases (Macdonald & Katsura, 1964; Upton & Wadsworth,  
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13 59 1966, 1972; Moore et al., 2011). Yet, many basaltic shield volcanoes, such as those located on  
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15 60 the islands of La Réunion, Hawaii, or Canary, occasionally produce small volumes of lava far  
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17 61 more differentiated than basalts. In most cases, these compositions might be related to small-  
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19 62 scale segregation of silicic liquids (up to 80 wt.% SiO<sub>2</sub>) during crystallization of thick basaltic  
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21 63 lava flows or lakes (Upton & Wadsworth, 1971; Helz, 2008; Martin & Sigmarsson, 2007).  
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23 64 However, there is evidence that extensive differentiation also affects isolated magma lenses  
24  
25 65 at depth. On the island of Hawaii, drilling of the Kilauea Lower East Rift Zone in 2005  
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27 66 encountered a melt of dacitic composition at 2488 m depth (Teplow et al., 2009). Andesite  
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29 67 lava erupted along the same rift in 2018 (Gansecki & Lee, 2018; Gansecki et al., 2019). In the  
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31 68 Canary archipelago, the October 2011 submarine eruption off El Hierro Island produced a  
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33 69 small volume of rhyolitic magma (Sigmarsson et al., 2013). On La Réunion Island, the Piton de  
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35 70 la Fournaise volcano produced a small volume of trachytic pumice during its largest historical  
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37 71 eruption in April 2007 (Salaün et al., 2010). The occurrence of silicic melts in the plumbing  
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39 72 system of basaltic volcanoes raises several questions related to (1) the source of the silicic  
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41 73 melts and their genetic link with the basalts, (2) the depth, conditions and time-scales of  
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43 74 magma storage, and (3) the degassing-crystallization history. Although the silicic melts are  
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45 75 generally thought to originate from isolated pockets of highly evolved magma, it is unclear  
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47 76 how such magma pockets can remain isolated within the plumbing system of highly active  
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49 77 basaltic volcanoes regularly fed by mantle melts. The contribution of evolved melts to the  
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51 78 compositional variability of basalts is suspected in some cases (Salaün et al. 2010), but remains  
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53 79 difficult to distinguish from source heterogeneity.  
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55 80 The eruption of trachytic melt at Piton de la Fournaise is particularly puzzling because this  
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57 81 volcano has produced lavas with limited compositional variations since 0.4 Ma, with  
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59 82 CaO/Al<sub>2</sub>O<sub>3</sub> mostly in the range of 0.65-0.85 (Albarède et al. 1997). To constrain the origin of  
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83 this anomalous melt, we conducted a comprehensive petrological and geochemical study  
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85 including analyses of major-trace element concentrations, volatile elements (H, C, S),  
radiogenic (Sr, Nd, Pb) and stable (Li, O) isotopes, and Th-U radioactive disequilibria. A major

finding is that the trachyte parental melt is older than Piton de la Fournaise shield edifice, and must pertain to an ancient volcano of La Réunion Island.

## GEOLOGICAL CONTEXT

### La Réunion Island

The island of La Réunion (Indian Ocean) is the present location of the hotspot that created the Deccan traps 66 Ma ago. The La Réunion edifice started to grow ~7 Ma ago on a NW-SE lithospheric fracture that has controlled the main volcano-tectonic features of the island and its slightly elongated shape (60 x 40 km). The emergent part of the island comprises an extinct volcano (Piton des Neiges) in the NW and a basaltic shield volcano (Piton de la Fournaise) in the SE (Fig. 1a). Piton des Neiges produced olivine basalts between 2.1 and 0.43 Ma ago, and increasingly differentiated lavas (hawaiite, benmoreite, mugearite and trachyte) until its final activity between 29 and 12 ka ago (Upton & Wadsworth, 1972; Gillot & Nativel, 1982; Deniel et al., 1992). According to most recent works (Smietana, 2011; Lénat et al., 2012; Valer et al., 2017a), Piton de la Fournaise started to grow 0.44 Ma ago on an ancient, now buried volcano (named “Les Alizés”), whose last differentiated lavas (hawaiites and mugearites) outcrop at the bottom of the Rivière des Remparts caldera (Fig. 1a). Between 0.44 Ma and 29 ka ago, Piton des Neiges and Piton de la Fournaise were active simultaneously.

### Piton de la Fournaise volcano

Four major collapses of Piton de la Fournaise volcano occurred 250, 150, 35 and 4.7 ka ago (Gillot et al., 1994; Merle et al., 2010), resulting in concentric calderas. The volcano has produced on average one eruption per year over the last three centuries, mostly inside the most recent caldera, named the Enclos Fouqué (Fig. 1a) (Stieltjes & Moutou 1989; Villeneuve & Bachèlery 2006). Piton de la Fournaise has a relatively simple plumbing system (Lénat et al., 2012; Michon et al., 2016): The central magma path feeding summit eruptions produces transitional basalts with restricted compositional variation ( $5 < \text{MgO} < 8$  wt.%), often referred to as Steady State Basalts (SSB) following Albarède et al. (1997). Magma erupted along the northeast and southeast rift zones contains up to 50% olivine (Boivin & Bachèlery, 2009). A

peripheral system feeds rare eccentric eruptions, producing lava slightly enriched in MgO (7.5–10 wt.%) and incompatible elements, and depleted in Ca relative to SSB (Famin et al., 2009; Valer et al., 2017b). The main magma reservoir feeding both the central and peripheral systems is thought to be located at a depth of about 7.5 km, 2–4 km west of the summit (Famin et al., 2009; Peltier et al., 2009; Lénat et al., 2012). Temporal geochemical fluctuations constrain the residence time of magmas in the main reservoir to between 10 and 30 years (Albarède, 1993; Sigmarsson et al., 2005; Vlastélic & Pietruszka, 2016). All Piton de la Fournaise lavas analysed so far have more than 5 wt.% MgO (Albarède et al., 1997), assuming that the 400–530 ka old plagioclase-ultraphyric basalts collected at the bottom of the Remparts caldera are late-stage products of the pre-existing Les Alizés volcano (Valer et al., 2017a). The most differentiated lavas of the historical period have 5.8–6.1 wt.% MgO and seem to correspond to magmas stored during the longest periods of inactivity (3 to 6 years) (Boivin & Bachèlery, 2009; Coppola et al., 2017).

#### THE APRIL 2007 ERUPTION AND THE TRACHYTIC PUMICES

After nine years of high activity, Piton de la Fournaise erupted between April 2 and May 1 2007 along the South-east Rift zone, at 590 m elevation within the Enclos Fouqué caldera (Fig. 1a). The eruption produced  $210 \times 10^6 \text{ m}^3$  of lava, the largest volume produced by an eruption of this volcano in at least two centuries (Bachèlery et al., 2010; Staudacher et al., 2009; Derrien, 2019). Between April 5 and 7, the summit of the volcano collapsed, while lava effusion rate transiently exceeded  $200 \text{ m}^3/\text{s}$  (Coppola et al., 2009). These two synchronous events were ascribed to the withdrawal of the shallow magma chamber (Staudacher et al., 2009). The eruption produced aphyric basalt with 7.0–7.6 wt.% MgO from April 2 to 5, and olivine-rich basalts subsequently (Di Muro et al., 2014).

When the site became accessible, in the early days of June 2007, white to grey pumices were found to the North West of the main eruptive vent (Piton Tremblet) (Fig. 1b). The nearby tree trunks, partially stripped of their bark and riddled with olivine crystals, were testament to the blast of an explosion in the area. The pumices are a few centimetres in size and include dark basaltic glass, either as very small drops interspersed within the pumice and/or as millimetre thick coating (Fig. 1c). Early field works noted that the pumices become darker towards the opening fracture, as their content in basaltic glass increases. The volume of pumice is

extremely small and unlikely to exceed a few cubic meters. During the following years, the 2007 pumice fallout was covered by younger lava flows. Such trachytic components might have been erupted in the past, but have not been found or preserved in the geological record due to their very minor volume.

Preliminary analyses (Falco, 2009) revealed that the pumices are trachytic in composition. To date, no study has focused on these samples, but their compositions were reported in two papers: Salaün et al. (2010) observed that the composition of the 2007 trachyte plots on the dominant fractionation trend of Piton de la Fournaise basalts. The authors suggested that trachytic melts form within rarely used eccentric magma paths and contaminate the basaltic melts, causing their small compositional variations. Vlastelic et al. (2011) showed that the pumice underwent extensive loss of water, halogens (Cl, F) and semi-volatile elements (Li, B and Cs), which they attributed to low-pressure, vapor-saturated crystallization during prolonged magma storage, or fluxing of vapours exsolved from deeper magma.

## SAMPLES AND METHODS

About 200 centimetre-sized pumice chips were collected to the west ("PN" group) and to the east ("PS" group) of the opening fracture (Fig. 1b). Within the PS fallout field, white pumices with very low amount of basaltic glass were found to the North of Piton Tremblet, at the border of the April 2007 lava flow (21°16'51"S – 55°46'29"E). They are referred to as sample 0704-TRA. A few chips from groups PN and PS were crushed and finely powdered in an agate mortar (samples 0704-PS and 0704-PN) to measure bulk major-trace element concentrations and Sr-Nd-Pb-Th-Li-O isotope compositions. One chip from the PN group (NPON) and two chips from the PS group (SPON and 0704-TRA) were selected for in situ analyses (EPMA and SIMS). Bulk and in situ analyses were also performed on the basaltic glass coating. In addition, trace elements and Li-Th-Pb isotopes were measured on single grains, glass and magnetic fractions from samples NPON, SPON and 0704-TRA. Analyses were performed at Laboratoire Magmas et Volcans (LMV, Clermont-Ferrand, France), Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France), Ecole Normale Supérieure (ENS, Lyon, France), and Stable Isotope Laboratory at the University of Oregon (Eugene, USA).

## Electron Microscopy

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5 183 Polished thin sections (samples SPON and NPON) and resin mount (sample 0704-TRA) were  
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7 184 surveyed by Scanning Electron Microscopy (JSM 5910LV, LMV) operating in Backscattered  
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9 185 Electron (BSE) imaging mode. The major element compositions were measured by Electron  
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11 186 Probe Microanalysis (Cameca SX 100, LMV) using a 15-kV accelerating voltage. Beam current  
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13 187 and spot size were 15-nA and 1 µm for minerals, and 8-nA and 20 µm for glass, respectively.  
14 188 The counting times on peak and background were 10 s.

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18 190 **Bulk major and trace elements**

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21 192 The two powders 0704-PS and 0704-PN were analysed for bulk major and trace element  
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23 193 content. Millimetre-sized grains of the basaltic coating and sample 0704-TRA were analysed  
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25 194 for trace elements only. Major elements were quantified at LMV by ICP-AES (HORIBA-Jobin-  
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27 195 Yvon ULTIMA C) after alkali fusion and nitric acid dissolution, as described by Gurioli et al.  
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29 196 (2018). For trace elements, different dissolution procedures were used to measure both  
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31 197 elements occurring in very low amounts and/or prone to contamination and elements hosted  
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33 198 in resistant minerals: conventional HF-HNO<sub>3</sub> attack at 90°C in Savillex vials, HF-HNO<sub>3</sub> attack  
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35 199 between 120 and 250°C in Parr pressure vessels (4749 type), ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>)  
36 200 dissolution at 230°C in PTFE vials following the method described by Zhang et al. (2012), and  
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38 201 alkali fusion. Trace elements were measured on the Agilent 7500 ICP-MS of the LMV as  
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40 202 described in Gurioli et al. (2018), with the exception of samples dissolved by alkali fusion,  
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42 203 which were measured on a Thermo Elemental X7 ICP-MS at CRPG. Trace element  
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44 204 concentrations acquired at LMV were calibrated externally (every 4 samples) with the USGS  
45 205 BHVO-2 standard dissolved as samples and using the recommended values of Chauvel et al.  
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47 206 (2011). The external reproducibility, inferred from repeated analysis of BHVO-2 as unknown  
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49 207 is 6% or lower except for Pb (15%) (Electronic Appendix 1). More information on sample  
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51 208 preparation and analysis is given in Vlastelic et al. (2013a).

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54 210 **Bulk C, H, S content**

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57 212 The concentrations of C, H and S of the powder samples 0704-PS and 0704-PN were measured  
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59 213 at LMV using a Flash 2000 CHNS-O elemental analyser from Thermo Fisher Scientific. One



milligram of powder and the same amount of  $V_2O_5$  were precisely weighted in a tin capsule using a microbalance, and introduced into the 950°C high-temperature reactor. The combustion gases ( $CO_2$ ,  $H_2O$  and  $SO_2$ ) were separated in the coupled chromatography column and quantified by thermal conductivity. Cystine ( $C_6H_{12}NO_4S_2$ ) was used for calibration. The 2 $\sigma$  errors of H and C measurements are in range of 12-18 % and 4-8 %, respectively.

### **Sr-Nd-Pb isotopes**

Three pumice samples (0704-PS, 0704-PN and 0704-TRA) and the basalt coating were analysed at LMV for bulk Sr-Nd isotopes. These samples, as well as chips from samples S-PON (n=1), N-PON (n=1) and 0704-TRA (n=6), were analysed for Pb isotopes. Samples (100 mg of powder or 5-10 mg grains) were dissolved with 5 ml of distilled 29M HF and 1 ml 14M  $HNO_3$ , at 90°C in Savillex vials for 24 hours. For chips, the same dissolution was used to measure Pb isotopes and trace elements. Sr and Pb were separated using Eichrom Sr specific resin (Deniel & Pin, 2001). Light Rare Earth Elements were extracted from the residual fraction using Tru.Spec resin, and Nd separated from the adjacent lanthanides using Ln.Spec resin (Pin & Zalduegui, 1997). Procedural blanks were < 0.03 ng for Pb, < 0.1 ng for Nd, and < 1 ng for Sr. These blanks are insignificant compared to the amounts of Sr, Nd and Pb extracted from samples, which are between  $5 \times 10^2$  (Pb) and  $2 \times 10^4$  (Sr) times larger.  $^{87}Sr/^{86}Sr$  and  $^{143}Nd/^{144}Nd$  were measured on a Thermo Fisher Scientific Triton Thermal Ionization Mass Spectrometer (TIMS), and were corrected for mass fractionation using  $^{86}Sr/^{88}Sr=0.1194$  and  $^{146}Nd/^{144}Nd=0.7219$ , respectively. Repeated measurement of the NBS SRM 987 and Ames standards during the course of the study yielded  $^{87}Sr/^{86}Sr=0.710243 \pm 9$  (2 $\sigma$ , n=20) and  $^{143}Nd/^{144}Nd=0.511958 \pm 8$  (2 $\sigma$ , n=16), respectively. Lead isotope compositions were measured on a Thermo Fisher Scientific Neptune Plus MC-ICPMS coupled to an Aridus II desolvating nebulizer system. The Pb instrumental mass fractionation was corrected during measurement by doping the Pb solutions with the TI NBS997 standard. The NBS981 standard was measured between every two samples to correct Pb ratios for instrumental drift and the slight difference in mass fractionation between Pb and TI. Data were normalized to the NBS981 standard using the values of Todt et al. (1996). Repeated analysis of the NBS981 standard every two samples yielded typical intra-session 2 $\sigma$  reproducibility of 100, 120 and 140 ppm for  $^{206}Pb/^{204}Pb$ ,  $^{207}Pb/^{204}Pb$  and  $^{208}Pb/^{204}Pb$ , respectively. The 2 $\sigma$  reproducibility of the  $^{208}Pb^*/^{206}Pb^*$  ratio

(defined as  $[(^{208}\text{Pb}/^{204}\text{Pb})_S - (^{208}\text{Pb}/^{204}\text{Pb})_{\text{CD}}] / [(^{206}\text{Pb}/^{204}\text{Pb})_S - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{CD}}]$  where subscripts S and CD refer to sample and Canyon Diablo meteorite, respectively) was better than 600 ppm.

### U-Th disequilibria

The rock powders (0704-PS and 0704-PN), glass (S-PON, N-PON, 0704-TRA) and magnetic (0704-TRA) fractions were analysed at LMV for Th isotopes. All samples were dissolved using conventional HF-HNO<sub>3</sub> attack. For glass and magnetic fractions, Th isotopes and trace elements were analysed on same dissolution. Thorium was extracted using TRU-Spec resin and purified using AG1-X8 anionic resin, following Carpentier et al. (2015). The  $^{230}\text{Th}/^{232}\text{Th}$  ratios were measured in static double collection mode on the same Neptune MC-ICPMS as for Pb isotopes. The small  $^{230}\text{Th}$  peak was measured on a secondary electron multiplier with adjustable quadrupole potential (RPQ). An in-house standard solution (ThS1) was repeatedly measured to correct for instrumental mass bias and faraday cup to secondary electron multiplier relative gain. Contribution of the  $^{232}\text{Th}$  tailing on  $^{230}\text{Th}$  was corrected using an exponential fit of the  $^{232}\text{Th}$  peak tail. Repeated analysis of Th Specpure and ThS1 standards yielded  $(^{230}\text{Th}/^{232}\text{Th}) = 0.157 \pm 0.002$  ( $2\sigma$ ,  $n=15$ ) and  $(^{230}\text{Th}/^{232}\text{Th}) = 1.022 \pm 0.003$  ( $2\sigma$ ,  $n=12$ ), respectively. The  $^{238}\text{U}/^{232}\text{Th}$  ratios were measured by ICP-MS, with a precision of 6 % estimated from the repeated analysis of BHVO-2 standard. The error on the  $^{238}\text{U}/^{232}\text{Th}$  ratio does not exceed the individual errors on U and Th concentrations due to the significant correlation of  $^{238}\text{U}$  and  $^{232}\text{Th}$  errors during ICPMS analysis.

### Bulk O isotope composition

Oxygen isotope compositions of samples 0704-PS and 0704-PN were analysed by laser fluorination in the Stable Isotope Laboratory at the University of Oregon following the method described by Bindeman et al. (2008). A 35W CO<sub>2</sub>-laser was used, and rock powders were reacted with purified BrF<sub>5</sub> to release oxygen. Gases were purified cryogenically using liquid N<sub>2</sub> and by using a Hg-diffusion pump to eliminate traces of F<sub>2</sub> gas formed by fluorination. Oxygen was then converted to CO<sub>2</sub> by reaction with platinum-graphite, and the yields were measured by a baratron gauge. Then the CO<sub>2</sub> was analysed on a Thermo Fisher scientific MAT 253 mass spectrometer. Internal precision varied from 0.14 to 0.20 ‰ ( $2\sigma$ ). The standards used with

these analyses include San Carlos olivine ( $\delta^{18}\text{O} = 5.25 \text{ ‰}$ ), Gore Mt Garnet (UWG2,  $\delta^{18}\text{O} = 5.80 \text{ ‰}$ , Valley et al., 1995) and OUG University of Oregon Garnet ( $\delta^{18}\text{O} = 6.52 \text{ ‰}$ ). The  $\delta^{18}\text{O}$  of standards varied between 0.01 and 0.14 ‰ over the course of the study, and were used to correct for day-to-day variability and absolute oxygen isotope compositions on the SMOW scale.

### **Bulk Li isotope composition**

In addition to Li data previously reported by Vlastelic et al. (2011), six grains of sample 0704-TRA and one grain of the basaltic coating (0704-PN-BAS) were analysed for bulk lithium isotope composition. About 50 mg of powder was dissolved in a mixture of concentrated  $\text{HClO}_4$  (0.3 ml) and HF (1 ml). Following Vlastelic et al. (2009a), we used 0.5M HCl and AG50W-X8 cationic resin to isolate Li in two steps. Lithium isotope compositions were measured on the Nu Plasma 500 MC-ICPMS of ENS Lyon coupled to a Nu DSN desolvator. Mass discrimination was monitored using IRMM-016, which was run between every sample analysis. Each sample was measured at least twice. Repeated analysis of the USGS BHVO-2 standard yielded  $^7\text{Li}/^6\text{Li} = +4.3\text{‰} \pm 0.4$  ( $2\sigma$ ,  $n=8$ ).

### **Lithium isotopes analysis by SIMS**

In-situ Li isotope compositions were measured on a polished section of sample 0704-TRA using the CRPG SIMS 1280 ion microprobe. The mass resolution was set to 2000 to separate  $^6\text{Li}^1\text{H}$  from  $^7\text{Li}$ . The measurements were made in single-collection mode using the central electron multiplier for mass 5.8 (for background),  $^6\text{Li}$  and  $^7\text{Li}$ , and with counting times in each cycle of 3, 12 and 4 s, respectively. Repose time was set to 3 s, 1 s and 1 s, respectively. One measurement consists of 20 cycles, with 40 s pre-sputtering and automatic centring of the secondary beam in the field aperture and in the contrast aperture and no energy offset was applied. A primary beam intensity of 8 nA was used to make the lithium isotope measurements with 20-25  $\mu\text{m}$  spot sizes. The count rates on  $^6\text{Li}$  ranged between 10000 counts/s in the basaltic glass and 500 counts/s in the trachyte glass, resulting in a one sigma counting statistic between  $\pm 1 \text{ ‰}$  and  $\pm 2.8 \text{ ‰}$  for  $^7\text{Li}/^6\text{Li}$ , respectively. The standards used were in house CRPG standards (a synthetic enstatite ENST-B and a natural basaltic glass NZ-06-14

from the Nazca ridge) as well as MPI-DING glass standards (ML3B, T1G, GOR132, GOR128, ALV2748). The external error of  $\delta^7\text{Li}$ , estimated from repeated analysis of one glass, is 3.7‰ (2 $\sigma$ ). Based on calibration before and after a session, variations of instrumental fractionation were within the external reproducibility.

**RESULTS**

Bulk analyses, including concentrations of major-trace elements and C-H-S, and Sr-Nd-Pb-Th-O-Li isotope compositions are reported in Electronic Appendix 1. Microprobe analyses of glass and minerals are reported in Electronic Appendix 2, while lithium isotope analyses by SIMS are given in Electronic Appendix 3.

**Mineralogy and petrology of the pumices**

The pumices show a hyaline texture with glass and microlites of feldspar in the matrix (Fig. 2). Their colour varies from white to medium grey. Inspection of thin sections indicates that the pumices contain 80 to 90 vol.% vesicle. Vesicles, ranging in size from several millimetres to a few micrometres, are rounded or elongated, isolated or coalescent, separated by very thin glass walls (a few tens to a few hundred  $\mu\text{m}$ ). Pumice fragments are often coated by a dark basalt glass (Fig. 2c). The yellowish-brown glass locally invades the pumice as fine droplets or thin films (Fig. 2a and c). Mixing between the two magmas is restricted to areas of a few tens of micrometres (Fig. 2c and f). In the trachytic liquid, microlites of  $<1\ \mu\text{m}$  to  $10\ \mu\text{m}$  of Na-rich alkali feldspar occur (anorthoclase,  $\text{An}_{4-11}\text{Ab}_{67-77}\text{Or}_{13-25}$ , see Fig. 2f and Electronic Appendix 2). In areas where the trachytic and basaltic liquids mix, the glass has variable compositions, depending on the relative proportions of the two liquids (Fig. 2d-f). Small crystals ( $<100\ \mu\text{m}$ ) of magnetite and dendritic microcrystals (ranging in size from a few to tens micrometres) of plagioclase (labradorite,  $\text{An}_{49-62}\text{Ab}_{37-49}\text{Or}_{1-2}$ , Electronic Appendix 2) are present. The mixed glass also contains clinopyroxene crystals ( $\text{En}_{33}\text{Fs}_{23}\text{Wo}_{44}$ ) with higher iron content than clinopyroxenes occurring in basalts (Falco, 2009). Other mineral phases, such as olivine, when present, are associated with the basaltic liquid. Pumice whole rock compositions and glass mainly plot in the trachyte field of the total alkali versus silica diagram, whereas yellowish-brown glasses are basalts (Fig. 3).

### Bulk trace element contents

Trace element patterns normalized to the average composition of common La Réunion basalts (referred to as steady state basalts) are shown on Figure 4 for the trachyte pumice and the basalt glass. The trachyte pattern is complex: Nb, Ta, Be and rare earth elements lighter than Eu define an enriched pattern, with normalized concentrations ranging from 2.1 for Sm up to 7.8 for Nb in sample 0704-TRA. Zirconium and Hf show positive anomalies, with  $Zr/Zr^*$  ( $Zr_N/(Sm_N \times Gd_N)^{0.5}$ ) ranging between 1.6 (0704-PN) and 3.0 (0704-TRA). Conversely, Cs, Cu, Li, B, Pb, Eu, Sr, Ba and U show negative anomalies. Lithium and Cs show the strongest anomalies, with  $Li/Li^*$  ( $Li_N/(Tm_N \times Yb_N)^{0.5}$ ) as low as 0.02 in sample 0704-TRA. The increasing recovery of Zr, Hf and heavy rare earth elements with dissolution strength (Electronic Appendix 4) indicates that the pumice contains zircon, and constrains its modal abundance to between 0.06 (0704-PN) and 0.16 wt.% (0704-TRA). The pumice samples generally have low compatible element contents (e.g., Ni <40 ppm), with the exception of chip#5 of sample 0704-TRA that obviously hosts some basalt (Electronic Appendix 1). The basalt pattern is flat, with incompatible element concentrations ranging between 0.53 and 0.57 times those of steady state basalts, due to the occurrence of ca. 50% cumulative olivine (Fig. 4). This characteristic is typical of April 2007 basalts erupted after April 5 (Di Muro et al., 2014). Only lithium shows a slight positive anomaly ( $Li/Li^*=1.2$ ). The homogeneous depletion of incompatible elements and the high Ni content of the basalt (887-1010 ppm, Electronic Appendix 1) are consistent with the occurrence of cumulative olivine.

### Bulk content of C, H and S

The samples 0704-PS and 0704-PN have between 487 and 727 ppm H, and between 373 and 970 ppm C (Electronic Appendix 1). The H content corresponds to 0.44-0.65 wt.%  $H_2O$ , which is higher than the value of  $0.2 \pm 0.1$  wt.% previously determined on the glass by Raman spectroscopy (Vlastelic et al., 2011). The C content corresponds to 0.14-0.36 wt.%  $CO_2$ . Sulphur content is below the detection limit of 50 ppm for both samples.

### Sr-Nd-Pb isotopic composition

The pumice samples show small variations of  $^{206}\text{Pb}/^{204}\text{Pb}$  (18.897-18.943),  $^{207}\text{Pb}/^{204}\text{Pb}$  (15.584-15.596) and  $^{208}\text{Pb}/^{204}\text{Pb}$  (38.979-39.027), a narrow range of  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.704213-0.704297), and constant  $\epsilon\text{Nd}$  ( $4.35 \pm 0.12$  ( $2\sigma$ )) (Electronic Appendix 1). These compositions plot well within the Sr-Nd-Pb isotope field of La Réunion Island lavas (Fig. 5), but show slightly higher  $^{87}\text{Sr}/^{86}\text{Sr}$  at given  $\epsilon\text{Nd}$  than Piton de la Fournaise historic lavas (Fig. 5a). The basalt coating plots within the field of the April 2007 eruption in Sr-Nd and Pb-Pb isotope spaces. It has a relatively unradiogenic Pb signature ( $^{206}\text{Pb}/^{204}\text{Pb}$  of 18.873, Fig. 5b) that characterizes the lavas emitted during the eruption paroxysm on April 5 (Vlastelic et al., 2009b).

### **$^{230}\text{Th}$ - $^{238}\text{U}$ disequilibria**

Thorium isotope compositions were measured on powders, glass and magnetic fractions (Electronic Appendix 1). The activity ratios ( $^{230}\text{Th}/^{232}\text{Th}$ ) range between 0.262 in 0704-PN powder and 0.654 in N-PON glass. These values are much lower than those reported for historical lavas, which show small variations between 0.915 and 0.944 (Sigmarsson et al., 2005; Pietruszka et al., 2009). Conversely, the ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios of the pumice samples are very similar to their ( $^{238}\text{U}/^{232}\text{Th}$ ) ratios, which range between 0.240 and 0.689. This translates into 0-14 % (average of 4.7%) excesses of  $^{230}\text{Th}$  over  $^{238}\text{U}$  (Fig. 6). However, errors of 6% on ( $^{238}\text{U}/^{232}\text{Th}$ ) ratios place five out of the six data points within error of equilibrium. Note that all Th isotope data are relative to the zircon-free phase, because the digestion method used may not fully dissolve zircons.

### **Oxygen isotopes**

The two pumice powders analysed have  $\delta^{18}\text{O}$  between +5.55 ‰ (sample 0704-PS) and +5.81 ‰ (sample 0704-PN) (Electronic Appendix 1). These values are within the range for mantle-derived magmas, but are higher than the  $\delta^{18}\text{O}$  of recent (1977-1992) steady state basalts, which varies between +5.34 and +5.52 ‰ with an average of +5.40 ‰ (Boivin & Bachèlery, 2009). They are closer to the  $\delta^{18}\text{O}$  range of Piton de la Fournaise 1977-1992 olivine rich lavas (+5.52 to +5.72 ‰, average of +5.60 ‰; Boivin & Bachèlery, 2009).

## Lithium isotopes

Vlastelic et al. (2011) previously noted that the low Li contents of samples 0704-PS and 0704-PN (1 and 1.4 ppm, respectively) correlates with extremely low  $\delta^7\text{Li}$  (-21 and -17‰, respectively). By comparison, bulk analysis of different chips from the new sample 0704-TRA yields even lower Li contents (between 0.48 and 0.13 ppm), but more variable and higher  $\delta^7\text{Li}$  (between -7.2 and +13.8 ‰, Electronic Appendix 1). In situ Li isotope and major element measurements were performed in sample 0704-TRA to constrain the origin of Li isotope heterogeneity (Fig. 7).  $\delta^7\text{Li}$  varies between -19.8 and -31.0 ‰ in the trachyte glass, and between -3.1 and -30.7 ‰ in the glassy regions with abundant sub-micrometric K-feldspars (Electronic Appendix 3). The interior of the trachyte pumice (7-9 mm from the basalt coating) is more depleted in Li than the external 1 mm layer, due to a larger amount of feldspar microlites in the glass and/or Li degassing. In situ analysis of the basaltic glass coating 0704-TRA yields  $\delta^7\text{Li}$  between +7.5 and +18.4 ‰, which is significantly heavier than bulk glass composition (+4.2 ‰). Reporting all data in a  $\delta^7\text{Li}$  vs. Li concentration plot (Fig. 8) highlights two main arrays: SIMS data acquired on the pure trachytic glass show a positive correlation between  $\delta^7\text{Li}$  and Li content, while most other data acquired on sample regions with variable microlite contents show the opposite relationship. The two arrays intercept at Li = 2 ppm and  $\delta^7\text{Li}$  = -35 ‰. Two SIMS analyses (b9 and b22) performed close to the pumice surface (Fig. 7) plot between this common component and the basalt composition (Fig. 8).

## DISCUSSION

### Isotope constraints on the origin of the trachyte melt

The isotope compositions of Sr, Nd and Pb indicate that the April 2007 trachyte shares the same source as La Réunion basalts (Fig. 5), and is not produced by partial melting of the underlying Indian Ocean crust, or another genetically unrelated lithology. For the same reason, partial melting of an enriched mantle lithology, as proposed for other Mauritian trachytes (Ashwal et al., 2016), or contamination from assimilated sediments (Sigmarsson et al., 2013), can also be ruled out. The mantle-like  $\delta^{18}\text{O}$  signature of the trachyte (+5.55 to +5.81

%) also precludes significant interaction with isotopically light (-8.67 to -4.9 ‰) hydrothermal fluids (Bénard et al., 2020). The basalt coating the pumice has a relatively unradiogenic Pb signature ( $^{206}\text{Pb}/^{204}\text{Pb}$  of 18.873, Fig. 5b) that characterizes the lavas emitted on April 5 2007, all other lavas from this eruption have  $^{206}\text{Pb}/^{204}\text{Pb}$  between 18.902 and 18.911 (Vlastelic et al., 2009b). The unradiogenic Pb isotope ratio indicates that the trachyte was emitted during the eruption paroxysm on April 5 when the lava effusion rate transiently exceeded 200 m<sup>3</sup>/s, the highest value ever measured at Piton de la Fournaise (Coppola et al., 2009). The mobilization and eruption of the trachyte is thus clearly related to the unusual dynamics and/or path of April 2007 magmas.

Previous studies (Falco, 2009; Salaün et al. 2010) noted that the Piton de la Fournaise 2007 trachyte plots at the end of the main differentiation trend of La Réunion basalts, showing a similar composition as Piton des Neiges trachytes (Fig. 3). Salaün et al. (2010) suggested that the major element composition of the trachyte is attainable through basalt crystallization, although they acknowledged that the low-pressure (<800 MPa) line of descent that fits basalt compositions does not reproduce more evolved compositions. Generally, available data supports the idea that the 2007 trachyte is a differentiation product of La Réunion common basalts. However, the extensive depletion (>90 %) of a number of volatile and semi-volatile elements (F, Cl, B, Cs, Cu, Li), and the significant depletion of less volatile U (26-68%) are testament to a complex history of storage and outgassing discussed here below.

### **Lithium isotope constraints on volatile element loss**

Lithium has proved useful to reconstruct magma degassing owing to its affinity for aqueous fluids and high diffusivity in silicate melts (Berlo et al., 2004; Kuritani & Nakamura, 2006; Kent et al., 2007; Rowe et al., 2008; Koga et al., 2008; Vlastelic et al., 2013a). Lithium isotopes also provide additional constraints on degassing processes (Beck et al., 2004; Schiavi et al., 2009; Vlastelic et al., 2011): at equilibrium conditions, preferential partitioning of  $^7\text{Li}$  into aqueous fluids (e.g., Wunder et al., 2006) decreases the  $^7\text{Li}/^6\text{Li}$  ratio in the residual melt. Conversely, out of equilibrium, faster diffusion of  $^6\text{Li}$  (Richter et al., 2003; Holycross et al., 2018) towards the silicate melt-fluid interface increases  $^7\text{Li}/^6\text{Li}$  of the melt. To a first order, the bulk Li depletion and low  $^7\text{Li}/^6\text{Li}$  of the pumice are consistent with equilibrium loss of Li. In detail, the in situ SIMS data show two main orthogonal arrays in the  $\delta^7\text{Li}$  versus Li plot that depart from



an end-member composition (Li=2ppm and  $\delta^7\text{Li} = -35 \text{ ‰}$ ) (Fig. 8). The array with a positive slope defined by the pure trachyte glass is thought to have preserved the equilibrium distribution of Li isotopes acquired prior to sample disruption. The array with a negative slope defined by the glass hosting sub-micrometric K-feldspars is consistent with disequilibrium loss of Li during the exhumation of the trachyte melt by the April 2007 magma. This second event of Li degassing might reflect slightly slower cooling of the interior of the pumice, which allowed crystal nucleation and Li diffusion towards the gas-melt interface. In support of this idea, Li is estimated to diffuse from melt to gas bubbles over time scales as short as seconds (see last figure of Vlastelic et al., 2013a). In the following, we model the array of the pure glass in order to constrain the degassing history of the trachyte melt prior to its exhumation. We use the term "degassing" *sensu lato* for the exsolution of gas or fluid, in the absence of constraints on the density of the exsolved phase.

We consider four scenarios, in which crystallization and degassing occurred simultaneously or successively, in open or closed system. For simultaneous crystallization and degassing in an open system we use the model previously developed for chlorine (Villemant & Boudon, 1999; Villemant et al., 2008) and subsequently modified by Vlastelic et al. (2011) to account for Li partitioning into minerals. During this fractional process referred to as FCD, fluids and crystals are extracted from the silicate melt immediately after their formation. The concentration of Li in the residual silicate melt ( $C^M$ ) varies with the initial melt content ( $C_0^M$ ) as follows (Eq. 1):

$$C^M = C_0^M \cdot F^{(\beta - 1)}$$

with

$$F = 1 - (1 + k)\Delta\text{Fluid}$$

and

$$\beta = \frac{D^{V-M} + kD^{S-M}}{k + 1}$$

where F is the mass fraction of residual silicate melt,  $\Delta\text{Fluid}$  is the mass fraction of fluid lost, and k the mass ratio of precipitated crystals to exsolved fluid. The latter (k) is assumed constant although this parameter might increase during degassing–crystallization evolution

(Villemant et al., 2008).  $D^{V-M}$  and  $D^{S-M}$  are the fluid-melt and crystal-melt partition coefficients, respectively. Writing Eq.1 for each Li isotope, and normalising yields (Eq. 2) :

$$\left(\frac{^7\text{Li}}{^6\text{Li}}\right)^M = \left(\frac{^7\text{Li}}{^6\text{Li}}\right)_0^M \cdot F^{(\beta_7 - \beta_6)}$$

where  $(^7\text{Li}/^6\text{Li})_0^M$  is the initial isotopic ratio of the melt, and subscripts 7 and 6 denote for  $^7\text{Li}$  and  $^6\text{Li}$  species, respectively. In the second scenario referred to as ECD, crystallization and degassing occur simultaneously in closed-system, with melt, crystals and fluids remaining in chemical equilibrium. The expression of Li concentration in the silicate melt is obtained by combining the mass balance equation and the definition of  $\beta$  (Eq.3):

$$C^M = \frac{C_0^M}{\beta + F(1 - \beta)}$$

And for Li isotopes (Eq. 4):

$$\left(\frac{^7\text{Li}}{^6\text{Li}}\right)^M = \left(\frac{^7\text{Li}}{^6\text{Li}}\right)_0^M \cdot \frac{\beta_6 + F(1 - \beta_6)}{\beta_7 + F(1 - \beta_7)}$$

In Eq. 2 and 4,  $D_7^{V-M}$  and  $D_6^{V-M}$  are related through the coefficient of isotopic fractionation between fluid and silicate melt ( $\alpha^{V-M}$ ) defined as (Eq. 5):

$$\alpha^{V-M} = \frac{\left(\frac{^7\text{Li}}{^6\text{Li}}\right)^V}{\left(\frac{^7\text{Li}}{^6\text{Li}}\right)^M} = \frac{D_7^{V-M}}{D_6^{V-M}}$$

where  $(^7\text{Li}/^6\text{Li})^V$  is the Li isotopic composition of the fluid.

For both FCD and ECD, the primary melt is assumed to have 5.5 ppm Li (average content of melt inclusions hosted in olivine crystals with forsterite contents in the range of 83.4-83.9 %, Di Muro et al., 2014). Because Li isotopes do not fractionate significantly during crystallization

(Tomascak et al., 1999; Schuessler et al., 2009), we assume that the initial Li isotopic composition is as in SSB ( $\delta^7\text{Li}=+3.5\text{‰}$ ), and  $D_7^{S-M} = D_6^{S-M}$  in Eq. 2 and 4. We then consider a two-step process where degassing occurs after fractional crystallization (FC). The Li content of the trachyte melt prior to degassing is estimated assuming no anomaly on trace element patterns ( $\text{Li}=\text{Li}_{\text{SSB}}\cdot[\text{Tm}/\text{Tm}_{\text{SSB}}+\text{Yb}/\text{Yb}_{\text{SSB}}]/2=11.8\text{ ppm}$ ), which implies a solid-melt partition coefficient of ca. 0.6. Subsequent degassing is modelled using Eqs. (1-2) for fractional degassing (open system) and Eqs. (3-4) for equilibrium degassing (closed-system) setting in both cases  $k=0$  (no crystallization). These two two-step processes are referred to as FC-FD and FC-ED, respectively.

For all four scenarios, we consider a dominantly aqueous fluid, with a concentration of 1.0 wt.% in primary melts (Bureau et al., 1999; Di Muro et al., 2014). The  $\text{H}_2\text{O}$  content of the trachyte melt prior to degassing (FC-FD and FC-ED processes) is estimated at 5.0 wt.% assuming 80% crystallization of an anhydrous mineral assemblage (Upton & Wadsworth, 1972). Taking 0.2 wt.% for the final water content in the degassed trachyte (Vlastelic et al., 2011), the amount of water lost ( $\Delta\text{Fluid}$ ) is 0.8 wt.% in the FCD and ECD scenarios (with  $k=80/0.8$ ) and 4.8 wt.% in the FC-FD and FC-ED scenarios. With these parameters, the target composition of the devolatilized trachyte ( $\text{Li}=2\text{ ppm}$  and  $\delta^7\text{Li} = -35\text{‰}$ ) requires  $D^{V-M}$  between 37 and 260 and  $\alpha^{V-M}$  between 1.022 and 1.053 depending on the crystallization-degassing scenario (Fig. 8). Only the FC-ED scenario with  $D^{V-M}=104$  and  $\alpha^{V-M}=1.048$  reproduces the linear array shown by the trachyte glass data (Fig. 8). This indicates that the exsolved fluid remained in equilibrium with the silicate melts, and suggests that the trachyte melt degassed in closed-system. The idea that the fluid phase was not extracted until the disruption of the trachyte melt by the basaltic magma is independently supported by the abnormally heavy  $^7\text{Li}/\text{Li}^6$  (+7 to +14‰) and slight positive Li anomaly of the basaltic glass coating the pumice (Fig. 4 and 8). This signature is best explained if the 2007 basalt assimilated or interacted with the  $^7\text{Li}$ -enriched vapour derived from the trachyte melt. The fluid in equilibrium with the trachyte glass (3.2-5.6 ppm Li and  $\delta^7\text{Li}$  between -19.8 and -31‰) must have 331-583 ppm Li and  $\delta^7\text{Li}$  between +16.1 and +26.1‰ (with  $D^{V-M}=104$  and  $\alpha^{V-M}=1.048$ ), and can thus easily contaminate the basalt. If differentiation took place in the lithospheric mantle (at 30 km depth), which cannot be ruled out, the parental melt would contain  $1.1 \pm 0.9\text{ wt.\% CO}_2$  in addition to 1.0

wt.% H<sub>2</sub>O (Boudoire et al., 2018), and  $D^{V-M}$  would be 17-67 % lower than estimated above (but  $\alpha^{V-M}$  would not change markedly).

### **Constraints on the density of the fluid phase from element partitioning between fluid and silicate melt**

Lithium isotope variations imply that the trachyte parental melt did not reach water saturation until the very late stage of crystallization. On the other hand, it is likely that the silicate melt reached sulphide saturation in response to the drop of oxygen fugacity related to titanomagnetite removal at MgO~5 wt.% (Collins et al., 2012). Lithium isotope evidence for equilibrium degassing (FC-ED process) provides the possibility to estimate fluid-melt partition coefficients for semi-volatile elements other than Li. The assumption behind this calculation is that semi-volatile elements behave similar to lithium and concentrate in the trachyte melt before being degassed. Concentrations of Cl, F, B, Cu and U in the trachyte melt prior to degassing are estimated assuming that the element ratios Cl/Nb, F/Nd, B/Nb, Cs/Th, Cu/Th and U/Th do not largely fractionate during crystallization, and are thus as in SSB (Electronic Appendix 1). Fluid-melt partition coefficients are inferred from Eq. (3) with  $\beta = D^{V-M}$  ( $k=0$ ) and  $\Delta\text{Fluid} = 4.8 \text{ wt.}\%$  (cf. previous section). In the absence of in situ glass data for the elements of interest, we use the bulk concentration of 0704-PS and 0704-PN. We find  $D^{V-M}$  in the range of  $7.1\text{--}17 \times 10^2$  for Cs,  $8.2\text{--}14 \times 10^2$  for Cu,  $2.4\text{--}4.1 \times 10^2$  for F,  $2.4\text{--}3.6 \times 10^2$  for Cl,  $2.4 \times 10^2$  for B and 8-47 for U. Note that these simple estimates are bulk partition coefficients of elements between the trachytic melt and a fluid which composition is not constrained. The corresponding concentrations of elements in the fluid in equilibrium with the trachyte melt are 2.8 wt.% Cl, 2.4 wt.% F, 1.2 wt.% Cu, 480 ppm B, 30 ppm Cs and 20-46 ppm U. Although the calculated  $D^{V-M}$  have a factor of two uncertainty, they are much larger than those estimated at low pressure between silicate melt and low-density vapours, which are generally close to unity or lower (Pokrovski et al., 2013). For instance, the partition coefficients of Li, Cs, and Cu between gas and magma are estimated to be lower than 0.1 at Tolbachik, Kudryavy and Erta Ale volcanoes (Zelenski et al., 2014). Conversely, the estimated  $D^{V-M}$  are comparable to the partition coefficients measured between dense brines and silicate melts at crustal conditions (600-1000 °C, 50-500 MPa) (Williams-Jones & Heinrich, 2005; Pokrovski et al., 2013). The estimated mobility of uranium is even higher than in crustal fluids (Peiffert et al.,

1996), and approaches U behaviour in subduction zones fluids (Bali et al., 2011). Such elevated partition coefficients reflect the complexation of metals and metalloids by halogen ions and hydration, which increase with fluid salinity, density and pressure. This effect is especially marked in the case investigated here as closed system degassing of the trachyte contributed to maintain high concentrations of water, Cl and F in the system. The high  $D^{V-M}$  estimated for Cu might also reflect to some extent the partitioning of Cu into liquid sulphides. Generally, these results indicate that the trachyte parental magma most likely differentiated deeper than the shallow magma reservoir of Piton de la Fournaise located at a depth of ca. 2.5 km.

### Uranium loss

The depletion of U relative to Th in the pumice, with Th/U up to 12.7 against 4.0 in parental basalts, indicates up to 68 % U removal. Fractional crystallisation of zircon, in which U strongly partitions relative to Th, can be shown to have barely increased the Th/U in the 2007 trachyte. Zircon is present in such a small abundance and sizes that it was not identified microscopically, only different chemical dissolution techniques revealed its presence in the pumice. To evaluate the fraction of zircon removed from the melt, we use the composition of the zircon-free glass (sample dissolution in PTFE vials using HF-HNO<sub>3</sub>) because the bulk rock contains accumulative zircon as evidenced by Zr-Hf positive anomalies in trace element patterns (Fig. 4). The zircon-free glass shows up to 50% Zr depletion (Zr/Zr\* of 0.5 in chip#1 of sample 0704-TRA, which has 199 ppm Zr; Electronic Appendix 1). That glass thus misses up to 200 ppm Zr, which corresponds to only 0.04% modal zircon (because the element zirconium (Zr) corresponds to approximately half the weight of a zircon). How much zircon fractionated from the trachyte melt can then be estimated for 80% fractional crystallisation of basalt (Upton & Wadsworth, 1972) by multiplying the modal proportion of zircon with that of the remaining melt proportion, namely  $0.04\% \times 20\%$ , or  $8 \times 10^{-3} \%$ . Assuming that U and Th do not significantly enter major minerals, and zircon-melt partition coefficients of 81 for U and 8.2 for Th (Wang et al. 2011), 80% crystallization of a mineralogical assemblage including  $8 \times 10^{-3} \%$  zircon increases the Th/U ratio by a factor of 1.01 only. Thus, the amount of zircon removed is too small to produce significant Th/U variations.

A more likely possibility is related to the increasing mobility of uranium in oxidising conditions. Pietruszka et al. (2009) suggested that some lavas of Piton de la Fournaise assimilated plutonic

rocks enriched in U through the circulation of hydrothermal fluids. In their model, hydrothermal fluids leach  $U^{6+}$  in the shallow oxidized layers of the volcanic edifice and precipitate  $U^{4+}$  in the deeper more reduced regions. In the case of the U depleted rhyolite pumice produced in 2011 at El Hierro (Canary islands), Sigmarsson et al. (2013) suggested that assimilation of sediments raised the oxygen fugacity of the mingled rhyolitic magmas to near Ni-NiO buffer, which enabled U volatilization as  $UF_6$ . As discussed above, neither radiogenic nor O isotopes provide evidence for assimilation of foreign material in the case studied here. Moreover, lack of U enrichment in Piton de la Fournaise gas sublimates, including sulphates and fluorides formed above thick lava flows (Vlastelic et al., 2013b), indicates that U is not significantly transported by low pressure - low density vapours. In keeping with Li isotope systematics, it is suggested that closed-system devolatilization of the trachyte melt during the very late stage of differentiation produced fluids enriched chlorine, fluorine and possibly carbonate (Upton & Wadsworth, 1972), leading to high solubility of U relative to Th. Whether the fluid exsolved and remained as an immiscible phase together with the degassed trachytic melt, or if it was integrated into hydrous phases (e.g., amphibole, chlorite, biotite ..) crystallising from the fluid phase remains an open question.

### Age of U loss

Constraints on the age of the U loss may be obtained from U-series decay products. Trachyte melt formed by 80% fractional crystallisation from a basalt should have identical U/Th as the parental magma, if the zircon proportion in the crystallising assemblage is very small. The very low U/Th is thus compatible with U-loss by volatile exsolution from the trachyte melt (Fig. 6a). Whether the volatile exsolution occurred instantaneously or progressively cannot be resolved by the present results. Nevertheless, the radioactive equilibrium between  $^{238}U$  and  $^{230}Th$  (Fig. 6a) indicates that the minimum time elapsed since U loss is close to five times the half-life of  $^{230}Th$ , i.e.  $5 \times 75.4 = 380$  ka, the time needed for reaching radioactive equilibrium between  $^{238}U$  and  $^{230}Th$ . The small  $^{230}Th$  excess measured in the glass fraction of sample 0704-TRA possibly results from the contamination of the trachyte glass with small amount of 2007 basalt with excess  $^{230}Th$  over  $^{238}U$ , which was the carrier magma for the old trachyte. This is consistent with the observation that the basaltic glass locally invades the pumice as fine droplets or thin films (Fig. 2a and c). However, such a contamination cannot explain the large variations of

( $^{230}\text{Th}/^{232}\text{Th}$ ) and ( $^{238}\text{U}/^{232}\text{Th}$ ) in the trachyte samples, which most likely reflect mixing with the U enriched fluids that did not escape. Indeed, the fluid composition is expected to plot on the equiline on the other side of the equipoint (Fig. 6b), and may mix to some degree with the trachyte melt if the system remained closed until the eruption.

The fractionation between U and Th is recorded at the end of  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay chains by  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$ . The ten trachyte samples analysed for Pb isotopes show subtle variations of the radiogenic  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  ratio (0.9895-0.9918) within the range of historical basalts (Fig. 9). The  $^{208}\text{Pb}^*/^{206}\text{Pb}^* - ^{232}\text{Th}/^{238}\text{U}$  isochron has a low and poorly defined slope of  $1.7(\pm 8.3) \cdot 10^{-5}$ , which translates into an age of  $0.37 \pm_{0.37}^{1.73}$  Ma. This imprecise age has little significance, but its upper limit within error constrains Th/U fractionation to be younger than 2.1 Ma. In any case, if the Th/U increase was older than 2.1 Ma,  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  of the trachyte would be significantly higher than the SSB value of  $0.991 \pm 0.002$  (Vlastelic et al., 2006). Taken together, U-series isotopes and  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  constrain U loss to have occurred between 0.38 and 2.1 Ma ago. Placing these ages in the history of La Réunion Island, we note that they span a time period extending from the oldest subaerial activity of Piton des Neiges to the early activity of Piton de la Fournaise (Fig. 10).

### Long-term trachyte storage

The surprisingly old age of U loss raises the possibility, not envisioned so far, that the trachyte derives from the remelting of ancient intrusive rocks of La Réunion Island. This possibility is consistent with the basalt/trachyte volume ratio of about  $10^8$ , and the high temperature ( $1188 \pm 16$  °C, Gurioli et al., 2018) and fast ascent of 2007 magmas, which potentially allowed important superheating above the liquidus. However, partial melting of gabbros with Zr deficit ( $\text{Zr}/\text{Zr}^*$  in the range of 0.37-0.53, Nauret et al., 2019) cannot produce the 2007 trachyte with a Zr excess ( $\text{Zr}/\text{Zr}^*$  of 1.6-3.0). Similarly, partial melting of plagioclase-free wehrlite cannot produce the observed negative Sr-Ba-Eu anomalies (Fig. 4). In contrast, partial defrosting, or melting of a solidified syenite intrusion is compatible with the 2007 trachyte composition. Depletion of Sr, Ba and Eu (Fig. 4) and low K/Zr would suggest feldspar-rich residue rather than alkali feldspar cumulate melting in the “trachyte attractor” hypothesis of Wolff (2017). Indeed, the major element concentrations of the 2007 trachyte are within the range of glasses formed by partial melts of syenite from Ascension Island (Harris & Bell, 1982), with the noticeable

exception of Na<sub>2</sub>O. Unfortunately, trace element concentrations have not been determined on those glasses to the best of our knowledge. The exsolved fluid phase would then have been stored in the ubiquitous hydrous phases (amphibole, chlorite and/or biotite) or interstitial cavities, such as those described by Upton & Wadsworth (1972) in microsyenites from Piton des Neiges.

In a second scenario, slow crystallization could have lasted at least approximately 0.4 Ma and a trachytic melt could still be available within the magma plumbing system, either as interstitial melt in a crystal mush or as melt lens. To survive over such time scale, a small volume of silicic magma requires a perfect balance of heat flux, so that melts neither solidify nor float and escape. To evaluate this possibility, we estimate the volume of Piton de la Fournaise plumbing system which temperature is maintained above the trachyte liquidus (about 800°C) due to the continuous flux of hot basaltic magma. The thermal power  $Q$  brought by the incoming magma depends on the magma flux ( $\phi$ ), the temperature difference between magma reservoir ( $T_{res}$ ) and injected magma ( $T_{inj}$ ), and the fraction of crystal removed ( $f$ ) at  $T_{res}$  according to (Eq. 6):

$$Q = \phi \rho (C_p (T_{inj} - T_{res}) + fL)$$

where  $\rho$  is the magma density (2600 kg/m<sup>3</sup>),  $C_p$  the heat capacity (1500 J/kg per K) and  $L$  the latent heat (4x10<sup>5</sup> J/kg) (Hawkesworth et al., 2000). Independent observations, including the age/volume ratio of La Réunion edifice (e.g. de Voogd et al., 1999) and the small Sr isotope variations of lavas (Vlastelic et al., 2018), suggest that the long-term magma production rate has remained relatively uniform and similar to the average rate over the last 60 years (0.5 m<sup>3</sup>/s, dense rock equivalent, Roult et al., 2012). Based on the MELTS modeling of Villemant et al. (2009), we set  $T_{inj} = 1304^\circ\text{C}$  and  $T_{res} = 1150^\circ\text{C}$  with  $f=0.2$  for Steady State Basalt with 92 ppm Ni (Electronic Appendix 1). Using these values,  $Q$  is estimated at  $4 \times 10^8$  W. We assume that this thermal power is uniformly emitted in a spherical plumbing system with a steady-state thermal structure. The temperature decreases from the centre to the boundary of the sphere according to Eq. 4.42 of Turcotte & Schubert (1982) (Eq. 7):

$$T_x = T_{x=r} + \frac{\rho H}{6k} (r^2 - x^2)$$



where  $r(m)$  is the radius of the sphere,  $x(m)$  the distance to its centre,  $H$  the heat supply in W per kg, and  $k$  the thermal conductivity (2.24 W/m per K). Substituting  $Q(W)$  for  $H(W/kg)$ , the sphere radius writes (Eq. 8):

$$r = \frac{Q}{8k\pi(T_c - T_{x=r})}$$

where  $T_c$  is the temperature at the centre of the sphere. Using a temperature of 1150°C at the center of the plumbing system (i.e.,  $T_c = T_{res}$ ) and 200°C at its boundary (2.5-4 km depth at 50-80°C/km, Dezayes et al., 2016), the sphere radius is estimated at 7.5 km. Note that this value is robust because  $Q$  is rather well constrained and the temperature difference between the center and the boundary of the plumbing system must be close to 1000°C. From Eq.7 the sphere with  $T > 800^\circ\text{C}$  has a radius of 4.6 km and its volume represents about ¼ of the plumbing system. This hot core could correspond to the central plumbing system of Piton de la Fournaise located below the enclos Fouqué caldera (Fig. 1; Michon et al., 2015). This simple model indicates that the thermal flux from hot basaltic magmas raising from the mantle is high enough to prevent magmas trapped within the central plumbing system of Piton de la Fournaise from total solidification. Whether the old trachyte erupted in 2007 is related to the fading sub-terrain magmatic activity of older volcanoes on La Réunion, Piton des Neiges or Les Alizés, is not clear but its origin could be contemporaneous with the initiation of Piton de la Fournaise volcano (Fig. 10).

## CONCLUSIONS

This paper aims to understand the eruption of a small volume of silicic melt during the largest historical eruption of the Piton de la Fournaise volcano. Such an event is puzzling because the volcano has regularly produced very homogeneous basalts since 0.44 Ma. The in-depth geochemical study of the pumice samples confirms previous suggestions that the trachyte is a differentiation product of a common basalt. On the other hand, the trachyte shows two particular geochemical features that may be testament to a long and complex history of differentiation and outgassing: (1) the extensive depletion of moderately volatile elements

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3 745 (Cs, B, Li, Cu) and uranium, together with large Li isotope fractionation are consistent with  
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5 746 closed system exsolution of dense fluids at a depth of several kilometres. (2) U-series isotopes  
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7 747 and radiogenic  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  constrain the time elapsed since U loss to between 0.4 and 2.1  
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9 748 Ma. Because this age is as old or older than Piton de la Fournaise shield edifice, the 2007  
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11 749 trachyte could be a product of an ancient volcano, such as Piton des Neiges or Les Alizés, which  
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13 750 declined about 0.4 Ma ago. Alternatively, it could result from the remobilization of the  
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15 751 interstitial melt of a micro-syenite intrusion, possibly not fully solidify due to the sustained  
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17 752 heat supply from hot basaltic magmas. The unusual dynamics of April 2007 eruption certainly  
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19 753 played a major role in remobilizing the old trachyte, providing the first direct evidence for  
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21 754 silicic melts in the plumbing system of Piton de la Fournaise basaltic volcano.  
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## Figure captions

### Figure 1

Location maps. (a) Shaded relief map of La Réunion Island showing major structural features, modified from Gailler and Lénat (2012). The boundary between Piton des Neiges (PdN) and Piton de la Fournaise (PdF) volcanoes, and the locations of the main places discussed in the text are shown. The main vent of the April 2007 eruption (Piton Tremblet shown with a star) is located within the Enclos Fouqué caldera, along the SE rift zone. Older calderas of Piton de la Fournaise are labelled. Note that the Rivière des Remparts caldera hosts the major outcrop of 400-530 ka old differentiated lavas, recently ascribed to the vanishing activity of an older volcano (named Les Alizés), which was active in the SE of the island prior to Piton de la Fournaise (Valer et al., 2017a). Seismic zones labelled [N30–40] and [N120] (dashed lines) are interpreted as representing magma path 40-30 and 20-11 km below sea level, respectively, below the western flank of Piton de la Fournaise (Michon et al. 2015, 2016; Boudoire et al., 2017). Following the April 2007 eruption, several earthquakes clustered 30km below sea level, 30 km to the west of Piton de la Fournaise summit [2007DEC], suggesting that the April 2007 magmas rose through a very eccentric region of the deep plumbing system. (b) Map of the April 2007 eruptive vent showing the opening fracture (dashed line), the Piton Tremblet (dark grey), the lava flow (light grey), and the pumice fallout (hatched field). The pumices were grouped according to their location relative to the opening fracture: the PN field ( $21^{\circ}16'53.5 \pm 4.5''\text{S} - 55^{\circ}46'19 \pm 4''\text{E}$ ) is located to the SW of the fracture whereas the PS field ( $21^{\circ}16'50 \pm 2''\text{S} - 55^{\circ}46'27 \pm 4''\text{E}$ ) is located to the NE. Few chips from each fields were powdered for bulk chemical analyses (0704-PN and 0704-PS samples). White pumices with trace of basaltic glass were found to the North of Piton Tremblet at the border of the April 2007 lava flow ( $21^{\circ}16'51''\text{S} - 55^{\circ}46'29''\text{E}$ ). They are referred to as sample 0704-TRA. Chips from the PN (N-PON) and PS (S-PON and 0704-TRA) fields were selected for in situ analysis. (a&b) Coordinates are in km (WGS84, UTM 40S). (c) Photo of the pumice and its basaltic glass coating (N-PON sample).

### Figure 2

Images of the pumice samples. (a) Close-up view of the relationship between basaltic (dark) and trachytic (white) glasses (N-PON sample). 1- Mixing zone with characteristic round

vesicles. 2- Fine droplets of basaltic liquid impregnating the trachytic pumice. (b) Scanning Electron Microscope (SEM) image of pumice 0704-PS showing a highly vesiculated texture with thin glassy vesicle walls. (c) Transmitted plane-polarized photomicrograph of SPON3 sample with brown glass coating trachytic glass; (d) Backscatter Scanning Electron Microscope (BSE) image of the same field as (c) Mgt = magnetite crystals. Plg = microlites of plagioclase. (e) BSE image of the transition from basaltic to trachytic liquids illustrating the gradual change in composition and crystallization of plagioclase (Plg) microcrystals in the basaltic glass (sample SPON3). (f) BSE image showing the development of abundant alkali feldspar (Fth) micro-crystallization in trachytic glass (sample SPON1). Note the presence of a cluster of magnetite crystals in the trachytic liquid close to its contact with a more basic liquid. In all panels, the yellow numbers express the SiO<sub>2</sub> content (wt.%).

### Figure 3

Total alkali vs. silica (TAS) diagram (Le Bas et al., 1986) showing representative compositions of the trachytic pumices. Bulk rock compositions (circles) are from this study and Falco (2009). The compositional fields of Piton des Neiges and Piton de la Fournaise volcanoes are reported.

### Figure 4

Trace element patterns of the April 2007 trachytic pumice and the basaltic coating. Concentrations are normalized to the average concentrations of steady-state basalts (SSB) given in Electronic Appendix 1. SSB are the dominant homogeneous basalts of La Réunion Island (Albarède et al., 1997). Pattern of 0704-PS is drawn using the data obtained with NH<sub>4</sub>HF<sub>2</sub> dissolution. Pattern of 0704-PS is drawn combining data obtained with Savillex (Li, Cs, Pb) and alkali fusion (other elements) dissolution methods. Pattern of 0704-TRA is the mean of analyses of chips #1-4 (Savillex) with Zr-Hf data from chip#7 analysis (Parr 250°C). Vertical lines indicate elements with negative anomalies.

### Figure 5

Sr-Nd-Pb isotope plots. The signature of the trachytic pumice and the basaltic coating is compared to that of La Réunion lavas in <sup>143</sup>Nd/<sup>144</sup>Nd vs <sup>87</sup>Sr/<sup>86</sup>Sr (a) and <sup>208</sup>Pb/<sup>204</sup>Pb vs <sup>206</sup>Pb/<sup>204</sup>Pb (b) spaces. The <sup>143</sup>Nd/<sup>144</sup>Nd ratios are shown using the εNd notation where  $\epsilon Nd = [(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR} - 1] \cdot 10^4$  with  $(^{143}Nd/^{144}Nd)_{CHUR} = 0.512638$ . Error

bars are shown in (a) and are within data symbols in (b). Data used to draw the La Réunion isotopic fields are from Fisk et al. (1988), Fretzdorff & Haase (2002), Bosch et al. (2008), Pietruszka et al. (2009), Smietana (2011), Vlastelic et al. (2005, 2007, 2009b, 2018).

# Figure 6

( $^{230}\text{Th}/^{232}\text{Th}$ ) versus ( $^{238}\text{U}/^{232}\text{Th}$ ) isochron plot. (a) The composition of historical lavas of Piton de la Fournaise (black field) is drawn using the data of Sigmarsson et al. (2005) and Pietruszka et al. (2009). Errors bars of ( $^{230}\text{Th}/^{232}\text{Th}$ ) and ( $^{238}\text{U}/^{232}\text{Th}$ ) are either shown or within symbol size. All but one trachyte samples plot within error on the equiline, which is indicative of  $^{230}\text{Th}$ - $^{238}\text{U}$  radioactive equilibrium. Indicative isochrons are shown for different values of  $t$ , using the equation:

$$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right) = \left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)^0 e^{-\lambda^{230}.t} + \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)(1 - e^{-\lambda^{230}.t})$$

where  $t$  is the age of Th/U fractionation and  $\lambda^{230}$  is the decay constants for  $^{230}\text{Th}$ . Dashed lines show 20% and 40%  $^{230}\text{Th}$ -excesses, i.e. ( $^{230}\text{Th}/^{238}\text{U}$ ) = 1.2 and 1.4, respectively. (b) Schematic illustration of how the 2007 trachyte formed. Fractional crystallisation yields trachyte melt with identical ( $^{230}\text{Th}/^{232}\text{Th}$ ) and ( $^{238}\text{U}/^{232}\text{Th}$ ) as the parental basalt (assumed to be identical to the recent basalts). During final magma differentiation ( $t=0$ ), exsolution of fluids in which U partitions, but not Th, yields U-poor trachyte melt (horizontal arrows) and important  $^{238}\text{U}$  -  $^{230}\text{Th}$  disequilibria. Both the  $^{238}\text{U}$ -depleted trachyte and the  $^{238}\text{U}$ -enriched fluid age and strive towards  $^{238}\text{U}$  -  $^{230}\text{Th}$  equilibrium (broken vertical arrows). Radioactive equilibrium is established after approximately 0.4 Ma with the U-depleted trachyte and the U-rich fluid having acquired a very low and very high ( $^{230}\text{Th}/^{232}\text{Th}$ ), respectively. At any time, the residual melt and the fluid plot on an isochron, on each side of the equipoint. If the system remained closed, mixing between melt and fluid could explain the large variation of melt composition along the equiline (Fig. 6 a). If the melt and the volatiles have remained as liquid and fluid phases since over 0.4 Ma, a special thermal regime is requested beneath Piton de la Fournaise. Alternatively, the trachyte crystallised as micro-syenite and the volatile phase as hydrous minerals both of which were defrosted by the primitive 2007 basalt. Both these possibilities are discussed in the text.

## Figure 7

Schematic cross section of sample 0704-TRA showing the loci of in situ Li isotope analyses. (a) Most analyses were done in the basalt coating (grey) and nearby in the trachyte (white). Ol: olivine crystals. (b) Three analyses were done in the interior of the pumice, 7-9 mm from the basalt coating. (c) Example of a SEM image acquired after SIMS measurements. These images were used to distinguish analyses performed on pure trachytic glass (light colour) from those done on glassy regions with abundant sub-micrometric K-feldspars (dark colour).

## Figure 8

$\delta^7\text{Li}$  versus Li concentration plot. Degassing and crystallization of a primary melt with 5.5 ppm Li and  $\delta^7\text{Li}=+3.5\text{‰}$  (star labelled PM) is modelled considering four scenarios: Fractional Crystallization (FC) followed by Fractional Degassing (FD) or Equilibrium degassing (ED); simultaneous crystallization and degassing in an open system (FCD) or closed system (ECD). Depending on the crystallization-degassing scenario, the target composition of the devolatilized trachyte (Li=2 ppm and  $\delta^7\text{Li} = -35\text{‰}$ ) requires  $D^{\text{V-M}}$  between 37 and 260 and  $\alpha^{\text{V-M}}$  between 1.022 and 1.053. Only the FC-ED scenario with  $D^{\text{V-M}}=104$  and  $\alpha^{\text{V-M}}=1.048$  reproduces the linear array shown by the trachyte glass data (white diamonds). See text for detailed description of the model and related equations and assumptions. The field of Piton de la Fournaise (dark grey) is drawn using the data of Vlastelic et al. (2011).

## Figure 9

$^{208}\text{Pb}^*/^{206}\text{Pb}^*$  versus  $^{232}\text{Th}/^{238}\text{U}$  isochron plot.  $^{208}\text{Pb}^*/^{206}\text{Pb}^* = [(^{208}\text{Pb}/^{204}\text{Pb})_{\text{S}} - (^{208}\text{Pb}/^{204}\text{Pb})_{\text{CD}}] / [(^{206}\text{Pb}/^{204}\text{Pb})_{\text{S}} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{CD}}]$  where subscripts S and CD refer to sample and Canyon Diablo meteorite, respectively.  $(^{208}\text{Pb}/^{204}\text{Pb})_{\text{CD}}=29.476$  and  $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{CD}}=9.307$  (Tatsumoto et al., 1973). The slope-age relationship in this isochron diagram is given by:

$$^{208}\text{Pb}^* / ^{206}\text{Pb}^* = \frac{\kappa_1 \mu_1 (e^{(\lambda^{232}.T)} - e^{(\lambda^{232}.t)}) + \kappa_2 \mu_2 (e^{(\lambda^{232}.t)} - 1)}{\mu_1 (e^{(\lambda^{238}.T)} - e^{(\lambda^{238}.t)}) + \mu_2 (e^{(\lambda^{238}.t)} - 1)}$$

where  $T=4.56$  Ga,  $t$  is the age of Th/U fractionation, and  $\lambda^{232}$  and  $\lambda^{238}$  are the decay constants for  $^{232}\text{Th}$  and  $^{238}\text{U}$ .  $\kappa$  and  $\mu$  are the  $^{232}\text{Th}/^{238}\text{U}$  and  $^{238}\text{U}/^{204}\text{Pb}$  atomic ratios, respectively. Subscripts 1 and 2 are relative to the intervals 4.56 Ga -  $t$  and  $t$  - 0 Ga, respectively. Indicative isochrons are shown for  $t$  in the range of 5 Ma – 4.56 Ga (plain lines). The regression line through trachyte data (dashed line) constrains Th/U fractionation to be younger than 2.1 Ma.

#### Figure 10

Temporal compositional evolution of La Réunion Island volcanoes. The  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio is used as a proxy for magma differentiation. Regression line through Piton des Neiges differentiated series (white triangles) is shown, whereas only temporal trends are shown for Piton des Neiges and Piton de la Fournaise shield stages because major elements and ages were not measured on same samples. The age estimated for the parental basalt of the 2007 trachyte is indicated (hatched area). The 2007 trachyte plots on the temporal compositional trend of the Piton des Neiges differentiated series, suggesting it could be a liquid remnant of the extinct volcano. Data source: McDougall (1971), Oversby (1972), Upton & Wadsworth (1972), Gillot & Nativel (1982), Albarède et al. (1997), Valer et al. (2017a).

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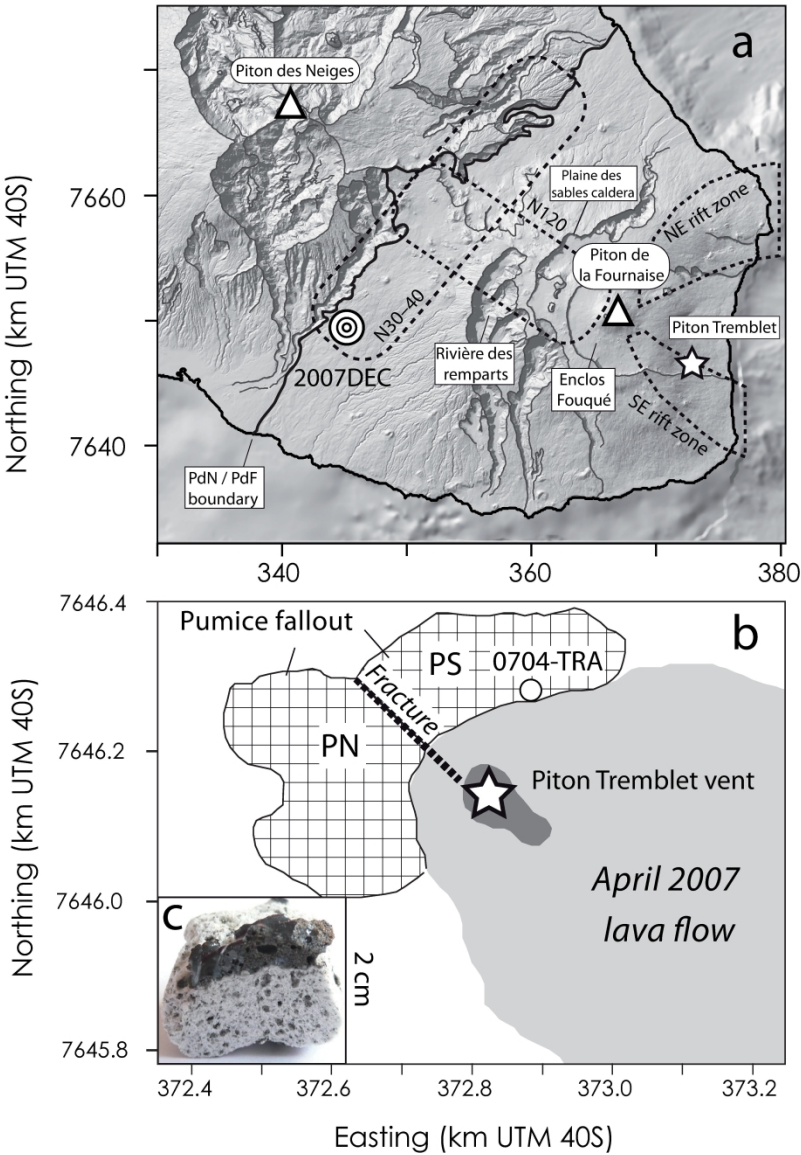
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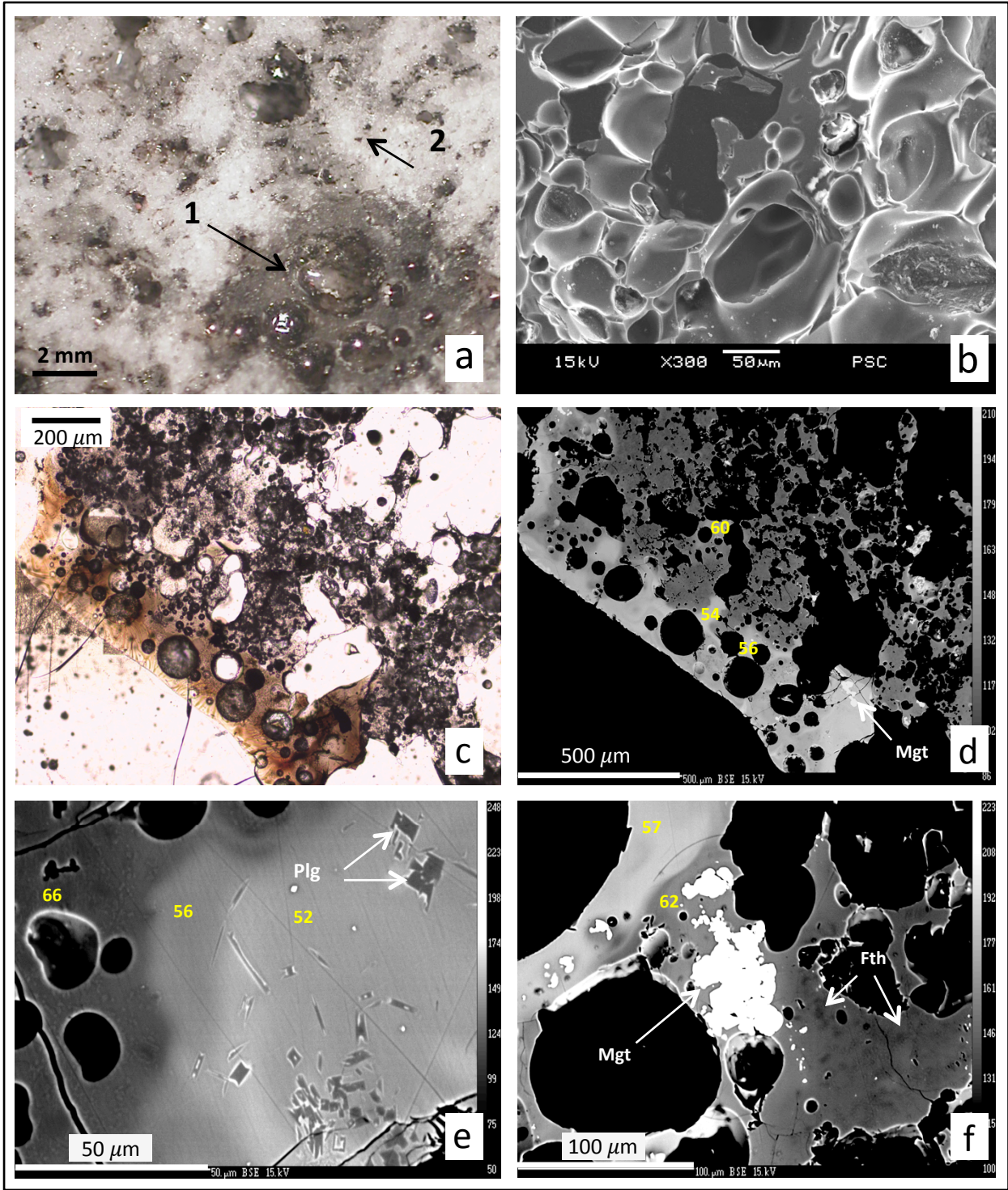
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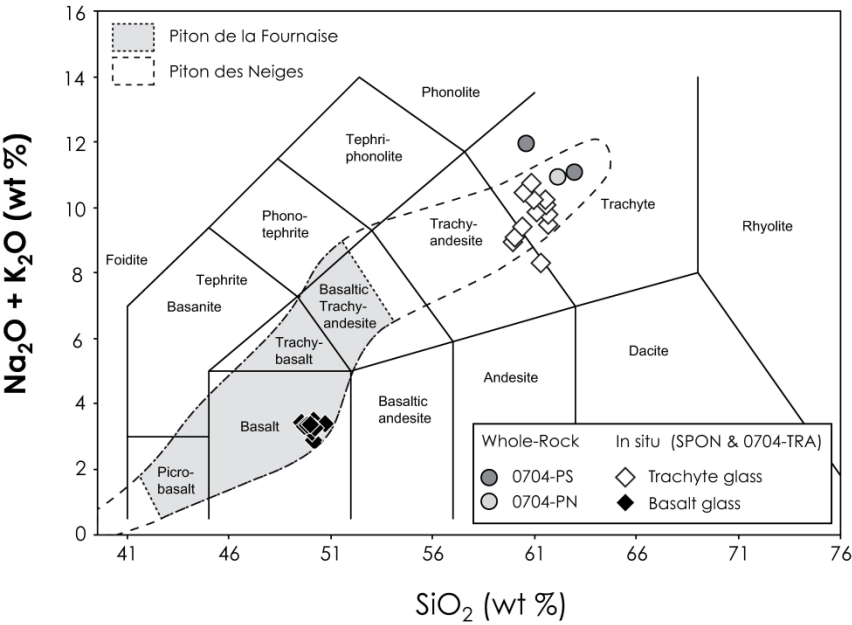
Location maps. (a) Shaded relief map of La Réunion Island showing major structural features, modified from Gailler and Lénat (2012). The boundary between Piton des Neiges (PdN) and Piton de la Fournaise (PdF) volcanoes, and the locations of the main places discussed in the text are shown. The main vent of the April 2007 eruption (Piton Tremblet shown with a star) is located within the Enclos Fouqué caldera, along the SE rift zone. Older calderas of Piton de la Fournaise are labelled. Note that the Rivière des Remparts caldera hosts the major outcrop of 400-530 ka old differentiated lavas, recently ascribed to the vanishing activity of an older volcano (named Les Alizés), which was active in the SE of the island prior to Piton de la Fournaise (Valer et al., 2017a). Seismic zones labelled [N30-40] and [N120] (dashed lines) are interpreted as representing magma path 40-30 and 20-11 km below sea level, respectively, below the western flank of Piton de la Fournaise (Michon et al. 2015, 2016; Boudoire et al., 2017). Following the April 2007 eruption, several earthquakes clustered 30km below sea level, 30 km to the west of Piton de la Fournaise summit [2007DEC], suggesting that the April 2007 magmas rose through a very eccentric region of the deep plumbing system. (b) Map of the April 2007 eruptive vent showing the opening fracture (dashed line), the Piton Tremblet (dark grey), the lava flow (light grey), and the pumice fallout (hatched field). The pumices

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3 were grouped according to their location relative to the opening fracture: the PN field ( $21^{\circ}16'53.5 \pm 4.5''\text{S} -$   
4  $55^{\circ}46'19 \pm 4''\text{E}$ ) is located to the SW of the fracture whereas the PS field ( $21^{\circ}16'50 \pm 2''\text{S} - 55^{\circ}46'27 \pm 4''\text{E}$ ) is  
5 located to the NE. Few chips from each fields were powdered for bulk chemical analyses (0704-PN and  
6 0704-PS samples). White pumices with trace of basaltic glass were found to the North of Piton Tremblet at  
7 the border of the April 2007 lava flow ( $21^{\circ}16'51''\text{S} - 55^{\circ}46'29''\text{E}$ ). They are referred to as sample 0704-  
8 TRA. Chips from the PN (N-PON) and PS (S-PON and 0704-TRA) fields were selected for in situ analysis.  
9 (a&b) Coordinates are in km (WGS84, UTM 40S). (c) Photo of the pumice and its basaltic glass coating (N-  
PON sample).

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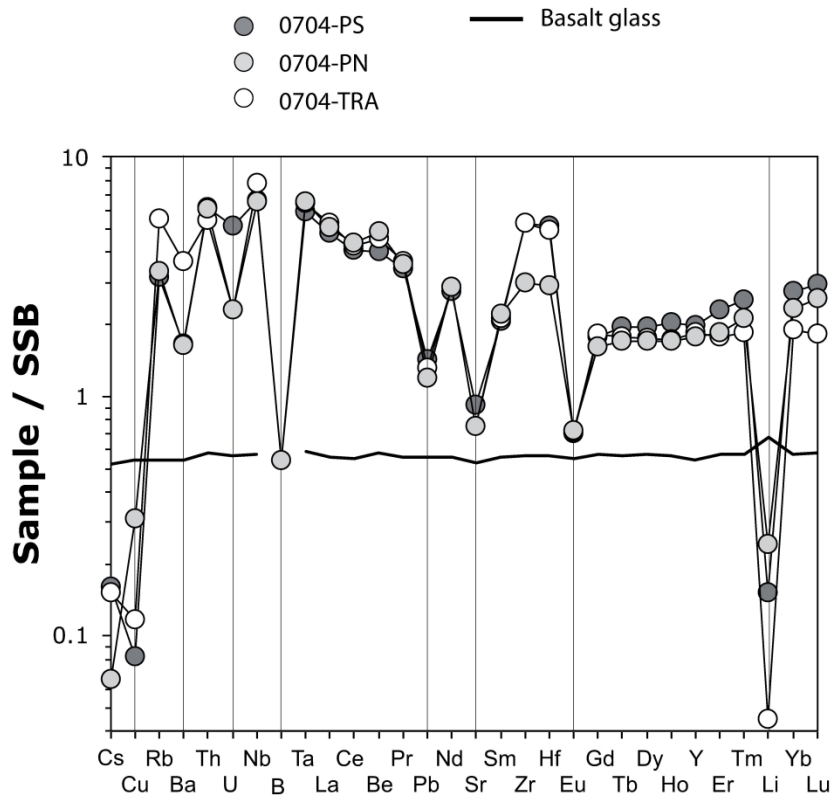


Total alkali vs. silica (TAS) diagram (Le Bas et al., 1986) showing representative compositions of the trachytic pumices. Bulk rock compositions (circles) are from this study and Falco (2009). The compositional fields of Piton des Neiges and Piton de la Fournaise volcanoes are reported.

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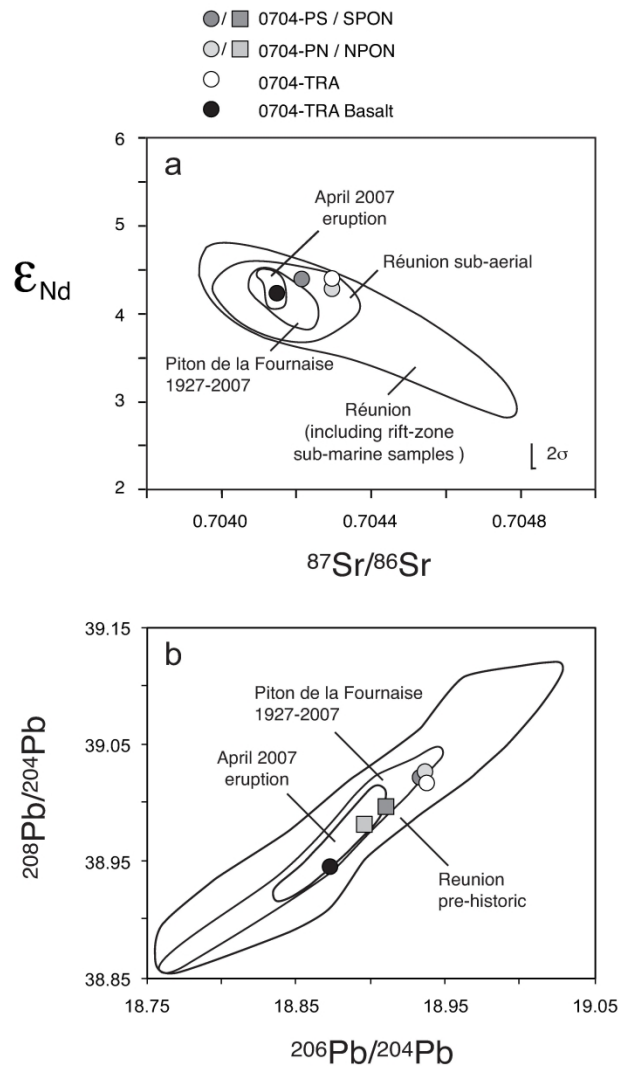
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Trace element patterns of the April 2007 trachytic pumice and the basaltic coating. Concentrations are normalized to the average concentrations of steady-state basalts (SSB) given in Electronic Appendix 1. SSB are the dominant homogeneous basalts of La Réunion Island (Albarède et al., 1997). Pattern of 0704-PS is drawn using the data obtained with  $\text{NH}_4\text{HF}_2$  dissolution. Pattern of 0704-PS is drawn combining data obtained with savillex (Li, Cs, Pb) and alkali fusion (other elements) dissolution methods. Pattern of 0704-TRA is the mean of analyses of chips #1-4 (savillex) with Zr-Hf data from chip#7 analysis (Parr 250°C). Vertical lines indicate elements with negative anomalies.

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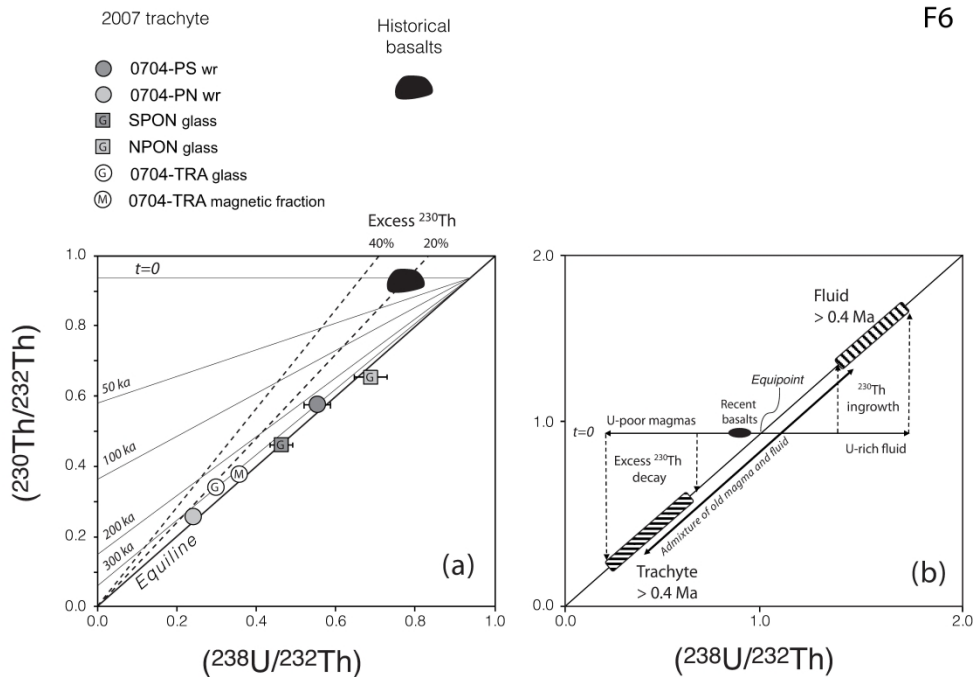
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Sr-Nd-Pb isotope plots. The signature of the trachytic pumice and the basaltic coating is compared to that of La Réunion lavas in  $^{143}Nd/^{144}Nd$  vs  $^{87}Sr/^{86}Sr$  (a) and  $^{208}Pb/^{204}Pb$  vs  $^{206}Pb/^{204}Pb$  (b) spaces. The  $^{143}Nd/^{144}Nd$  ratios are shown using the  $\epsilon_{Nd}$  notation where  $\epsilon_{Nd} = [(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR} - 1] \cdot 10^4$  with  $(^{143}Nd/^{144}Nd)_{CHUR} = 0.512638$ . Error bars are shown in (a) and are within data symbols in (b). Data used to draw the La Réunion isotopic fields are from Fisk et al. (1988), Fretzdorff & Haase (2002), Bosch et al. (2008), Pietruszka et al. (2009), Smietana (2011), Vlastelic et al. (2005, 2007, 2009b, 2018).

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F6

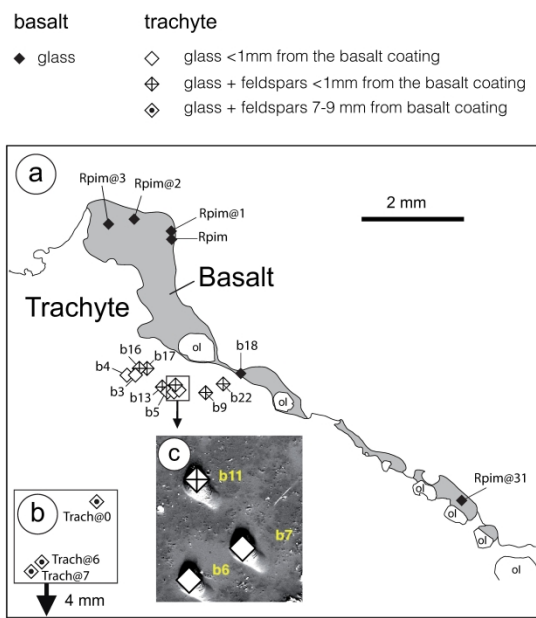


$(^{230}\text{Th}/^{232}\text{Th})$  versus  $(^{238}\text{U}/^{232}\text{Th})$  isochron plot. (a) The composition of historical lavas of Piton de la Fournaise (black field) is drawn using the data of Sigmarsson et al. (2005) and Pietruszka et al. (2009). Errors bars of  $(^{230}\text{Th}/^{232}\text{Th})$  and  $(^{238}\text{U}/^{232}\text{Th})$  are either shown or within symbol size. All but one trachyte samples plot within error on the equiline, which is indicative of  $^{230}\text{Th}$ - $^{238}\text{U}$  radioactive equilibrium. Indicative isochrons are shown for different values of  $t$ , using the equation:  $(^{230}\text{Th}/^{232}\text{Th}) = (^{230}\text{Th}/^{232}\text{Th})_0 \cdot e^{-\lambda^{230} \cdot t} + (^{238}\text{U}/^{232}\text{Th}) \cdot (1 - e^{-\lambda^{230} \cdot t})$  where  $t$  is the age of Th/U fractionation and  $\lambda^{230}$  is the decay constants for  $^{230}\text{Th}$ . Dashed lines show 20% and 40%  $^{230}\text{Th}$ -excesses, i.e.  $(^{230}\text{Th}/^{238}\text{U}) = 1.2$  and  $1.4$ , respectively. (b) Schematic illustration of how the 2007 trachyte formed. Fractional crystallisation yields trachyte melt with identical  $(^{230}\text{Th}/^{232}\text{Th})$  and  $(^{238}\text{U}/^{232}\text{Th})$  as the parental basalt (assumed to be identical to the recent basalts). During final magma differentiation ( $t=0$ ), exsolution of fluids in which U partitions, but not Th, yields U-poor trachyte melt (horizontal arrows) and important  $^{238}\text{U}$  -  $^{230}\text{Th}$  disequilibria. Both the  $^{238}\text{U}$ -depleted trachyte and the  $^{238}\text{U}$ -enriched fluid age and strive towards  $^{238}\text{U}$  -  $^{230}\text{Th}$  equilibrium (broken vertical arrows). Radioactive equilibrium is established after approximately 0.4 Ma with the U-depleted trachyte and the U-rich fluid having acquired a very low and very high  $(^{230}\text{Th}/^{232}\text{Th})$ , respectively. At any time, the residual melt and the fluid plot on an isochron, on each side of the equipoint. If the system remained closed, mixing between melt and fluid could explain the large variation of melt composition along the equiline (Fig. 6 a). If the melt and the volatiles have remained as liquid and fluid phases since over 0.4 Ma, a special thermal regime is requested beneath Piton de la Fournaise. Alternatively, the trachyte crystallised as micro-syenite and the volatile phase as hydrous minerals both of which were defrosted by the primitive 2007 basalt. Both these possibilities are discussed in the text.

279x195mm (600 x 600 DPI)



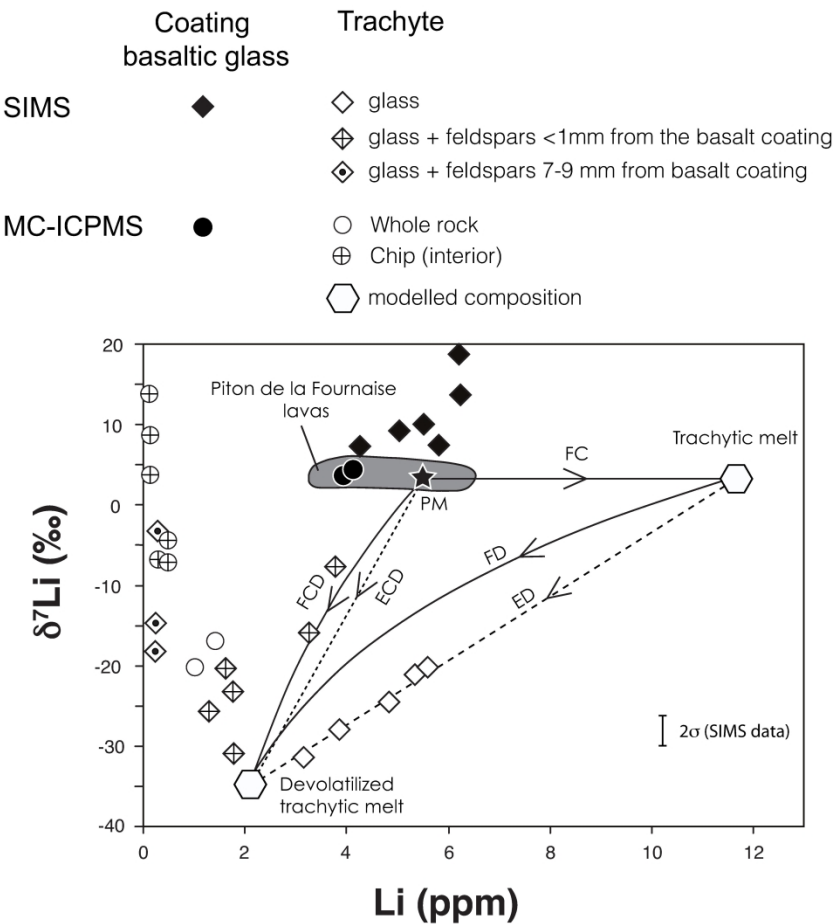
F7



Schematic cross section of sample 0704-TRA showing the loci of in situ Li isotope analyses. (a) Most analyses were done in the basalt coating (grey) and nearby in the trachyte (white). Ol: olivine crystals. (b) Three analyses were done in the interior of the pumice, 7-9 mm from the basalt coating. (c) Example of a SEM image acquired after SIMS measurements. These images were used to distinguish analyses performed on pure trachytic glass (light colour) from those done on glassy regions with abundant sub-micrometric K-feldspars (dark colour).

197x371mm (600 x 600 DPI)

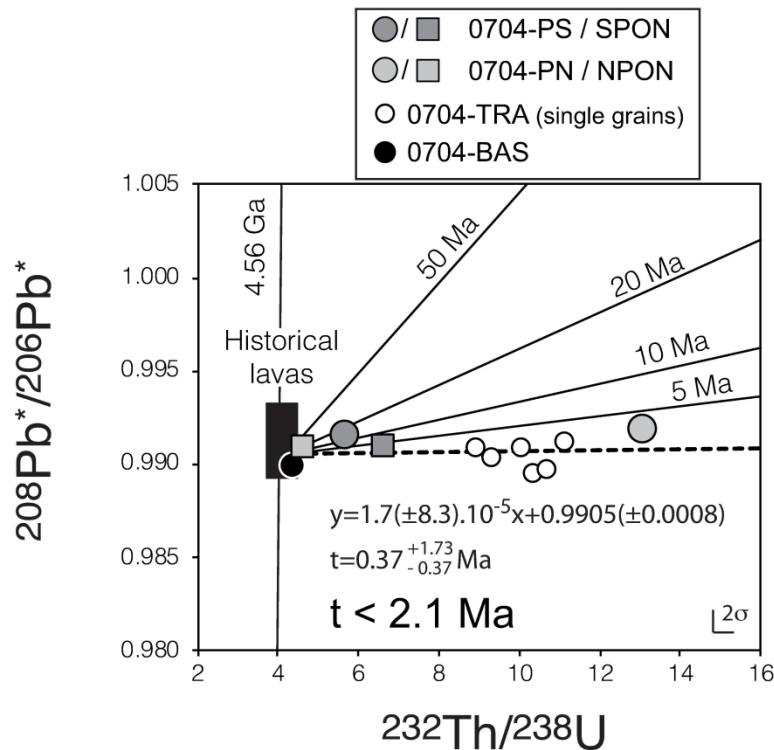
F8



$\delta^7\text{Li}$  versus Li concentration plot. Degassing and crystallization of a primary melt with 5.5 ppm Li and  $\delta^7\text{Li} = +3.5\text{‰}$  (star labelled PM) is modelled considering four scenarios: Fractional Crystallization (FC) followed by Fractional Degassing (FD) or Equilibrium degassing (ED); simultaneous crystallization and degassing in an open system (FCD) or closed system (ECD). Depending on the crystallization-degassing scenario, the target composition of the devolatilized trachyte (Li = 2 ppm and  $\delta^7\text{Li} = -35\text{‰}$ ) requires  $D^{\text{V-M}}$  between 37 and 260 and  $\alpha^{\text{V-M}}$  between 1.022 and 1.053. Only the FC-ED scenario with  $D^{\text{V-M}} = 104$  and  $\alpha^{\text{V-M}} = 1.048$  reproduces the linear array shown by the trachyte glass data (white diamonds). See text for detailed description of the model and related equations and assumptions. The field of Piton de la Fournaise (dark grey) is drawn using the data of Vlastelic et al. (2011).

189x273mm (600 x 600 DPI)

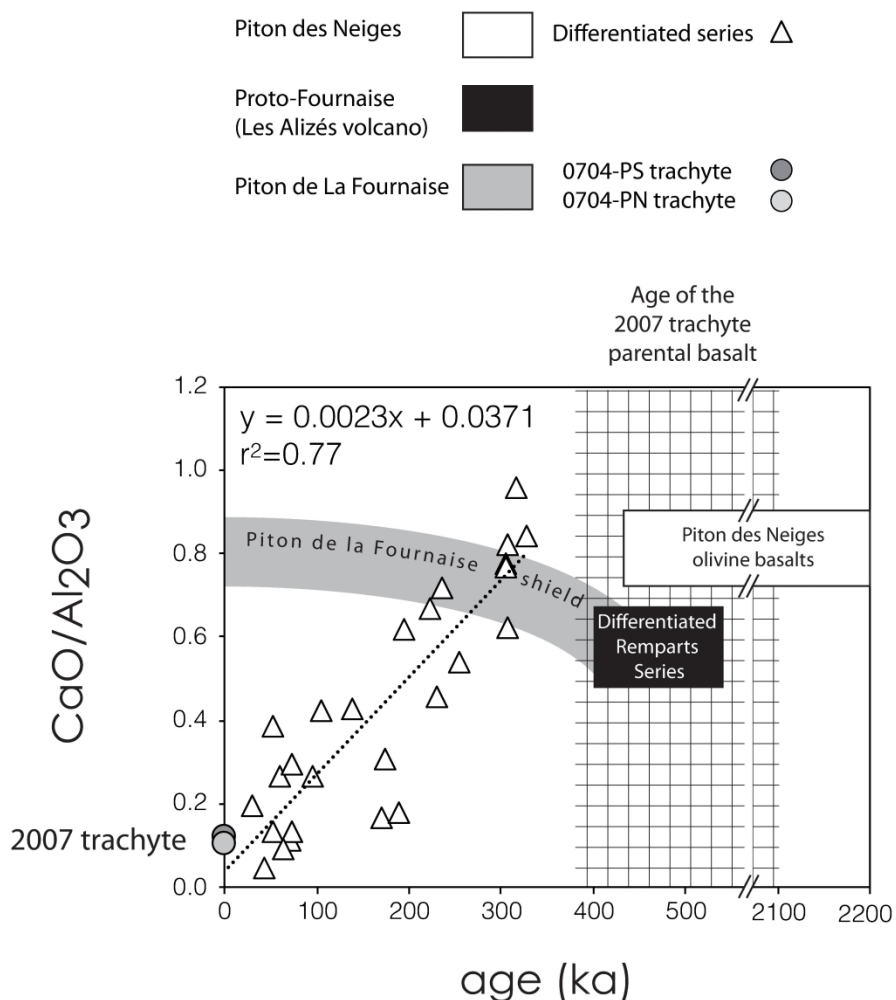
F9



$^{208}\text{Pb}^*/^{206}\text{Pb}^*$  versus  $^{232}\text{Th}/^{238}\text{U}$  isochron plot.  $^{208}\text{Pb}^*/^{206}\text{Pb}^* = [(^{208}\text{Pb}/^{204}\text{Pb})_S - (^{208}\text{Pb}/^{204}\text{Pb})_{\text{CD}}] / [(^{206}\text{Pb}/^{204}\text{Pb})_S - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{CD}}]$  where subscripts S and CD refer to sample and Canyon Diablo meteorite, respectively.  $(^{208}\text{Pb}/^{204}\text{Pb})_{\text{CD}} = 29.476$  and  $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{CD}} = 9.307$  (Tatsumoto et al., 1973). The slope-age relationship in this isochron diagram is given by:  $^{208}\text{Pb}^*/^{206}\text{Pb}^* = [\kappa_1\mu_1(e^{\lambda^{232}\text{T}} - e^{\lambda^{232}\text{t}}) + \kappa_2\mu_2(e^{\lambda^{232}\text{t}} - 1)] / [\mu_1(e^{\lambda^{238}\text{T}} - e^{\lambda^{238}\text{t}}) + \mu_2(e^{\lambda^{238}\text{t}} - 1)]$  where  $T=4.56$  Ga,  $t$  is the age of Th/U fractionation, and  $\lambda^{232}$  and  $\lambda^{238}$  are the decay constants for  $^{232}\text{Th}$  and  $^{238}\text{U}$ .  $\kappa$  and  $\mu$  are the  $^{232}\text{Th}/^{238}\text{U}$  and  $^{238}\text{U}/^{204}\text{Pb}$  atomic ratios, respectively. Subscripts 1 and 2 are relative to the intervals 4.56 Ga -  $t$  and  $t$  - 0 Ga, respectively. Indicative isochrons are shown for  $t$  in the range of 5 Ma - 4.56 Ga (plain lines). The regression line through trachyte data (dashed line) constrains Th/U fractionation to be younger than 2.1 Ma.

178x180mm (600 x 600 DPI)

F10



Temporal compositional evolution of La Réunion Island volcanoes. The CaO/Al<sub>2</sub>O<sub>3</sub> ratio is used as a proxy for magma differentiation. Regression line through Piton des Neiges differentiated series (white triangles) is shown, whereas only temporal trends are shown for Piton des Neiges and Piton de la Fournaise shield stages because major elements and ages were not measured on same samples. The age estimated for the parental basalt of the 2007 trachyte is indicated (hatched area). The 2007 trachyte plots on the temporal compositional trend of the Piton des Neiges differentiated series, suggesting it could be a liquid remnant of the extinct volcano. Data source: McDougall (1971), Oversby (1972), Upton & Wadsworth (1972), Gillot & Nativel (1982), Albarède et al. (1997), Valer et al. (2017a).

186x245mm (600 x 600 DPI)