1	Deciphering textural and chemical zoning of K-feldspar megacrysts from Mt. Amiata Volcano
2	(Southern Tuscany, Italy): insights into the petrogenesis and abnormal crystal growth
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15	Abstract
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17	This study reports the complex textural and chemical features of K-feldspar megacrysts (up
18	to 5 cm long) hosted in trachydacitic lava flows, lava domes, and <i>coulées</i> from Mt. Amiata volcano
19	(Tuscan Magmatic Province, Central Italy). Backscattering and cathodoluminescence imaging,
20	coupled with core to rim major and trace elements patterns, reveal complex zoning, and resorption
21	surfaces associated with sharp chemical variations (e.g., Sr and Ba). These zoning patterns
22	originated by disequilibrium and re-equilibration events, related to the repeated influx of mafic
23	magmas or convective motions in the trachydacitic magma reservoir. Multiple mafic magma
24	refilling occurences are also supported by the field record of abundant microgranular magmatic
25	enclaves in the studied products. Our results highlight that the abnormal dimension of the studied
26	K-feldspars originates by the interplay between petrological and kinetic processes involving: (i)

27	extensive dissolution; (ii) heterogeneous nucleation; (iii) alternation of spasmodic growth events in
28	disequilibrium and near-equilibrium crystallization. The repeated influx of hotter magmas and
29	reheating can determine the thermal condition to the growth of few, large K-feldspar megacrysts.
30	Also, the strong textural and chemical similarities observed in the K-feldspar megacrysts from Mt.
31	Amiata volcanic rocks and Mt. Capanne monzogranite (Elba Island, Central Italy) support the
32	hypothesis of a phenocrystic origin of intrusive K-feldspar megacrysts.
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34	Keywords
35	K-feldspar megacrysts; feldspar microtexture; chemical zoning; trace elements; magma mixing;
36	dissolution/recrystallization; Mount Amiata, Italy.
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38	1. Introduction
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40	The origin of K-feldspar megacrysts in igneous rocks (both plutonic and volcanic) is a
41	fascinating and still debated petrologic argument. K-feldspar megacrysts, up to 15-20 cm long, are
42	quite common in plutonic rocks (Cox et al., 1996; Gagnevin et al., 2004, 2005; Moore and Sisson,
43	2008; Paterson and Vernon, 2002; Słaby et al., 2007, 2017; Vernon, 1986) and one of the leading
44	open questions about their origin refers to the timing of their growing (i.e. the so called "late" or
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46 47 48 49	"early" formation hypothesis). The late formation hypothesis implies a porphyroblastic growth under subsolidus conditions, by textural coarsening promoted by thermal cycling, possibly associated with fluid migration (Glazner and Johnson, 2013; Johnson and Glazner, 2010). On the contrary, the early formation hypothesis favours a magmatic origin suggesting that K-feldspar megacrysts develop as phenocrysts from the melt phase of magma. Vernon (1986) presented and

53 Vernon, 2010; Vernon and Paterson, 2008). Oscillatory zoning of many K-feldspar megacrysts has 54 been considered as evidence of their magmatic origin by Vernon (1986). In addition, oscillatory 55 zoning and resorption surfaces related to chemical and textural discontinuities, have been 56 commonly linked to the intrusion of hotter magmas into a silicic magma reservoir and/or convection 57 (Cox et al., 1996; Gagnevin et al., 2008; Moore and Sisson, 2008; Słaby et al., 2007, 2017). These 58 authors consider the presence of mafic to felsic enclaves in some megacrystic granitic rocks an 59 additional evidence of magma mixing. Assuming a phenocrystic origin, several hypotheses have 60 been advanced as to why feldspar crystals reach very large dimensions. According to Vernon 61 (1986) the large size of the K-feldspar is strictly connected with the crystal kinetics (nucleation and 62 growth rate), in particular, the nucleation difficulty of the K-feldspar in granitic melts (see also 63 Vernon, 2004, pp 46-54; Vernon, 2010). Higgins (1999) suggests that K-feldspar megacrysts are 64 formed by textural coarsening which is promoted by temperature cycling, during which the magma 65 temperature is buffered close to the liquidus temperature of the K-feldspar for a long time. According to Moore and Sisson (2008), repeated reheating of the granitic pluton in the Sierra 66 67 Nevada Batholith, due to surges of new, hotter melt, provides the ideal environment for the growth 68 of the extraordinarily large K-feldspars.

69 Although less common, K-feldspar megacrysts (i.e., sanidine megacrysts) are also found in 70 volcanic rocks. Examples are the trachytic to rhyolitic lavas and lava domes from Mt. Amiata and 71 Roccastrada (Tuscany, Central Italy; Balducci and Leoni, 1981) and other volcanic occurrences in 72 different magmatic setting (e.g., Perini et al., 2003; Higgins, 2011; Moussallam et al., 2015). In 73 these case studies, there are no doubts about the magmatic origin of the megacrysts. However, as 74 for the megacrysts in plutonic environment, the mechanisms and the dynamics governing their 75 formation and growth are still widely debated deserving further investigations. As an example, 76 Balducci and Leoni (1981) suggested that the unusual dimensions of sanidine megacrysts are linked 77 to the high growth rate of K-feldspars in trachytic and rhyolitic melts. Higgins (2011), following the 78 same model applied in plutonic context (Higgins, 1999), proposed that megacrysts in dacites from

the Taapaca volcano are the result of textural coarsening cycles that were enabled by repeated variations of the magma temperature (around the liquidus temperature of the sanidine) in response to injections of more mafic magmas. Finally, Moussallam et al. (2015) suggested that the anorthoclase megacrysts from Erebus volcano (Antartica) originated by complex dynamics occurring in a vigorously convecting reservoir, and bi-directional magma transport between the reservoir and the overlying lava lake via the conduit.

85 The primary aim of this study is to shed new light on the processes and the dynamics 86 governing the origin and crystallization of K-feldspar megacrysts in igneous rocks by focusing on 87 the textural characteristics and compositional zoning of K-feldspar megacrysts hosted in 88 trachydacitic effusive products from Mt. Amiata Volcano (Tuscany, Central Italy). We used in-situ 89 major and trace element analyses on crystals and glasses combined with high-resolution electron 90 back-scattered and cathodoluminescence imaging. In particular, we focus on compatible trace 91 elements in K-feldspars (i.e., Sr and Ba). The slow diffusivities of these elements, in both alkali 92 feldspar and plagioclase, preserve the primary chemical heterogeneity under variable thermal 93 conditions for extended periods (Cherniak, 2002; Singer et al., 1995), making chemical zoning of 94 the feldspar one of the more robust geochemical indicators of magma evolution (e.g., Cox et al., 95 1996; D'Oriano et al., 2017; Gagnevin et al., 2004, 2005; Ginibre et al., 2004; Słaby et al., 2007, 96 2008). Moreover, the study of the K-feldspar megacrysts is largely facilitated in effusive rocks 97 because volcanic crystals keep the original zoning almost unaltered. Otherwise, despite the plutonic 98 K-feldspar megacrysts preserve magmatic shape and microstructures (e.g. oscillatory zoning) 99 (Vernon, 2004; Vernon and Paterson, 2008; Vernon, 2010), they typically show evidence of 100 subsolidus exsolution, which make accurate chemical analysis difficult to obtain (Vernon, 1986).

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102 **2. Geological background**

Mt. Amiata, sited in southern Tuscany, is the youngest volcano (about 300-230 ka; Laurenzi et al., 2015) of the Tuscan Magmatic Province (TMP), which comprises several mafic to silicic intrusive and effusive centres spread out in southern Tuscany and Tuscan archipelago. They include high-potassium calc-alkaline (HKCA), shoshonitic (SHO), potassic alkaline (KS) and ultrapotassic lamproitic rocks (Peccerillo et al., 2017 and references therein).

109 According to geochemical and isotopic constraints (e.g. Cadoux and Pinti, 2009; Conticelli 110 et al., 2015; Cristiani and Mazzuoli, 2003; Giraud et al., 1986; Peccerillo et al., 1987; Poli et al., 111 1984; Rombai et al., 1995; Van Bergen et al., 1983), Mt. Amiata experienced a complex 112 compositional evolution, also involving magma mixing processes, between an ultra-potassic mafic 113 magma (with geochemical characteristics typical of the Roman Magmatic Province, RMP) and a 114 calc-alkaline silicic magmatic system probably crustal-derived (with geochemical characteristics 115 typical of the TMP). The roof of the shallow reservoir has been estimated at depth of 5-7 Km 116 (Gianelli et al., 1988).

The volcanic activity of Mt. Amiata mainly developed along an ENE-WSW-trending 117 118 structural alignment, and it is dominated by the emplacement of lava flows, lava domes, and 119 coulées. The most recent geological interpretation suggests two main periods of activity 120 corresponding to an older Bágnore Synthem and a younger Mt. Amiata Synthem, separated by a 121 major unconformity (Principe et al., 2017, 2018; Vezzoli and Principe, 2017). The Bágnore 122 Synthem comprises two Subsynthems (Fig. 1) and is characterized by the emission of several lava 123 flows (up to 8 km long) and the emplacement of only one exogenous lava dome with coulées, 124 included inside Montearioso Subsynthem. The Mt. Amiata Synthem comprises three Subsynthems, 125 among which the oldest Valle Gelata Subsynthem (Fig. 1) is characterized by both extensive lava 126 flows that reach 4-6 km in length and exogenous lava domes; while the younger two Subsynthems 127 (named Madonna degli Scout and Prato della Contessa; Fig. 1) include several exogenous lava 128 domes with coulées and small lava flows.

129	The composition of the erupted products ranges from latite to trachydacite (SiO ₂ = 57-68 wt			
130	% and $Na_2O+K_2O = 7-9$ wt %; Fig. 2) (Cadoux and Pinti, 2009; Conticelli et al., 2015; Ferrari et al.,			
131	1996; La Felice et al., 2017; Poli et al., 1984; Rombai et al., 1995). Also, they contain, in variable			
132	proportion, millimetric to pluri-decimetric size metasedimentary xenoliths and microgranular			
133	magmatic enclaves. The latter are characterized by compositions ranging from trachybasalt to latite			
134	$(SiO_2 = 47-59 \text{ wt }\% \text{ and } Na_2O+K_2O = 5-8 \text{ wt }\%; Fig. 2)$ (Rombai et al., 1995; Van Bergen et al.,			
135	1983). In general, Mt. Amiata lava flows are highly porphyritic, medium to coarse grained, with a			
136	glassy groundmass commonly showing perlitic fractures, and, sometimes, spherulitic textures. The			
137	most abundant phenocrysts are plagioclase and K-feldspar (mainly fragments of broken crystals),			
138	orthopyroxene and biotite, ±clinopyroxene. Embayed quartz, and other accessory minerals (i.e.,			
139	apatite, ilmenite, and zircon) are rare. All the lava domes, coulées, and the few short lava flows of			
140	the younger Mt. Amiata Synthem have similar mineral paragenesis, but are characterized by the			
141	distinctive presence of K-feldspar megacrysts (from 1 to 5-6 cm long) coupled with abundant			
142	microgranular, magmatic enclaves (Cadoux and Pinti, 2009; Conticelli et al., 2015; Ferrari et al.,			
143	1996; La Felice et al., 2017).			
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145	3. Methods			
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147	3.1 Sampling			

The investigated K-feldspar megacrysts were collected from three samples (AMT60, AMT95, AMT110) belonging to the three Subsynthems of the younger Mt. Amiata Synthem (see Fig. 1 for location map). In particular, AMT60 was collected from the Coderino lava flow (Coderino formation, Valle Gelata Subsynthem; Principe et al., 2017), AMT 95 comes from the top of the Mt. Amiata exogenous lava dome (La Vetta formation, Madonna degli Scout Subsynthem; Principe et al., 2017), and AMT110 was sampled from a lava *coulées* of the La Montagnola exogenous lava dome (La Montagnola formation, Prato della Contessa Subsynthem; Principe et al., 2017). Some crystals were collected in the field, extracting them from more friable vesicular lava samples; others were manually separated from the host rock in the laboratory. Unbroken megacrysts, or partially fractured crystals in which the original shape was easily reconstructed, were selected. They were cut through the approximate geometric centre in order to expose all the growing layers including the innermost core. Twenty megacrysts were processed for chemical and textural analyses. Among them five megacrysts were selected for trace element analysis.

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3.2 Petrography and textural study

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165 The modal abundance (volume fraction) of K-feldspar megacrysts larger than 1 cm were 166 carried out on samples-hand specimens. The samples were cut into slabs 10-20 cm in length (total surface $\sim 0.1 \text{ m}^2$ for each sample) and scanned using a planar scanner (600 dpi). The margins of K-167 168 feldspar megacrysts larger than 1 cm were outlined in a vector-drafting program (Adobe Illustrator). 169 Crystal outlines were then filled and exported as TIFF files, and the obtained greyscale images were 170 processed using the ImageJ software (Schindelin et al., 2012). The modal content of <1 cm crystals 171 was determined on thin sections using an optical microscope equipped with a point counter. In each 172 sample, ~ 2000 points were counted excluding bubbles.

173 Textural investigations were performed at the Istituto Nazionale di Geofisica e Vulcanologia 174 (INGV), in Pisa (Italy) using an optical microscope and a Zeiss EVO MA 10 Scanning Electron 175 Microscope (SEM), capturing selected Back Scattered Electron (BSE) and cathodoluminescence 176 (CL) images. The entire image of each K-feldspar megacryst was assembled from a mosaic of 50-120 greyscale images.

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179 *3.3 Mineral and glass analyses*

Preliminary major element composition of minerals was performed using a Zeiss EVO MA 10 SEM, equipped with an Oxford ISIS micro-analytical EDS system at the INGV, Pisa (Italy). The analytical error, calculated using international standards, is generally lower than 2% for oxides with concentrations >10 wt%, lower than 10% for oxides between 1 and 10 wt%, and better than 30% for concentrations < 1 wt%.

186 Trace elements composition of selected K-feldspars, plagioclases, and glasses were performed at the Dipartimento di Fisica e Geologia, University of Perugia (Italy) by Laser Ablation-187 188 Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). The instrumentation consisted in a 189 Teledyne Photon Machine G2 laser ablation device, equipped with a two-volume HelEx 2 cell, and coupled to a Thermo Fischer Scientific iCAP Q quadrupole mass spectrometer (Petrelli et al., 190 2016a). A circular 20 μ m spot size, a repetition rate of 8Hz, and a laser fluence of ~3.5 Jcm⁻¹ have 191 192 been utilized. Ablation times were about 30 seconds per spot, preceded by a 25 second background 193 measurement and followed by 25 seconds of washout. Data reduction was completed with the Iolite 194 3 software (Paton et al., 2011). The NIST SRM 610 (Pearce et al., 1997) glass and the USGS 195 BCR2G (Wilson, 1997) reference materials were used as calibrator and quality control, 196 respectively. The SiO₂ concentrations obtained by electron microprobe were used as internal 197 standard. Under the reported analytical conditions, the precision is better than 10% for 198 concentrations above 0.1 ppm and better than 5% above 20 ppm; accuracy is always better than 199 10% (Petrelli et al., 2016b).

Major elements analyses at the same locations of trace element determinations (i.e., close to LA craters) were performed using a JEOL JXA-8200 electron microprobe (EMP) equipped with a WDS/EDS combined system at the INGV, Rome (Italy). A beam size of 5- μ m was used for feldspars and a defocused beam, with a spot size of 10 μ m, for glasses (15 kV voltage, 5 nA beam current). The accuracy of WDS analyses was calculated using international standards (SiO₂<1%; Al₂O₃<2%; Na₂O<9%; K₂O<2%; CaO<2%).

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4. Results

4.1 Petrochemical data

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211 The studied rocks are trachydacite with SiO₂ \sim 61.5-62.3 wt %, K₂O \sim 5.5-6.0 wt %, and MgO ~ 1.7-2.6 wt % (Table 1, Fig. 2). They have a crystal content of 35-37 vol% (Table 2) mainly 212 213 composed of plagioclase (11-13 vol%; An 45-86), K-feldspar (11-14 vol%; Or 76-83), 214 orthopyroxene (5 vol%; Mg# 42-58), clinopyroxene (1-5-vol%; Mg# 59-89; Fs 6-24; Wo 39-51), 215 biotite (2-4 vol%), and minor ilmenite. Among the K-feldspars a 3.5-5% by volume are megacrysts 216 with an average length of 2-3 cm and a maximum length of 5-6 cm. They are commonly euhedral 217 although are rarely completely intact, and can present smoothly rounded margins. K-feldspar 218 phenocrysts <1cm are mostly fragments of broken crystals. Megacrysts and phenocrysts have the 219 same major-element chemical composition ~Or 76-83 (Fig. 3). Millimetric to decimetric 220 microgranular magmatic enclaves with amoeboid shape are abundant. They may contain K-feldspar 221 megacrysts inherited from the host silicic rock. Metasedimentary xenoliths of tabular shape and 222 aggregates of minerals (mainly plagioclase, orthopyroxene, and biotite) are also present. Sample 223 AMT60 has a glassy groundmass with perlitic texture that locally is highly vesicular with fibrous 224 glass portions. Sample AMT110 has heterogeneous groundmass showing flow banding with 225 alternating glassy portions with perlitic cracks, and microcrystalline portions characterized by 226 devitrification textures (spherulites) with the precipitation of secondary minerals in vesicles (e.g., 227 cristobalite). Sample AMT 95 shows hypocrystalline groundmass with abundant plagioclase, K-228 feldspar and clinopyroxene microlites. The glassy groundmass analyzed in AMT60 and AMT110 229 has a homogenous rhyolitic composition with SiO₂ ~75-76 wt %, Al₂O₃ ~11.7-12.3 wt %, and K₂O 230 ~6.9-7 wt %.

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232 4.2 *K-feldspar megacrysts*

234 Macroscopic shape

The studied K-feldspar megacrysts are simple prismatic crystals and tabular Carlsbad twins. The crystals are mostly characterized by a {010} tabular habit with the maximum elongation parallel to the c-axis (Fig. 4a, c). A precise quantitative information on their size and shape is limited because the crystals are mostly embedded in the groundmass, and the best exposure is found only on weathered surfaces (Fig. 4a, b, c). Megacrysts usually show a dusty internal portion, crowded with mineral, melt inclusions and vesicles surrounded by a clear corona (Fig.4d).

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242 *Microscopic texture*

243 Backscattered electron and cathodoluminescence images highlight that compositional and 244 textural zoning is ubiquitous in the investigated K-feldspar megacrysts. Zoning is well shown by 245 different grey tones both in BSE and CL images (Fig. 5a1, a2). Although there is no systematic 246 correlation between brightness in CL images and chemical composition of the mineral (Marshall, 247 1988), a comparison between BSE and CL images show that zoning pattern in CL (Fig. 5a2) images 248 reproduce the zoning observed in BSE (Fig. 5a1), which are conversely strictly related to chemical 249 changes. Thus, in this case, changes of the grey tone in CL images is also associated with 250 compositional variations and can be discussed as evidence of chemical zoning. CL images were 251 mostly used for describing the texture of the studied crystals, because they highlight better than 252 BSE images the complicated zoning of the studied feldspar.

At the microscopic scale, the dusty internal portion of the crystals exhibits a complex texture due to the occurrence of large patchy zoned cores crowded with minerals grains and large melt inclusions with irregular shape and vesicles (see in particular Fig. 5a, b, c, d). The cores are commonly surrounded by approximately concentric thick layers, each of them passing towards the outer edge, from bright, patchy zoned layers, to Dark Oscillatory zoned Layers (hereafter DOL) (Fig. 5a, b, c). Deep resorption surfaces mainly develop on the DOL and are highlighted by 259 irregular shapes, deep embayments, rounded boundaries or unconformities. Remnants of deeply 260 resorbed DOL are abundant (Fig. 5a2, b, c). Several deep resorption surfaces are recognized in the 261 largest megacrysts, where the dusty internal portion spreads over almost all the crystal volume (Fig. 5a, b, c). The smaller megacrysts record fewer dissolution events and usually show a patchy zoned 262 263 core crowded with inclusions (minerals, glass, and vesicles) (Fig. 5d, e). Concentric alignments of 264 mineral grains are found in many megacrysts and commonly surround highly irregular resorption surfaces associated with dissolution events (Fig. 5b, c, d). They follow the layer boundaries, are 265 266 euhedral to subhedral and can be distributed with their long axes parallel to the layer boundary. 267 When the megacryst engulfs mineral grains, large pockets filled with glass formed around the 268 inclusion. Zoned plagioclase, up to 1-2 mm long, is the most abundant inclusion mineral, followed 269 by biotite, pyroxene, oxides, apatite, and small (few micrometres) grains of zircon. The dusty 270 internal portion of the crystals is surrounded by a concentric, oscillatory zoned corona, 2-3 mm 271 thick, which has the same textural characteristics of the interior DOL.

Within the DOL, a progressive shift from bright to dark zones is observed in each layer, whereas the contact among dark and bright zones is abrupt. The external boundaries of the darker layers are subhedral to anhedral with rounded and/or lobate shape and can cross-cut the previous layers. The thickness of each layer ranges from 250-300 μ m to few tens of μ m. These surfaces originated by a relatively weak (or less disrupting) dissolution event during which at least 150 μ m of the crystal can be resorbed (Fig. 6).

K-feldspar aggregates are also found in the analyzed samples. In particular, in sample AMT95 many megacrysts result from clustering and intergrowth of several millimetre-sized crystals. Large crystal aggregates with irregular shape can form the core of the megacrysts. Mutual attachment of several grains is well shown by the zoning patterns inside the megacrysts that mirror different optical orientation between adjacent growing grains (Fig. 5e). After aggregation, the grain clusters develop a common overgrowth.

Chemical zoning

286 Five representative K-feldspar megacrysts were selected for the study of major and trace 287 element variations. The megacrysts are sanidine with composition ranging between Or76 and Or83 288 (An 1-4, Ab 16-21) and large trace elements variability (Ba \sim 1100-8800 ppm; Sr \sim 650-2350 ppm; 289 Eu ~2.5-7.3 ppm; Rb ~350-450 ppm). Core to rim compositional transects reveal chemical 290 oscillatory zoning patterns coupling the textural discontinuities observed in BSE and CL images. In 291 detail, Figure 7 displays Ba and Sr variation within the studied crystals. The area rimward of the 292 main resorbed surfaces shows a Ba increase commonly of 1000-2000 ppm, up to 4000 ppm. The 293 transition from low- to high Ba layers is generally sharp, whereas Ba content in layers between two 294 resorbed surfaces usually decreases outward the crystal (Fig 7b). As a whole, Sr content variations 295 reproduce the Ba trend with an increase rimward of the resorbed surfaces from 100-200 ppm up to 296 800 ppm. The patchy zoned areas show irregular oscillations, while the DOLs, both within the dusty 297 area and the outer corona, exhibit more regular trends characterized by saw-tooth zoning with a 298 gradual Ba decrease outwards of each layer (Fig. 6). The Ba content in each layer varies from about 299 100 up to 350 ppm. The rims (<200 µm) have Ba and Sr contents of ~1570-2540 ppm and ~650-300 890 ppm, respectively.

301 There is not a clear correlation between the mol% Or and the abundance of compatible trace 302 elements. Rb positively correlates with Ba, Sr and Eu (Fig. 8). Two compositional groups are 303 distinguished in the Rb/Sr vs. Ba diagram: i) the main group shows an increase of Rb/Sr ratio from 304 ~0.3 to ~0.6 which is coupled with a Ba decrease from ~5000 to ~1000 ppm; ii) the patchy cores of 305 the crystals AMT60 cr2 and AMT95 cr1 and the patchy layer between 1 and 2 cm from the rim 306 within AMT110 cr2 show higher Ba contents and, as a whole, depict a line of descent in the range 307 Rb/Sr ratio 0.15 - 0.60 and Ba 8800-3800 ppm. This second compositional group is also 308 characterized by a distinct enrichment of Pb and Li (Fig. 8 and Supplementary Table 1). The 309 different enrichment of trace elements is not related to a specific texture. Indeed, all the high-Ba

310 portions within the crystals have patchy texture, but patchy textured zones with relatively low-Ba311 content are also present.

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313 Plagioclase inclusions

Mineral inclusions in the K-feldspar megacrysts show variable dimension from tens of micrometres to 1-2 mm. The dimension of the largest inclusions is comparable with that of the phenocrysts in the groundmass.

317 Plagioclase is the most abundant mineral inclusion. It usually results from the clustering of 318 small grains (Fig 6 and Fig. 9a, b) and shows cores with a wide compositional variation, from An48 319 to An78, rimmed by an An-poor layer (An 45-58) with euhedral outer margins. Sporadic crystals 320 show a direct zoning from An69 to An48 with euhedral growth boundaries (Fig. 9c). Cores host 321 many melt inclusions and bubbles with either irregular or elongated nearly rectangular shaped, 322 aligned parallel to the main axis of the crystal. Embayment enclosed by euhedral edges are also 323 present on the rim. Melt inclusions and bubbles appear to be embedded during the crystal growth or 324 when two grains with irregular boundary attached (Fig. 9a, b). Although these crystal shapes are not 325 the typical skeletal or hopper texture that originates at high crystal growth rate under high 326 undercooling (Fenn, 1977; Lofgren, 1974), the entrapment of large melt pockets and the formation 327 of large embayments enclosed by euhedral edges point to a fairly high growth rate.

328 Complex resorption and growth features characterize the larger crystals (~ 1-2 mm). The 329 cores are characterized by the occurrence of nearly homogeneous, strongly resorbed areas An50-330 An55 (dark grey in Fig. 9d) and sieve textured, patchy zoned sectors (bright zones in Fig. 9d) with 331 composition ranging between An60 and An80. The An rich zones are intensely altered into hydrous 332 aluminium silicates (allophane). The outer rims have nearly homogeneous composition ~An50. 333 Compatible trace elements in the plagioclase inclusions increase with An increasing. Sr ranges from 334 \sim 700 ppm in An-poor plagioclase up to \sim 1100 ppm in the An-rich patchy zones. As Sr, also Eu 335 increases from 2.5 ppm in the An-poor zones to 3.9 ppm in the An-rich zones (Fig. 10).

336 Both the texture and composition of plagioclase inclusions show characteristics comparable 337 to those of the plagioclase phenocrysts in the groundmass. A few phenocrysts contain composite 338 inclusions formed by mutual attachment of several plagioclase crystals; each of them is 339 characterized by a patchy core (~An50-70) with abundant melt inclusions and an oscillatory zoned 340 mantle (~An45-55) (Fig. 9e). In these crystals, the texture of the cores presents strong similarities 341 with that of the smaller plagioclase inclusions (or cluster of small grains) (Fig. 9a, b, e; 342 Supplementary Table 1). Conversely, most plagioclase phenocrysts present the same complex 343 growth/dissolution textures of the larger (1-2 mm) inclusions (patchy and/or oscillatory zoning, 344 sieve texture, dissolution surfaces, secondary alteration into allophane; Fig. 9f). The chemical 345 composition of the phenocrysts ranges from An50 to An89 (Fig. 9e, f), with variable content of Sr 346 (600-1300 ppm), Eu (1.9-3.9 ppm), and the outer layers have sodic composition (An45-60) and 347 relatively low contents of compatible trace elements (Sr 600-900 ppm, Eu 1.9-3.1 ppm) (Figs. 3, 10; 348 Supplementary Table 1).

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5. Discussion

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352 Textural evidence of repeated dissolution and growth events are ubiquitous in the studied K-353 feldspar megacrysts. Compositional transects across megacrysts highlight repeated variations of 354 compatible trace elements from low-Ba (Ba ~1800 ppm) to high-Ba zones (up to 8800 ppm) with 355 deeply resorbed surfaces related to sharp chemical changes. These crystal textures and characteristic 356 chemical zoning are commonly related to disequilibrium due to recharge events of the shallow 357 magma reservoir by deeper mafic magmas, producing convective dynamics within the systems 358 (e.g., Bateman, 1995; Couch et al., 2001; Ginibre et al., 2002a, 2002b; Huppert et al., 1984; Kahl et 359 al., 2013; Perugini and Poli, 2012; Singer et al., 1995; Turner and Campbell, 1986). The abundance 360 of mafic to intermediate (trachybasalt to latite) microgranular enclaves at Mt. Amiata is field 361 evidence for repeated influxes of hotter magma in the resident trachydacitic magma reservoir.

5.1 The origin of the chemical zoning in K-feldspar megacrysts

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We combined compatible Ba and Sr and semi-compatible Rb trace element contents in Kfeldspar, whole rock, and glassy groundmass to retrace the petrogenetic processes occurring in the magmatic system during the growth of the studied K-feldspar megacrysts.

368 The composition of the different layers within the megacrysts was inverted to the melt 369 composition in which the crystal grew, using the formula:

$$C_{melt}^{\alpha} = C_{Kfel}^{\alpha} / K d_{Kfel/l}^{\alpha}$$

where C^{α}_{melt} is the concentration of the α element in the melt (or liquid), C^{α}_{Kfel} is the 370 concentration of the element α in K-feldspar, and Kd^{α}_{Kfel/l} is the partition coefficient. The partition 371 372 coefficient K-feldspar/melt were calculated using the average composition of the glassy 373 groundmass (table 1) and ten K-feldspar compositions measured in the rims 200 µm thick of the 374 megacrysts, in the samples AMT60 and AMT110, assuming chemical equilibrium between the glassy groundmass and the rim of the crystals. The average Kd ($\pm \sigma$) obtained are $Kd_{Kfel/l}^{Ba} = 8 \pm$ 375 2, $Kd_{Kfel/l}^{Rb} = 0.8 \pm 0.02$, $Kd_{Kfel/l}^{Sr} = 5 \pm 0.3$. The calculated compositions of the glass in 376 equilibrium with the different layers within the K-feldspar megacrysts are widely variable, in the 377 378 range Ba 110-1100 ppm, Sr 130-470 ppm and Rb 340-570 ppm (Fig. 11).

Obtained results were compared with fractional crystallization (FC), assimilation plus fractional crystallization (AFC), and magma-mixing (MM) models performed using the PETROMODEL spreadsheet (Ersoy, 2013). The partition coefficients plagioclase/melt ($Kd_{pl/l}^{Ba} =$ 0.16 ± 0.04 and $Kd_{pl/l}^{Sr} = 5 \pm 0.3$) were calculated using the average composition of the glassy groundmass (Table 1) and the composition of the euhedral rims of the phenocrysts (on 9 rim compositions). The partition coefficients between mafic minerals and melt in silicic rocks were taken from the GERM Partition Coefficients Database (https://earthref.org/GERM/). The FC trends 386 were calculated using the modal proportion of minerals measured in the studied samples (Table 2). 387 The volume percent of each component was transformed in weight percent using a density of 2.5 g/cm³ for rhyolitic melt and the densities given in the literature for minerals. The AFC process was 388 389 simulated using the composition of a metasedimentary xenolith (AMT 23 in Conticelli et al., 2015) 390 as assimilant. Shoshonite and andesite enclaves (from Conticelli et al., 2015) were used as mafic 391 end-member in the MM process calculations. All the calculations were performed assuming that the 392 bulk partition coefficient of trace elements remains constant throughout the process. The results of 393 the modelling are reported in Figure 11.

394 PETROMODEL calculations indicate that the composition of the glassy groundmass cannot 395 be reproduced from the whole rock composition by fractional crystallization. In detail, the analyses 396 of the natural glasses fall above the FC line of descent due to a high Ba and Sr contents (Fig. 11a, 397 b). On the contrary, the composition of the glassy matrices can be successfully modelled by the 398 AFC process involving about 25 wt% of assimilant. AFC is possibly combined with mixing 399 processes during the magma evolution. These results agree with the models proposed in the 400 literature for explaining the petrogenetic evolution of the Mt. Amiata magmas, which include 401 fractional crystallization and magma mixing (Conticelli et al., 2015 and references therein), 402 associated with assimilation of metasedimentary xenoliths (Van Bergen and Barton, 1984). Going 403 deeper into details, from the Rb vs. Sr diagram (Fig. 11a), it emerges that the melt compositions, calculated starting from the high-Ba K-feldspars, fit the mixing lines between rhyolitic melts and 404 405 mafic magmas. The mafic end member involved in the mixing process is commonly <30 wt% and 406 increases up to 40 wt% for the composition referred to the K-feldspar with higher Sr contents (Fig. 407 11a). Thus, we suggest that the compositional heterogeneity of the K-feldspar megacrysts may be 408 associated with the extent of hybridization of the melt in which they regrow, within the shallow, 409 trachydacitic magma body that fed the Mt. Amiata volcanic activity.

However, in the Rb vs. Ba diagram (Fig. 11b), the calculated melts fall far above the FC,
AFC, and MM trends. Two main factors may be responsible for the anomalous high contents of Ba:

412 i) the choice of the partition coefficients, and ii) a possible crystal-melt disequilibrium. The choice 413 of the partition coefficients is critical for such kind of modelling. In particular the partition coefficient K-feldspar/liquid for Ba. The value of $Kd_{Kfel/l}^{Ba} = 8$ obtained by crystal/melt 414 415 equilibrium in this work is consistent with the values commonly used in the silicic rocks (see for example Slaby et al., 2007), but the $Kd_{Kfel/l}^{Ba}$ given in literature cover a broad range of values from 416 417 1 to 20-25, depending on the chemical composition of the crystal and the melt and the physical 418 conditions (GERM Partition Coefficients Database; Icenhower and London, 1996; Leeman and Phelps, 1981). If a fairly high value of $Kd_{Kfel/l}^{Ba} = 15$ is used to invert the feldspar composition to 419 420 the melt in equilibrium, the melt compositions obtained approximate to mixing lines (Fig. 11b), and 421 the extent of hybridization is consistent with that obtained by the Sr contents. However, departure 422 from the equilibrium during magma-mixing can strongly affect the partition coefficients between 423 crystal and liquid (see for example Albarède and Bottinga, 1972; Loomis, 1982; Singer et al., 1995; 424 Arzilli et al., 2018), and non-equilibrium partitioning during magma mixing may induce an 425 enrichment of Ba content rimward of resorption surfaces in K-feldspar megacrysts (Gagnevin at al., 426 2005). Arzilli et al. (2018) founded that disequilibrium crystal growth in alkali feldspar produces a 427 strong increasing of the partition coefficient of the compatible trace elements (e.g. Ba and Sr), higher growth rates corresponding to higher apparent $Kd_{Kfel/l}^{Ba}$ and $Kd_{Kfel/l}^{Sr}$ values. Accordingly, 428 429 we argue that disequilibrium phenomena related to dissolution and crystal regrowth are responsible 430 for the anomalous Ba enrichment observed in the studied K-feldspar megacrysts. Likely a relatively 431 low degree of undercooling (lower than 30-50 °C used in the experiments of Arzilli et al., 2018) can 432 produce apparent increasing of the most compatible element (Ba), having a minor effect on Sr. Disequilibrium conditions are also consistent with a fairly high crystal-growth rate inferred by the 433 434 textural features of the Ba-rich layers and the hosted plagioclases (see discussion below).

The different partitioning of Ba, Rb, and Sr observed in studied K-feldspars (Fig. 8) points to distinct chemical signatures of the melt in which the crystals grew. This indicate that the chemical zoning in the K-feldspar megacrysts reproduces both the different degree of hybridization
of the magmas, and the heterogeneity of the primary mafic magmas that periodically refilled the
trachydacitic magma reservoir of Mt. Amiata volcano (Conticelli et al., 2015; Poli and Peccerillo,
2016; Van Bergen, 1985).

441 The textural and chemical zoning of the dark oscillatory layers (DOL) can reflect the 442 convection within the silicic magma reservoir that repeatedly moves the crystals through zones with 443 variable chemical characteristics and temperature (e.g., Couch et al., 2001; Cox et al., 1996; 444 D'Oriano et al., 2017; Ginibre et al., 2002a, b; Moussallam et al., 2015). Weak dissolution may also 445 be originated from re-heating of the magma induced by the arrival of hotter magma from depth, 446 without physical mixing with the resident trachydacite. The saw-tooth pattern of the zoning is likely 447 enhanced by the discharge during the dissolution of K-feldspar chemical components into the melt 448 adhering to the crystal, and the subsequent crystallization of a K-feldspar in which an initially high-449 Ba content decreases as growth proceeds (Fig. 6). We rule out that saw-tooth patterns are attributed 450 to a diffusion-controlled growth kinetics at the boundary layer around the growing crystal (Allègre 451 et al. 1981; L'Heureux, 1993), because this growth model produces oscillatory layers on a scale of 10-30 μ m, that are much thinner than that observed in the DOL (up to 300 μ m). 452

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5.2 Inferences from the plagioclase inclusions

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The plagioclase hosted in the megacrysts, as well as many phenocrysts in the groundmass, present a variety of textures, from patchy to direct or oscillatory zoning, and from skeletal to deeply resorbed shapes, and variable chemical composition. The composition of the rims of the phenocrysts, in textural equilibrium with the groundmass glass, is around An50, whereas bytownitic compositions, up to An 89 are largely present in patches and layers within the crystals (both phenocrysts and inclusions). 462 Some An-rich plagioclase cores might represent remnants of metasedimentary xenoliths 463 (Van Bergen and Barton, 1984), but zoning commonly found in the plagioclase, both within the 464 megacrysts and in the groundmass, points to a magmatic origin. Similarly, a xenocrystic origin from 465 mafic magmas is not consistent with the trace element chemistry. As already done for K-feldspar, 466 the composition of the An rich plagioclase (An65-An89) was inverted to the melt composition in which the crystal grew using the content of Sr in plagioclase and $\operatorname{Kd}_{pl/l}(C_{melt}^{Sr} = C_{pl}^{Sr}/Kd_{pl/l}^{Sr})$. The 467 partition coefficient for Sr in plagioclase strongly depend on the An component, Sr content 468 decreasing with An content increasing (Blundy and Wood, 1991). Using a $Kd_{pl/l}^{Sr} = 2$ (among the 469 470 lowest values given in the GERM Partition Coefficient Database) the plagioclase with composition 471 An65-80 is in equilibrium with melts having Sr content of 350-600 ppm, which is lower than that of 472 the enclaves (600-850 ppm, Conticelli et al., 2015). Only few points An84-89 in the cores of the 473 phenocrysts give melt in equilibrium with Sr ~800-900 ppm and have likely a xenocrystic origin. 474 As an alternative, the high An content in the plagioclase An65-80 must be favored by a high water 475 content of the new hotter magma which stabilizes the anorthite component. A rapid growth under 476 high undercooling mostly related to degassing has been proposed as a possible mechanism for the 477 origin of the patchy zoning in igneous plagioclase (e.g., Anderson, 1984; Landi et al., 2004). We 478 speculate that volatile loss during magma mixing, inducing nucleation and rapid growth, may have 479 originated the patchy zoned texture which typifies many small plagioclase inclusions or aggregates 480 of small crystals (e.g., Fig 9a, b) and their chemical variation from An-rich to An-poor 481 compositions. This is also consistent with their shape (skeletal to hopper) which testify a fairly high 482 growth rate (Lofgren, 1974). The small plagioclase inclusions and the clusters of small grains 483 hosted in the K-Feldspar megacrysts likely formed during a single crystallization event promoted by 484 the rapid variations of the magma conditions. The primary evidence supporting this conclusion is 485 the absence of resorption surfaces, or abrupt changes in the chemical composition, which on turn 486 are abundant in the large plagioclase inclusions and phenocrysts. Ultimately, textural data indicate

487 that crystallization of the small plagioclase inclusions was nearly contemporaneous to (or 488 immediately preceded) the crystallization of the host high-Ba K-feldspar. The unstable magma 489 conditions also participated in causing the chemical disequilibrium in the high-Ba K-feldspar above 490 discussed.

- 491 The larger plagioclase inclusions (Fig. 9d) have the same textural and chemical features of
 492 most of the plagioclase phenocrysts. They record repeated dissolution and recrystallization events
 493 due to refilling and magma mixing at different extent before their trapping.
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5.3 The origin of the patchy texture in K-feldspar

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497 The patchy cores of the K-feldspar megacrysts from Mt. Amiata might be derived from 498 events of dissolution and renewed growth of the crystal (either homogeneous or chemically zoned) 499 due to mixing with hotter mafic magma or heating events, as suggested for similar textures both in 500 volcanic (e.g., D'Oriano et al., 2017; Ginibre et al., 2004) and intrusive (e.g., Cox et al., 1996; 501 Gagnevin et al., 2004, 2005; Słaby et al., 2017; Vernon, 1986) igneous rocks. The large pockets of glass present in the cores (e.g., Fig. 5c) are commonly explained as embayments due to dissolution, 502 503 subsequently sealed by regrowth of the crystal. However, as shown in Fig. 5e, the early formation 504 of aggregates of K-feldspar participated in developing the texture and zoning of the megacrysts 505 cores. During the crystal clustering and growth, melt pockets and grains of minerals were trapped. 506 Post entrapment crystallization on the rims of the melt pockets can give chemical zoning that does 507 not follow the crystal boundary or regular crystal shapes, resulting in a general patchy zoning. 508 Successive events of dissolution and regrowth can further develop the patchy zoning and modify the 509 original texture up to hide the morphology of the early aggregates. The patchy Ba-rich layers within 510 the K-feldspar likely originated by not-equilibrium crystal growth, which was enhanced by 511 spasmodic events induced by magma-mixing.

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515 Textural and chemical zoning in the K-feldspar megacrysts hosted in the Mt. Amiata 516 effusive products indicate that these crystals grew as phenocrysts in a silicic magma reservoir 517 during repeated dissolution and crystallization events.

The K-feldspar dimension in the studied products is however unusual, because most of the silicic effusive products contain K-feldspar phenocrysts, but do not develop large megacrysts. The megacrystic lava dome and *coulées* at Mt. Amiata host a quantity of microgranular magmatic enclaves that is larger than observed in megacryst-free lava flows (Conticelli et al. 2015; Ferrari et al. 1996; Van Bergen et al. 1983), although quantitative data are not yet available. This suggests a correlation between repeated influx of hotter magma from the depth and the formation of the Kfeldspar megacrysts.

525 According to Vernon (1986, 2010), the large size of the megacrysts is evidently due to 526 nucleation difficulties for K-feldspar in silicic melts, but we argued that repeated influx of new 527 hotter magma could favour the growth of megacrysts in the trachydacite magmas of Mt. Amiata. 528 The data here presented indicate that reheating during magma mixing increases the temperature of 529 the system above the liquidus temperature of the K-feldspar inducing dissolution. After dissolution, 530 cooling and degassing in the chaotic mixed system moves again the system below the liquidus 531 temperature and crystallization resumes under a certain amount of undercooling. The degree of 532 undercooling for K-feldspar should be low to medium, as discussed in section 5.1. At low/medium 533 undercooling (e.g. 20-40 °C in the experiments carried out by Arzilli and Carroll (2013) on 534 trachytic melts at 100 MPa) growth dominates crystallization process, while nucleation dominates 535 at high undercooling (Fenn, 1977; Arzilli and Carroll, 2013). At low/medium undercooling, 536 heterogeneous nucleation can be favoured because a lower activation energy required respect to 537 homogeneous nucleation (Vernon, 2004, p. 46-51 and reference therein). As a result, after an event 538 of dissolution, crystal kinetics favours the rapid growth of K-feldspar layers (with abundant

539 inclusions of mineral grains and melt) on existing K-feldspars. When equilibrium is restored, the 540 crystal growth of the existing crystals, continue in the convective magma chamber (DOL). In 541 addition, layer discontinuities in the DOL highlight dissolution of about 150 µm of crystal and a 542 thicker portion is possibly resorbed during more disruptive magma-mixing. Thus, small crystals that 543 possibly formed in the trachydacitic magma chamber during cooling and convection, may be totally 544 resorbed during a mixing event. In this view, repeated reheating of the magma chamber can favour 545 the formation of few large crystals rather than abundant small phenocrysts. Higgins (1999, 2011) 546 suggested that megacrysts develop from the host magma by coarsening ("Ostwald ripening") 547 promoted by cycling changes of the temperature in response to the influx of mafic magmas. Based 548 on the textural feature of the megacrysts shown in the present work, crystallization kinetics favored 549 the formation of large aggregates of K-feldspars which can become the nuclei of new megacrysts 550 (Fig.5 e). However, the process that promotes aggregation of few large crystals (mm sized in Fig. 551 5e) appears to be different from the "Ostwald ripening" mechanism, which should involve 552 coarsening of a number of small nuclei (or many small crystals). These aggregates can be better 553 explained as *synneusis* structures (Stull, 1979; Vance, 1969), that is mutual attachment of crystals 554 probably related to magmatic turbulence induced by magma mixing and/or convection. Mutual 555 attachment of crystals can be one of the factors that participate in the formation of large megacrysts. 556 A schematic cartoon illustrating the growth mechanisms of the K-feldspar megacrysts is shown in 557 Fig. 12.

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5.5 Comparison with megacrystic plutons

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A comparison among the K-feldspar megacrysts of Mt. Amiata and those hosted in intrusive products of the Tuscan Magmatic Provinces (e.g. the monzogranitic Mt. Capanne Pluton, Elba island; Gagnevin et al., 2004, 2005) reveals strong similarities in both the chemical zoning and texture, although a detailed comparison of the chemical zoning is hampered by the formation of pertitic textures in the intrusive K-feldspar. Both plutonic megacrysts from Mt Capanne and volcanic megacrysts from Mt Amiata, highlight repeated dissolution and regrowth episodes, associated with large trace-elements chemical zoning, suggesting a similar growth history. A phenocrystic origin of the K-feldspar megacrysts in plutonic rocks has been widely favoured in the most recent literature. The study of K-feldspar megacrysts from Mt. Amiata and their comparison with ones from Mt. Capanne pluton, also support this interpretation.

Mt. Capanne pluton is also characterized by the occurrence of abundant microgranular 571 572 enclaves with variable composition, and according to Gagnevin et al. (2008), the abundance of 573 megacrysts is positively correlated with the volumetric abundance of the mafic inclusions. As 574 discussed for Mt. Amiata products, this suggests that the repeated influxes of hotter magma into a 575 shallow magma body may favour the growth of the extraordinary large K-feldspar crystals. We 576 argue that reiterated reheating of the silicic magma chamber in which K-feldspar crystallize is one 577 mechanism that can provide thermal conditions for the growth of the large crystals (as also suggested by Moore and Sisson, 2008). 578

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6. Conclusions

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582 The study of the K-feldspar megacrysts hosted in the trachydacitic lava flows, lava domes 583 and *coulées* of Mt. Amiata evidences a complex crystallization history which was driven by 584 successive disequilibrium and re-equilibration events, due to the influx of hotter magmas and 585 convection in the magma reservoir. Magma mixing events are testified by deeply resorbed surfaces 586 and disequilibrium crystal regrowth. The variable chemical composition of the K-feldspars is 587 related to a different extent of hybridization during magma-mixing, and to chemical heterogeneities 588 characterizing the mafic magmas that refilled the silicic reservoir. Finally, the fairly rapid growth 589 rate inducing chemical disequilibrium was highlighted by the anomalous Ba enrichment rimwards 590 of the resorption surfaces.

591 We suggest that the K-feldspar megacrysts from Mt. Amiata originate by the interplay of 592 crystal kinetics and repeated reheating due to magma mixing. A single magma mixing event 593 involves reheating and K-feldspar dissolution, during which the microphenocrysts can be resorbed 594 entirely, (ii) after dissolution a low nucleation rate favours heterogeneous crystallization, and a 595 fairly rapid crystal re-growth. After the destabilization events, equilibrium is restored, and the 596 crystals continue to grow under nearly equilibrium conditions in a convective magma chamber, 597 where a low nucleation rate makes difficult the formation of new nuclei. Repeated magma influx 598 and reheating can determine the thermal condition ideal to the growth of these large crystals.

The textural and chemical similarities observed in K-feldspar megacrysts from Mt. Amiata lava domes and *coulées* and Mt. Capanne pluton (Tuscan Magmatic Province) show that megacrysts from these rocks have the same growth history and support the hypothesis of a phenocrystic origin of intrusive K-feldspar megacrysts.

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615 Figure captions

Figure 1 – Synthematic map of Mt. Amiata with the location of the sampling sites (yellow
dots). In the legend a comparison between the stratigraphic units recognized by Principe et al.
(2017, 2018), Vezzoli and Principe (2017) and the previous stratigraphic subdivisions (Marroni et
al., 2015; Ferrari et. al. 1996; Mazzuoli and Pratesi, 1963) is shown.

Figure 2 – T.A.S. (Total Alkali-Silica) diagram for silicic lava flows and lava domes (light
grey dots) and magmatic enclaves (dark grey diamonds). Triangles represent the rocks studied in
this work. Data from Rombai et al., 1995; Ferrari et al., 1996; Cristiani and Mazzuoli, 2003;
Cadoux and Pinti, 2009; Conticelli et al., 2015; La Felice et al. 2017.

Figure 3 – Feldspar ternary diagram for K-feldspar (both megacrysts >1 cm and phenocrysts
and fragments <1 cm) and plagioclase phenocrysts represented in terms of albite (Ab), anorthite
(An) and orthoclase (Or) end-members.

Figure 4 – Examples of K-feldspar megacrysts from Mt. Amiata: (a) megacryst weathered
out of the friable vesicular groundmass; (b) megacryst embedded in the groundmass; (c) entire
simple prismatic crystal elongated parallel to (010) face; (d) broken megacryst showing internal
dusty zone and a most homogeneous external rim.

631 Figure 5 – Mosaic of BSE (a1) and CL (a2, b, c, d, e) images of K-feldspar megacrysts showing the textural features mentioned in the text. Crystals are cut through the approximate 632 633 geometric centre and nearly perpendicular (a) or parallel (b, c, d) to (010). a) Comparison between 634 images obtained with BSE (a1, left half) and CL (a2, right half) detectors. The rectangles indicate 635 the overlap area; a), b), c) images show the typical dusty internal portions formed by a large patchy 636 zoned core surrounded by several zoned layers with rounded to resorbed boundaries and concentric 637 alignments of mineral grains; d) a relatively small crystal composed by a patchy zoned core 638 crowded with melt inclusions, vesicles and mineral grains, surrounded by a concentric, oscillatory 639 zoned corona; e) the megacryst is formed by clustering of several crystals (e.g. A, B, C), as shown 640 by angular discordances of the growth layers. The shape of the megacryst is determined by the post aggregation overgrowth. DOL= dark oscillatory layers. Dashed line indicates the boundary between
 different zones as indicate in the text. Arrows indicate resorption surfaces.

A high-resolution version of the images is available as Virtual Microscope (eSlide VM...) (or
supplementary material)

Figure 6 – Enlargement of the corner at the bottom left of the Figure 5d. The CL image
illustrates the oscillatory textures in DOL (dark oscillatory layers). Arrows indicate resorption
surfaces. The numbers are Ba ppm content.

Figure 7 – (a), (b), (c) Ba and Sr (ppm) rim to core profiles across selected K-feldspar
megacrysts. CL images are parts of K-feldspar megacrysts in Figure 5.

Figure 8 – Or mol% vs. Rb ppm (a) and selected trace elements binary diagrams (b-f) for Kfeldspar megacrysts.

652 Figure 9 – Plagioclase inclusions in K-Feldspar megacrysts AMT 60 cr2 (a, b, c,), AMT 653 110 cr2 (d) and plagioclase phenocrysts from AMT110 (e, f). (a, b) plagioclase clusters (CL 654 images) formed by aggregation of more grains. Large irregular melt pockets are embedded during 655 the crystal growth; (c) BSE images of a plagioclase inclusion with direct chemical zoning; (d) BSE 656 images show patchy zoned cores (An50-An77) encircled by a mantle with oscillatory zoning and 657 corroded surfaces; (e) CL image of a plagioclase phenocryst composed by a main crystal and at 658 least three smaller euhedral grains attached. They are characterized by patchy zoned cores with 659 large melt inclusions and bubbles, encircled by oscillatory zoned mantles; (f) the BSE image 660 display a plagioclase phenocryst with sieve texture and extensive patchy zoning. The An 85 zones are altered into allophane. Single numbers are An mol%; double numbers are An mol% and Ba ppm 661 (An-Ba). 662

Figure 10 – An mol% vs. Sr ppm (a) and Eu ppm vs. Sr ppm (b) binary diagrams for
plagioclase inclusions and phenocrysts.

Figure 11 – Binary plots Rb vs. Sr (a) and Rb vs. Ba (b) showing the results of geochemical
 modeling for fractional crystallization (FC), assimilation and fractional crystallization (AFC) and

magma mixing (MM) processes (Ersoy, 2013). See text for explanation. Diamonds: micaceous
(filled) and andesitic (empty) enclaves from Conticelli et al. (2015); Square: metasedimentary
xenolith from Conticelli et al. (2015); triangles: whole rock composition from La Felice et al.
(2017); large circle: groundmass glass composition.

671 **Figure 12** – Schematic cartoon illustrating the growth mechanisms of the K-feldspar megacrysts. 672 (a) Nucleation and growth of few crystals in trachydacite magma. Mutual attachment of crystals can form crystal aggregates; (b) magma mixing and reheating induce dissolution of the K-feldspars; the 673 674 smallest crystals can be totally resorbed; (c) temperature decrease and degassing during mixing 675 promote a new event of crystallization: patchy cores form and a Ba-rich patchy corona with 676 abundant mineral inclusions growths; (d) the system re-equilibrate after mixing event and an 677 oscillatory corona growth in a convective magma body. A low nucleation rate hampers the growth 678 of new crystals. New dissolution and regrowth cycles result from reiterated magma influxes.

- 680 Table 1 Major and trace elements composition of whole rocks from La Felice et al. (2017)
 681 and groundmass glasses (this work). bdl= below detection limit.
- Table 2 Modal analyses in vol% of phenocrysts in the analyzed samples. Abbreviations:
 plg=plagioclase; K-fel=K-feldspar; opx=orthopyroxene; cpx=clinopyroxene; bt=biotite; ox=Fe-Ti
 oxydes; qtz=quartz; gdm= groundmass.
- 685 Supplementary Table 1 Major and trace element compositions of K-Feldspar (a) and
 686 plagioclase (b).
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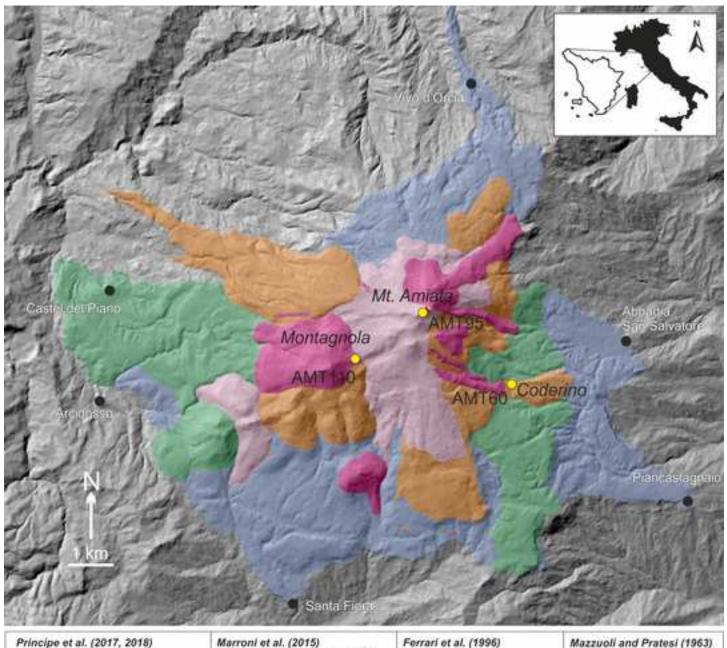
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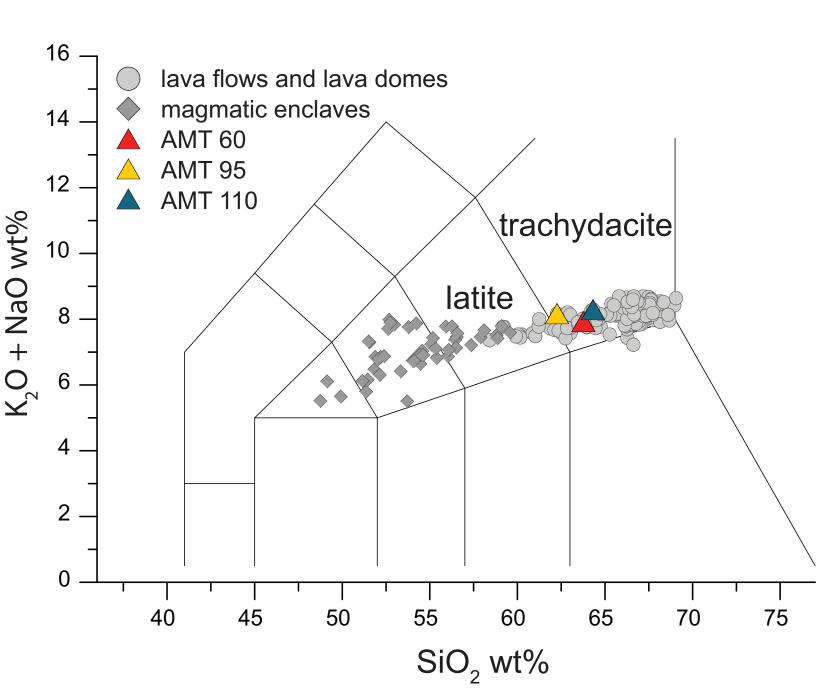
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Monte Amiata Synthem	Olivine Latite Final Lavas (231 ka *)	Olivine Latitic Lava flows	Trachytic Lava flows
Prato della Contessa Subsynthem Madonna degli Scout Subsynthem	Dome and Massive Lava Flow Complex (301-294 ka *)	Domes and Lava flows Complex	Quartz-latitic Complex B
Valle Gelata Subsynthem Bågnore Synthem	Basal Trachydacitic Complex	Basal Trachydacitic Complex	Quartz-latitic Lava flows
Montearioso Subsynthem Bagnólo Subsynthem		Upper unit Lower unit	Quartz-latitic Complex A



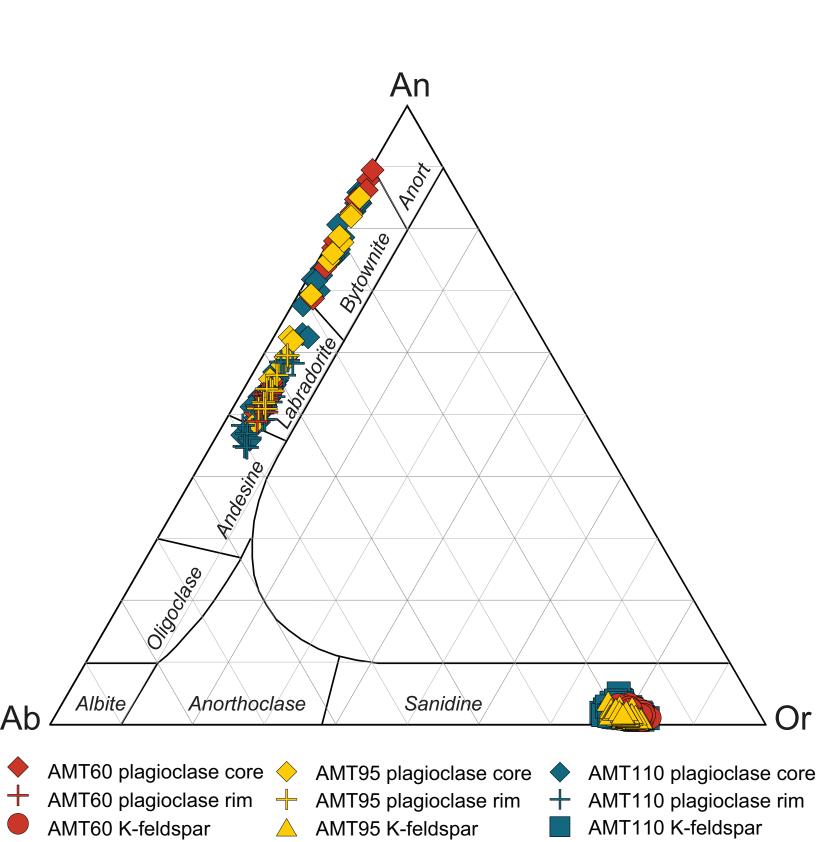


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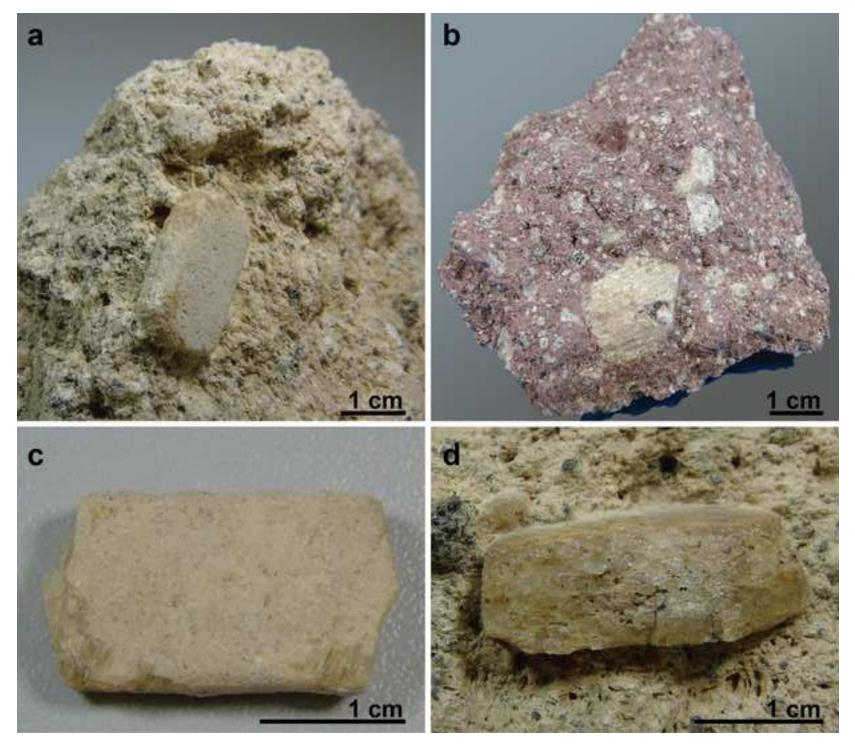
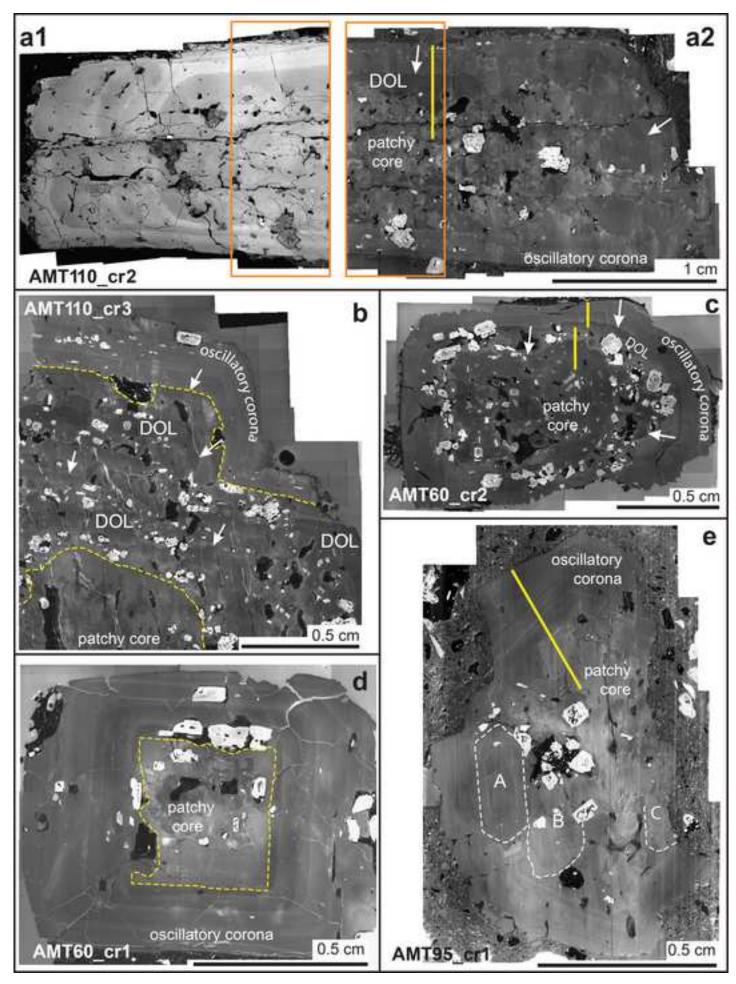
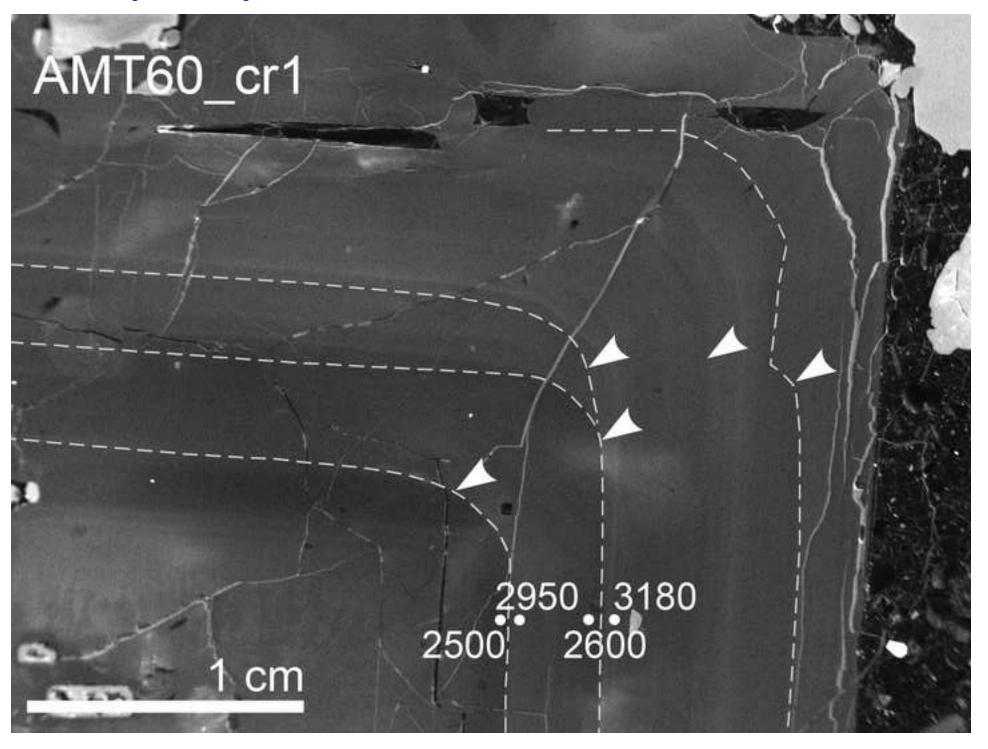
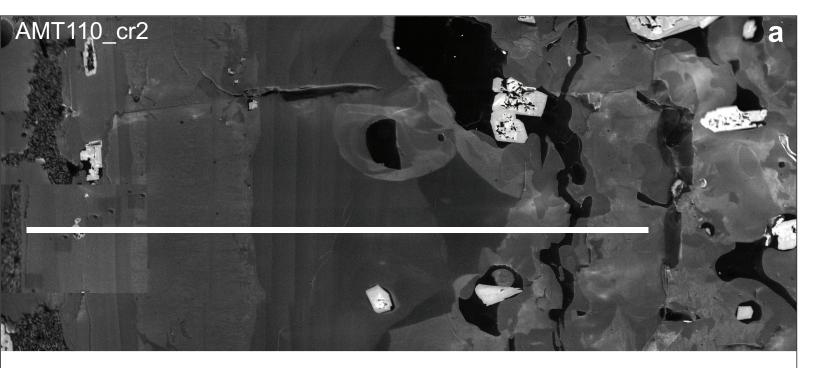
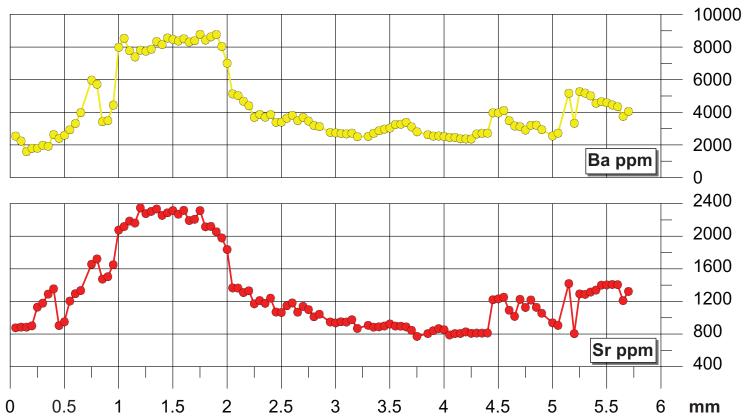


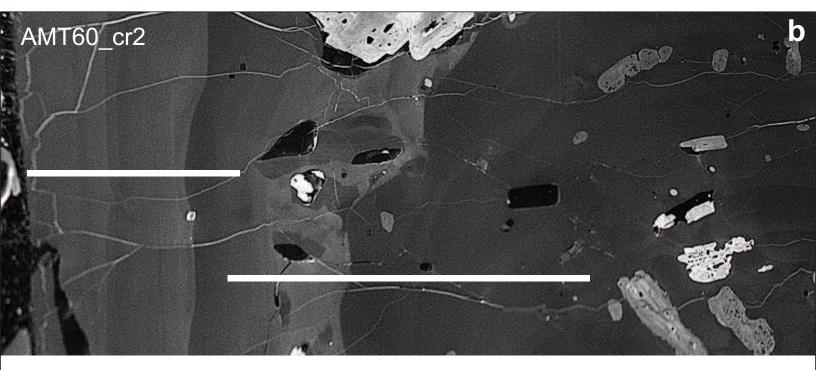
Figure5 Click here to download high resolution image

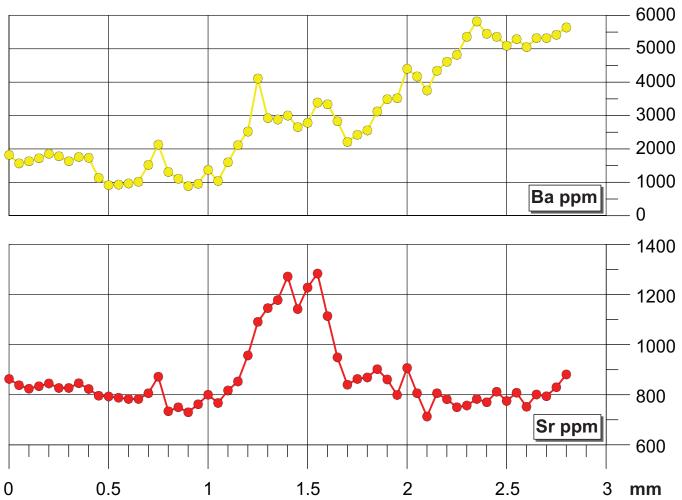


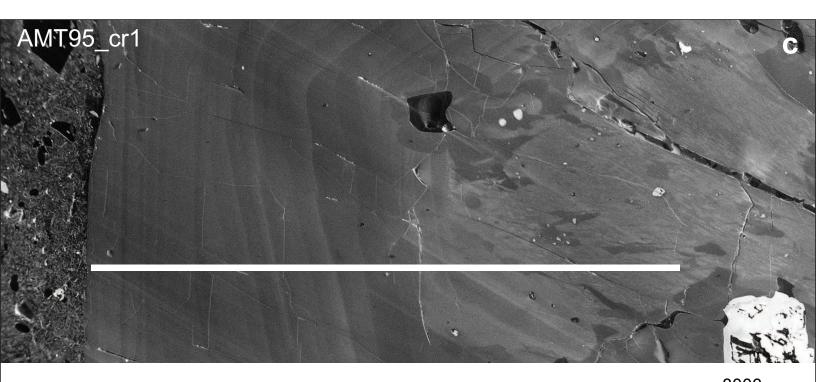


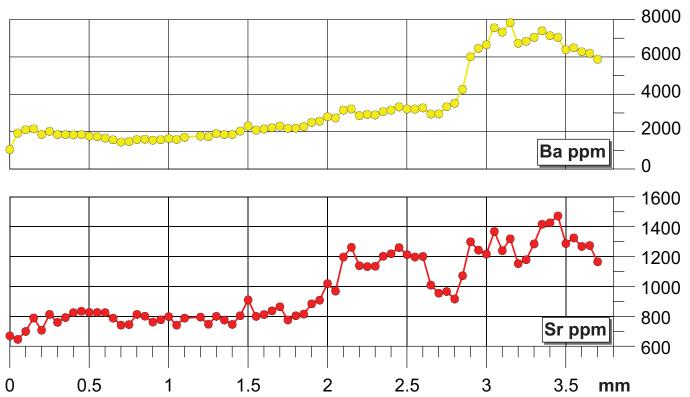


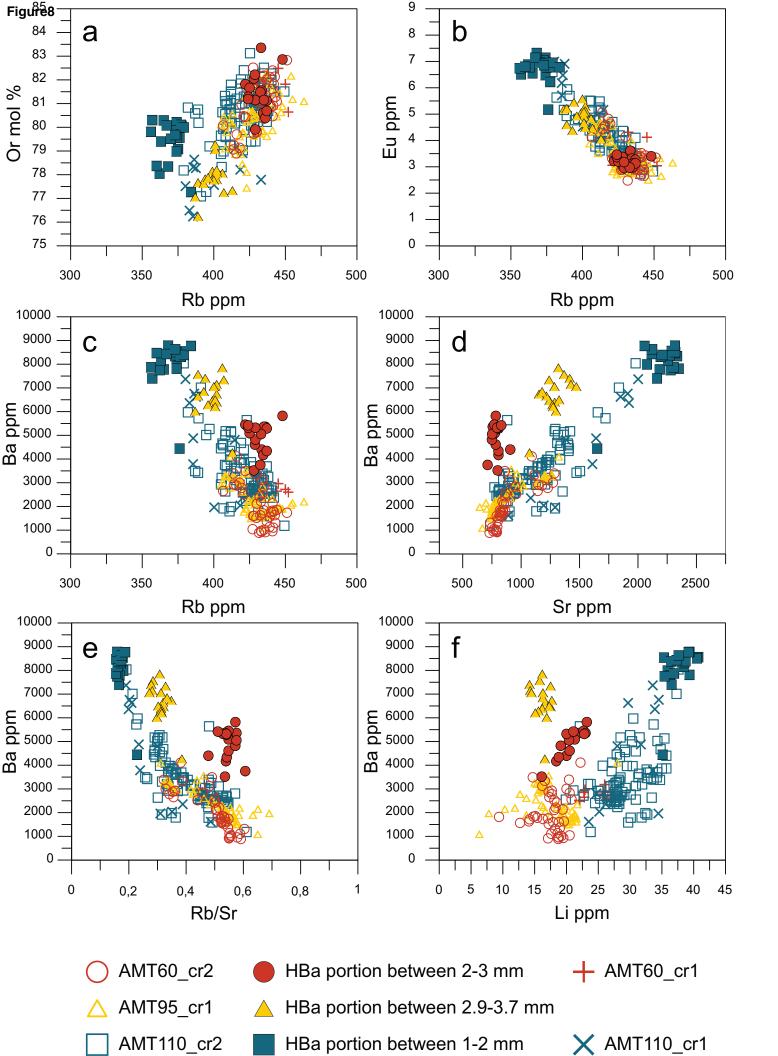


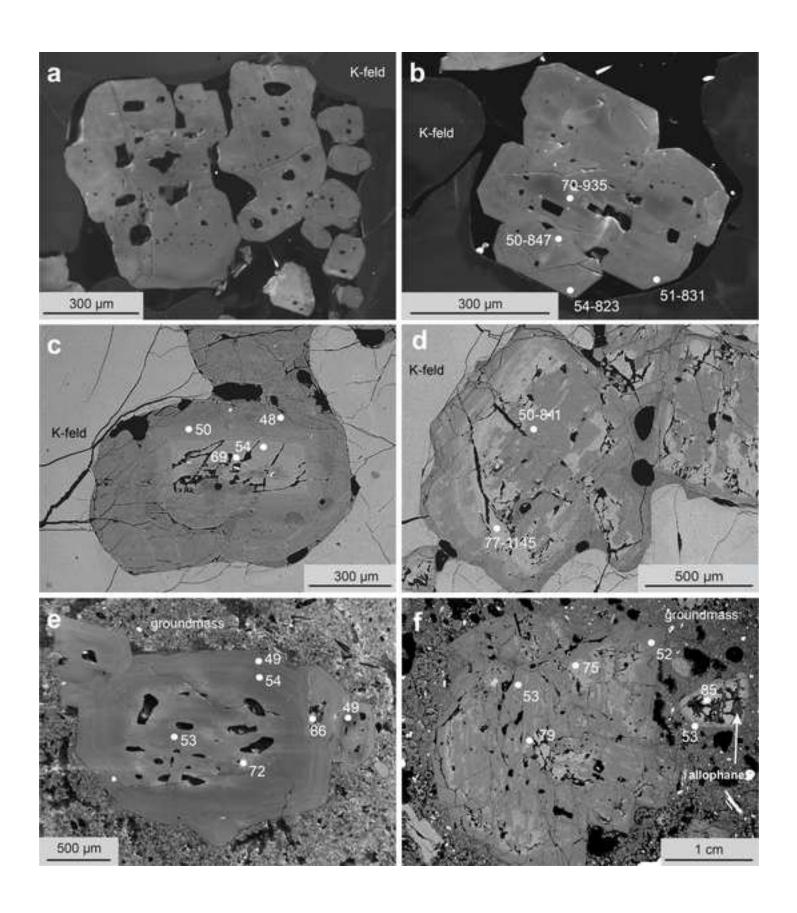


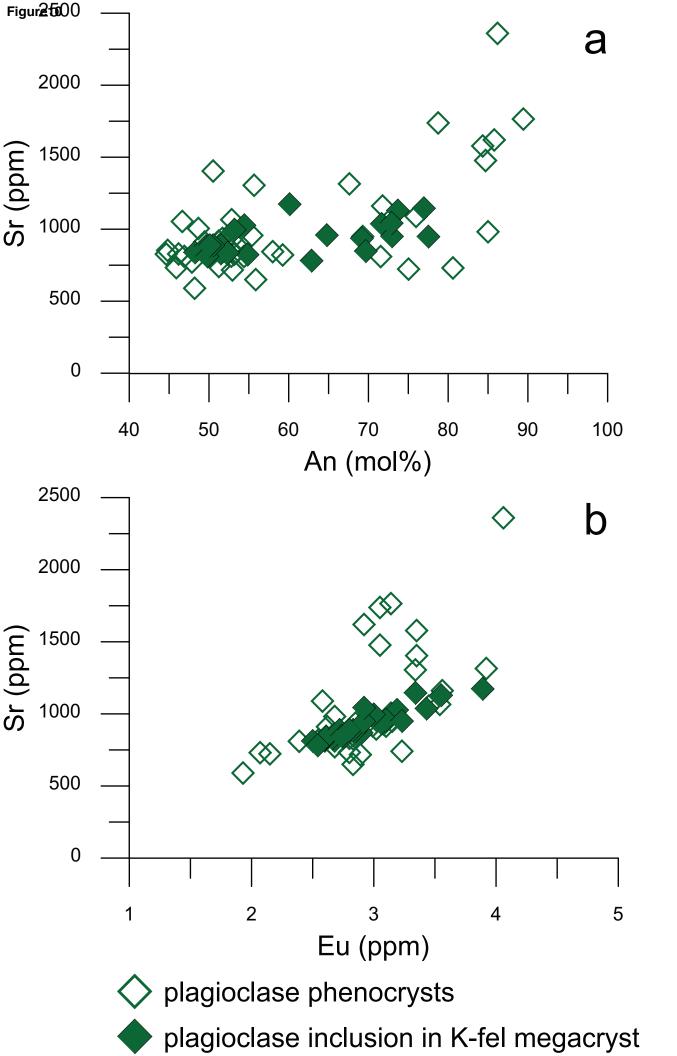


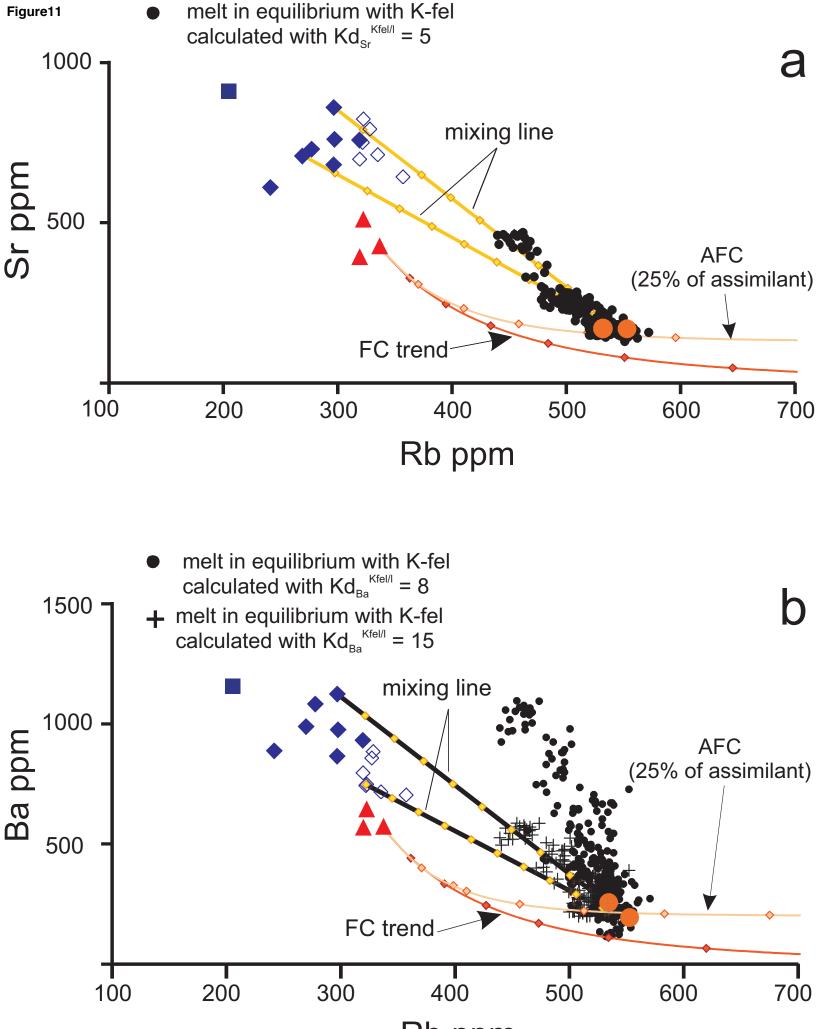












Rb ppm

Figure12

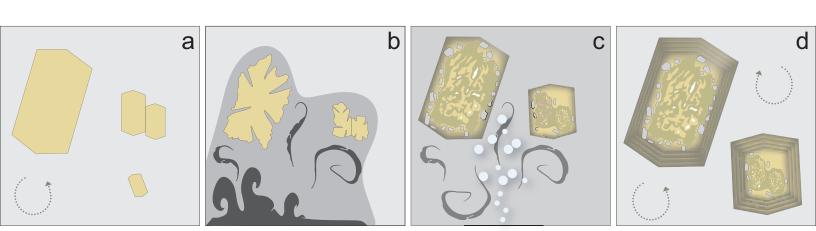


Table 1 – Major and trace elements composition of whole rocks from La Felice et al. (2017)and matrix glasses (this work). bdl= below detection limit.

		A MT05	A M/T 1 10		n	A N/T 1 10	
SAMPLE	AMT60 Coderino	AMT95 Amiata top	AMT110 Montagnola	AMT6		AMT110	
Locality	whole rock		Montagnota	Coderino		Montagnola	
	whole rock	K		glasses average (10)		glasses average (6)	
SiO ₂ %	61.70	61.50	62.30	76.09	<i>st.dev.</i> 1.14	75.21	<i>st.dev.</i> 1.05
TiO_2	0.57	0.63	0.60	0.28	0.05	0.23	0.04
Al_2O_3	17.00	16.35	16.25	11.73	0.03	12.28	0.34
Fe_2O_3	4.36	4.84	4.23	0.84	0.32	12.28	0.08
MnO	0.07	0.08	0.07	0.04	0.21	0.03	0.03
MgO	1.93	2.58	1.74	0.02	0.05	0.05	0.03
CaO	3.27	4.50	3.45	0.68	0.05	0.87	0.10
Na ₂ O	2.13	2.12	2.20	2.17	0.27	2.12	0.15
K ₂ O	5.54	5.95	5.83	7.02	0.22	6.92	0.25
Cr_2O_3	0.01	0.01	0.01	7.02	0.22	0.72	0.25
P_2O_5	0.19	0.23	0.19				
LOI	4.81	1.62	2.14				
Total	101.58	100.41	99.01	98.86	1.06	98.87	1.09
Ba ppm	565	642	565	193	45	255	29
Ce	151	139	144	169.8	8.0	175.2	5.8
Cr	40	50	30	bdl		bdl	
Cs	35.9	35.6	33	76.2	5.1	73.7	1.8
Dy	5.99	5.32	5.25	6.43	0.31	6.58	0.38
Er	3.08	2.67	2.65	3.27	0.18	3.22	0.12
Eu	1.46	1.73	1.6	0.61	0.12	0.62	0.07
Ga	21.5	19.5	20.4	18.79	1.45	18.03	0.68
Gd	8.07	7.74	7	8.20	0.55	8.36	0.65
Hf	8.6	7	7.5	5.76	0.22	5.63	0.32
Но	1.19	1.03	0.99	1.22	0.06	1.23	0.11
La	83.3	76.7	79.8	90.2	3.5	91.3	2.3
Lu	0.44	0.38	0.37	0.46	0.02	0.44	0.03
Nb	17.5	15.4	18.1	15.1	0.8	15.8	0.5
Nd	68.1	63.4	62.7	65.1	3.0	68.0	2.5
Pr	18.25	16.45	16.85	18.10	0.87	18.66	0.60
Rb	319	322	337	553	31	534	12
Sm	11.6	11.05	10.95	11.28	0.54	12.11	0.62
Sn	11	9	10				
Sr	387	504	421	166	43	165	25
Ta	1.4	1.2	1.4	1.82	0.11	1.78	0.09
Tb	1.12	1.04	0.96	1.14	0.06	1.17	0.07
Th	44.3	39.4	41.8	69.1	3.3	68.4	1.9
Tm	0.5	0.44	0.43	0.48	0.03	0.48	0.04
U	12.65	11	11.2	18.5	1.1	18.5	0.5
V	55 7	84 7	59 7	3.0	0.5	8.7	0.9
W Y	7 33.1	7 29.2	7 28.8	33.9	1.5	35.4	1.7
r Yb	2.64	29.2	28.8	3.11	0.25	3.01	0.12
Zr	333	2.43 260	299	165.4	6.2 6.2	170.3	10.7
Zr As	535 54	200 27	299	103.4	0.2	170.5	10.7
AS Co	8	14	8	1.13	0.35	1.88	0.53
Cu	12	23	16	2.41	2.05	1.88	0.33
Li	12	110	110	2.41	2.03 16	224	13
Ni	120	20	11	0.58	0.22	bdl	-
Pb	59	20 54	57	80.9	7.0	70.7	2.9
Sc	9	12	9	10.9	0.4	12.7	0.5
Zn	59	62	57	31.1	7.9	29.6	4.2
 11		<u>.</u>		51.1	1.2	27.0	

Table 2 – Modal analyses in vol% of phenocrysts in the analyzed samples. Abbreviations: plg=plagioclase; K-fel=K-feldspar; opx=orthopyroxene; cpx=clinopyroxene; bt=biotite; ox=Fe-Ti oxydes; qtz=quartz; gdm= groundmass.

Sample	AMT60	AMT95	AMT110
plg	13.2	11.6	12.8
K-fel	14.2	10.6	11.0
opx	5.2	5.0	5.3
cpx	1.3	5.1	1.7
bt	2.9	2.4	3.6
OX	0.2	0.0	0.5
qtz	0.1	0.1	0.3
gdm	63.0	65.2	64.8
Total	100	100	100