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1

2 **(Revision 2) Experimental investigation of trace element partitioning between amphibole and**
3 **alkali basaltic melt: towards a more general partitioning model with implications for amphibole**
4 **fractionation at deep crustal levels**

5

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20

21 **ABSTRACT**

22 Time-series experiments were carried out in a piston cylinder apparatus conducted at 0.8 GPa and
23 1030-1080 °C using as starting material a hydrous K-basalt melt to determine the element partition
24 coefficients between amphibole and silicate glass. Major, minor, and trace element compositions of

25 amphibole and glass were determined with a combination of electron microprobe and laser ablation
26 inductively coupled plasma mass spectrometry. Results show that the main mineral phase is calcic
27 amphibole, and the coexisting glass compositions range from basaltic trachyandesite to andesite. We
28 estimated the ideal radius, the maximum partition coefficient and the apparent Young's modulus of the
29 A, M1-M2-M3, and M4-M4' sites of amphibole. The influence of melt and amphibole composition,
30 temperature, and pressure on the partition coefficients between amphiboles and glasses has also been
31 investigated by comparing our data with a literature dataset spanning a wide range of pressures (0.6-2.5
32 GPa), temperatures (780-1100 °C), and compositions (from basanite to rhyolite). Finally, we modelled
33 a deep fractional crystallization process using the amphibole-melt partition coefficients determined in
34 this study, observing that significant amounts of amphibole crystallization (>30 wt%) well reproduce
35 the composition of an andesitic melt similar to that of the calcalkaline volcanic products found in
36 Parete and Castelvoturno bore-holes (NW of Campi Flegrei, Italy).

37

38 **Keywords:** amphibole; trace element partition coefficient; lattice strain model; Campi Flegrei

39

40

INTRODUCTION

41 The occurrence of amphibole in rocks encompassing the entire range of silica activities in terrestrial
42 igneous suites, coupled with its capacity to incorporate significant concentrations of geochemically
43 important trace elements, underscores the likely importance of this phase in the chemical evolution of
44 both mantle- and crustal-derived magmas (Brenan et al. 1995; Tiepolo et al. 2007). During the last
45 decades, the behavior of trace element partitioning between calcic amphiboles and silicate melts has
46 been investigated at different pressures (0.2-2.7 GPa), temperatures (750-1150 °C), and system
47 compositions (e.g., Nicholls and Harris 1980; Adam et al. 1993; Adam and Green 1994, 2003; Sisson
48 1994; LaTourrette et al. 1995; Brenan et al. 1995, 1998; Klein et al. 1997; Tiepolo et al. 1999, 2000a,

49 2020b, 2007; Hilyard et al. 2000a; Zhang et al. 2019). It is widely accepted that the resulting partition
50 coefficients depend on the chemical compositions of mineral and melt phases, pressure, temperature,
51 and H₂O-content of the melt, as well as on the redox conditions (Blundy and Wood 2003; Adam and
52 Green 2006; Aigner-Torres et al. 2007; Severs et al. 2009; van Kan Parker et al. 2010; Hill et al. 2011;
53 Fabbrizio et al. 2021). Moreover, Blundy and Wood (1994) provided a theoretical framework based on
54 the lattice strain model (Brice 1975) for the interpretation of trace element partitioning. So far, it has
55 been applied successfully to trace element partitioning between pyroxene (e.g., Wood and Blundy
56 1997; Schmidt et al. 1999; Adam and Green 2006; Sun and Liang 2012, 2013; Mollo et al. 2018;
57 Bonechi et al. 2021; Fabbrizio et al. 2021), olivine (e.g., Zanetti et al. 2004; Sun and Liang 2013),
58 garnet (e.g., Draper and van Westrenen 2007; van Westrenen and Draper 2007; Sun and Liang 2013),
59 amphibole (e.g., LaTourrette et al. 1995; Adam and Green 2006; Tiepolo et al. 2007; Wan et al. 2009;
60 Nandedkar et al. 2016; Shimizu et al. 2017; Zhang et al. 2019; Cannà et al. 2022), phlogopite (e.g.,
61 LaTourrette et al. 1995; Schmidt et al. 1999; Fabbrizio et al. 2010), leucite (e.g., Schmidt et al. 1999;
62 Fabbrizio et al. 2008), feldspars (e.g., Icenhower and London 1996; Fabbrizio et al. 2009) and their
63 coexisting melts. Despite numerous investigations on the partition between crystals and melt, there are
64 still some mineral phases, including amphibole, for which data are limited or missing. In this study we
65 provide new data on amphibole major, minor, and trace elements partition coefficients derived from
66 crystallization experiments on a hydrous K-basaltic melt at 0.8 GPa and 1030-1080 °C. In detail, we
67 analysed major and trace elements in amphiboles and glasses of the experimental runs by using an
68 electron microprobe and laser ablation-inductively coupled plasma-mass spectrometry, respectively.
69 We determined the concentrations of large ion lithophile elements, rare earth elements, high field
70 strength elements, and transition metals in experimental phases and then, we used the obtained data to
71 calculate the partition coefficients between amphiboles and glasses. In addition, we estimated the ideal
72 radius, the maximum partition coefficient, and the apparent Young's modulus of the A, M1-M2-M3,

73 and M4-M4' sites of amphibole. Also, we reviewed the influence of melt and amphibole compositions,
74 temperature, and pressure on the behavior of partition coefficients between amphiboles and glasses by
75 integrating our data with a literature data set (LEPR database and data from Nandedkar et al. 2016,
76 Zhang et al. 2019, and Cannà et al. 2022) spanning a wide range of pressures (0.6-2.5 GPa),
77 temperatures (780-1100 °C) and compositions (from basanite to rhyolite). Finally, we observed
78 whether a composition approaching the APR16 one is able, through the crystallization of amphibole in
79 a deep differentiation process, to produce an andesite melt with trace element abundances similar to
80 those of the calc-alkaline volcanic products found in Parete and Castelvoturno bore-holes (NW of
81 Campi Flegrei, Italy).

83 METHODS

84 Samples' description

85 Crystallization experiments were performed by using the end loaded piston cylinder apparatus at the
86 HP-HT Laboratory of the Earth Sciences Department (Sapienza University, Rome, Italy). Experiments
87 were carried out at isobaric conditions of 0.8 GPa, 1030-1080 °C, with an initial H₂O content ≥ 3 wt%,
88 and durations from 0.25 to 9 hours. Experiments were performed at different duration to observe the
89 variation of trace elements concentration with time in both disequilibrium and equilibrium conditions.
90 We used as starting materials the powder of a natural primitive K-basalt (APR16) and its glass
91 (APR16GL, Table 1), prepared by melting the APR16 powder in a Fe-saturated Pt container for 15 min
92 using a CO/CO₂ gas mixing furnace installed at the Bayerisches Geoinstitut (Bayreuth, Germany) at
93 1400 °C, atmospheric pressure and oxygen fugacity corresponding to the NNO (nickel-nickel oxide)
94 buffer. The as-fused starting material did not contain crystalline phases, as analysed by both
95 microprobe and SEM image analyses. Then, the obtained glassy starting material was ground in an
96 agate mortar under acetone. The natural primitive K-basalt (APR16 sample) was found as scoria clast

97 in the deposits of the Solchiaro hydromagmatic eruption (~22 ka ago; Morabito et al. 2014) located in
98 Procida Island (Campi Flegrei, Italy). This K-basalt is characterized by 12 vol% of forsteritic olivine
99 and diopsidic clinopyroxene phenocrysts dispersed in a groundmass made of olivine, clinopyroxene,
100 plagioclase, Ti-magnetite, alkali feldspar, and glass (D'Antonio et al. 1999; De Astis et al. 2004).
101 Although amphibole is not present in outcropped products, its stability has been experimentally
102 observed when using APR16 as a starting composition, equilibrated at $P = 0.8$ GPa when water
103 contents are > 7 wt.% (Bonechi et al. 2017; Perinelli et al. 2019; Bonechi et al. 2020a, 2020b).

104

105 **Experimental techniques**

106 The detailed experimental procedure is described by Perinelli et al. (2019) and by Bonechi et al.
107 (2020a, 2020b). Here we report the main aspects. Assemblies were 1.25 cm in diameter, and consisted
108 of CaF₂ outer sleeve, graphite furnace, and crushable magnesia spacers were used.

109 The experimental charges were prepared loading Au₇₅Pd₂₅ capsules with ~40 mg of sample powder. In
110 each experiments, we added water in known amounts by using a 1.0 μ L microsyringe (Table 2). Loss
111 of H₂O by vaporization during welding was prevented by freezing the crucible with nitrogen. The
112 welded capsule was weighed, stored in a furnace at 110 °C for at least 1 h, and then weighed again to
113 confirm the absence of water leaks. Moreover, to minimize possible loss of H₂ during the experiments
114 the charges were surrounded by pyrophyllite powder (Freda et al. 2001). The temperature was
115 controlled by a factory-calibrated W₃Re₉₇-W₂₅Re₇₅ (type D) thermocouple and maintained with an
116 uncertainty of ± 5 °C. For the experimental run-up, we used the “hot piston-out” procedure (Johannes
117 et al. 1971; Presnall et al. 1978) in which the assembly was first cold-pressurized to a value ~10% over
118 the target pressure and then heated to the final run temperature. This technique allows to closely
119 approach the run pressure through the stress relaxation within the assembly upon heating, requiring
120 only minor upward pressure adjustments during the experiment in most cases (Watson et al. 2002). The

121 heating rate was imposed at 150 °C/min. The samples were maintained at the target pressure and
122 temperature for a given duration (nominal duration; Table 2), and then quenched by turning off the
123 power. The temperature drop below 500 °C was of <5 s (average cooling rate of 150 °C/s). All the runs
124 were self-buffered; an estimation of experimental fO_2 was made by using the theoretical model of Barr
125 and Grove (2010), which is based on the temperature-and fO_2 -dependent partitioning of Fe between
126 the AuPd capsule and coexisting melt. Thus, we measured the post-run Fe content in the sample-holder
127 as closely as possible to the capsule-sample boundary of a near-liquidus anhydrous experiment.
128 Applying the Barr and Grove (2010) approach the calculated fO_2 were of NNO -0.5 for the near-
129 liquidus run and NNO -0.8 and NNO -1.1 for the longest runs of this study (Bonechi et al. 2020a). As a
130 whole, the estimated range of fO_2 values agree with those estimated for similar furnace assemblages
131 (Conte et al. 2009; Weaver et al. 2013; Perinelli et al. 2019; Bonechi et al. 2020a). Finally, we
132 determined the undercooling (ΔT ; Table 2) that is the difference between the liquidus temperature and
133 the nominal temperature of the experiment (Bonechi et al. 2020a, 2020b; Bonechi 2020). For
134 calculations, the liquidus temperature (T_L) of APR16 experiments was taken from Procida K-basalt
135 experimental data (1095 °C; Perinelli et al. 2019, Bonechi et al. 2020a).

136

137 **Analytical techniques**

138 **Textural investigations and major element determinations.** Back-scattered electron (BSE)
139 images used to investigate textural aspects of both natural and experimental samples were collected by
140 Scanning Electron Microscopy using a FEI-quanta 400 equipped for microanalysis with an EDAX
141 Genesis system at the Earth Sciences Department, Sapienza University of Rome. Major elements were
142 analysed at the CNR-Istituto di Geologia Ambientale e Geoingegneria di Roma, with a Cameca SX50
143 electron microprobe equipped with five wavelength dispersive spectrometers. Quantitative analyses
144 were performed using 15 kV accelerating voltage and 15 nA beam current. As standards we employed

145 metals for Mn and Cr, Jadeite for Na, Wollastonite for Si and Ca, Orthoclase for K, Corundum for Al,
146 Magnetite for Fe, Rutile for Ti, Periclase for Mg, Apatite for P. Counting times for all elements were
147 20 s on peak and 10 s on both backgrounds. Light elements (Na, K) were counted first to prevent loss
148 by volatilization. The PAP correction method was used. Minerals were analysed using a beam diameter
149 of 1 μm whereas to minimize alkali loss during glass analysis, the beam was defocused to 15 μm . To
150 evaluate the accuracy of the analyses, repeated analyses of three international secondary standards
151 (Kakanui augite, Icelandic Bir-1, and rhyolite RLS132 glasses from USGS) were made before any
152 series of measurements. The mean precision from the standard value was about 1% for SiO_2 , 2% for
153 Al_2O_3 , 5% for K_2O , CaO and FeO , and 8-10% for other elements. The analytical precision (2 sigma
154 error) is $\leq 1\%$ for elements in the concentration range >10 wt% oxide, 5% for elements in the range 2–
155 10 wt% oxide, and better than 10% for elements in the range 0.5-2 wt% oxide. The water contents of
156 experimental glasses were estimated according to the by-difference method (Devine et al. 1995;
157 Humphreys et al. 2006). We are aware that this method is not fully reliable given the estimation is
158 affected by *i*) element concentrations not measured by EMPA and *ii*) surface charge effects (Hughes et
159 al. 2019) leading to an overestimation of H_2O concentration. However, the obtained H_2O values show a
160 good linear correlation (correlation coefficient $R^2 = 0.97$) with those determined by micro-Raman
161 spectroscopy measurements on residual melts of equilibrium experiments performed on the same
162 composition, at the same P, T, and initial hydrous conditions (cf. Perinelli et al. 2019).

163

164 **Laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS).** LA-ICP-MS
165 analyses of the experimental samples were performed at the Department of Physics and Geology,
166 University of Perugia (Italy). The instrumentation consisted of a Teledyne/Photon Machine G2 LA
167 device equipped with a Two-Volume ANU HeEx 2 cell and coupled with a Thermo Fisher Scientific
168 quadrupole-based iCAP-Q ICP-MS. The analyses of amphibole crystals and glasses were performed

169 using a circular laser beam of 12-20 μm diameter, a frequency of 10-15 Hz and a laser density on the
170 sample surface of 3.5 J/cm². Oxide formations was checked on the NIST SRM 612 by monitoring and
171 maintaining the ratio ThO/Th ratio below 0.005. The NIST SRM-610 standard reference material was
172 used as calibrant and Ca, previously analysed by EPMA, as internal standard. Under these operating
173 conditions precision and accuracy are better than 10% for most of the elements (Petrelli et al. 2007,
174 2008, 2016). In detail, at beam sizes equal or larger than 15 μm , precision (measured as one sigma) and
175 accuracy (expressed as relative deviation from the reference value) are of the order of 10% (Petrelli et
176 al. 2016). Accuracy is better or equal to 10% and 13% at beam sizes of 15 and 10 μm , respectively,
177 while when the spatial resolution is increased to 12 μm , accuracy remains better than 15% (Petrelli et
178 al. 2016).

179

180

RESULTS

181 **Texture, phase relationships and chemical composition of experimental samples**

182 All the experimental samples investigated in this study, except the APR16-ST1 run, are described in
183 detail in the previous work of Bonechi et al. (2020a) dealing with phase equilibria and crystallization
184 kinetics in the APR16 K-basalt. Here we briefly report a description of the main aspects.

185 *Texture and phase relationships.* All the experimental products that for simplicity we have grouped
186 into the C3A (i.e., C3Aa, C3Ab, C3Ad runs) and C3B (C3Ba, C3Bb, C3Bc, C3Bd runs) suites, show a
187 high crystallinity (Fig. 1a, b and Table 2) as a consequence of the imposed undercooling ($\Delta T = 150$ -
188 200 °C), that yields strong supersaturation conditions in the K-basaltic melt, enhances the nucleation
189 kinetics in the sample during the early stage of experiments, and affects the phase modal proportions
190 (Bonechi et al., 2020a and reference therein). Amphibole (Amph) occurs in all the experiments as
191 euhedral crystals of ~40 μm in size, along with clinopyroxene (Cpx) + oxide (Ox) \pm plagioclase (Plg) \pm
192 orthopyroxene (Opx) (Table 2). Both tiny crystals of Cpx and Opx (up to ~5 μm sized) are euhedral in

193 shape, as the larger (~40 μm in size) Ox grains. Subhedral to euhedral plagioclase has dimensions of
194 about 10 μm or less (Bonechi et al. 2020a). Glass is present in all the experimental runs, but it was
195 analysed only in those with glass portions large enough to be examined.

196 About the APR16-ST1 experiment (Fig. 1c and Table 2), it is similar to the two runs with the longest
197 duration, i.e., C3Ad and C3Bd, in both texture and mineral assemblage. It is formed by abundant Amph
198 showing well-developed crystal face and dimensions up to ~50 μm , combined with idiomorphic Cpx of
199 ~5 μm in size and euhedral Ox (sized up to ~40 μm). Glass pools larger than 60 μm occur within all the
200 capsule. It is also characterized by large (up to 100 μm) and numerous vesicles present throughout the
201 sample as a result of the high amount of water added before the experiment ($\text{H}_2\text{O}_i = 8 \text{ wt}\%$), which
202 favored the achievement of saturation conditions (APR16 H_2O solubility ~10 wt%; Perinelli et al.
203 2019).

204 *Chemical composition.* Chemical compositions of Amph are reported in Table S1 of Supplementary
205 Material 2. According to the Hawthorne et al. (2012) classification, all the crystallized Amph is calcic,
206 and its composition varies from magnesiohornblende and edenite to pargasite and
207 magnesiohastingsite. Cpx compositions are diopsidic ($\text{Wo}_{46-48}\text{En}_{39-43}\text{Fs}_{10-14}$), whereas the
208 orthopyroxene crystals found in the APR16-C3Bc run is enstatitic ($\text{Wo}_4\text{En}_{73}\text{Fs}_{23}$). Oxide crystals are
209 generally hercynites, while in the APR16-C3Aa run Cr-rich spinels also occur. Plagioclase grains
210 occurring in the shortest runs (0.25-3 h) are bytownitic (An_{72}) and labradoritic (An_{62}) in composition.
211 As regards Amph, the calculated Amph-melt Fe-Mg exchange coefficient (i.e., $^{\text{Amph-liq}}K_{\text{DFe-Mg}} =$
212 $(\text{FeO}/\text{MgO})^{\text{Amph}}/(\text{FeO}/\text{MgO})^{\text{liq}}$) for the runs of the C3A and C3B suites varies between ~0.3 and ~1,
213 showing an almost linear decrease with increasing time (Bonechi et al. 2020a) and a non-achievement
214 of equilibrium conditions in many of the experiments. Indeed, only the magnesiohastingsites
215 crystallized in the runs at 9 h (i.e., APR16-C3Ad and APR16-C3Bd with $^{\text{Amph-liq}}K_{\text{DFe-Mg}} = 0.34$ and
216 0.40, respectively) attained Amph-liquid equilibrium conditions ($^{\text{Amph-liq}}K_{\text{DFe-Mg}} = 0.28 \pm 0.11$; Putirka

217 2016). In addition to these, also the magnesiohastingsite crystallized in the run APR16-ST1, carried out
218 for 2 h in saturation conditions ($H_2O_i = 8$ wt.%; Table 2), achieved Amph-liquid equilibrium conditions
219 ($K_{DFe-Mg}^{Amph-liq} = 0.32$). As regards the other phases, instead, Cpx and Plg result to be always in
220 disequilibrium conditions. Chemical compositions of synthetic glasses, that according to TAS diagram
221 (Le Bas et al. 1986) range from basaltic trachy-andesite to andesite (Fig. S1 of Supplementary Material
222 1), are reported in Table S2 of Supplementary Material 2.

223

224

225 **Trace and REE content**

226 Average compositions of trace elements concentrations analysed by LA-ICP-MS technique in Amph,
227 and coexisting glass are reported in Table 3.

228 *Amphibole*. Figure 2 shows the trace elements concentrations in Amph normalized to chondrite C1
229 after Anders and Grevesse (1989) for LILEs (Large-Ion Lithophile Elements), REEs (Rare Earth
230 Elements), HFSEs (High Field Strength Elements), and TEs (Transition Elements). The abundance of
231 LIL elements (e.g., Rb and Ba) of Amph from all experiments are comparable among them except for
232 Pb which shows significant differences in its content. The chondrite-normalized REE patterns display
233 enrichment of light REE (LREE) over heavy REE (HREE) (i.e., $La_N/Yb_N = 3.5-6.2$, where the subscript
234 N denotes chondrite-normalized values) with a maximum at La_N (~ 74). All Amph exhibit no Eu
235 anomaly ($Eu/Eu^* = 0.98-1.06$; $Eu/Eu^* = Eu_N/(Sm_N \times Gd_N)^{1/2}$) indicating the absence or scarce
236 crystallization of coexisting plagioclase. Finally, the concentration of tetravalent HFSEs (i.e., Hf, Zr,
237 Ti) is lower than that of pentavalent cations (i.e., Ta and Nb), while as regards TEs, it is possible to see
238 evident troughs at Co and Ni compared to the nearby elements.

239 *Glass*. Figure 3 shows the trace elements concentration in the experimental glasses normalized to
240 chondrite C1 after Anders and Grevesse (1989) for LILEs, REEs, HFSEs, and TEs. Generally, all the

241 experimental glasses match the trend of the APR16 sample (Mazzeo et al. 2014) and of the APR16
242 suite of Bonechi et al. (2021), except for Ni abundances, which are relatively higher. C1-normalized
243 trace element patterns are L-MREE (Light/Middle rare earth element) enriched ($La_N = 105-128$,
244 $La_N/Sm_N = 3.0-4.6$, $La_N/Yb_N = 5.6-9.5$) and nearly flat in the HREE region ($Ho_N/Yb_N = 0.7-1.1$). All
245 the considered glasses have absent or slightly positive Eu anomaly ($Eu/Eu^* = 1.01-1.11$). Moreover,
246 pentavalent HFSEs (i.e., Ta and Nb) are more abundant than tetravalent cations (i.e., Zr, Hf, Ti).

247

248

249

DISCUSSION

250 Partition coefficients

251 Table 4 reports the trace elements Amphibole-melt D -values obtained in the present study for the
252 longest experiments of the C3A and C3B suites and for APR16-ST1 run, where amphiboles are in
253 equilibrium with the melt. Unfortunately, due to the impossibility to obtain reliable trace element
254 concentrations of the glasses in the runs with shorter duration and in disequilibrium, we could not
255 quantitatively compare the partition coefficients in both disequilibrium and equilibrium conditions.
256 However, the trace element concentrations measured in Amph do not show significant variation except
257 a slight decrease or increase in the ones at equilibrium conditions (i.e., APR16-C3Ad, APR16-C3Bd,
258 APR16-ST1; Table 3 and Fig. S2 of Supplementary Material 1). Qualitatively, this seems to suggest
259 higher Amph-melt D -values for incompatible elements (e.g., LILE, REE, HFSE) and lower Amph-melt
260 D -values for compatible elements (e.g., TE) in disequilibrium conditions, due to an excessive
261 accumulation or depletion of trace elements, depending on their degree of compatibility or
262 incompatibility, at the crystal-melt interface with a consequent disequilibrium element uptake during
263 crystal growth (Bonechi et al. 2021 and reference therein). Figure 4 shows the partition coefficients
264 between amphibole and melt for LILEs, REEs, HFSEs, and TEs. LILEs are incompatible (e.g., D_{Sr}

265 ≤ 0.6 , $D_{Ba} \leq 0.5$). Noteworthy is the behaviour of lithium that, in agreement with literature data (e.g., D_{Li}
266 $= 0.3$ in Dostal et al. 1983), results in incompatible behavior in the APR16-ST1 amphiboles but
267 becomes almost compatible in crystals from the APR16-C3Ad ($D_{Li} = 0.84$) and APR16-C3Bd ($D_{Li} =$
268 0.75) runs (Table 4). This contrasting behaviour may have been induced by the different initial H_2O
269 content (H_2O_i) between the APR16-C3Ad/Bd ($H_2O_i = 3-4$ wt%) and APR16-ST1 ($H_2O_i = 8$ wt%)
270 experiments, which influenced the kinetic of Amph growth. Indeed, although the ΔT , that is one of the
271 parameters controlling the crystal growth regime, is high for all experiments (Table 2), the H_2O -
272 saturated condition of APR16-ST1 run ($\Delta T = 100$ °C) still allowed for slow Amph growth and
273 selectivity in elements partitioning from the beginning of the experiment, whereas H_2O -undersaturated
274 condition of APR16-C3Ad/Bd experiments ($\Delta T = \sim 140-200$ °C) probably promoted an initial rapid,
275 disequilibrium growth of Amph and less selectivity in elements partitioning. The experimental duration
276 of APR16-C3Ad/Bd experiments (9 h), may not have been enough for the diffusive re-equilibration of
277 some elements such as lithium, whose abundance in APR16-C3Ad/Bd runs is always higher than in
278 APR16-ST1 one (Table 3). LREEs (e.g., $D_{La} \leq 0.4$) are always more incompatible than MREE and
279 HREEs, which in some cases result to be compatible with Amph (e.g., D_{Tb} in all the considered runs,
280 D_{Sm} to D_{Tm} in APR16-C3Bd, and D_{Sm} , D_{Er} in APR16-ST1). As regards HFSEs, tetravalent and
281 pentavalent-charged cations are always incompatible (D_{Nb} and $D_{Ta} \leq 0.7$; D_{Zr} and D_{Hf} between 0.5 and
282 0.8), with the exception of Ti. Finally, trace element partition coefficients of TEs (i.e., D_{Co} , D_{Cr} , D_{Ni} ,
283 D_{Sc} , and D_V) range from slightly incompatible to highly compatible. In particular, D_V vary between 0.7
284 and 1.3, whereas D_{Co} , D_{Sc} , D_{Ni} , and D_{Cr} are between 2 and 9.

285

286 **Lattice strain model (LSM)**

287 At equilibrium, the amph/melt partition coefficient can be quantitatively described by the near-
288 parabolic relationship (Brice 1975; Blundy and Wood 1994; Wood and Blundy 2001):

289

$$D_j^{crystal-melt} = D_0 \exp \left[\frac{-4\pi EN_A}{RT} \left(\frac{r_0}{2} (r_j - r_0)^2 - \frac{1}{3} (r_0 - r_j)^3 \right) \right] \quad (1),$$

291

292 where D_0 is the amphibole-melt partition coefficient for the strain-free substitution; r_0 is the optimum
293 radius for the lattice site; r_j is the ionic radius of the element of interest in the appropriate co-ordination
294 taken from Shannon (1976); E is the apparent Young's modulus for the lattice site (GPa); R is the gas
295 constant ($8.3144 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); N_A is Avogadro constant and T is the temperature in K. The apparent
296 Young's modulus E controls the tightness of the parabola, and D_0 determines the apex of the parabola
297 with corresponding ideal lattice site r_0 .

298 To apply the lattice strain model (LSM) and fit the experimentally determined trace element partition
299 coefficients, we used the SIMPLE FIT program (Dalou et al. 2018), a lattice strain model fit by a
300 differential-evolution-constrained algorithm (Storn and Price 1997) adapted to be error weighted. In
301 presence of a small number of measured trace elements, the program failed to produce good fits.
302 Therefore, following Dalou et al. (2018), we reduced the parameter space from the default range (D_0
303 min and/or D_0 max; E min and/or E max; r_0 min and/or r_0 max) to overcome this limitation. Best-fit
304 parabolas determined for monovalent, divalent, trivalent, and tetravalent cations are plotted in Figure 5.
305 Fit parameters E , D_0 , and r_0 and related errors for monovalent, divalent, trivalent, and tetravalent
306 cations in A, M1-M2-M3, and M4-M4' sites are reported in Table 5.

307

308 **Onuma diagrams for monovalent, divalent, trivalent, and tetravalent cations**

309 The partitioning behaviour for cations (D_i) with the same valence is conveniently shown in Onuma
310 diagrams (Onuma et al. 1968) as a function of the ionic radius, indicating which elements are
311 compatibles/incompatibles in a given site or which ones are fractionated between two distinct sites. The
312 parabolic fits of monovalent cations indicate that they are incorporated in the larger A-site permitting a

313 very good constraining of its lattice strain parameters, especially for APR16-ST1 run. The best fits for
314 the monovalent cations of the runs APR16-C3Ad and APR16-C3Bd were obtained by fixing the E
315 value equal to that determined by the fit of APR16-ST1.

316 The larger divalent elements (Ca, Sr, Pb, Ba) enter the XII-fold A-site, whereas smaller cations enter
317 into the M4-site with Mg, Co, Fe, Mn that seem to be fractionated between the VIII-fold and the VI-
318 fold sites, Ni enters exclusively into the smaller VI-fold site. However, given that cations entering in
319 the M4 sites plot only on the right-limb of the parabola it is not possible to fully constrain these fits.
320 Also, the limited amount of data for the larger divalent cations prevented us from deriving the parabolic
321 fits for these elements (Fig. 5). The parabolic distribution of the trivalent (i.e., REE, Sc, Cr, and Al)
322 partition coefficients indicates that amphiboles crystallized close to equilibrium conditions (Fig. 5).
323 One of the three structurally distinct octahedral (VI-folds) sites, M1, M2, or M3 hosts Sc, Cr, and Al
324 whereas the REEs enter all in the larger VIII-fold M4 and M4' sites. Given the apexes of the parabolic
325 fits in all the runs are located near the ionic radius of Gd, the REEs should preferentially occupy the
326 M4' site (Bottazzi et al. 1999; Tiepolo et al. 2000b). Europium partition coefficients fall on the
327 parabolas of the REE showing that all Eu is trivalent. Finally, tetravalent cations are fractionated
328 between the VIII-fold (U, Th) and the VI-fold sites (Ti, Zr, Hf), while pentavalent cations (i.e., Nb, Ta,
329 V) enter the small VI-fold site.

330

331 **Comparison with the parameterized lattice strain model for REE of Shimizu et al. (2017)**

332 Shimizu et al. (2017) used previous published experimental REE and Y partitioning data between
333 amphibole and silicate melt, the lattice strain model, and nonlinear least-squares regression method to
334 parameterize key partitioning parameters in the lattice strain model for REEs as a function of pressure,
335 temperature, and both amphibole and melt compositions. We compared our D_{REE} with those obtained
336 applying the model (Hybrid mode using mineral and melt chemistry) of Shimizu et al. (2017). As

337 shown in Figure 6, $D_{\text{REE}}^{\text{Amph-glass}}$ predicted by Shimizu et al. (2017) correlates quite well with those
338 measured in this study ($R^2 = 0.68-0.74$). In particular, the most compatible elements show a good
339 agreement with the Shimizu et al. model while the elements that most differ from the model are the
340 most incompatible ones (e.g., La, Ce). This deviation can be explained considering the analytical
341 difficulties in measuring these incompatible elements due to possible micro/nano inclusion of glass
342 and/or the limited spot size. Moreover, the combination of the small spot size (12 μm), used for the
343 measurement of the trace element concentrations, with the potential presence of defect substitutions,
344 kinetic effects and boundary layers in the melt can have a significant effect on the measurement error
345 of the most incompatible elements making their analytical determination extremely difficult or
346 impossible (Fabrizio et al. 2021) .

347

348 **Influence of melt composition, pressure, and temperature on trace element partitioning**

349 To determine the main influencing variables affecting the partition coefficients (e.g., melt composition,
350 Amph composition, temperature, pressure), we performed multiple linear regression analyses using our
351 data joint to those of a database of existing experimental amphibole-melt partition coefficients (LEPR
352 database and data from Nandedkar et al. 2016, Zhang et al. 2019, and Cannaò et al. 2022) spanning a
353 wide range of conditions (0.6-2.5 GPa, 780-1100 °C; Table S3 of Supplementary Material 2) and
354 starting compositions from basalt to rhyolite (Fig. S1 of Supplementary Material 1). The experiments
355 crystallized calcic amphiboles in the range pargasite-edenite-hastingsite-magnesiohastingsite-
356 magnesiohorneblende (Fig. S3 of Supplementary Material 1). In the regression analysis, the natural
357 logarithms of $D^{\text{Amph/L}} (\ln D)$ were treated as independent variables while melt composition (X_{nf}/X),
358 Amph composition ($\text{Mg}\#_{\text{Amph}}$), P, and T were considered as dependent variables. X_{nf}/X is defined as
359 the sum of the molar fractions of network-forming cations (X_{nf} , i.e., Si and the fraction of Al balanced
360 by alkalis) normalized to the sum of all cations on a molar basis (X ; Tiepolo et al. 2000b), while

361 $Mg\#_{Amph}$ is defined as $Mg/(Mg+Fe^{2+}+Fe^{3+})$. Instead of the NBO/T value (i.e., NBOs are the non-
362 bridging oxygen atoms and T are the cations in tetrahedral coordination) that is usually used to express
363 the structural organization of a melt and requires the knowledge of the H_2O content and the Fe^{2+}/Fe^{3+}
364 ratio of the melt, we decided to use the parameter X_{nf}/X because it allows making a wider comparison
365 with the literature data for many of which H_2O content and Fe^{2+}/Fe^{3+} ratio data are missing. We
366 obtained a fine correlation ($R^2 > 0.8$) for Fe, Ho, Tb, and Tm (Figure 7 and Supplementary Material 3),
367 whose partition coefficients are greatly influenced by X_{nf}/X , T and $Mg\#_{Amph}$. Particularly, Fe ($R^2 = 0.83$
368 and $SEE = \pm 18$), Ho ($R^2 = 0.87$ and $SEE = \pm 4$) and Tm ($R^2 = 0.86$ and $SEE = \pm 3$) are affected by
369 X_{nf}/X , T and $Mg\#_{Amph}$, while Tb ($R^2 = 0.91$ and $SEE = \pm 2$) by X_{nf}/X and $Mg\#_{Amph}$. For Ca, Ce, Dy, Er,
370 Eu, Gd, K, Lu, Mg, Mn, Nb, Nd, Pr, Sm, Ti, Yb (Supplementary Material 3) we obtained satisfactory
371 correlation ($R^2 = 0.7-0.8$) observing, also in this case, the main influence of X_{nf}/X followed by
372 $Mg\#_{Amph}$, P, and T. Finally, we observed a moderate correlation ($R^2 = 0.6-0.7$) for Al, Hf, La, Ta, Zr
373 (Supplementary Material 3) while for the remaining elements (e.g., Ba, Cr, Na, Ni, Rb, Sr) we did not
374 observe a clear trend ($R^2 < 0.5$). As regards Pb, Th and U, instead, we noted the influence of X_{nf}/X , T
375 and P, without finding any good correlations ($R^2 \sim 0.5$; Supplementary Material 3). We noticed, indeed,
376 that our runs and those of Zhang et al. (2019) show higher D_{Pb} , D_{Th} , and D_U than those of the other data
377 considered in the comparison. The observed variation may also be related either to melt polymerization
378 either to the effect of the redox conditions on the oxidation state of U (Tiepolo et al. 2007). Whether or
379 not the significant increase in $^{Amph/L}D_i$ for Pb, Th, and U is related to variations of melt structure, oxide
380 phases crystallization or oxygen fugacity is beyond the scope of this study.

381 *Melt composition.* The influence of melt composition on partitioning is essentially related to its degree
382 of polymerization: the higher the structural organization of the melt, the lower the probability of
383 hosting those cations not fitting tetrahedral coordination due to their ionic radius and charge (Tiepolo et
384 al. 2007). As shown in Supplementary Material 3, at X_{nf}/X ranging between 0.5 and 0.8, the relation

385 between $D_{\text{REE}}^{\text{Amph/L}}$ and melt composition is approximately linear as observed in Tiepolo et al. (2000b).
386 As regards HFSE, $D_{\text{Ti}}^{\text{Amph/L}}$ is exponentially correlated with melt composition (Supplementary Material
387 3). As observed also in the work of Tiepolo et al. (2007), at higher X_{ntf}/X values (>0.6) the variation of
388 $D_{\text{Ti}}^{\text{Amph/L}}$ with melt composition is stronger, and two separate trends can be distinguished. The first
389 trend is similar to that observed for REE (Dy and Yb). The second trend, defined by the samples from
390 Hilyard et al. (2000), Tiepolo et al. (2000a), Xiong et al. (2005), and Liu et al. (2015), in agreement
391 with what previously observed in the work of Tiepolo et al. (2007), suggests the prevalence of
392 structural control on $D^{\text{Amph/L}}$ for Ti^{4+} over that of the melt. A similar strong crystal structure control has
393 been observed on $D_{\text{Ca}}^{\text{Amph/L}}$, $D_{\text{Fe}}^{\text{Amph/L}}$, $D_{\text{K}}^{\text{Amph/L}}$, $D_{\text{Mg}}^{\text{Amph/L}}$.
394 *Pressure.* The role of pressure on the $D^{\text{Amph/L}}$ of the LIL elements was specifically investigated by
395 Adam and Green (1994) and Dalpé and Baker (2000). Dalpé and Baker (2000) noted that $D^{\text{Amph/L}}$ for
396 the elements with ionic radii farther from the r_0 of the A-site are much more strongly affected by
397 pressure than those with ionic radius closer to the r_0 . The dependence of $D^{\text{Amph/L}}$ for Rb on pressure is
398 much stronger than that of Na or K (Dalpé and Baker 2000). However, in this study, as possible to see
399 for Ba in Supplementary Material 3, no obvious correlation between LILE and pressure can be noted.
400 The effect of pressure on the overall variation of the $D_{\text{REE}}^{\text{Amph/L}}$ was investigated by Adam and Green
401 (1994). These authors showed that $D^{\text{Amph/L}}$ for Lu and Sm decrease by up to a factor of about two with
402 increasing pressure from 0.5 to 2.0 GPa. We observed a similar behaviour with a decrease of D_{REE} (La,
403 Ce, Eu, Nd, Sm) with increasing pressure from 0.5 to 3 GPa in the comparison of our data with the
404 database of existing experimental amphibole-melt partition coefficients (Supplementary Material 3).
405 Adam and Green (2003) showed that the negative correlation observed between D_{REE} and pressure is
406 not predicted by the thermodynamic model of Wood and Blundy (1997) and concluded that variations
407 in $D_{\text{REE}}^{\text{Amph/L}}$ mostly depend on the volume-reducing substitutions occurring at the octahedra and the
408 tetrahedra, which increase the activities of +3 and +4 ions, and decrease those of +1 ions, in sites with

409 VIII-fold co-ordination as pressure increases. A specific study on the influence of pressure on the
410 $D_{\text{HFSE}}^{\text{Amph/L}}$ was carried out by Adam and Green (1994), who documented a decrease of the $D_{\text{Ti}}^{\text{Amph/L}}$
411 by a factor of 2 with increasing pressure from 0.5 to 2.0 GPa. According to this observation, we noted
412 for the dataset considered, a decrease of D_{Ti} , D_{Zr} , and D_{Hf} with increasing pressure up to ~3 GPa for the
413 considered data set.

414 *Temperature.* Adam and Green (1994) observed that D -values for Ti and REE are relatively insensitive
415 to changes in temperature contrasting with the results of many previous studies (e.g., Nicholls and
416 Harris 1980; Ray et al. 1983; Green and Pearson 1985). The reason for this is not immediately obvious
417 but may be related to the complex inter-element substitutions which occur between crystallographic
418 sites as temperature varies. Even the recent studies of Li et al. (2017) and Shimizu et al. (2017)
419 observed the influence of temperature on trace element partitioning. Particularly, Li et al. (2017)
420 observed a decrease of D_{Ti} and D_{Nb} with increasing temperature, while Shimizu et al. (2017) noticed
421 that D_0 for REE negatively correlates with temperature. However, to date, the influence of temperature
422 on amphibole/melt trace element partitioning has been found only in a few experimental works in the
423 literature probably due to the relatively small thermal stability field of the amphibole and/or the relation
424 between temperature and melt polymerization. Noteworthy, in the runs of this study we identified the
425 influence of temperature on the partitioning of several trace elements between amphibole and melt,
426 which can be well observed considering the D_0 values reported in Table 5. As regards the divalent
427 cations, we noted that D_0 increases with decreasing T in M1-M2-M3 site while it decreases with
428 decreasing T in M4-M4' one (Fig. 8a). This trend suggests that the decrease in T favors the entry of
429 Mn, Fe, Co, Mg in VI-fold coordination into the M1-M2-M3 site. As regards the trivalent cations, we
430 noted that D_0 decreases with decreasing T in M1-M2-M3 site while it increases with decreasing T in
431 M4-M4' one (Fig. 8b). In this case, REEs are favored with respect to Al, Cr, Sc as the T decreases, in
432 agreement with what was observed by Shimizu et al. (2017). Finally, as regards tetravalent cations (Ti,

433 Hf, Zr), D_0 tends to decrease with increasing T in M1-M2-M3 site (Fig. 8c), agreeing with what was
434 previously observed for D_{Ti} in the work of Li et al. (2017).

435 The trends of the D_0 for divalent, trivalent, and tetravalent cations in M1-M2-M3 and M4-M4' sites as
436 a function of temperature, observed in Figure 8, are well in agreement with the trends of the respective
437 D_i considered in the multiple linear regression (Supplementary Material 3). For instance, we noted a
438 positive correlation for D_{Al} (trivalent in M1-M2-M3), and a negative correlation for D_{Fe} , D_{Mg} (divalent
439 in M1-M2-M3), D_{Dy} , D_{Eu} , D_{Ho} , D_{Nd} (trivalent in M4-M4'), and D_{Ti} , D_{Hf} (tetravalent in M1-M2-M3).

440

441

IMPLICATIONS

442 A unique aspect of the investigated composition (a primitive K-basalt from the Campi Flegrei Volcanic
443 District) lies in the compositional evolution of its experimental liquids as a function of the amount of
444 water in the melt, which covers the field of basalt, trachybasalt, and shoshonite for water content <3
445 wt%, and that of basaltic andesite and andesite for water content >4 wt% (Perinelli et al. 2019),
446 approaching in term of major elements those of the 2 Ma old, calc-alkaline volcanic products found in
447 Parete and Castelvoturno bore-holes (north-west of Campi Flegrei; Beccaluva et al. 1991 and
448 references therein) (Fig. S4 of Supplementary Material 1). The trace element compositions of the
449 experimental residual glasses, on the other hand, do not correspond to those of the calc-alkaline rocks
450 of Campi Flegrei. This difference is not surprising because geochemical models of magmatic suites
451 deriving from metasomatic mantle sources should be computed on co-magmatic end-members (e.g.,
452 Gaeta et al. 2016, 2021) and ~2 Ma separate the APR16 basalt from the old calc-alkaline rocks of
453 Campi Flegrei. The presence of tephra dated at 2.214 ± 0.034 Ma and rich in amphibole with relative
454 high Mg# (60-64; Florindo et al. 2021; Fig. S5 of Supplementary Material 1) indicates, on the other
455 hand, the importance of the amphibole in the pre-eruptive systems of the volcanic districts of the
456 circum-Tyrrhenian region.

457 We used submarine basalt to trachybasalt compositions from the Pontine archipelago area to model the
458 trace element abundances due to the fractional crystallization of amphibole. These rocks have been
459 interpreted to be the primitive/intermediate lithologies representing parental compositions for the >1
460 Ma, peralkaline felsic rocks outcropping in the western Pontine Islands (Conte et al. 2016, 2020). In
461 addition, the Pontine submarine lithotypes share orogenic trace element signatures exhibited by the
462 calc-alkaline volcanic products of the Campi Flegrei. This and the results obtained from H₂O-saturated
463 experiments on APR16 prompted us to test the hypothesis whether a composition similar to those
464 submarine basalts, approaching that of APR16 (i.e., SiO₂ = 49.31-50.31 wt%, Na₂O+K₂O = 3.81-5.39
465 wt%, Mg# = 0.72-0.64; Conte et al. 2016, 2020), is able of producing andesites with the trace elements
466 abundances such as those recovered in the Parete and Castelvoturno bore-holes by a differentiation
467 process that involves the crystallization of amphibole. Thus, using as parental magma the trace element
468 composition of submarine TD4B basalt (Conte et al. 2016), we calculated the concentration of selected
469 elements in residual melts due to crystal-liquid fractionation process (FC). To model the FC process,
470 we used the Excel© spreadsheet program “FC-AFC-FCA and mixing modeler” (Ersoy and Helvacı
471 2010) considering: *i*) a fractionate mineral assemblage formed by amphibole + clinopyroxene + oxides
472 in proportion as in the experiments producing an andesitic residual melt (Table 2), *ii*) the partition
473 coefficients amphibole-melt determined in this study, *iii*) the partition coefficients clinopyroxene-melt
474 from the longest experiments determined by Bonechi et al. (2021). Modelling results indicate that the
475 pattern of natural andesite, is well reproduced for a calculated residual liquid fraction of 44% (Fig. 9), a
476 value close to the experimental 40% (Table 2), with the exception of Cs and Rb. As for Cs and Rb, the
477 fractionation behavior of these elements cannot be accurately modelled starting from TD4B basalt
478 composition. This result could be due either to the mobility and the incompatibility ($D < 1$) of these
479 elements either to the presence of a parental magma with different Cs and Rb concentrations.

480

481

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753

754

755 **Figures captions**

756 **Figure 1.** Backscattered images of experimental samples. Details of the experimental conditions are
757 reported at the bottom of each image. Amph shows euhedral habit and maximum size of ~40 μm ;
758 pyroxene and oxide show euhedral habit with sizes up to ~5 μm and 40 μm , respectively. In Figure 1a
759 some tiny quench crystals are present. Black holes with size ≤ 5 μm are saturation bubbles.
760 Abbreviation: Amph: amphibole; Px: pyroxene; Ox: oxide; Gl: glass.

761 **Figure 2.** C1-normalized (Anders and Grevesse 1989) trace elements abundances for synthetic
762 amphiboles. C3A suite (1080 °C) is reported in green, C3B (1030 °C) in light blue and APR16-ST1
763 (1050 °C) in blue. Symbols indicate different experimental dwell time: circle 0.15 h, asterisk 2 h,
764 triangle 3 h, diamond 6 h and square 9 h.

765 **Figure 3.** C1-normalized (Anders and Grevesse 1989) trace elements abundances for analysed
766 synthetic glasses. Symbols are as in Figure 2. Red crosses indicate data for the APR16 natural samples
767 from Mazzeo et al. (2014). For comparison we reported C1-normalized trace elements abundances for
768 synthetic glasses of Bonechi et al. (2021), indicated with the yellow field.

769 **Figure 4.** Calculated $^{Amph/Glass}D$ values for trace elements in experimental samples. Symbols are as in
770 Figure 2.

771 **Figure 5.** Onuma diagrams for amphibole-liquid partition coefficients for mono-, di-, tri-, and
772 tetravalent cations versus ionic radii (in Å; Shannon 1976) for VI-, VIII- and XII-fold coordinated sites
773 along with the results of the lattice strain fits in A, M1-M2-M3, M4-M4' sites for samples (a) APR16-
774 C3Ad (1080 °C), (b) APR16-C3Bd (1030 °C), (c) APR16-ST1 (1050 °C). The dotted curves represent
775 the fits of the lattice strain model to $^{Amph/Glass}D_i$ values while symbols represent measured $^{Amph/Glass}D_i$
776 values. Cations are indicated as follow: monovalent in orange, divalent in green, trivalent in light blue,
777 tetravalent in yellow and pentavalent in purple. Cations in site-A are indicated with triangles, in site
778 M4-M4' with circles and in site M1-M2-M3 with squares. Empty symbols indicate elements not
779 considered in the fits of the LSM.

780 **Figure 6.** (a) Amphibole-melt REE partition coefficients calculated in this study and those calculated
781 using the model of Shimizu et al. (2017). Symbols are as in Figure 2. Solid lines indicates partition
782 coefficients calculated in this study while dashed lines those obtained with the model. (b) Comparison
783 between the experimentally measured partition coefficients to those predicted using the model of
784 Shimizu et al. (2017). The solid line represents 1:1 ratio, and dashed lines represent 2:1 and 1:2 ratios.

785 **Figure 7.** Calculated and predicted $\ln D_{Tb}$ is compared for the available database of existing
786 experimental amphibole-melt partition coefficients (LEPR database and data from Nandedkar et al.
787 2016, Zhang et al. 2019, and Cannà et al. 2022; Table S3 of Supplementary Material 2 and
788 Supplementary Material 3). Solid and dashed grey lines are 1:1, 1:2 and 2:1 lines, while green dashed
789 line is the regression line. Embedded table reports the parameters and related errors obtained from the
790 regression analysis. For creating the model and to avoid over-fitting of the data the t-stat (calculated as
791 the ratios between the coefficients and their standard errors and thus representing a measure of the
792 precision with which the regression coefficients are measured; e.g., Rawlings et al. (1998)) were
793 checked for all variables, looking for the t-stat ≥ 5 , and the P-value (a measure of how the overall result
794 of the regression is statistically significant; e.g., Rawlings et al. (1998)) was checked in order to
795 achieve the maximum value similarly to the approach used in Putirka et al. (2003).

796 **Figure 8.** Diagrams showing the variation in the strain-free partition coefficient (D_0) for the amphibole
797 as function of temperature for divalent (a), trivalent (b) and tetravalent (c) cations in VI-fold
798 coordinated M1-M2-M3 site and in VII-fold coordinated M4-M4' site. Symbols are as in Figure 5.
799 Arrows indicate the trends observed for D_0 as function of temperature variation.

800 **Figure 9.** Primitive Mantle normalized (McDonough and Sun 1995) trace elements patterns of TD4B
801 basalt (Conte et al. 2016) and the predicted composition of differentiated melts obtained after 56% of
802 fractional crystallization of TD4B basalt assumed as primitive parental melt of andesitic magma of
803 Campi Flegrei (sample from Parete borehole; Beccaluva et al. 1991). The reported degree of
804 fractionation (FC) reflects the crystallized phase assemblage and proportions determined for run
805 APR16-C3Bd (amphibole (35) + clinopyroxene (24) + oxide (1)) that produced andesitic residual glass.
806 The modelled compositions were calculated by using the Excel® spreadsheet program of Ersoy and
807 Helvacı (2010).

808

809

810 **Tables captions**

811 **Table 1** Composition (wt%) of APR16 rock sample and APR16GL starting material

812 **Table 2** Experimental run conditions, melt water contents, phases assemblage and proportions in run
813 products

814 **Table 3** Major and trace element concentrations (ppm) for synthetic amphibole crystals and glasses

815 **Table 4** Major and trace elements partition coefficients between amphibole and glass for experimental
816 samples

817 **Table 5** Best fits for E , r_0 and D_0 obtained by regression of amphibole/glass partition coefficients of
818 monovalent, divalent, trivalent and tetravalent cations in A, M1-M2-M3, M4-M4' sites

819

820 **Supplementary materials**

821 **Supplementary Material 1** contains supplementary figures

822 **Supplementary Material 2** contains supplementary tables

823 **Supplementary Material 3** contains multiple linear regression analyses

Figure 1

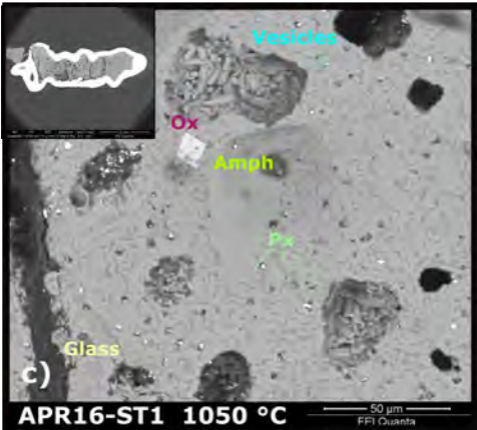
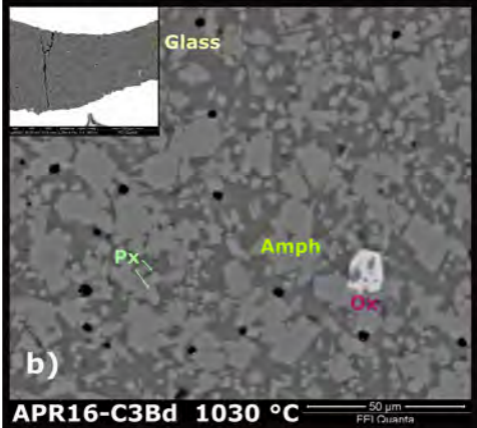
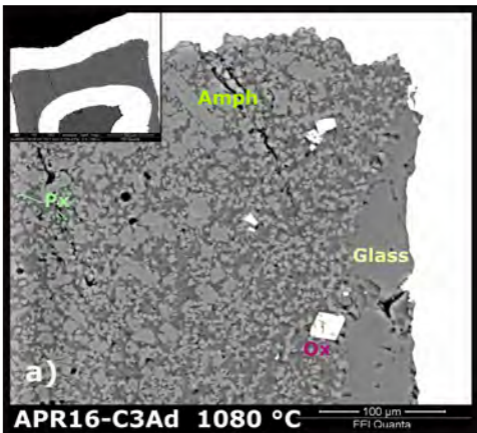


Figure 3

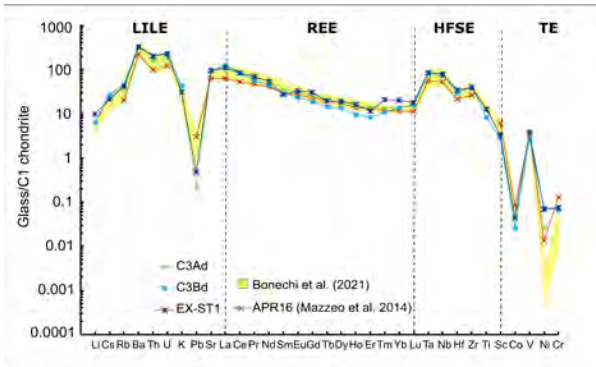
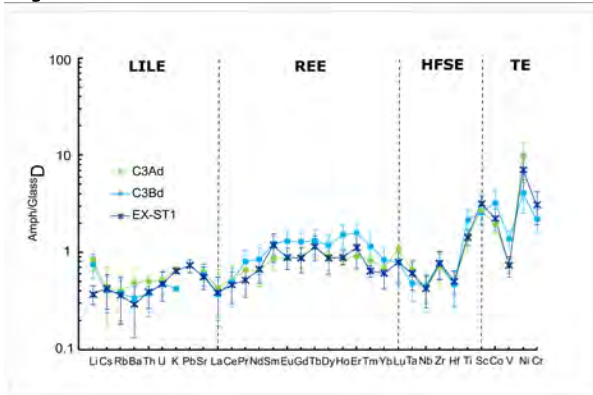


Figure 4



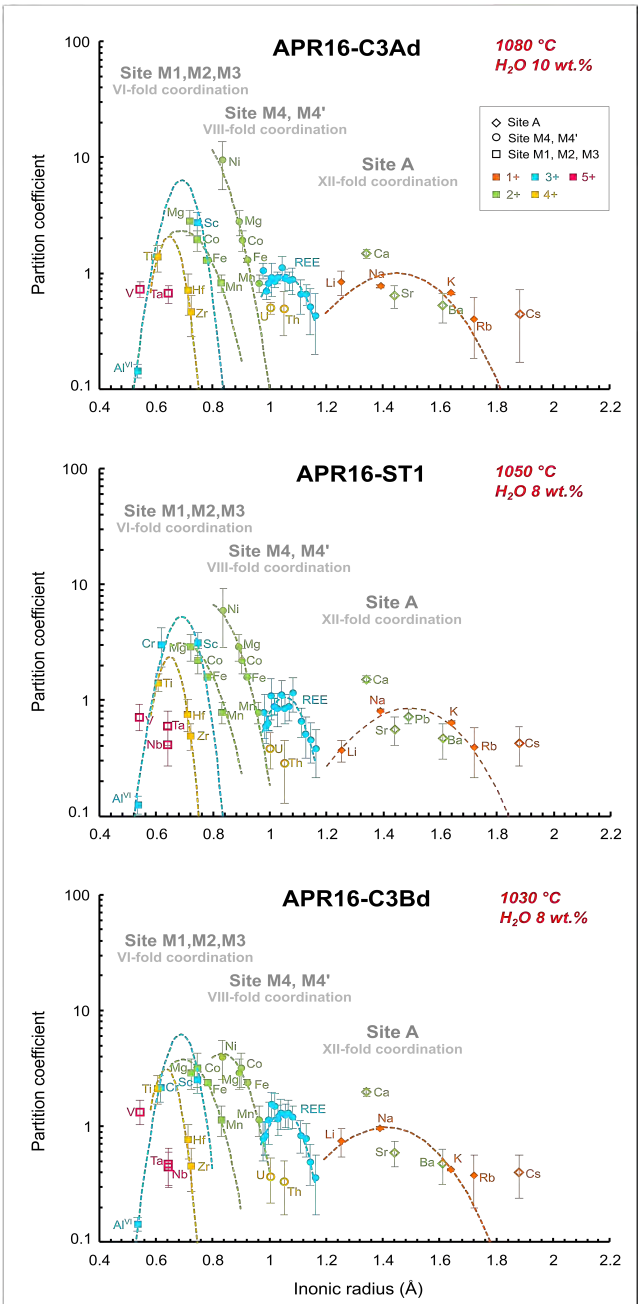
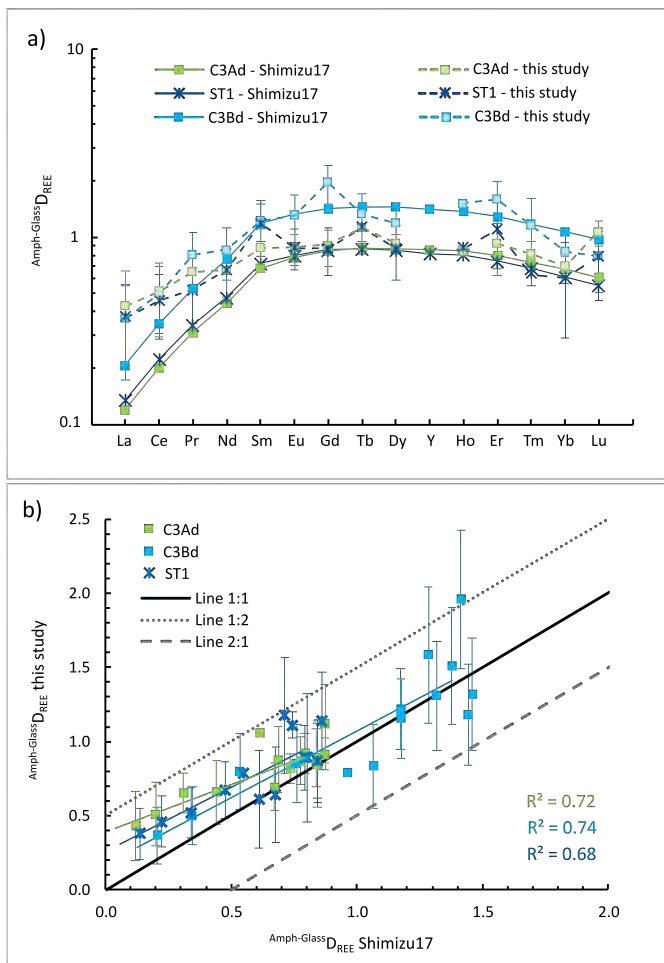
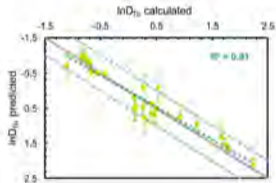


Figure 6



$$\ln D_{Tb} = 8.985 * X_{ni} / X + 4.141 * Mg\#_{Anph} - 8.285$$



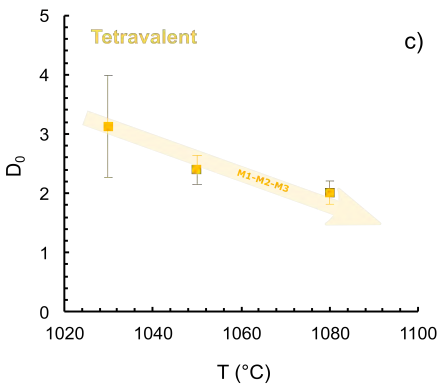
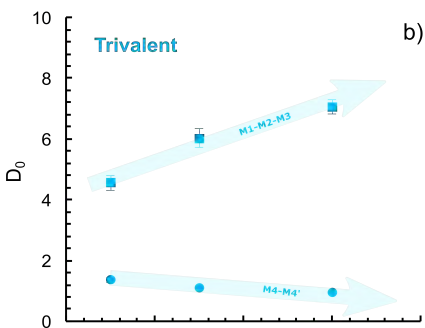
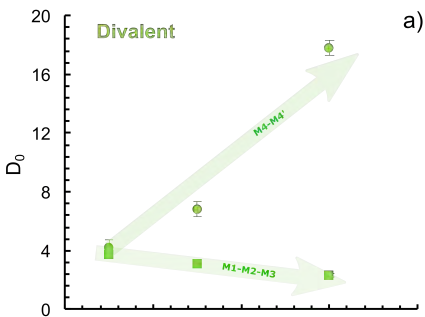
Regression Statistics

Multiple R	0.96
R Square	0.91
Adjusted R Square	0.91
Standard Error	0.28
Observations	27

ANOVA

	df	SS	Significance F
Regression	2	19.60	1.82E-13
Residual	24	1.86	
Total	26	21.46	

	Coefficients	Standard Error	t Stat	P-value
Intercept	-8.28	0.77	-10.72	1.23E-10
X Variable 1	8.99	0.60	15.01	1.06E-13
X Variable 2	4.14	0.65	6.41	1.24E-06



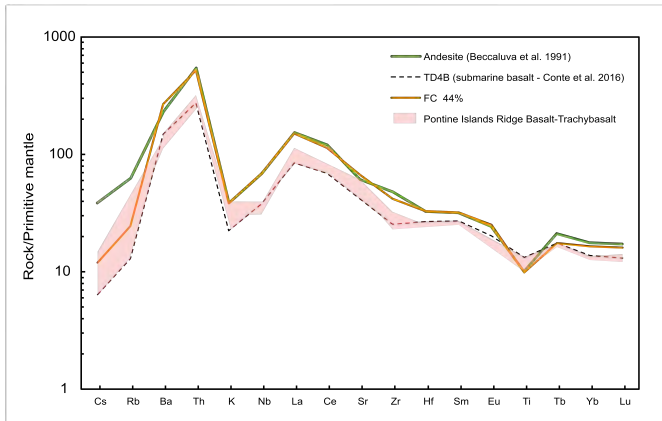


Table 1 Composition (wt%) of APR16 rock sample and APR16GL starting material

Sample	APR16	APR16GL
SiO ₂	48.89	49.3 (0.46)
TiO ₂	1.23	1.33 (0.03)
Al ₂ O ₃	15.65	15.31 (0.14)
FeO _{tot}	8.08	7.79 (0.13)
MnO	0.14	0.14 (0.05)
MgO	8.89	9.31 (0.07)
CaO	11.64	12.02 (0.09)
Na ₂ O	2.88	2.86 (0.05)
K ₂ O	1.52	1.60 (0.02)
P ₂ O ₅	0.31	0.55 (0.02)
Total	99.23	99.31 (0.29) ^y
L.O.I.	0.61	-
Mg# *	0.66	0.68

*[MgO/(MgO+FeO_{tot})] molar, assuming all Fe²⁺ and Fe³⁺ as FeO_{tot}. Chemical composition of APR16 is from D'Antonio et al. (1999); APR16GL composition is from Perinelli et al. (2019). ^y For APR16GL the analysis is normalized to 100 but the original total is reported. Standard deviation is reported in parenthesis.

Table 2 Experimental run conditions, melt water contents, phases assemblage and proportions in run products

Run #	T (°C)	T _L (°C)	ΔT (°C)	Time (h)	H ₂ O _i (wt%)	Phases	H ₂ O _f EPMA (wt%)	Σr ²	% ΔFe [§]
APR16-C3Aa*	1080	1218	138	0.25	4	Gl + Amph + Cpx + Plg + Ox			
APR16-C3Ab*	1080	1218	138	3	4	Gl + Amph + Cpx + Plg + Ox	7.5		
APR16-C3Ad	1080	1233	153	9	3.3	Gl(55) + Amph(24) + Cpx(20) + Ox(1)	10.2	0.41	-1
APR16-C3Ba*	1030	1224	194	0.25	3.8	Gl + Amph + Cpx + Plg + Ox	10.6		
APR16-C3Bb*	1030	1225	195	3	3.7	Gl + Amph + Cpx + Plg + Ox	9.5		
APR16-C3Bc*	1030	1232	202	6	3.4	Gl + Amph + Cpx + Opx + Ox			
APR16-C3Bd	1030	1216	186	9	4.2	Gl(40) + Amph(35) + Cpx(24) + Ox(1)	8.3	0.18	-1
APR16-ST1	1050	1150	100	2	8	Gl(51) + Amph(36) + Cpx(13) + Ox(1)	8.1	0.31	

Gl = glass; Amph = amphibole; Cpx = clinopyroxene; Opx = orthopyroxene; Plg = plagioclase; Ox = oxide minerals. ΔT is the difference between the liquidus temperature and the nominal temperature of the experiment. T_L is the liquidus temperature (°C) determined on the basis of phase relations experimental data from Perinelli et al. (2019). H₂O_f EPMA = water content in the melt determined by the by-difference calculation method (respect to the total of EMP analyses); % Percent of relative Fe loss from starting material based on difference between the starting material and calculated bulk composition of experiment obtained from mass-balance calculations. Σr² values from mass balance calculation. *Crystals too small for analysis and not considered for mass balance calculations.

Table 3 Major and trace element concentrations (ppm) for synthetic amphibole crystals and glasses

Run#	APR16-C3Aa	APR16-C3Ab	APR16-C3Ad	APR16-C3Ba	APR16-C3Bb	APR16-C3Bc	APR16-C3Bd	APR16-ST1
Phase	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass	Amph glass
Na*	18472 (838)	16766 (307)	16469 (351) 21514 (213)	14763 (265)	13353 (302)	10831 (452)	17211 (513) 17730 (231)	16840 (433) 20698 (211)
K*	11456 (102)	11124 (52)	11207 (103) 16769 (206)	11207 (98)	13448 (92)	10709 (232)	8965 (272) 21168 (209)	9630 (312) 15025 (204)
Ca*	80121 (5800)	82051 (6100)	83337 (5980) 56892 (3850)	84409 (4800)	86196 (6400)	88912 (5100)	84909 (5150) 43026 (3105)	90556 (4350) 59608 (3400)
Fe*	82005 (4451)	65526 (2350)	59774 (2310) 46327 (950)	71123 (1890)	66537 (1930)	76952 (2100)	70812 (2250) 29382 (890)	68635 (1850) 42285 (850)
Mg	51270 (4251)	55950 (3402)	71267 (16478) 25466 (2086)	57857 (3171)	56380 (1819)	79820 (18651)	56740 (13767) 19200 (3389)	77962 (14804) 26575 (4189)
Al	83550 (13055)	75983 (5265)	79183 (11744) 100157 (5379)	87900 (2712)	89100 (1880)	100340 (5010)	79311 (15056) 103500 (35003)	79892 (10591) 109100 (18949)
Mn	1269 (112)	1199 (79)	1048 (173) 1283 (46)	1373 (93)	1355 (23)	1557 (142)	1153 (197) 995 (135)	1048 (139) 1381 (207)
Ti	6426 (788)	7453 (904)	8157 (2071) 5949 (324)	7266 (195)	7280 (86)	8838 (2971)	7906 (2131) 3633 (239)	7787 (1151) 5452 (509)
Zr	107 (19)	90 (4)	69 (26) 149 (15)	105 (3)	106 (1)	101 (9)	75 (24) 163 (40)	77 (16) 154 (24)
Nb	12 (2)	10.1 (0.6)	7.4 (3.3) 17.6 (1.4)	12 (1)	11.9 (0.4)	13 (2)	8 (2) 20 (5)	8 (2) 19 (4)
Hf	2.9 (0.6)	2.1 (0.3)	2.3 (0.9) 3.2 (0.3)	2.7 (0.4)	2.7 (0.6)	3.3 (0.4)	2.4 (0.8) 3.04 (0.01)	2.7 (0.5) 3.6 (0.9)
Ta	0.71 (0.14)	0.7 (0.1)	0.66 (0.11) 0.99 (0.05)	0.7 (0.1)	0.7 (0.1)	0.6 (0.1)	0.6 (0.2) 1.2 (0.1)	0.7 (0.1) 1.2 (0.3)
Th	3.32 (0.86)	2.1 (0.3)	2.31 (0.94) 4.7 (0.4)	3.0 (0.2)	2.8 (0.1)	2.7 (0.5)	1.9 (0.9) 5.8 (0.3)	1.7 (0.8) 5.9 (1.6)
U	1.06 (0.28)	0.82 (0.08)	0.75 (0.05) 1.5 (0.1)	1.0 (0.1)	0.9 (0.1)	0.9 (0.1)	0.7 (0.3) 1.9 (0.4)	0.7 (0.2) 1.8 (0.4)

Rb	61 (16)	40 (3)	34 (18) 86 (7)	62 (11)	61 (3)	38 (7)	39 (17) 103 (20)	35 (14) 87 (18)
Sr	518 (107)	435 (32)	429 (91) 679 (24)	484 (96)	539 (15)	555 (43)	422 (88) 708 (103)	407 (80) 733 (136)
Cs	2.7 (0.8)	1.6 (0.4)	1.8 (0.1) 4.1 (0.5)	2.7 (0.4)	2.3 (0.1)	2.2 (0.1)	2.0 (0.7) 5 (1)	1.7 (0.5) 4 (1)
Ba	507 (125)	414 (37)	377 (104) 729 (56)	491 (100)	523 (11)	450 (61)	376 (111) 791 (139)	354 (93) 761 (164)
Pb	9 (5)	1.4 (0.7)	bdl 0.51 (0.07)	17 (9)	31 (23)	1.44 (0.36)	0.83 (0.18) bdl	0.85 (0.13) 1.17 (0.03)
Sc	40 (5)	42 (3)	50 (10) 18 (2)	43 (3)	43 (1)	50 (5)	41 (7) 16 (3)	60 (9) 19 (3)
V	189 (18)	208 (23)	163 (26) 223 (3)	209 (12)	210 (2)	264 (61)	198 (39) 146 (18)	154 (30) 212 (31)
Cr	337 (41)	355 (30)	525 (173) bdl	377 (15)	375 (7)	436 (68)	381 (96) 175 (9)	612 (208) 200 (28)
Co	36 (8)	38 (3)	44 (8) 23 (2)	45 (4)	46 (2)	52 (18)	42 (12) 13 (2)	49 (10) 22 (3)
Ni	119 (37)	135 (16)	184 (70) 13 (4)	148 (22)	165 (16)	167 (66)	149 (52) 37 (5)	241 (75) 40 (17)
La	16.7 (3.3)	13.3 (0.7)	11 (5) 25 (1)	17 (1)	17 (1)	16 (1)	11 (5) 30 (8)	10 (4) 26 (5)
Ce	34 (4)	30 (1)	25 (10) 48 (1)	35 (1)	35 (1)	37 (4)	25 (9) 50 (7)	23 (7) 50 (10)
Pr	4.2 (0.8)	3.8 (0.3)	3.8 (0.8) 48 (1)	4.4 (0.3)	4.6 (0.1)	4.6 (0.4)	4 (1) 5 (1)	3 (1) 6 (1)
Nd	18.4 (2.9)	18.5 (1.3)	16.2 (5.2) 25 (1)	21 (2)	19.8 (1.7)	23.7 (2.9)	17 (4) 20 (4)	16 (3) 24 (5)
Sm	4.4 (0.5)	4.8 (0.5)	4.5 (1.0) 5.2 (0.5)	5 (1)	5.1 (0.7)	5.5 (1.5)	5 (1) 4.1 (0.4)	5 (1) 4 (1)
Eu	1.6 (0.3)	1.6 (0.3)	1.5 (0.2) 1.7 (0.4)	1.8 (0.4)	1.8 (0.3)	2.0 (0.4)	1.7 (0.4) 1.3 (0.2)	1.6 (0.3) 1.8 (0.3)
Gd	4.9 (0.9)	4.8 (0.5)	4.4 (0.9) 4.9 (0.4)	4.6 (0.8)	4.9 (0.4)	5.4 (1.6)	4.7 (1.1) 3.7 (0.1)	5.2 (1.2) 6 (1)

Tb	0.7 (0.1)	0.7 (0.1)	0.8 (0.2) 0.74 (0.04)	0.8 (0.1)	0.7 (0.1)	0.8 (0.2)	0.7 (0.2) 0.53 (0.01)	0.8 (0.2) 0.7 (0.1)
Dy	3.8 (0.5)	3.9 (0.9)	3.6 (0.2) 3.9 (0.4)	4.2 (0.6)	4.1 (0.5)	5.0 (0.8)	3.8 (1.1) 3.22 (0.01)	4 (1) 4.6 (0.9)
Ho	0.8 (0.1)	0.8 (0.2)	0.7 (0.1) 0.85 (0.05)	0.8 (0.1)	0.9 (0.1)	1.0 (0.1)	0.8 (0.2) 0.53 (0.06)	0.8 (0.1) 0.9 (0.1)
Er	2.2 (0.5)	1.93 (0.32)	2.02 (0.62) 2.2 (0.2)	2.3 (0.2)	2.4 (0.2)	2.4 (0.8)	2.1 (0.5) 1.32 (0.13)	2.0 (0.4) 1.8 (0.6)
Tm	0.27 (0.05)	0.34 (0.03)	0.27 (0.03) 0.33 (0.04)	0.35 (0.01)	0.4 (0.1)	0.37 (0.13)	0.3 (0.1) 0.26 (0.04)	0.32 (0.04) 0.50 (0.03)
Yb	1.88 (0.32)	2.1 (0.3)	1.6 (0.1) 2.3 (0.3)	1.96 (0.04)	2.5 (0.5)	2.11 (0.27)	1.83 (0.43) 2.2 (0.5)	1.97 (0.47) 3.2 (0.7)
Lu	0.35 (0.08)	0.4 (0.1)	0.37 (0.02) 0.35 (0.05)	0.34 (0.03)	0.3 (0.1)	0.29 (0.06)	0.3 (0.1) 0.38 (0.05)	0.34 (0.12) 0.43 (0.08)

Notes: Amph = amphibole; standard deviation is reported in brackets. *Data from EPMA.

For single analysis Int2SE (i.e., analytical error) is reported also in brackets but in italic; bdl = below detection limit.

Table 4 Major and trace elements partition coefficients between amphibole and glass for experimental samples

Run#	APR16-C3Ad	APR16-C3Bd	APR16-ST1
Na*	0.77 (0.02)	0.97 (0.03)	0.81 (0.02)
K*	0.67 (0.01)	0.42 (0.01)	0.64 (0.02)
Ca*	1.46 (0.12)	1.97 (0.16)	1.52 (0.10)
Fe*	1.29 (0.05)	2.41 (0.12)	1.62 (0.05)
Mg	2.79 (0.69)	2.95 (0.88)	2.93 (0.77)
Al	0.79 (0.12)	0.76 (0.29)	0.73 (0.17)
Al ^{IV}	0.64	0.60	0.61
Al ^{VI}	0.14	0.15	0.12
Mn	0.82 (0.14)	1.16 (0.25)	0.79 (0.16)
Li	0.84 (0.20)	0.75 (0.21)	0.37 (0.08)
Ti	1.37 (0.36)	2.16 (0.60)	1.43 (0.25)
Zr	0.46 (0.18)	0.46 (0.19)	0.50 (0.13)
Nb	0.42 (0.14)	0.45 (0.15)	0.42 (0.15)
Hf	0.71 (0.28)	0.78 (0.25)	0.77 (0.24)
Ta	0.67 (0.12)	0.48 (0.17)	0.61 (0.20)
Th	0.49 (0.20)	0.34 (0.16)	0.29 (0.16)
U	0.50 (0.05)	0.37 (0.16)	0.39 (0.13)
Cs	0.44 (0.27)	0.40 (0.16)	0.43 (0.16)
Rb	0.40 (0.21)	0.38 (0.18)	0.40 (0.18)
Sr	0.63 (0.14)	0.60 (0.15)	0.56 (0.15)
Ba	0.52 (0.15)	0.48 (0.16)	0.47 (0.16)
Pb			0.73 (0.11)
Sc	2.73 (0.62)	2.56 (0.65)	3.16 (0.69)
V	0.73 (0.12)	1.36 (0.32)	0.73 (0.18)
Cr		2.18 (0.56)	3.06 (1.12)
Co	1.93 (0.38)	3.23 (1.05)	2.23 (0.55)
Ni	9.42 (4.15)	4.03 (1.51)	6.03 (3.17)
La	0.43 (0.23)	0.37 (0.19)	0.38 (0.17)
Ce	0.51 (0.22)	0.50 (0.19)	0.46 (0.17)
Pr	0.66 (0.13)	0.80 (0.26)	0.52 (0.17)
Nd	0.66 (0.21)	0.85 (0.26)	0.67 (0.19)
Sm	0.88 (0.22)	1.22 (0.27)	1.18 (0.39)
Eu	0.87 (0.16)	1.31 (0.37)	0.89 (0.22)
Gd	0.89 (0.20)	1.27 (0.47)	0.87 (0.25)
Tb	1.12 (0.26)	1.32 (0.38)	1.14 (0.33)
Dy	0.92 (0.11)	1.18 (0.34)	0.87 (0.28)
Ho	0.85 (0.10)	1.51 (0.41)	0.89 (0.15)
Er	0.92 (0.29)	1.58 (0.40)	1.11 (0.43)
Tm	0.82 (0.13)	1.15 (0.46)	0.64 (0.09)
Yb	0.69 (0.10)	0.84 (0.27)	0.61 (0.19)
Lu	1.06 (0.16)	0.79 (0.28)	0.79 (0.32)

Table 5 Best fits for E , r_0 and D_0 obtained by regression of amphibole/liquid partition coefficients of monovalent, divalent, trivalent and tetravalent cations in A, M1-M2-M3, M4-M4' sites

		APR16-C3Ad	APR16-ST1	APR16-C3Bd
Monovalent	A			
	D_0	0.97±0.20	0.86±0.06	0.98±0.11
	r_0	1.449±0.049	1.495±0.008	1.419±0.030
	E	<i>30±4</i>	<i>30±4</i>	<i>30±4</i>
Divalent	M1, M2, M3			
	D_0	2.32±0.14	3.11±0.09	3.77±0.30
	r_0	0.689±0.006	0.686±0.008	0.697±0.013
	E	209±5	200±1	247±37
	M4, M4'			
	D_0	17.77±0.51	6.84±0.53	4.24±0.47
	r_0	0.709±0.002	0.776±0.008	0.834±0.015
	E	202±2	227±20	259±48
Trivalent	M1, M2, M3			
	D_0	7.08±0.09	6.04±0.28	4.56±0.25
	r_0	0.689±0.004	0.688±0.002	0.688±0.004
	E	785±12	805±10	696±27
	M4, M4'			
	D_0	0.9550±0.0002	1.1004±0.0018	1.3541±0.0634
	r_0	1.0514±0.0001	1.0558±0.0007	1.0511±0.0006
	E	200±1	299±4	303±17
Tetravalent	M1, M2, M3			
	D_0	2.004±0.194	2.39±0.24	3.12±0.86
	r_0	0.6475±0.0038	0.6477±0.0034	0.6368±0.0117
	E	1195±143	1247±137	1181±429

Note: D_0 : strain-compensated partition coefficient. E : Young Modulus of the lattice site (GPa). r_0 : optimum site radius (Å). D_0 , r_0 and E were calculated using the SIMPLE program (Dalou et al. 2018). E values of the monovalent cations (reported in italic) for APR16-C3Ad and APR16-C3Bd runs have been set equal to that determined for run APR16-ST1.