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1	REVISION 1
2	Trace-element partitioning between plagioclase alkali feldspar. Ti-magnetite biotite apatite and
2	evolved potassic liquids from Campi Elegrei (Southern Italy)
5	evolved polassie inquids from Campi Pregret (Southern hary).
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19	Abstract
20	Partition coefficients $(^{Min/L}D)$ for a series of geochemically relevant elements have been
20	Partition coefficients (D) for a series of geochemicany relevant elements have been
21	calculated from combined EMP/LA-ICP-HRMS analyses of plagioclase, alkali feldspar, Ti-
22	magnetite, biotite, apatite and trachytic/trachyphonolitic melt pairs in selected Campi Flegrei
23	pyroclastic rocks. $P^{UL}D$ and $K_{fs/L}D$ values are generally very low for most of the trace-elements but
24	Sr, Ba and Eu. The $K_{fs/L}D$ for the latter elements record a systematic increase as the melt

25 composition changes from trachyte to trachyphonolite, likely due to increasing structural compliance of the sanidine in the trachyphonolites related to larger Na/K values. Conversely, 26 *Kfs/LD* values for transitional, highly-charged incompatible elements (e.g., LREE) decrease from 27 trachyte to trachyphonolite, possibly in response to the decrease of melt polymerization. Min/LD 28 values for titanomagnetite generally decrease with the increasing melt evolution, the highest 29 30 values being those measured for Ti, V and Sc. Titanium, Ba, Sc. Rb, Nb, Ta and V are compatible in biotite in equilibrium with trachytic melt, whereas Cs, Sr and Pb are incompatible 31 and REE are strongly incompatible, as supported by the extremely low $^{Bt/L}D_V$ (0.003-0.008). 32 Partition coefficients for apatite and trachyphonolitic glass pairs are high for Sr, REE 33 (particularly MREE) and Y, large for Th, U and V, generally low for HFSE and variable for other 34 LILE. The comparison of measured ^{Min/L}D values for Campi Flegrei trachytes/trachyphonolites 35 with other sets of partition coefficients reported in literature for evolved potassic systems 36 suggests that a reliable dataset for magma evolution modelling requires: (i) a thorough 37 preliminary selection of natural samples; (ii) the adoption of accurate microanalytical techniques; 38 (iii) the direct measurement of $^{Min/L}D$ values for each specific melt composition. 39

Keywords: Campi Flegrei, partition coefficients, plagioclase, alkali feldspar, Ti-magnetite,
biotite, apatite, LA-ICP-HRMS

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Introduction

Although trace-element partition coefficients are a powerful and widely used tool in modelling the evolution of magmatic systems, reliable datasets that describe the trace-element partitioning behaviour in highly differentiated potassic alkaline liquids are still scarce or lacking. In a companion paper, Fedele et al. (2009) reported the results of detailed EMP/LA-ICP-HRMS investigations aimed at obtaining an internally consistent set of trace-element partition coefficients for clinopyroxene/melt

pairs from selected Campi Flegrei trachytic/trachyphonolitic samples. These samples resulted 49 particularly suitable for partitioning studies in virtue of their glassy nature and their moderately 50 porphyritic character. In addition, the employed microanalytical technique allowed the authors to 51 reliably assess the attainment of mineral/glass chemical equilibrium and to consequently recognize 52 suitable sites for the correct evaluation of the mineral/liquid partition coefficients. Major- and trace-53 54 element analyses of plagioclase, alkali feldspar, Ti-magnetite, biotite and apatite from the same Campi Flegrei samples investigated by Fedele et al. (2009) are here presented in order to complete 55 the study on the trace-element partitioning for the typical paragenesis of evolved potassic melts. 56

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Geological background

The Campi Flegrei is an active volcanic field covering an area running from the city of Naples 59 to its western suburbs, whose last eruption occurred in AD 1538 (D'Oriano et al. 2005 and 60 references therein). Fumarolic and hydrothermal phenomena (plus sporadic bradiseismic crises) 61 are the only evidence of ongoing a volcanic activity, which has been predominantly explosive, 62 characterized by a great number of eruptions building numerous (mainly monogenetic) volcanic 63 edifices and very rare effusive manifestations of limited areal extent (e.g., Morra et al. 2010; 64 Melluso et al. 2012 and references therein). The Campi Flegrei district is characterized by a 65 nested caldera structure whose genesis is attributed to the two most explosive events of the area 66 (Perrotta et al. 2006): the Ignimbrite Campana (IC, ~39 ka; De Vivo et al. 2001) and the Tufo 67 Giallo Napoletano (TGN, ~15 ka; Deino et al. 2004) eruptions. 68

69 Campi Flegrei juvenile products have a potassic alkaline affinity, belonging to the slightly 70 silica-undersaturated shoshonitic series of the "orogenic" Italian Plio-Pleistocene Roman 71 Province (e.g., Lustrino et al. 2011 and references therein). Rock compositions range from rare This is a preprint, the final version is subject to change, of the American Mineralogist (MSA) Cite as Authors (Year) Title. American Mineralogist, in press. (DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-2015-4995

shoshonitic basalts to predominant trachytes-trachyphonolites-phonolites (e.g., Morra et al. 2010
and references therein).

The investigated samples belong to the Breccia Museo Formation (BM; Perrotta and Scarpati 74 1994; Melluso et al. 1995; Fedele et al. 2008), interpreted as the proximal facies deposit of the IC 75 eruption (Fedele et al. 2008 and references therein). The juvenile products of the BM are 76 77 pumices, obsidians and spatter clasts, showing trachytic to phonolitic compositions. The phenocryst load is generally ~5-12% (estimated as the area occupied by phenocrysts over a total 78 area of a thin section), represented mainly by sanidine, plagioclase, clinopyroxene, biotite, 79 opaque oxides and apatite (in decreasing order of abundance) set in a completely glassy 80 groundmass (Fig. 1). 81

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Analytical techniques

The major element composition of the mineral phases and the glassy matrix has been determined by Electron Microprobe analyses (EMP) at the CNR-IGAG (Rome, Italy), using an automated CAMECA SX50 microprobe in full WDS mode. An acceleration potential of 20 kV with a sample current of 20 nA (measured on brass) was applied. The beam size was varied as a function of the analyzed phase, with a particularly large beam size (300 μ m²) for the glass phases. Natural and synthetic oxides and silicates were used as standards. On-line corrections for drift, dead-time and background were applied to the raw data. Precision is 2% (relative).

Trace-element contents in mineral phases and host glass were determined on 100 µm-thick thin sections by Laser Ablation - Inductively Coupled Plasma – High Resolution Mass Spectrometry (LA-ICP-HRMS) at IGG-CNR (Pavia, Italy). The microprobe consists of a doublefocusing sector-field analyzer (Finnigan Mat, Element I) coupled with a Q-switched Nd:YAG laser source (Quantel Brilliant). The fundamental emission of the laser source (1064 nm, in the

near-IR region) was converted to 213 nm by three harmonic generators. Helium was used as 96 97 carrier gas and mixed with Ar downstream of the ablation cell. Spot diameter was varied in the 98 range of 40-60 µm. Quantification was carried out using the NIST SRM 610 glass as external standard (Pearce et al. 1996). Si was used as internal standard for plagioclase, K-feldspar, biotite 99 and glass, while Ca was used for apatite and Ti for magnetite. Detection limits are in the range 100 101 100-500 ppb for Sc, Ti and Cr, 10-100 ppb for V, Rb, Sr, Zr, Cs, Ba, Gd and Pb, 1-10 ppb for Y, 102 Nb, La, Ce, Nd, Sm, Eu, Tb, Dy, Er, Yb, Hf and Ta, and usually <1 ppb for Pr, Ho, Tm, Lu, Th 103 and U. Precision and accuracy (both better than 10% for concentrations at ppm level) were 104 assessed by means of repeated analyses of NIST SRM 612 and BCR-2g standards. The composition of the glass beneath the thin section has been documented before the sample analysis 105 in order to promptly recognize the piercing of the rock and to eliminate any glass contribution. 106 The gas background was measured for 60 s, as in any other routine analysis, whereas signals 107 108 during ablation were acquired for approximately 20-50 s. Analyses were performed with 10 Hz 109 repetition rate of laser and ~1-2.5 mJ/sec laser power. Full details as in Miller et al. (2007). Precautions have been taken to avoid any bias on the analytical results. Memory effects have 110

111 been taken into account leaving more than one minute between two consecutive analyses and analyzing glasses after the minerals. Spurious signals related to memory effects usually affect 112 more blanks (because less time is passed after the previous analysis), thus determining a 113 worsening of the detection limits and hindering the quantification of elements at ultra-trace 114 concentration level. Surface contamination during sample polishing and/or handling before the 115 116 micro-analytical measurement and occurrence of micro-inclusions of glass/fluid have been 117 monitored by detailed inspection of the signal profiles acquired during ablation. Only intervals 118 with parallel signals have been integrated. Anomalous signal contributions at the beginning of the

ablation (due to surface contamination) and/or randomly occurring during ablation (possibly
related to inclusions and/or memory effect) has been accurately documented and excluded by
integration.

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Results

124 The selected BM juvenile samples (Melluso et al. 1995) are single obsidian (samples AI, AN and I) and single spatter (B, C and R) clasts, about 15-20 cm in diameter (Fig. 1). Following the 125 126 R₁R₂ classification diagram (De La Roche et al. 1980; Fig. 2), rocks are trachytes (AI, AN and C, plotting as trachytes in the TAS diagram) and trachyphonolites (B, I and R, phonolites in the TAS 127 diagram). Trachytic samples are vitrophyric (phenocryst load $\sim 10-12\%$), with phenocrysts of 128 sanidine (\sim 50-55%), clinopyroxene (\sim 15-20%), plagioclase (\sim 15-20%), biotite (\sim 5-10%) and 129 magnetite (<1%) set in a glassy matrix. Trachyphonolitic samples are also vitrophyric and have 130 131 lower phenocryst load (\leq 5%) and a phenocrysts assemblage consisting of sanidine (\sim 75%), plagioclase (~15-20%) and clinopyroxene (~5-8%) plus accessory magnetite, biotite and apatite. 132 An increase of SiO₂ (from 58.9-59.8 to 60.4-60.7 wt%), Na₂O (2.61-3.36 to 6.25-6.45 wt%), 133 incompatible elements (e.g., Zr from 175-255 to 681-733 ppm, La 38-48 to 116-119 ppm) and 134 135 P.I. [0.77-0.81 to 0.95-0.97; P.I. = peralkaline index = molar (Na+K)/Al], associated with a decrease of MgO (from 1.08-1.73 to 0.37-0.92 wt%), CaO (2.53-3.14 to 1.62-1.78 wt%), K₂O 136 (9.14-9.52 to 7.17-7.22 wt%), Ba (519-1210 to 23-93 ppm) and Sr (502-819 to 24-78 ppm) is 137 138 recorded in the trachyte/trachyphonolite transition.

Major- and trace-element composition of the observed mineral phases is reported in the following section, with the only exception being clinopyroxene for which full description and discussion were presented in Fedele et al. (2009). Enclosing glass compositions were similarly investigated in Fedele et al. (2009) and so they will be only briefly summarized below.
Compositional data are given in Tables 1, 2, 3, 4 and 5, completed by the Electronic Appendix.

145 Glasses

Glasses from BM trachyte samples are characterized by trachytic compositions with: 1) $SiO_2 =$ 146 147 59.9-61.9 wt%, Na₂O = 2.73-4.71 wt%, K₂O = 8.17-9.40 wt% and P.I. = 072-092; 2) low MgO (0.61-0.81 wt%) and CaO (2.17-2.54 wt%); 3) Mg# [Mg# = molar Mg/(Mg+Fe+Mn)] in the 148 149 range of 0.24-0.28; 4) relatively high abundances for strongly incompatible elements such as 150 LILE, (e.g., Rb, Cs, Ba, and Sr), LREE, HFSE (e.g., Zr and Nb); 5) very low Sc, V and Cr (Table 1). Primitive mantle-normalized (McDonough and Sun 1995) multi-element diagrams are LREE 151 enriched (La_N = 66.1-95.2, La_N/Sm_N = 4.0-5.3, La_N/Yb_N = 12.2-17.6) and nearly flat for HREE 152 $(Ho_N/Yb_N = 0.98-1.32)$, with peaks at Th, U and Pb, and troughs at Sr and Ti (Fig. 3). Two 153 "anomalous" glass compositions have been observed within sample AI (one having a 154 trachyphonolitic composition), characterized by a relative Na₂O enrichment, FeO, MgO and CaO 155 depletion, slightly lower Mg#, higher REE, Y and HFSE and troughs at Sr, Ba and Eu. 156 Analyzed BM trachyphonolites have trachyphonolitic glasses that show higher Na₂O (5.23-157 158 6.37 wt%), P.I. (0.86-0.97), REE, Y, HFSE and Pb and lower MgO (0.26-0.56 wt%), CaO (1.63-2.42 wt%), K₂O (6.53-7.40 wt%), Mg# (0.12-0.23), Sc, V, Sr and Ba with respect to trachytic 159 glasses (Table 1). Primitive mantle-normalized patterns are LREE enriched (e.g., $La_N = 126-253$, 160 161 $La_N/Yb_N = 8.21-16.5$) and nearly flat in the HREE region, which stronger LREE/MREE (e.g.,

La_N/Sm_N 4.31-6.99) and weaker MREE/HREE fractionation (Sm_N/Yb_N 1.91-2.79; Fig. 4) with respect to glasses from trachytic samples. Normalized patterns also show marked troughs at Ba, Sr and Eu. Trachyphonolitic glasses can be thus considered to represent slightly more differentiated melts with respect to trachytic ones. Glasses from sample R show some chemical variability pointing to slightly "transitional" compositions between trachytic and trachyphonoliticglasses.

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169 Feldspars

Trachytes. Plagioclase occurs as subhedral tabular phenocrysts/microphenocrysts, commonly 170 171 showing a turbid appearance (due to abundant glass inclusions) and corroded rims (Fig. 1a,b,c). Analyzed crystals are bytownites (An₇₈₋₈₇Ab₁₁₋₁₉Or₁₋₅; Fig. 2) with moderate variability both in 172 major (e.g., AI = 1.76-1.87 apfu, Ca = 0.76-0.90 apfu, Na = 0.11-0.18 apfu; Table 2) and trace-173 174 elements (e.g., Sr = 2424-3078 ppm, Ba = 100-219 ppm, Rb = 0.6-17 ppm, Pb = 5-7 ppm; Table 3). Primitive mantle-normalized incompatible element diagrams have peaks at Sr. Ba and Eu and 175 with very high Eu/Eu* [7.21-11.8, where Eu/Eu* = $Eu_N/(Sm_N \times Gd_N)^{1/2}$] and the typical 176 LREE/MREE and LREE/HREE fractionation (Fig. 3). 177

Alkali feldspar crystals are large homogenous tabular/columnar sanidine phenocrysts, up to \sim 7 mm long (Fig. 1a,b,c) with a narrow compositional range (An₂₋₄Ab₁₂₋₁₆Or₈₀₋₈₆; Fig. 2) in both major and trace-elements, except for Sr (basically 1023-2042 ppm; a analysis has 308 ppm), Ba (597 up to >10000 ppm; a single has 112 ppm) and, less evidently, Rb (143-223 ppm; Tables 2 and 3). Similarly to plagioclases, primitive mantle-normalized diagrams for BM alkali feldspars are markedly fractionated (Fig. 3), showing peaks at Rb, Ba, Sr and Eu and low HREE.

Trachyphonolites. Plagioclase is represented by subhedral-euhedral tabular microphenocrysts (Fig. 1d,e,f). Two distinctive plagioclase types were observed: a bytownite ($An_{83-86}Ab_{14-16}Or_{0-1}$) and an andesine-oligoclase ($An_{26-32}Ab_{59-62}Or_{10-13}$; Fig. 2). The calcic plagioclase, observed only in sample B, matches the plagioclase of trachytic samples, with high Sr (>2200 ppm) and Ba (~115 ppm) and low K₂O (~0.01 apfu) and incompatible elements (typically below or only barely above the detection limits; Table 2 and 3). On the other hand, the Na-rich variety is remarkably

190 richer in LREE, while it has much lower Sr (176-303 ppm) and Ba (25-34 ppm). Primitive 191 mantle-normalized patterns for the two plagioclase types have similar shape, both slightly LREE/HREE enriched and with peaks at LILE and Eu. The Ca-rich phenocrysts, still very similar 192 to the plagioclase of the trachytic samples, are systematically poorer in the most incompatible 193 elements (e.g., Th, La and Ce) and Pb, and have more evident peaks at Ba and Sr with respect to 194 the Na-rich ones, which show higher LREE and slightly higher Eu peaks (Eu/Eu* ~13.4; Fig. 4). 195 Alkali feldspar is the dominant phenocryst phase, represented by euhedral columnar 196 197 microphenocrysts ~ 1 mm long (Fig. 1d,e,f), occasionally up to 5-6 mm. Analyzed alkali feldspars 198 are sanidines with a homogeneous composition (i.e., An₃₋₄Ab₃₄₋₃₇Or₅₈₋₆₃), considerably poorer in K (0.57-0.63 apfu) and richer in Na (0.33-0.37 apfu) with respect to their equivalents from BM 199 trachytes. Trace-element abundances are similarly homogeneous, characterized by lower Sr (157-200 201 188 ppm) and Ba (270-309 ppm) and higher Rb (238-269 ppm), Pb (26-30 ppm) and LREE with respect to sanidine from trachytes. Primitive mantle-normalized diagrams are quite similar to 202 those of alkali feldspars from BM trachytes, with less pronounced peaks at Ba, Sr and Eu, and 203 higher Rb, Cs and LREE (Fig. 4). With respect to coexisting plagioclases, alkali feldspars from 204 trachyphonolites are richer in Cs, Rb, Ba, Pb, Eu and Ti (the latter two with a lower extent) and 205 206 poorer in Sr and REE.

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208 Opaque oxides

Opaque oxides occur as accessory small subhedral-euhedral microphenocrysts in both trachytes and trachyphonolites (Fig. 1b,e), sometimes included in clinopyroxene and biotite crystals. The opaques belong to the spinel s.s. and can be classified as Ti-magnetites (Fig. 5a), characterized by higher Al_2O_3 and MgO (3.88-4.33 and 2.42-2.74 wt%, respectively) and lower TiO₂ (5.68-5.78 wt%, ulvöspinel content ~17 mol%) in trachytes with respect to trachyphonolites (Al₂O₃ = 1.93 wt%, MgO = 1.49 wt%, TiO₂ = 9.50 wt%, ulvöspinel content = 26.6 mol%; Table 4). Vanadium is typically enriched (1961-2398 ppm and 823 ppm, respectively for trachytes and trachyphonolites), whereas Cr (113-157 and 51 ppm), Zr (22-24 and 69 ppm), Nb (8-10 and 51 ppm) and Sc (8-9 and 4 ppm) are low. Other trace-element contents are typically very low, most of them being below the detection limits (Table 5; Fig. 6).

- 219
- 220 Biotite

Trioctahedral biotite mica crystals [according to the nomenclature of Rieder et al. (1999); Fig. 221 222 5b] have been observed and analyzed only in the trachytic samples, where they occur as sporadic euhedral microphenocrysts with the typical lamellar habit (Fig. 1a,b) and a characteristic brown 223 to pale vellow pleochroism. Analyzed individuals show moderately high Mg# (~0.66) and TiO₂ 224 (~4.8 wt%; Table 4) and generally very low trace-element concentrations (especially for Y and 225 226 the REE, typically <0.1 ppm or even below the detection limits), with the exception of LILE (e.g., Rb = 294-307 ppm, Sr = 69-95 ppm, Ba = 2903-5275 ppm), V (426-486 ppm), HFSE (e.g., 227 Zr \sim 22 ppm, Nb = 41-48 ppm, Ta = 1.68-1.85 ppm; Table 5) and Sc (\sim 12 ppm), many of which 228 have peaks in the primitive mantle-normalized diagrams of Fig. 7a. 229

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231 Apatite

Apatite was observed only in trachyphonolitic sample I as very small microphenocrysts with 232 233 prismatic habits. The apatite is relatively rich in Ca (9.96 apfu, almost completely filling the M1 and M2 sites) and F (3.83 wt%, fluorapatite/hydroxyl-fluorapatite) and poor in Si (0.17 apfu; 234 Table 4), Y, Th, U and REE (e.g., Y = 1486 ppm, Th = 110 ppm, La = 3635 ppm, Ce = 7325 235 ppm; Table 5). Thus, the analyzed crystal approaches the composition of pure apatite end-236 britholite 237 member [i.e., $Ca_5(PO_4)_3(F,OH),$ with minor silico-phosphate,

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238 (Ca,REE,Y,Th,U)₅(SiO₄,PO₄)₃(F,OH); Fig. 5c], and it can be classified as *fluorapatite/hydroxyl-*239 *fluorapatite*. The primitive mantle-normalized pattern has a marked LREE/HREE- (La_N/Yb_N 240 ~38) and LREE/MREE- enrichment (La_N/Sm_N ~4.4), with troughs at Ba, Pb, Sr, Eu and V (Fig. 241 7b). Apatite is the main mineral repository of Th and U.

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Discussion

The trace-element concentrations analyzed by LA-ICP-HRMS for mineral phases and 244 coexisting glasses within the studied BM samples were used for the calculation of mineral/liquid 245 partition coefficients for trachytic and trachyphonolitic systems. The reliability of such Min/LD 246 values is obviously dependent on the effective attainment of equilibrium conditions. The overall 247 chemical homogeneity of both trachytic and trachyphonolitic glasses allows assuming they 248 reasonably represent the composition of the fractionating magma. However, a more detailed 249 inspection of both major- and trace-element glass composition showed some variability in 250 samples AI and R, possibly suggesting the persistence of local heterogeneities. Chemical 251 variability is particularly wide for trachytic sample AI (with glasses ranging from trachytic to 252 trachyphonolitic in composition), whereas it is less pronounced for trachyphonolite R (with only 253 254 glass analysis, R-3-VETROC, slightly deviating from the others in terms of lower Y, REE, Pb, Th and U concentrations, more similar to the values of trachytic glasses). In the light of the above 255 observations, in order to correctly define the equilibrium partitioning and calculate ^{*Min/L*} values: 256 for BM trachytes, trachyphonolitic glass analyses from sample AI were discarded, whereas 257 trachytic glasses from the same sample were taken, given their similar composition with 258

respect to those from samples AN and C;

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• for BM trachyphonolites, only the single anomalous glass analysis from sample R was discarded, whereas glass analyses from sample I were taken.

262 In the following sections the extent to which analyzed minerals satisfy criteria of phenocrystmatrix equilibrium is considered. It is worth noting here that the incorporation of trace-elements 263 coming from the coexisting melts into a mineral structure is commonly ruled by the match in 264 valence and ionic radius between the major-element cation and the trace-element(s) substituting 265 after it. Lattice-site elastic-strain models are adopted to unravel the role of the crystal-chemical 266 control on trace-element incorporation in minerals and their partitioning between solid and melt. 267 In these models (Nagasawa 1966; Brice 1975) trace-elements are regarded as impurities 268 introduced in a perfectly elastic and isotropic crystal lattice that minimise its perturbation by 269 270 relaxing the adjacent sites and distributing the surplus elastic or electrostatic energy through the 271 lattice. The equations of Beattie (1994) and Blundy and Wood (1994) describe the relationships among partition coefficients, ionic radii and ionic charges. Fedele et al. (2009) used the Blundy 272 273 and Wood (1994) mathematical treatment to fit the partition coefficients of series of isovalent cations entering structure sites of clinopyroxene in equilibrium with BM trachyte-trachyphonolite 274 melts. In principle, the same approach could be extended to the $^{Min/L}D$ of this study. However, the 275 276 limited number of crystals suitable to measure equilibrium partitioning and the limited number of elements hosted by most of the mineral phases considered here makes the modelling of obtained 277 Min/LD according to commonly adopted lattice-site elastic-strain models less reliable. Thus, the 278 Min/LD are compared with those predicted according to semi-empirical parameterizations or 279 straightforwardly to literature data. 280

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282 Plagioclase

Assessment of equilibrium. Several lines of evidence indicate that Ca-rich bytownitic 283 284 plagioclase crystals in trachytic samples cannot be regarded as the crystallization product of a trachytic-trachyphonolitic melt. Rather, they more likely represent a xenocryst phase. First of all, 285 petrographic evidence of textural disequilibrium is provided by the occurrence of corroded rims 286 287 (Fig. 1a,b,c,d), which suggest crystal/melt re-equilibration reactions. Secondly, the chemistry of 288 these plagioclases plots on the less differentiated end of the entire Campi Flegrei trend (see Fig. 2), in the compositional field of crystals in equilibrium with the less evolved shoshonitic basalts, 289 290 shoshonites and latites (e.g., Armienti et al. 1983; Beccaluva et al. 1990; D'Antonio and Di Girolamo 1994; Fedele et al. 2006). These observations are in keeping with previous studies that 291 292 documented for BM trachytes-phonolites and other Campi Flegrei evolved rocks the presence of xenocryst Mg-rich clinopyroxene crystals originally equilibrated in less evolved, nearly-primitive 293 294 melts and the concurrent occurrence of (xenocryst) Ca-rich and (equilibrium) Na-rich (labradorite-andesine, An₃₅₋₅₅) plagioclase (Melluso et al. 1995, 2012; Orsi et al. 1995; Civetta et 295 al. 1997; de Vita et al. 1999; Pappalardo et al. 2002, 2008; Fulignati et al. 2004; Fedele et al. 296 2008, 2009). Chemical disequilibrium is also confirmed by the significantly lower An contents 297 298 (i.e., An₄₃₋₅₁ and An₅₂₋₅₅ for dry and wet magmatic systems, respectively) of putative plagioclase in equilibrium with host BM trachytes according to the equation of Bédard (2006). On this basis, 299 300 the analyzed plagioclases from the studied BM trachytes cannot be in chemical equilibrium with the coexisting glass and, consequently, were not used for the calculation of PULD for trachytic 301 liquids. Similar considerations indicate that the Ca-rich plagioclase is not in equilibrium with BM 302 trachyphonolites. Only Na-rich plagioclase meets textural and chemical requirements to be 303 regarded as a liquidus phase for Campi Flegrei evolved trachytic melts (Fig. 2). Accordingly, its 304 composition approaches that calculated assuming equilibrium with host trachyphonolitic melt 305

306 (i.e., An_{23-38} and An_{43-51} for dry and wet magmatic systems, respectively) according to the 307 equation of Bédard (2006). The composition of this plagioclase was therefore used for the 308 calculation of trace-element partition coefficients by dividing average trace-element abundances 309 for minerals and coexisting glasses, as reported in Table 6.

Calculated *PVLD* **values and comparison with literature data.** The only compatible elements 310 are Sr (^{PUL}D values ranging from 9.5 to 15). Ba (1.5-2.6) and Eu (1.1-1.4), whereas all the other 311 trace-elements show a strongly (e.g., LILE, HFSE, M-HREE, Y and Ti, with $^{Pl/L}D \leq 0.08$) to 312 moderately (e.g., Sc = 0.42-0.48, Pb = 0.20-0.24, La = 0.17-0.20, Ce = 0.10-0.12) incompatible 313 behaviour (Fig. 8a). The presented PULD values are basically consistent with data obtained using 314 the theoretical model of Bédard (2006), based on plagioclase anorthite molecular values and 315 MgO concentration of supposed equilibrium melt, thus supporting the hypothesis of 316 plagioclase/trachyphonolite equilibrium (Fig. 8b). The fit is particularly good for the key 317 elements Rb, Ba, Sr and Eu and acceptable for LREE. On the other hand, partition coefficients 318 for Th. U. HFSE (Ti excluded) and HREE are guite overestimated, although still displaying 319 incompatible behaviour. Fig. 8b also shows the results of the application of the Bédard (2006) 320 model to the Ca-rich plagioclase of both BM trachytes and trachyphonolites. The mismatch in the 321 calculated ^{*PUL*}D values for the key elements, especially Sr and Eu resulting strongly incompatible, 322 is a further evidence for the xenocryst nature of such plagioclase. 323

The literature data for Campi Flegrei trachytes and trachyphonolites (Table 6) show several differences with the present dataset. Villemant (1988) measured $^{Feldspar/L}D$ in trachytetrachyphonolite melts, obtaining values that are significantly higher for Ba (9.5 to 16.6) and Rb (0.52-0.97) and markedly lower for Sr (2-6.6) and Eu (0.85-1.17). The contrasting results mainly arise from the different sampling and analytical solutions. The data of Villemant (1988) data were obtained by INAA (Instrumental Neutron Activation Analysis) on mineral separates and

330 associated groundmass. Such a bulk technique is not able to avoid sampling bias related to the 331 presence of either phases not completely equilibrated with the coexisting melt and/or occasional 332 glass contamination, differently from *in situ* microanalytical investigations carried out by LA-ICP-HRMS (Fedele et al. 2009). Presumably, feldspar separates analysed by Villemant (1988) 333 included alkali feldspars and, probably, xenocryst Ca-rich plagioclase. This clearly results in a 334 wide broadening of Feldspar/LD values. The higher K2O contents of the former facilitate the 335 336 entrance of Ba and Rb in the crystal lattice, while hampering that of Sr, which, in contrast better enters Ca-rich plagioclase. 337

Compared to the PULD values reported here, Pappalardo et al. (2008) obtained lower values for 338 Ba (0.90 and 0.05 for trachyphonolites and trachytes, respectively), Sr (1.40 and 7.80 for 339 trachytes and trachyphonolites, respectively) and Eu (0.90-0.80). It is to notice that he dataset of 340 Pappalardo et al. (2008), though restricted to only seven trace-elements, was obtained by SIMS 341 342 (Secondary Ions Mass Spectrometry), a microanalytical technique that furnishes *in-situ* chemical 343 information more comparable with that obtained by LA-ICP-HRMS. However, the lack of an accurate assessment that equilibrium conditions were attained led the authors themselves to 344 consider their values compositional ratios rather than effective partition coefficients. Literature 345 data for other trace-elements are too scattered and $P^{I/L}D$ values generally too low to allow a 346 systematic comparison with the present dataset, even though a generally stronger correspondence 347 can be easily envisaged, as it is the case of LREE and MREE in trachyphonolitic systems. 348

Finally, as regards the comparison with $^{Pl/L}D$ for other highly-differentiated systems (Table 6), the following observations can be reported: (a) phonolites display similar $^{Pl/L}D$ for all the traceelements, although basically displaced to higher values, especially for the compatible Ba (1.73-7.33), Sr (11.7-49.8) and Eu (0.99-2.18); (b) with the exception of systematically lower $^{Pl/L}D_{Sr}$ (0.94-4.2), partition coefficients for sodic trachytic liquids are generally largely variable with

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354 respect to those for potassic BM trachyphonolites (e.g., Eu and Ba range from incompatible to strongly compatible; (c) rhyolites generally have wide PULD ranges for the key elements, 355 displaying higher values with respect to BM trachyphonolites (i.e., $P_{LL}D_{Rb} = 0.06-0.76$, $P_{LL}D_{Eu} = 0.06-0.76$ 356 2.0-7.9, ${}^{PUL}D_{Pb} = 0.27$ -2.2), whereas Sc is markedly more incompatible (0.01-0.06); (d) high 357 silica rhyolites have largely variable $PULD_{Ba}$ (1.0-19.55), generally lower $PULD_{Sr}$ (4.04-13.1) and 358 higher ${}^{PUL}D_{Eu}$ (3.65-5.62) and ${}^{PUL}D_{Pb}$ (0.35-0.97) compared to the corresponding values reported 359 here for BM trachyphonolites. 360

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362 Alkali feldspar

Assessment of equilibrium. The textural evidence and the homogeneous major element 363 composition (well within the literature range for alkali feldspars from Campi Flegrei evolved 364 365 rocks; Fig. 2) confirm that alkali feldspar crystals from BM are in equilibrium with coexisting glasses. Nevertheless, some variability that may be source of uncertainty in the calculation of 366 appropriate $K_{fs/L}D$ values is observed at the trace-element scale; this is the case, for instance, of 367 Ba, Sr and Rb. This variability likely reflects the effects of slight differences in the fractionation 368 trend that led the melt to be progressively Ba- and Sr-poorer. On this basis, it seems reasonable to 369 370 argue that the crystals showing the strongest Ba and Sr enrichment (namely, C-1-SAN40-7 and C-1-SAN40-3 and AI-4-SAN15-4, from samples C and AI, respectively) were segregated from 371 slightly less evolved liquids (see also the lower Rb, Pb and L-MREE abundances), and therefore 372 they are unsuitable for the calculation of $K_{fs/L}D$ values. Similarly, the trace-element composition 373 of sanidine AN-4-SAN11-1 from trachyte AN is virtually identical to that of the other sanidine 374 crystals from BM trachytes (Table 3), but it is characterised by significantly lower Ba (112 ppm) 375 and Sr (308 ppm) contents (possibly due to analytical issues) to assume complete equilibrium. 376 This sample was therefore discarded. In virtue of their notably smaller Ba and Sr variability, the 377

remaining sanidine crystals were assumed to better represent trachytic liquidus phases. Their compositions were therefore used in the calculation of $K_{fs/L}D$ values reported in Table 7.

Calculated ${}^{Kfs/L}D$ values and relevant changes from trachytes to trachyphonolites. With ${}^{Kfs/L}D$ values in the range of 2.5-5.4 and 2.5-3.1, Ba and Sr, respectively, are the only compatible elements in trachytes (Fig. 9). Europium oscillates from slightly incompatible to slightly compatible (0.87-1.2), whereas Rb and Pb behave as slightly/moderately incompatible elements (0.70-0.81 and 0.47-0.57, respectively). Finally, ${}^{Kfs/L}D_{Ti}$ and ${}^{Kfs/L}D_{Sc}$ are respectively between 0.13 and 0.24 and between 0.35 and 0.54, whereas the remaining trace-elements (mainly LREE) show a strongly incompatible behaviour (${}^{Kfs/L}D \leq 0.1$).

The sanidine crystals in trachyphonolites have a homogeneous K₂O-poorer and Na₂O-richer 387 composition that is consistent with Campi Flegrei literature data as for both the compositional 388 range and the chemical changes at the transition from trachytes to trachyphonolites (Fig. 2). The 389 assessment of the attainment of crystal/liquid equilibrium is thus more straightforward, and the 390 calculation of $K_{fs/L}D$ more reliable (Table 7). Compared to trachytes, trachyphonolites are 391 characterized by higher Kfs/LD values for Ba (16-21), Sr (7.5-8.8) and, less markedly, Eu (1.2-1.4), 392 whereas the remaining trace-elements are characterized by a slight decrease of $K_{fs/L}D$ values (still 393 showing a moderately to strongly incompatible behaviour; Fig. 9). Rubidium and Pb are 394 moderately incompatible (0.50-0.60 and 0.34-0.45, respectively), both recording a slight decrease 395 of $K_{fs/L}D$ values with respect to trachytes. 396

The general decrease of ${}^{Kfs/L}D$ values for incompatible elements at the trachyte-trachyphonolite transition (extended also to ${}^{Cpx/L}D$ values; Fedele et al. 2009) is possibly related to a decrease of melt polymerization, as observed by White et al. (2003) for the transition from alkaline to peralkaline systems (i.e., with P.I. \geq 1.0). In the case of Rb, the decrease of ${}^{Kfs/L}D$ seems also related to the lower presence of the orthoclase molecule in the alkali feldspar, given the great 402 geochemical similarity of Rb and K (both in terms of charge and size; e.g., Mahood and Stimac 403 1990, White 2003). A similar linear relation between Or content and ${}^{Kfs/L}D_{Rb}$ has been previously 404 documented for peralkaline (White et al. 2003) and peraluminous silicic systems (Icenhower and 405 London 1996).

In contrast, the partitioning of compatible elements in alkali feldspar seems barely affected by 406 variations in melt polymerization (White et al. 2003). Thus, the observed increase of $K_{fs/L}D$ for Ba 407 and Sr must be related to other causes. One possibility is that both elements substitute for Na in a 408 Ca-poor alkali feldspar and, therefore, their partition coefficients increase as a consequence of the 409 410 higher Ab content in the alkali feldspar of trachyphonolites. Again, a similar feature has been observed by White (2003) and White et al. (2003) for peralkaline systems. Finally, the mild 411 increase of $K_{fs/L}D_{Eu}$ with increasing degree of evolution cannot be simply explained, due to the 412 concomitant occurrence of Eu^{2+} and Eu^{3+} . These latter can have variable, sometimes contrasting. 413 behaviour as a function of the variations in the oxidation state, melt polymerization and lattice 414 features. However, it is proposed that the slight increase of $K_{fs/L}D_{Eu}$ can be the result of a 415 dominant effect of Eu^{2+} (which is supposed to become more compatible in trachyphonolites, 416 having the same ionic radius and charge of Sr) over Eu^{3+} (supposed to be more incompatible in 417 418 trachyphonolites like Sm and Gd).

419 **Comparison with literature data.** Similarly to ${}^{Pl/L}D$, also ${}^{Kfs/L}D$ for Campi Flegrei trachyte-420 trachyphonolite melts show some major differences with literature datasets, particularly as for Ba 421 and Sr. As for trachytic systems, both ${}^{Feldspar/L}D$ from Villemant (1988) and ${}^{Kfs/L}D$ from 422 Pappalardo et al. (2008) show a much wider spectrum of values relative to those of this study 423 (Table 7). The markedly lower ${}^{Feldspar/L}D_{Ba}$ (down to 1.13) and higher ${}^{Feldspar/L}D_{Sr}$ (up to 6.6) by 424 Villemant (1988) are likely ruled by dominant Ca-rich plagioclase. In contrast, the notably higher 425 ${}^{Feldspar/L}D_{Ba}$ values (up to 16.6) by Villemant (1988) and the wide range of ${}^{Kfs/L}D_{Ba}$ values (0.3 to

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426 13) by Pappalardo et al. (2008) are probably the result of localized heterogeneities in the 427 analyzed samples. As for trachyphonolites, our ${}^{Kfs/L}D$ are notably higher for Ba and only slightly 428 higher for Sr and Eu, the latter being slightly incompatible according to Pappalardo et al (2008). 429 As a whole, it is proposed that the observed differences result from the sampling and analytical 430 issues previously discussed in the plagioclase section.

431 A comparison between present data and literature data for other evolved systems is shown in Table 7. The trachytes of White et al. (2003) display lower ${}^{Kfs/L}D_{Rb}$ (0.24-0.37), higher ${}^{Kfs/L}D_{Eu}$ 432 (2.04-2.10) and largely variable $K_{fs/L}D_{Ba}$ (1.11-12.74, quite within the range of the data presented 433 here) and $\frac{K_{fs/L}}{D_{sr}}$ (0.45-4.81, only barely comparable with present data for trachytes). Such 434 differences are probably the effect of numerous factors, including variations in bulk-rock SiO_2 435 and P.I. (both influencing the degree of melt polymerization) and in crystal chemistry as well 436 (White et al. 2003). As for sodic trachytes, $K_{fs/L}D_{Ba}$ (5.2-5.9) roughly compares with that 437 measured in BM trachytes, $K_{fs/L}D_{Rb}$ is definitely lower (0.11-0.26), whereas $K_{fs/L}D_{Sr}$ (3.6-10) and 438 $^{Kfs/L}D_{Fu}$ (0.4-2.5) cover the entire range of the present dataset and even extends to higher values. 439 Pantellerites and comendites (peralkaline rhyolites) are characterized by an overall decrese of 440 partition coefficients for incompatible elements and Rb with respect to BM trachytes-441 trachyphonolites. This decline of $K_{fs/L}D$ at the trachyte/pantellerite transition should be probably 442 ascribed to a decrease of melt polymerization, as observed by Mahood and Stimac (1990) and 443 White et al. (2003). In contrast, compatible elements display a broad range of $K_{fs/L}D$, with values 444 445 that are lower and higher relative to those for BM trachytes and typically lower compared to those for BM trachyphonolites (e.g., ${}^{Kfs/L}D_{Ba} = 0.66-10.35$, ${}^{Kfs/L}D_{Sr} = 0.40-2.79$). This probably 446 447 reflects the influence of numerous interplaying factors in their partitioning (as mentioned above; see White et al. 2003). As for rhyolitic systems, LILE (e.g., ${}^{Kfs/L}D_{Rb} = 0.31-2.4$, ${}^{Kfs/L}D_{Pb} = 0.99-$ 448 4.1) and Eu (2-9.06) display higher partition coefficients, whereas Sr shows Kfs/LD values 449

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intermediate between BM trachytes and trachyphonolites (i.e., 4.5-7.3) and Ba basically encompasses the range for analyzed trachytes and trachyphonolites (1-24). Finally, high-silica rhyolites show roughly similar, although widely variable, ${}^{Kfs/L}D_{Rb}$ (0.11-0.74) and ${}^{Kfs/L}D_{Ba}$ (1.0-20.9) with respect to BM trachytes and trachyphonolites, whereas ${}^{Kfs/L}D_{Sr}$, ${}^{Kfs/L}D_{Eu}$ and ${}^{Kfs/L}D_{Pb}$ are remarkably higher.

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456 Ti-magnetite

Titanomagnetite crystals from both trachytes and trachyphonolites do not show any textural 457 458 evidence for disequilibrium and display compositions that are well within the range reported for opaque oxides from Campi Flegrei evolved products (i.e., ulvöspinel contents basically between 459 16 and 29%, with only a few higher values in the range 40-62%; Fig. 5a). As a comparison, Ti-460 magnetite crystals in the slightly less evolved (latite-trachyte) pyroclastic rocks from the nearby 461 Ischia district have slightly higher ulvöspinel (~35-46%), TiO₂ (10.4-15.6 wt%) and MgO 462 contents (2.40-5.04 wt%) and lower FeOtot (72.1-77.9 wt%). The analyzed crystals can be 463 reasonably considered as the direct product of segregation from their coexisting 464 trachytic/trachyphonolitic glasses and therefore are used for the calculation of $^{Mt/L}D$ values, 465 466 reported in Table 8.

The very low trace-element concentration of analyzed Ti-magnetite crystals is apparent from Fig. 10a, in which only Ti ($^{Mt/L}D_{Ti} = 18-19$ for trachytes, 25 for trachyphonolites) and V ($^{Mt/L}D_V =$ 44-49 and 55) show a strongly compatible behaviour. Scandium varies from moderately compatible in trachytes ($D_{Sc} = 1.7$) to barely incompatible (0.96) in trachyphonolites. Interestingly, Sc is the only trace-element for which a clear decline in $^{Mt/L}D$ values can be observed as melt changes in composition from trachyte to trachyphonolite. Among the remaining trace-elements, only HFSE have $^{Mt/L}D$ above 0.1 (and typically \leq 0.4; Fig. 10a). A general trend of increasing compatibility of Ti and HFSE can be envisaged at the trachyte-trachyphonolite transition, likely related to the increase of Ti and Fe/Mg and the concurrent decrease of Al. This trend, along with evidence that ${}^{Mt/L}D_{Ti,V,Sc} > {}^{Mt/L}D_{HFSE}$ and ${}^{Mt/L}D_{Th,U} < 0.035$, are consistent with results and related considerations reported by Nielsen et al (1994) for basic to intermediate systems.

As a whole, strongly incompatible elements (e.g., LILE, LREE and MREE) are typically 479 below the detection limits in our dataset, whereas, a moderately incompatible to slightly 480 compatible behaviour is reported by Villemant (1988) for some of them (e.g., La, Eu and Tb; 481 Table 8). These high $^{Mt/L}D$ values are most probably due to unusually REE-rich contents that 482 reflect the presence of late-stage phase inclusions (e.g., apatite, zircon, rutile; see Nielsen et al. 483 1994). Differences in the adopted analytical techniques (see above) may also explain the strongly 484 compatible behaviour of Sc (with ${}^{Mt/L}D_{Sc}$ increasing from 3.80-7.95 to 9.70 at the 485 trachyte/trachyphonolite transition) measured by Villemant (1988). 486

Finally, large differences are observed between ${}^{Mt/L}D$ for trachytic-trachyphonolitic liquids and 487 those for other differentitated systems (Table 8). The most remarkable are reported in the 488 following: (a) phonolites display generally higher ${}^{Mt/L}D$ values (e.g., ${}^{Mt/L}D_U = 0.725$, ${}^{Mt/L}D_{Ta} =$ 489 0.164-0.90, ${}^{Mt/L}D_{Sc} = 2.85-5.38$); (b) in Na-trachytes Ta is compatible (${}^{Mt/L}D_{Ta} = 0.28$ or 1.13-490 2.35) and Sc strongly compatible ($^{Mt/L}D_{Sc} = 1.88-10.42$); (c) rhyolites and high-silica rhyolites 491 show higher ^{Mt/L}D values for all the trace-elements, including the more incompatible ones, some 492 of which can also turn to strongly compatible (e.g., ${}^{Mt/L}D_{Th}$ up to 13.1, ${}^{Mt/L}D_{Ta}$ up to 4.5, ${}^{Mt/L}D_{Y}$ up 493 to 3.21). 494

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496 Biotite

The biotite crystals recovered in AI trachyte have a broadly similar composition, fully consistent with existing literature data for Campi Flegrei differentiates (i.e., Mg# = 0.61-0.74), as well as for those from similar rocks from Ischia (i.e., Mg# = 0.63-0.76; Fig. 5b). Only Ba and (less evidently) Sr and V exhibit a more marked chemical variability (Table 5), and so two sets of $B\nu LD$ values were calculated (Table 9 and Fig. 10b), dividing the composition of each biotite crystal meeting the requirements of textural and chemical equilibrium by the average composition of coexisting trachytic glass.

The most compatible elements are, in order of decreasing ^{Bt/L}D values, Ti (14), V (8.8-10.0), 504 Ba (5.7-10) and Sc (2.2-2.3). As for the other trace-elements, both LILE and HFSE range from 505 strongly incompatible (e.g., Th, U, Pb, Sr, Zr, Hf), to moderately/barely incompatible (Cs, Ta), to 506 slightly compatible (Rb, Nb). Differently from the other analyzed mineral phases, an overall good 507 correspondence exists between Bt/LD values reported here and those measured by Villemant 508 (1988), particularly for key elements such as Rb and Sr, but also for HFSE (e.g., Ta and Hf). 509 Some discrepancies, such as the generally wider range of literature data (e.g., ${}^{Bt/L}D_{Sc} = 2.81-5.56$, 510 $^{Bt/L}D_{Ba} = 1.04-21.5$) possibly result from crystal and/or glass compositional heterogeneities. 511

The present dataset is remarkably different from the previous ones reported for biotite in 512 equilibrium with other evolved liquids, for which generally higher ${}^{Bt/L}D$ values for all the most 513 514 relevant trace-elements are reported (Table 9). Partition coefficients for phonolitic systems are 515 quite similar to those reported here for trachytes, with values that are basically slightly higher for Rb, lower for Ta (which is clearly incompatible) and one order of magnitude higher for Sc. 516 Rhyolites and high-silica rhyolites are characterized by a notable increase of $^{Bt/L}D$ values for 517 almost the entire spectrum of analyzed trace-elements, some of which display a particularly wide 518 range (e.g., ${}^{Bt/L}D_{Cs} = 1.2-3.1$, ${}^{Bt/L}D_{Rb} = 3.0-9.7$, ${}^{Bt/L}D_{Ba} = 3.7-7.0$). 519

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521 Apatite

The few data available for Campi Flegrei trachyte-phonolite apatites display a wide 522 compositional variability, covering the range from near-pure apatite (similar to that reported here) 523 to terms rich in the britholite silico-phosphate component (i.e., Si+REE > 6 apfu; Fig. 5c). It could 524 525 be hypothesized that the britholite-rich compositions are found in differentiated holocrystalline trachytes and trachyphonolites (Melluso et al. 2012), as the extreme enrichment in lanthanides, 526 Th and U of the melt facilitates their entrance in the apatite-britholite crystal lattice, mainly at the 527 528 expense of CaO (whose abundance progressively decreases with magma evolution). In the Campi Flegrei volcanic products such substitutions are associated with a decrease of F, which prefers to 529 enter fluorite and F-bearing Ca-Zr-disilicates (Melluso et al. 2012). A similar increase of Si, 530 LREE and Y (as well as of Fe) has been documented in the apatite crystals from Pantelleria at the 531 transition from trachytes to pantelleritic trachytes and pantellerites (Mahood and Stimac 1990). In 532 addition, Macdonald et al. (2013) documented the occurrence of both (relatively) early 533 crystallizing apatite and late crystallizing britholite in some Paleogene granites from Scotland and 534 Northern Ireland. Therefore, in light of the above considerations and in the absence of evidence 535 536 in favour of textural and/or chemical disequilibrium, the analyzed apatite crystal from trachyphonolite sample I can be confidently considered as a liquidus phase. Calculated $^{Ap/L}D$ are 537 538 reported in Table 10 and in Fig. 10b.

539 Yttrium and REE are all strongly compatible, with ${}^{Ap/L}D$ values generally >20, except for the 540 heavier HREE, whose partition coefficients record a clear decrease with increasing atomic 541 number, from 17 (Er) to 7.8 (Lu). Highest values (\geq 30) are for MREE, consistently with both 542 theoretical and experimental data (see Prowatke and Klemme 2006). Large ion litophile elements 543 range from strongly/moderately incompatible (e.g., Pb, Ba, U) to moderately compatible (Th), up to strongly compatible (Sr), whereas HFSE are all strongly incompatible (e.g., ${}^{Ap/L}D_{Ti} = 0.05$; concentrations for all the other HFSE are below the detection limits) and and V is compatible $({}^{Ap/L}D_V = 2.0)$. The latter can be explained by the ordering of V at Z site, in substitution of P (e.g., Pan and Fleet 2002).

Up to the present study, the only $^{Ap/L}D$ literature data available for apatite/evolved liquid 548 equilibria refer to more than 20 year-old studies (see Table 9). The dataset of Prowatke and 549 Klemme (2006) is not considered here because it refers to partitioning between apatite and 550 synthetic silicate melts of less evolved composition (approximately ranging from basalt to 551 andesite) at high P and T conditions (1.0 GPa and 1250 °C). As a whole, an overall good 552 correspondence is observed with literature data for apatite/phonolite equilibrium. REE show a 553 trend of increasing compatibility from LREE to MREE (e.g., ${}^{Ap/L}D_{La} = 14.4$, ${}^{Ap/L}D_{Nd} = 54.3$, 554 $^{Ap/L}D_{E\mu} = 102$) followed by a reversal to lower values for HREE (e.g., $^{Ap/L}D_{L\mu} = 3.69$), with values 555 significantly lower for LREE and HREE and markedly higher for MREE relative to those of this 556 557 study. Similar observations can be made for sodic trachytes and pantellerites, which basically mimic the general trend observed in this study although their $A_{P/L}D$ are generally higher, 558 particularly for U and LREE. Finally, data for granitic systems indicate a much higher 559 560 compatibility of HREE with respect to LREE, differently from evidence for Campi Flegrei trachyphonolites and the other evolved systems discussed above. 561

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Implications

The present study provides a new dataset of partition coefficients for plagioclase, alkali feldspar, Ti-magnetite, biotite and apatite equilibrated with trachytic-trachyphonolitic potassic systems. The new set of $^{Min/L}D$ values has been obtained thanks to preliminary petrographic observations that suggested suitable textural conditions (i.e., glassy texture, low to moderate 568 phenocryst load) and the adoption of *in situ* microanalytical techniques that confirmed chemical 569 equilibrium between the analyzed mineral phases and coexisting melts.

Analyzed plagioclases include both Na- and Ca-rich terms, with only the former having equilibrated with trachyphonolitic liquids, whereas the latter formed from less evolved melts (possibly shoshonitic basalt). ^{PUL}D calculated for Na-rich terms are characterised by high values for Sr, Ba and Eu. A marked increase of $^{Kf_{N}L}D$ for the compatible elements Ba, Sr (and Eu that varied from slightly incompatible to slightly compatible in trachytes) and a clear (though small) decrease of the remaining trace-elements (all incompatible at various extent) characterize the transition from trachytes to trachyphonolites.

As regards Ti-magnetite, Ti, V and Sc are compatible elements in evolved trachytic-577 trachyphonolitic systems, as broadly expected. A systematic decrease of $^{Mt/L}D$ values (with the 578 only exception of ${}^{Mt/L}D_{sc}$) is observed at the transition from trachytes to trachyphonolites. The 579 highest ^{Bt/L}D values for trachytic liquids were calculated for Ti, Ba and Sc, whereas the remaining 580 HFSE and LILE show a variable partitioning behaviour (from strongly, moderately and slightly 581 incompatible to slightly compatible). The REE are strongly incompatible elements. 582 Apatite/trachyphonolite partition coefficients are high for Sr, Y and REE (the latter with $A_{P/L}D$ 583 values up to \sim 40), very low for HFSE and largely variable for the remaining LILE. 584

The comparison with the few sets of $^{Min/L}D$ available in literature for similar systems revealed significant differences for the main trace-elements entering in the crystal lattice of the analyzed mineral phases. Such discrepancies are possibly related to the different analytical methods (i.e., LA-ICP-HRMS vs. INAA) and/or to the lack of an accurate evaluation of the attainment of equilibrium conditions, thus confirming the importance of a preliminary sample selection and the adoption of *in situ* microanalytical techniques. On the other hand, the differences observed between our $^{Min/L}D$ and those for other differentiated systems, although in part related to the heterogeneity of the datasets available for comparative purposes, stress out once again the need that each system must be separately considered (Mahood and Stimac 1990, White et al. 2003, Fedele et al. 2009). The different physical (T, P, fO_2 , degree of polymerization) and chemical parameters (major element content, degree of peralkalinity), as well as changes in mineral chemistry and in fractionating mineral assemblage plus various kinetic effects (e.g., growth rate) can play a great influence on the mineral/liquid partitioning and need to be adequately addressed.

It should be finally stressed that the determination of mineral/liquid partition coefficients for highly evolved systems such as those investigated here can significantly improve the understanding of magma evolution processes. As huge silica- and alkali-rich magma reservoirs are commonly characterized by explosive eruptions (e.g., Mason et al. 2004 and references therein), a detailed knowledge and modelling of the magmatic evolution can also contribute to a correct evaluation of the volcanic hazard and related risks.

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613

References

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614	Armienti, P., Barberi, F., Bizouard, H., Clocchiatti, R., Innocenti, F., Metrich, N., Rosi, M., and
615	Sbrana, A. (1983) The Phlegrean Fields: magma evolution within a shallow chamber. Journal
616	of Volcanology and Geothermal Research, 17, 289-311.
617	Bacon, C.R., and Druitt, T.H. (1988) Compositional evolution of the zoned calcalkaline magma
618	chamber of Mt. Mazama, Crater Lake, Oregon. Contributions to Mineralogy and Petrology 98,
619	224-256.
620	Beattie, P. (1994) Systematics and energetics of trace-element partitioning between olivine and
621	silicate melts: Implications for the nature of mineral/melt partitioning. Chemical Geology,
622	117, 57-71.
623	Beccaluva, L., Di Girolamo, P., Morra, V., and Siena, F. (1990) Phlegraean Fields volcanism
624	revisited: A critical re-examination of deep eruptive systems and magma evolutionary
625	processes. Neues Jahrbuch fur Geologie und Paläontologie Monatshefte, 5, 257-271.
626	Bédard, J.H. (2006) Trace element partitioning in plagioclase feldspar. Geochimica et
627	Cosmochimica Acta, 70, 3717-3742.
628	Blundy, J., and Wood, B. (1994) Prediction of crystal-melt partition coefficients from elastic
629	moduli. Nature, 372, 452-454.
630	Brice, J.C. (1975) Some thermodynamic aspects of the growth of strained crystals. Journal of
631	Crystal Growth, 28, 249-253.
632	Carmichael, I.S.E. (1967) The iron-titanium oxides of salic volcanic rocks and their associated
633	ferromagnesian silicates. Contributions to Mineralogy and Petrology, 14, 36-64.
634	Civetta, L., Orsi, G., Pappalardo, L., Fisher, R.V., Heiken, G., and Ort, M. (1997) Geochemical
635	zoning, mingling, eruptive dynamics and depositional processes - the Campanian Ignimbrite,
636	Campi Flegrei caldera, Italy. Journal of Volcanology and Geothermal Research, 75, 183-219.

- D'Antonio, M., and Di Girolamo, P. (1994) Petrological and geochemical study of mafic
 shoshonitic volcanics from Procida-Vivara and Ventotene Islands. Acta Volcanologica, 5, 6980.
- 640 Deino, A.L., Orsi, G., de Vita, S., and Piochi, M. (2004) The age of the Neapolitan Yellow Tuff
- caldera-forming eruption (Campi Flegrei caldera Italy) assessed by 40 Ar/ 39 Ar dating method.
- Journal of Volcanology and Geothermal Research, 133, 157-170.
- 643 De La Roche, H., Leterrier, P., Grandclaude, P., and Marchal, E. (1980) A classification of
- volcanic and plutonic rocks using R1-R2 diagram and major element analyses. Its
 relationships with current nomenclature. Chemical Geology, 29, 183-210.
- de Vita, S., Orsi, G., Civetta, L., Carandente, A., D'Antonio, M., Deino, A., di Cesare, T., Di
- 647 Vito, M.A., Fisher, R.V., Isaia, R., Marotta, E., Necco, A., Ort, M., Pappalardo, L., Piochi, M.,
- and Southon, J. (1999) The Agnano-Monte Spina eruption (4100 years BP) in the restless
- 649 Campi Flegrei caldera (Italy). Journal of Volcanology and Geothermal Research, 91, 269-301.
- 650 De Vivo, B., Rolandi, G., Gans, P.B., Calvert, A., Bohrson, W.A., Spera, F.J., and Belkin, H.E.
- (2001) New constraints on the pyroclastic eruptive history of the Campanian Volcanic Plain
- (Italy). Mineralogy and Petrology, 73, 47-65.
- Di Girolamo, P., Melluso, L., Morra, V., and Secchi, F.A.G. (1995) Evidence of interaction
- between mafic and differentiated magmas in the youngest phase of activity at Ischia island
- (Italy). Periodico di Mineralogia, 64, 393-411.
- 656 D'Orazio, M., Armienti, P., and Cerretini, S. (1998) Phenocryst/matrix trace-element partition
- 657 coefficients for hawaiite-trachyte lavas from the Ellittico volcanic sequence (Mt. Etna, Sicily,
- Italy). Mineralogy and Petrology, 64, 65-88.

- D'Oriano, C., Poggianti, E., Bertagnini, A., Cioni, R., Landi, P., Polacci, M., and Rosi, M. (2005)
- 660 Changes in eruptive style during the A.D. 1538 Monte Nuovo eruption (Phlegrean Fields,
- Italy): the role of syn-eruptive crystallization. Bulletin of Volcanology, 67, 601-621.
- 662 Ewart, A., and Griffin, W.L. (1994) Application of proton-microprobe data to trace-element
- partitioning in volcanic rocks. Chemical Geology, 117, 251-284.
- Fedele, L., Morra, V., Perrotta, A., and Scarpati, C. (2006) Volcanological and geochemical
 features of the products of the Fiumicello eruption, Procida island, Campi Flegrei (southern
- Italy). Periodico di Mineralogia, 75, 43-72.
- 667 Fedele, L., Scarpati, C., Lanphere, M., Melluso, L., Morra, V., Perrotta, A., and Ricci, G. (2008)
- The Breccia Museo formation, Campi Flegrei, southern Italy: geochronology, chemostratigraphy and relationship with the Campanian Ignimbrite eruption. Bulletin of Volcanology, 70, 1189-1219.
- Fedele, L., Zanetti, A., Morra, V., Lustrino, M., Melluso, L., and Vannucci, R. (2009) Insights on
 the clinopyroxene/liquid trace element partitioning in natural trachyte-trachyphonolite
 systems: an EMP/LA-ICP-MS case study from Campi Flegrei (southern Italy). Contributions
 to Mineralogy and Petrology, 158, 337-356.
- Fowler, S.J., Spera, F.J., Bohrson, W.A., Belkin, H.E., and De Vivo, B. (2007) Phase equilibria
 constraints on the chemical and physical evolution of the Campanian Ignimbrite. Journal of
 Petrology, 48, 459-493.
- Fulignati, P., Marianelli, M., Proto, M., and Sbrana, A. (2004) Evidences for disruption of a
- 679 crystallizing front in a magma chamber during caldera collapse: an example from the Breccia
- 680 Museo unit (Campanian Ignimbrite eruption, Italy). Journal of Volcanology and Geothermal
- 681 Research, 133, 141-155.

8/13

- 682 Ghiara, M.R., Lirer, L., and Munno, R. (1979) Mineralogy and geochemestry of the "low-
- 683 potassium series" of the Campania volcanics (South Italy). Chemical Geology, 26, 29-49.
- Icenhower, J., and London, D. (1996) Experimental partitioning of Rb, Cs, Sr and Ba between
 alkali feldspar and peraluminous melt. American Mineralogist, 81, 719-734.
- Icenhower, J.P., and London, D. (1997) Partitioning of flourine and chlorine between biotite and
- 687 granitic melt: experimental calibration at 200 MPa H₂O. Contributions to Mineralogy and
- 688 Petrology 127, 17-29.
- 689 Leeman, W.P., and Phelps, D.W. (1981) Partitioning of rare earths and other trace elements
- between sanidine and coexisting volcanic glass. Journal of Geophysical Research, 86, 1019310199.
- Lemarchand, F., Villemant, B., and Calas, G. (1987) Trace element distribution coefficients in
 alkaline series. Geochimica et Cosmochimica Acta, 51, 1071-1081.
- Lustrino, M., Duggen, S., and Rosenberg, C.L. (2011) The Central-Western Mediterranean:
- Anomalous igneous activity in an anomalous collisional tectonic setting. Earth-Science
 Reviews, 104, 1-40.
- 697 Macdonald, R., Bagiński, B., Dzierźanowski, P., and Jokubauskas P. (2013) Apatite-supergroup
- 698 minerals in UK Palaeogene granites: composition and relationship to host-rock composition.
- European Journal of Mineralogy, 25, 461-471.
- Mahood, G.A., and Hildreth, W. (1983) Large partition coefficients for trace elements in high-
- silica rhyolites. Geochimica et Cosmochimica Acta, 47, 11-30.
- Mahood, G.A., and Stimac, J.A. (1990) Trace-element partitioning in pantellerites and trachytes.
- Geochimica et Cosmochimica Acta, 54, 2257-2276.
- Mason, B.G., Pyle, D.M., and Oppenheimer, C. (2004) The size and frequency of the largest
- explosive eruptions on Earth. Bulletin of Volcanology, 66, 735-748.

- McDonough, W.F., and Sun, S.-s. (1995) The composition of the Earth. Chemical Geology, 120,
 223-253.
- Melluso, L., Morra, V., Perrotta, A., Scarpati, C., and Adabbo, M. (1995) The eruption of the Breccia Museo (Campi Flegrei, Italy): Fractional crystallization processes in a shallow, zoned magma chamber and implications for the eruptive dynamics. Journal of Volcanology and
- 711 Geothermal Research, 68, 325-339.
- 712 Melluso, L., de' Gennaro, R., Fedele, L., Franciosi, L., and Morra, V. (2012) Evidence of
- crystallization in residual, Cl-F-rich, agpaitic, trachyphonolitic magmas and primitive Mg-rich
- basalt-trachyphonolite interaction in the lava domes of the Phlegrean Fields (Italy). Geological
- 715 Magazine, 149, 532-550.
- 716 Miller, C., Zanetti, A., Thöni, M., and Konzett, J. (2007) Eclogitisation of gabbroic rocks:
- Redistribution of trace elements and Zr in rutile thermometry in an Eo-Alpine subduction zone
 (Eastern Alps). Chemical Geology, 239, 96-123.
- Morra, V., Calcaterra, D., Cappelletti, P., Colella, A., Fedele, L., de' Gennaro, R., Langella, A.,
- Mercurio, M., and de' Gennaro, M. (2010) Urban geology: relationships between geological
- setting and architectural heritage of the Neapolitan area. In M. Beltrando, A. Peccerillo, M.
- 722 Mattei, S. Conticelli, and C. Doglioni, Eds, Geology of Italy. Journal of the Virtual Explorer,
- 723 36, paper 26. doi:10.3809/jvirtex.2010.00261.
- Nagasawa, H. (1966) Trace element partition coefficient in ionic crystals. Science, 152, 769-771.
- Nagasawa, H. (1970) Rare earth concentrations in zircon and apatite and their host dacite and
- granites. Earth and Planetary Science Letters, 9, 359-364.
- 727 Nagasawa, H. (1973) Rare-earth distribution in alkali rocks from Oki-Dogo Island, Japan.
- Contributions to Mineralogy and Petrology, 39, 301-308.

- Nash, W.P., and Crecraft, H.R. (1985) Partition coefficients for trace elements in silicic magmas.
- Geochimica et Cosmochimica Acta, 49, 2309-2322.
- Nielsen, R.L., Forsythe, L.M., Gallahan, W.E., and Fisk, M.R. (1994) Major- and trace-element
 magnetite-melt equilibria. Chemical Geology, 117, 167-191.
- 733 Orsi, G., Civetta, L., D'Antonio, M., Di Girolamo, P., and Piochi, M. (1995) Step-filling and
- development of a three-layer magma chamber: the NYT case history. Journal of Volcanology
- and Geothermal Research, 67, 291-312.
- Pan, Y., and Fleet, M.E. (2002) Compositions of the apatite-group minerals: substitution
 mechanisms and controlling factors. Reviews in Mineralogy and Geochemistry, 48, 13-49.
- Pappalardo, L., Civetta, L., de Vita, S., Di Vito, M., Orsi, G., Carandente, A., and Fisher, R.V.
- (2002) Timing of magma extraction during the Campanian Ignimbrite eruption (Campi Flegrei
- Caldera). Journal of Volcanology and Geothermal Research, 114, 479-497.
- 741 Pappalardo, L., Ottolini, L., and Mastrolorenzo, G. (2008) The Campanian Ignimbrite (southern
- 742 Italy) geochemical zoning: insight on the generation of a super-eruption from catastrophic
- ⁷⁴³ differentiation and fast withdrawal. Contributions to Mineralogy and Petrology, 156, 1-26.
- 744 Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., and
- 745 Chenery, S.P. (1996) A compilation of new and published major and trace element data for

NIST SRM 610 and NIST SRM 612 glass reference materials. Geostandards Newsletter, 21,
115-144.

- Perrotta, A., and Scarpati, C. (1994) The dynamics of the Breccia Museo Eruption (Campi
 Flegrei Italy) and the significance of spatter clasts associated with lithic breccias. Journal of
- Volcanology and Geothermal Research, 59, 335-355.

- 751 Perrotta, A., Scarpati, C., Luongo, G., and Morra, V. (2006) The Campi Flegrei caldera boundary
- in the city of Naples. In B. De Vivo, Ed., Volcanism in the Campania Plain: Vesuvius, Campi
- Flegrei and Ignimbrites. Developments in Volcanology, 9, p 85-96. Elsevier, Amsterdam.
- Piochi, M., Civetta, L., and Orsi, G. (1999) Mingling in the magmatic system of Ischia (Italy) in
- the past 5 ka. Mineralogy and Petrology, 66, 227-258.
- Piochi, M., Mastrolorenzo, G., and Pappalardo, L. (2005) Magma ascent and eruptive processes
- from textural and compositional features of Monte Nuovo pyroclastic products, CampiFlegrei, Italy. Bulletin of Volcanology, 67, 663-678.
- Poli, S., Chiesa, S., Gillot, P.-Y., Gregnanin, A., and Guichard, F. (1987) Chemistry versus time
- in the volcanic complex of Ischia (Gulf of Naples, Italy): evidence of successive magmatic
- cycles. Contributions to Mineralogy and Petrology, 95, 322-335.
- Prowatke, S., and Klemme, S. (2006) Trace element partitioning between apatite and silicate
 melts. Geochimica et Cosmochimica Acta, 70, 4513-4527.
- Rieder, M., Cavazzini, G., D'yankonov, Y.S., Gottardi, G., Giggenheim, S., Koval, P.V., Müller,
- G., Neiva, A.M.R., Radoslovich, E.W., Robert, J.-L., Sassi, F.P., Takeda, H., Weiss, Z., and
- Wones, D.R. (1999) Nomencalture of the micas. Mineralogical Magazine, 63, 267-279.
- 767 Scarpati, C., Cole, P., and Perrotta, A. (1993) The Neapolitan Yellow Tuff A large volume
- multiphase eruption from Campi Flegrei, Southern Italy. Bulletin of Volcanology, 55, 343-356.
- Stormer, J.C. (1983) The effect of recalculation on estimates of temperature and oxygen fugacity
- from analyses of multicomponent iron-titanium oxides. American Mineralogist, 68, 586-594.
- 572 Streck, M.J., and Grunder, A.L. (1997) Compositional gradients and gaps in high-silica rhyolites
- of the Rattlesnake Tuff, Oregon. Journal of Petrology, 38, 133-163.

8/13

- Stix, J., and Gorton, M.P. (1990) Variations in trace element partition coefficients in sanidine in
- the Cerro Toledo Rhyolite, Jemez Mountains, New Mexico: Effects of composition,
 temperature and volatiles. Geochimica et Cosmochimica Acta, 54, 2697-2708.
- 777 Villemant, B. (1988) Trace element evolution in Phlegreaen Fields (central Italy): fractional
- crystallization and selective enrichment. Contributions to Mineralogy and Petrology, 98, 169-
- 183.
- Watson, E.B., and Green, T.H. (1981) Apatite/liquid partition coefficients for the rare earth
 elements and strontuim. Earth and Planetary Science Letters, 56, 405-421.
- 782 White, J.C. (2003) Trace-element partitioning between alkali feldspar and peralkalic quartz
- trachyte to rhyolite magma. Part II: Empirical equations for calculating trace-element partition
- coefficients of large-ion lithophile, high field-strength and rare-earth elements. American
 Mineralogist, 88, 330-337.
- White, J.C., Holt, G.S., Parker, D.F., and Ren, M. (2003) Trace-element partitioning between
 alkali feldspar and peralkalic quartz trachyte to rhyolite magma. Part I: Systematics of traceelement partitioning. American Mineralogist, 88, 316-329.
- 789 Wörner, G., Beusen, J.-M., Duchateau, N., Gijbels, R., and Schmincke, H.-U. (1983) Trace
- relement abundances and mineral/melt distribution coefficients in phonolites from Laacher See
- Volcano (Germany). Contributions to Mineralogy and Petrology, 84, 152-173.
- 792
- 793

Figure captions

Figure 1. Thin section microphotographs (plane polarized light) showing the most relevant petrographic features of the analyzed BM samples. a) phenocrysts/microphenocrysts of alkali feldspar (large crystal at the right), biotite (dark lamella at the left) plagioclase (small dusty individuals with corroded rims at the center and upper center) and clinopyroxene (small light

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798 grey crystals at the upper left) set in a glassy groundmass; b) phenocrysts of alkali feldspar (at the 799 left), biotite (light grey lamella at the center) plagioclase (dusty crystal with corroded rims at the 800 upper center), clinopyroxene (grey crystals at the right and lower right) and opaque oxides (black individual at the right) set in a glassy groundmass; c) phenocrysts of alkali feldspar (big crystal at 801 the right) and plagioclase (small dusty individuals with irregular rims at the left and lower left) 802 803 set in a vescicular glassy matrix; d) phenocrysts of alkali feldspar and plagioclase in a glassy 804 groundmass; e) phenocrysts/microphenocrysts of alkali feldspar (large crystal at the center), 805 plagioclase (tabular crystal at the left) and opaque oxides (black individuals at the lower left) in a 806 glassy groundmass; f) phenocrysts/microphenocrysts of alkali feldspar (large crystal at the left) and plagioclase (tabular crystals at the center and at the right) in a glassy groundmass. 807

Figure 2. Composition of plagioclase and alkali feldspar crystals from the analyzed BM 808 trachytes and trachyphonolites. Small black symbols are for feldspars from the Campi Flegrei 809 district literature (CF; Armienti et al. 1983; Beccaluva et al. 1990; Civetta et al. 1997; de Vita et 810 al. 1999; D'Antonio and Di Girolamo 1994; D'Oriano et al. 2005; Fedele et al. 2006, 2008; 811 Fowler et al. 2007; Melluso et al. 1995, 2012; Orsi et al. 1995; Pappalardo et al. 2002, 2008; 812 Piochi et al. 2005) equilibrated with melts of various compositions. The inset at the upper right 813 814 shows the composition of the investigated BM whole rock samples (with sample labels in italics) according to R_1R_2 classification (De La Roche et al. 1980). 815

Figure 3. Primitive mantle-normalized [after McDonough and Sun (1995)] trace-element abundances for the analyzed plagioclase (Na- and Ca-rich terms, see text), alkali feldspar and associated glass from the investigated BM trachyte samples AI (a), AN (b) and C (c).

Figure 4. Primitive mantle-normalized [after McDonough and Sun (1995)] trace-element abundances for the analyzed plagioclase (Na- and Ca-rich varieties, see text), alkali feldspar and associated glass from the investigated BM trachyphonolite samples B (a), I (b) and R (c).

Figure 5. a) $Fe^{2+}+Mn+Mg-Ti-Fe^{3+}$ classification diagram for the opaque oxides from the 822 analyzed BM trachytes and trachyphonolites. Smaller symbols are literature data for Campi 823 824 Flegrei trachytes-phonolites (black dots; Armienti et al. 1983, Melluso et al. 1995, 2012, Orsi et 825 al. 1995, Civetta et al. 1997, Pappalardo et al. 2002, 2008, Fedele et al. 2008) and for Ischia latites-trachytes (crosses; Piochi et al. 1999). b) Mg-Al-Fe+Mn classification diagram for the 826 827 biotite crystals from the analyzed BM trachytes. Smaller symbols are literature data for Campi Flegrei trachytes-phonolites (Armienti et al. 1983, Melluso et al. 1995, 2012, Orsi et al. 1995, 828 Civetta et al. 1997, Fulignati et al. 2004, Fedele et al. 2008, Pappalardo et al. 2008) and for Ischia 829 trachytes-phonolites (Ghiara et al. 1979, Poli et al. 1987, Di Girolamo et al. 1995, Piochi et al. 830 1999). c) Ca+P vs. Si+REE diagram for the apatite crystals from the analyzed BM 831 trachyphonolites. Smaller symbols are literature data for Campi Flegrei trachytes-phonolites 832 (Fulignati et al. 2004; Fedele et al. 2008; Melluso et al. 2012; authors' unpublished data). 833

Figure 6. Primitive mantle-normalized [after McDonough and Sun (1995)] trace-element abundances for the analyzed Ti-magnetite and associated glass from the investigated BM trachytes (a and b) and trachyphonolites (c).

Figure 7. Primitive mantle-normalized [after McDonough and Sun (1995)] trace-element abundances for the analyzed biotite (a), apatite (b) and associated glasses from the investigated BM trachytes and trachyphonolites (respectively).

Figure 8. a) Calculated ${}^{Min/L}D$ values for trace-elements for plagioclase from the investigated BM trachyphonolites. b) ${}^{Min/L}D$ values for trace-elements calculated applying the model of Bédard (2006) to analyzed plagioclase crystals and coexisting glasses. It is to note that for Eu and Ta the regression equation used is based on the MgO content of the host melt, rather than on plagioclase An content.

- Figure 9. Calculated ^{*Min/L*}D values for trace-elements for alkali feldspar from the investigated
- 846 BM trachytes and trachyphonolites.
- Figure 10. Calculated $^{Min/L}D$ values for trace-elements for Ti-magnetite (a), biotite and apatite
- (b) from the investigated BM trachytes and trachyphonolites.

rock	AI	(T)	AN	(T)	C ((T)	В (Гр)	Ι (Τ	p)	R (*	Гр)
	n =	9, 9	n =	7,7	n =	0,4	n = -	4, 4	n = 4	4, 6	n =	1,3
	Average	S.Dev.										
SiO_2	60.8	0.44	61.3	0.42	na		60.4	0.33	60.6	0.34	61.8	
TiO ₂ (EMP)	0.39	0.07	0.40	0.03	na		0.46	0.03	0.49	0.04	0.43	
Al_2O_3	18.6	0.13	18.9	0.17	na		19.3	0.46	19.5	0.33	17.6	
Cr ₂ O ₃	0.04	0.02	0.04	0.00	na		0.05	0.00	0.00	0.00	0.00	
FeO	3.35	0.26	3.18	0.09	na		3.03	0.08	2.99	0.04	3.33	
MnO	0.15	0.06	0.10	0.02	na		0.26	0.02	0.27	0.08	0.27	
MgO	0.68	0.08	0.64	0.02	na		0.32	0.04	0.43	0.08	0.50	
CaO	2.34	0.23	2.40	0.10	na		1.70	0.05	1.81	0.24	2.42	
Na ₂ O	3.63	0.61	3.44	0.27	na		6.09	0.17	6.16	0.14	5.23	
K ₂ O	8.80	0.41	8.95	0.34	na		6.89	0.05	6.81	0.23	7.40	
BaO	0.10	0.05	0.13	0.04	na		bdl	bdl	0.01	0.01	0.00	
F	0.14	0.03	na		na		0.41	bdl	0.43	0.00	na	
SO_3	0.17	0.07	na		na		0.05	bdl	0.07	0.00	na	
Cl	0.20	0.18	0.44	0.06	na		0.78	0.41	0.79	0.42	0.32	
Sum	99.2	0.45	99.8	0.29			99.3	0.84	100.0	0.43	99.3	
Mg#	0.26	0.01	0.26	0.00			0.15	0.01	0.19	0.03	0.20	
P.I.	0.83	0.06	0.81	0.04			0.91	0.04	0.90	0.04	0.94	
Sc	6	0.5	5	0.2	5	0.5	5	0.3	4	0.3	4	0.2
V	43	11.8	45	1.5	57	2.7	14	0.5	15	1.0	16	2.9
TiO ₂ (ICP)	0.32	0.03	0.32	0.01	0.34	0.02	0.36	0.02	0.37	0.01	0.43	0.07
Rb	298	42.6	279	16.5	276	21.6	453	28.4	451	16.8	496	23.0
Sr	388	172	360	24	529	73	20	1	25	8	21	3
Y	28	8.9	25	1.3	23	1.4	71	4.3	66	3.9	63	9.3
Zr	296	135	232	9	202	11	853	26	809	53	935	197
Nb	50	24.6	37	1.8	32	1.7	134	5.9	137	10.5	145	32.8
Cs	13	4.9	13	0.6	12	1.2	32	2.3	31	2.1	46	4.3
Ba	418	257	236	14	574	117	13	1	18	4	15	3
La	65	24	55	3	49	5	152	9	148	8	146	12
Ce	120	49	97	7	84	9	270	17	271	23	285	35
Pr	12	4.2	10	0.9	9	1.3	25	1.2	26	1.9	27	3.1
Nd	45	14	40	4	37	4	84	2	92	8	96	9
Sm	7.9	2.1	7.7	0.9	7.2	1.0	14.5	0.5	15.6	1.1	17.8	2.0
Eu	1.84	0.31	2.30	0.23	2.52	0.28	1.32	0.06	1.48	0.15	1.26	0.15

Table 1. Average major (EMP, in wt%) and trace element (LA-ICP-HRMS, in ppm) analyses for representative glass from the selected trachytic (T) and trachyphonolitic (Tp) Campi Flegrei BM samples (data from Fedele et al. 2009)

Gd	6.4	1.3	6.1	0.7	5.8	0.5	12.6	1.0	12.7	0.9	13.4	1.7
Tb	0.94	0.15	0.81	0.06	0.76	0.09	1.90	0.16	1.93	0.14	1.76	0.17
Dy	5.7	1.5	4.8	0.6	4.4	0.6	12.6	1.6	12.0	1.0	12.2	1.3
Но	1.06	0.27	0.92	0.09	0.85	0.06	2.38	0.23	2.28	0.24	2.49	0.34
Er	2.99	0.99	2.53	0.20	2.34	0.14	6.93	0.51	6.94	0.57	7.34	1.34
Tm	0.43	0.14	0.37	0.05	0.37	0.03	1.02	0.02	1.00	0.08	1.12	0.23
Yb	3.1	1.0	2.4	0.2	2.3	0.3	7.0	0.3	6.8	0.5	8.4	2.1
Lu	0.45	0.16	0.36	0.04	0.33	0.07	1.02	0.02	1.04	0.07	1.15	0.13
Hf	6.6	2.8	5.1	0.5	4.9	0.5	16.5	0.7	16.0	1.1	19.4	3.8
Та	2.4	1.1	1.8	0.1	1.6	0.2	6.3	0.3	6.1	0.3	7.2	1.6
Pb	42.6	5.4	39.9	3.3	38.0	3.8	62.8	3.2	63.2	3.4	84.3	5.1
Th	21.8	10.1	16.8	1.2	15.7	1.7	59.9	1.4	61.1	3.3	67.6	10.1
U	7.6	3.9	5.7	0.4	4.7	0.6	18.5	0.8	19.2	0.9	18.7	2.0

Notes: S.Dev. = standard deviation; n = number of analyses (reported for major and trace elements, separated with a comma); Mg# = molar [Mg/(Mg+Fe+Mn)]. P.I. = molar (Na+K)/Al. bdl = below detection limits; na = not analyzed.

rock		AI (Tr	achyte)			AN (T	rachyte)			C (Tra	achyte)			В	(Trachy	ohonolite	e)		I (Ti	rachyphon	olite)		R (Trachyp	honolite)	1
phase	Ca	a-Pl]	Kfs	С	a-Pl	I	Kfs	С	a-Pl]	Kfs	N	a-Pl	C	a-Pl]	Kfs	Na-Pl	ŀ	Kfs	N	a-Pl	K	ſs
	n	= 9	n	= 4	n	= 6	n	= 4	n	= 6	n	= 4	n	= 3	n	= 5	n	= 3		n	= 3	n	= 6	n	= 2
	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.		Av.	S.Dev.	Av.	S.Dev.	Av.	S.Dev.
SiO ₂	46.3	0.75	63.6	0.28	46.5	0.64	64.8	0.57	46.2	0.66	64.1	1.26	60.1	0.57	46.0	0.34	64.5	0.23	60.0	65.0	0.19	61.1	0.62	65.9	0.02
Al_2O_3	33.8	0.48	19.2	0.15	32.9	0.40	18.8	0.25	33.1	0.43	18.9	0.25	24.2	0.11	33.8	0.22	19.3	0.10	24.7	19.4	0.37	23.7	0.28	19.0	0.06
FeO _{tot}	0.66	0.07	0.19	0.06	0.68	0.07	0.20	0.04	0.69	0.06	0.25	0.03	0.42	0.03	0.67	0.03	0.27	0.04	0.37	0.22	0.05	0.41	0.04	0.28	0.02
CaO	16.7	0.59	0.50	0.12	16.2	0.76	0.49	0.07	17.1	0.67	0.44	0.04	5.69	0.28	16.8	0.24	0.68	0.12	6.04	0.68	0.03	6.13	0.42	0.76	0.10
Na ₂ O	1.53	0.20	1.59	0.16	1.78	0.24	1.54	0.04	1.46	0.19	1.27	0.05	6.97	0.15	1.54	0.10	3.97	0.18	6.95	3.86	0.10	6.88	0.17	4.03	0.09
K ₂ O	0.32	0.19	13.6	0.24	0.31	0.07	13.7	0.23	0.35	0.09	13.7	0.24	1.87	0.11	0.13	0.03	10.4	0.33	1.83	10.4	0.12	1.80	0.17	10.1	0.28
BaO	0.08	0.02	0.46	0.28	0.07	0.03	0.08	0.02	0.12	0.07	0.62	0.49	0.03	0.01	0.10	0.09	0.05	0.01	bdl	0.04	0.02	0.02	0.00	0.15	0.00
SrO	0.16	0.08	bdl		0.22	0.11	0.21	0.08	0.36	0.10	0.08	0.02	bdl		0.23	0.06	bdl		bdl	bdl		0.08	0.00	0.06	0.00
	99.5	0.36	99.2	0.30	98.7	0.96	99.7	0.40	99.4	0.51	99.3	0.51	99.3	0.45	99.2	0.24	99.2	0.23	99.8	99.5	0.47	100	0.44	100	0.11
Si	2.14	0.03	2.95	0.00	2.17	0.02	3 00	0.02	2.15	0.02	2.99	0.04	2.71	0.01	2.14	0.01	2.95	0.01	2.69	2.97	0.02	2.74	0.03	3 00	0.00
Al	1.84	0.03	1.05	0.00	1.81	0.02	1.02	0.01	1.81	0.03	1.04	0.02	1.28	0.01	1.85	0.01	1.04	0.01	1 30	1.04	0.01	1.25	0.01	1.02	0.00
Fe	0.03	0.00	0.01	0.00	0.03	0.00	0.01	0.00	0.03	0.00	0.01	0.00	0.02	0.00	0.03	0.00	0.01	0.00	0.01	0.01	0.00	0.02	0.00	0.01	0.00
Ca	0.83	0.03	0.03	0.01	0.81	0.04	0.02	0.00	0.85	0.03	0.02	0.00	0.27	0.01	0.83	0.01	0.03	0.01	0.29	0.03	0.00	0.29	0.02	0.04	0.00
Na	0.14	0.02	0.14	0.01	0.16	0.02	0.14	0.00	0.13	0.02	0.11	0.00	0.61	0.01	0.14	0.01	0.35	0.02	0.60	0.34	0.01	0.60	0.01	0.36	0.01
K	0.02	0.01	0.81	0.02	0.02	0.00	0.81	0.01	0.02	0.01	0.82	0.02	0.11	0.01	0.01	0.00	0.61	0.02	0.10	0.60	0.01	0.10	0.01	0.58	0.02
Ba	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	5.00		5.00		5.00		5.00		5.00		5.00		5.00		5.00		5.00		5.00	5.00		5.00		5.00	
Ab%	14.3	1.87	14.6	1.46	16.8	2.33	14.6	0.06	13.9	1.72	12.1	0.31	61.4	0.96	14.7	0.99	35.5	1.52	60.5	34.9	0.45	60.1	0.98	36.4	0.94
Or%	1.94	1.22	82.9	1.93	1.95	0.38	82.9	0.36	2.21	0.51	85.6	0.40	10.9	0.55	0.89	0.28	61.2	2.08	10.5	61.7	0.58	10.3	1.17	59.8	1.42
An%	83.8	2.80	2.54	0.61	81.3	2.65	2.49	0.36	83.9	2.13	2.30	0.17	27.7	1.51	84.4	1.18	3.33	0.60	29.0	3.41	0.14	29.5	1.65	3.77	0.48
Notes: S.	Dev. = s	standard	deviatio	n; n = nu	mber of	analyses	; Ab% =	albitite a	mol%; (Or% = ort	hoclase	e mol%; A	n% = and	orthite mo	l%. bdl :	= below	detectio	n limits.							

Table 2. Average (Av.) major element concentrations (EMP, in wt%) and calculated structural formulae (apfu, atoms per formula unit, on 8 oxygens and 5 cations) for representative plagioclase (Ca-Pl and Na-Pl) and alkali feldspar (Kfs) crystals from the selected trachytic (T) and trachyphonolitic (Tp) Campi Flegrei BM samples. The full dataset is reported in the Electronic Appendix

Table 3. Average (Av.) trace element compositions (LA-ICP-HRMS, in ppm) for representative plagioclase (Ca-Pl and Na-Pl) and alkali feldspar (Kfs) crystals from the selected trachytic (T) and trachyphonolitic (Tp) Campi Flegrei BM samples. The full dataset is reported in the Electronic Appendix

rock	AI	(Trachy	/te)		AN (Tra	achyte)			C (Tra	chyte)		В	(Trachyp	ohonoli	te)	I (Trachyp	phonolite)	R	(Trachy	phonoli	ite)
phase	Ca-Pl	K	ſfs	Ca	-Pl	K	Kfs	Са	a-Pl	K	ſs	Na-Pl	Ca-Pl	ŀ	Kfs	Na-Pl	Kfs	N	a-Pl	K	Kfs
		n	= 2	n =	= 2	n	= 3	n	= 4	n	= 2			n	= 2			n	= 3	n	= 2
		Av.	S.Dev	Av.	S.Dev	Av.	S.Dev	Av.	S.Dev	Av.	S.Dev			Av.	S.Dev			Av.	S.Dev	Av.	S.Dev
Sc	1.7	2.6	0.4	bdl		1.7	0.0	0.8	0.0	0.9	0.0	2.3	1.4	2.5	0.6	1.9	2.1	bdl		bdl	
V	bdl	bdl		bdl		bdl		2.6	1.6	bdl		bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Ti	55.2	208	37.5	57.8	0.18	340	83.3	103	44.5	221	18.5	181	49.0	291	9.19	172	291	178	2.94	289	5.78
Rb	1.2	200	22.6	0.8	0.1	212	12.4	6.9	5.9	170	26.6	11.7	b.d.l.	251	8.2	10.9	269	11.9	1.0	250	11.4
Sr	2420	1140	29.9	2550	93.7	814	360	2780	253	1810	231	303	2220	173	15.3	238	188	199	17.5	183	2.2
Y	0.40	0.04	0.00	0.45	0.00	bdl		0.76	0.48	0.11	0.00	0.19	0.29	bdl		0.28	bdl	0.20	0.04	bdl	
Zr	0.46	b.d.l.		0.38	0.00	bdl		4.09	4.12	bdl		bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Nb	0.18	0.04	0.02	0.08	0.00	bdl		0.82	0.91	bdl		bdl	bdl	bdl		bdl	bdl	0.07	0.03	0.14	0.00
Cs	bdl	0.72	0.03	bdl		0.97	0.03	0.47	0.31	0.77	0.11	bdl	bdl	1.22	0.06	bdl	1.03	bdl		1.19	0.06
Ba	101	2930	1530	122	10.8	664	481	186	19.6	6340	3920	34.4	115	289	18.5	27.5	282	28.1	2.8	310	0.3
La	12.2	2.75	1.44	11.41	0.29	4.63	0.70	10	2.62	1.66	0.34	25.4	7.89	7.94	0.52	29.50	9.12	27.8	1.69	7.98	0.20
Ce	16.7	1.85	1.05	15.80	0.14	2.94	0.48	14	3.40	1.06	0.28	26.1	10.8	4.94	0.48	31.73	6.31	29.1	1.97	5.53	0.15
Pr	1.30	0.10	0.04	1.31	0.11	0.18	0.04	1.36	0.33	0.08	0.02	1.61	0.98	0.28	0.03	2.19	0.33	1.89	0.04	0.28	0.01
Nd	3.99	0.16	0.07	4.55	0.18	0.31	0.11	4.80	1.21	0.13	0.05	4.30	3.06	0.38	0.02	5.86	0.65	5.58	0.44	0.46	0.02
Sm	0.50	0.05	0.01	0.48	0.11	bdl		0.61	0.14	0.03	0.00	0.33	0.43	0.04	0.00	0.44	0.08	0.30	0.02	bdl	
Eu	1.37	1.37	0.32	1.64	0.12	2.39	0.22	1.53	0.02	1.40	0.21	1.50	1.14	1.65	0.17	1.81	1.91	1.74	0.17	1.73	0.07
Gd	0.37	bdl		0.35	0.00	bdl		0.50	0.10	bdl		0.35	0.21	bdl		bdl	bdl	bdl		bdl	
Tb	bdl	bdl		0.02	0.00	bdl		0.05	0.02	bdl		bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Dy	bdl	bdl		bdl		bdl		0.23	0.12	bdl		bdl	0.20	bdl		0.17	bdl	bdl		bdl	
Но	bdl	bdl		bdl		bdl		0.04	0.02	bdl		bdl	0.01	bdl		bdl	bdl	bdl		bdl	
Er	bdl	bdl		bdl		bdl		0.13	0.00	bdl		bdl	bdl	bdl		0.06	bdl	bdl		bdl	
Tm	bdl	bdl		bdl		bdl		bdl		bdl		bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Yb	bdl	bdl		bdl		bdl		bdl		bdl		0.01	bdl	bdl		bdl	bdl	bdl		bdl	
Lu	bdl	bdl		bdl		bdl		bdl		bdl		bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Hf	bdl	bdl		bdl		bdl		0.28	0.00	0.03	0.00	bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Та	bdl	0.03		bdl		bdl		0.12	0.00	bdl		bdl	bdl	bdl		bdl	bdl	bdl		bdl	
Pb	5.84	16.3	2.34	5.89	0.14	22.7	0.96	5.97	0.76	14.4	2.46	15.1	5.19	26.2	0.03	15.3	28.2	17.2	0.78	29.0	0.52
Th	0.06	bdl		0.03	0.00	bdl		0.35	0.37	bdl		bdl	bdl	bdl		0.01	bdl	bdl		bdl	
U	0.01	bdl		0.01	0.00	bdl		0.12	0.13	bdl		0.01	bdl	bdl		bdl	bdl	bdl		0.01	0.00

Notes: S.Dev. = standard deviation; n = number of analyses; bdl = below detection limits.

rock	AI (T)	AN (T)	I (Tp)		AI	(T)		I (Tp)
sample	AI-2-MAGN18-3	AN-2-MAGN 10-2	I-5-MAGN22-9		AI-1-BIOT14-10	AI-3-BIOT36-12		I-5-APAT22-3
phase	Mt	Mt	Mt		Bt	Bt		Ap
TiO ₂	5.78	5.68	9.50	SiO_2	36.4	36.3	SiO_2	1.03
Al_2O_3	4.43	3.88	1.93	TiO ₂	4.83	4.87	FeO _{tot}	0.28
FeO _{tot}	79.4	80.3	80.3	Al_2O_3	14.5	14.9	CaO	52.0
MnO	0.56	0.58	1.96	Cr_2O_3	0.01	0.00	F	3.83
MgO	2.74	2.42	1.49	FeO _{tot}	13.9	14.2	P_2O_5	42.5
	92.9	92.8	95.2	MnO	0.17	0.23		99.7
				MgO	15.9	15.7	O=F	1.61
Fe_2O_3	52.8	53.5	49.3	CaO	0.01	0.02	Tot	98.1
FeO	31.8	32.1	36.0	K_2O	9.22	9.29		
Usp%	17.4	17.0	26.6	Na ₂ O	0.31	0.25	T site (6	cations)
				BaO	0.29	0.62	Si	0.17
Si	0.00	0.00	0.00	Cl	0.08	bdl	Р	5.83
Ti	0.16	0.16	0.27	SrO	bdl	0.17	M1+M2	sites (10 cations)
Al	0.19	0.17	0.08		95.7	96.5	Ca	9.96
Fe ⁺³	1.48	1.51	1.38				Fe	0.04
Fe ⁺²	0.99	1.01	1.12	Mg#	0.67	0.66		
Mn	0.02	0.02	0.06					
Mg	0.15	0.14	0.08	Si	5.42	5.38		
				Ti	0.54	0.54		
				Al ^{IV}	2.04	2.08		
				Al^{VI}	0.52	0.54		
				Mg	3.52	3.48		
				Fe	1.73	1.76		
				Mn	0.02	0.03		
				\square_{M1}	0.20	0.20		
				Κ	1.75	1.76		
				Na	0.09	0.07		
				$\Box_{\mathbf{A}}$	0.16	0.17		

Table 4. Major element concentrations (EMP, in wt%) and calculated structural formulae (in apfu, atoms per formula unit) for representative Ti-magnetite (Mt, 3 cations and 4 oxygens basis), biotite and (Bt and Ap, 16 cations and 24 oxygens) from the selected trachytic (T) and trachyphonolitic (Tp) Campi Flegrei BM samples

Notes: FeO and Fe₂O₃ in Ti-magnetite calculated following Carmichael (1967). Ulvöspinel mol% (Usp%) calculated according to Stormer (1983). \Box A and \Box M1 for the biotite are the vacancies in the dodecahedral site A and in the octahedral site M1. St.Dev. = standard deviation; n = number of analyses; Mg# = molar Mg/(Fetot+Mg+Mn). bdl = below detection limits.

Table 5. Trace element compositions (LA-ICP-HRMS, in ppm) for re-	epresentative Ti-magnetite (Mt	t), biotite (Bt) and apatite (A	Ap) from the selected
trachytic (T) and trachyphonolitic (Tp) Campi Flegrei BM samples			

rock		AI (T)		AN (T)	I (7	Гр)
sample	AI-2-MAGN18-3	AI-1-BIOT14-10	AI-3-BIOT36-12	AN-2-MAGN 10-2	I-5-MAGN22-9	I-5-APAT22-3
phase	Mt	Bt	Bt	Mt	Mt	Ар
Sc	9.3	12.2	13.0	8.4	4.3	bdl
V	2400	426	486	1960	823	29.8
Cr	113	15.4	13.9	157	50.8	bdl
Rb	bdl	307	294	bdl	bdl	bdl
Sr	bdl	68.8	95.3	bdl	bdl	81.0
Y	0.11	0.07	0.20	0.31	0.25	1490
Zr	21.9	21.5	22.1	23.9	69.3	bdl
Nb	8.5	47.6	40.9	10.3	50.6	bdl
Cs	bdl	3.22	3.29	bdl	bdl	bdl
Ва	bdl	2900	5270	bdl	bdl	8.02
La	bdl	bdl	bdl	bdl	bdl	3630
Ce	bdl	bdl	bdl	bdl	bdl	7330
Pr	bdl	bdl	bdl	bdl	bdl	879
Nd	bdl	bdl	bdl	bdl	bdl	3570
Sm	bdl	bdl	bdl	bdl	bdl	518
Eu	bdl	bdl	bdl	bdl	bdl	43.4
Gd	bdl	bdl	bdl	bdl	bdl	412
Tb	bdl	bdl	bdl	bdl	bdl	47.7
Dy	bdl	bdl	bdl	bdl	bdl	273
Но	bdl	bdl	bdl	bdl	bdl	48.6
Er	bdl	bdl	bdl	bdl	bdl	117
Tm	bdl	bdl	bdl	bdl	bdl	13.1
Yb	bdl	bdl	bdl	bdl	0.06	65.2
Lu	bdl	bdl	bdl	bdl	bdl	8.08
Hf	0.56	0.57	0.62	0.66	2.10	bdl
Та	0.44	1.85	1.68	0.46	2.21	bdl
Pb	bdl	1.85	2.39	bdl	0.59	13.7
Th	bdl	bdl	0.03	0.05	0.01	110
U	0.01	0.03	0.03	0.02	0.04	14.4

Notes: St.Dev. = standard deviation; n = number of analyses; bdl = below detection limits.

1 4010 0.	Culturated	D values i	of the sele	eteu Divi tit	renyphonon				
		Pl/Tp			Feld/T	Feld/Tp	Pl/T	Pl/Tp	Pl/Ph
sample	В	Ι	R		Vil	1988	Pap	2008	Wo1983
Rb	0.03	0.02	0.02		0.7-0.97	0.52			0.018-0.052
Ва	2.6	1.5	1.8		1.13-16.6	9.50	0.05	0.90	1.725-7.33
Th	0.0001	0.0002			0.01-0.03	0.01			0.001-0.008
U	0.0007				0.01-0.03	0.01			
La	0.17	0.20	0.19		0.08-0.10	0.09	0.40	0.18	0.251-0.343
Ce	0.10	0.12	0.10				0.20	0.10	0.129-0.212
Pb	0.24	0.24	0.20						
Sr	15	9.5	9.5		2-6.6		1.40	7.80	11.66-49.8
Pr	0.065	0.086	0.069						
Nd	0.051	0.064	0.058				0.15	0.05	0.055-0.168
Sm	0.023	0.028	0.017				0.08	0.02	0.080-0.130
Eu	1.1	1.2	1.4		0.85-1.06	1.17	0.90	0.80	0.991-2.178
Gd	0.03								
Ti	0.08	0.08	0.07						
Dy		0.01							
Ŷ	0.003	0.004	0.003						
Er		0.01							
Yb	0.001								0.003-0.009
Sc	0.48	0.42			0.03-0.07	0.26			0.015-0.055
		Pl/NaT			Pl/Rhy		Pl/	hsR	
	Nag1973	Lem1987	D'O1998	N&C1985	B&D1988	I&L1996	E&G1994	S&G1997	
Rb		0.06	0.074	0.06-0.19	0.30	0.07-0.76	0.011-0.029	0.13-0.34	
Ba	0.265-3.40		0.78	0.56-3.3	0.48	1.07-18.38	1.00-1.8	6.95-19.55	
Th		0.01	0.010	0.03-0.08	0.01			0.03	
U		0.01	0.018	0.05-0.13					
La		0.05	0.21	0.30-0.45	0.30			0.070-0.17	
Ce	0.0115-0.223		0.13	0.21-0.34	0.22			0.032-0.104	
Pb			0.27	0.42-2.2			0.35-0.97		
Sr	0.94-3.18		4.2	6.8-33	4.40	7.96-23.05	4.04-12.2	10.5-13.1	
Pr	0.0078-0.219		0.100						
Nd			0.080	0.14-0.29	0.19				
Sm			0.046	0.11-0.23	0.12			0.008-0.019	
Eu	1.52-2.35	0.27	0.65	3.8-7.9	2.00			3.75-5.62	
Gd									
Ti									
Dy	0.043-0.220		0.021	0.07-0.18					
Y			0.021	0.04-0.21			0.022-0.084		
Er	0.037-0.219		0.017						
Yb	0.037-0.227		0.021	0.06-0.13	0.10			0.012-0.026	
Sc		0.01		0.02-0.06	0.01				

Table 6. Calculated $^{P/L}D$ values for the selected BM trachyphonolites (Pl/Tp)

Notes: Also shown are literature data for Campi Flegrei trachytes (Pl/T) and trachyphonolites (from Vil1988 = Villemant 1988 and Pap2008 = Pappalardo et al. 2008), for phonolites (Pl/Ph; from Wo1983 = Wörner et al. 1983), sodic trachytes (Pl/NaT; from Nag1973 = Nagasawa 1973, Lem1987 = Lemarchand et al. 1987 and D'O1998 = D'Orazio et al. 1998), rhyolites (Pl/Rhy; from N&C1985 = Nash and Crecraft 1985, B&D1988 = Bacon and Druitt 1988 and I&L1996 = Icenhower and London 1996) and high-silica rhyolites (Pl/hsR; from E&G1994 = Ewart and Griffin 1994 and S&G1997 = Streck and Grunder 1997). Data from Villemant (1988) refer to feldspar/liquid equilibria (Feld/T and Feld/Tp), not taking into account whether plagioclase or alkali feldspar.

Table 7.	Calculated Kfs/L I	D values for the	selected BM	trachytes (K	(Ifs/T) and tr	achyphonolites	s (Kfs/Tp)						
		Kfs/T			Kfs/Tp	••		Feld/T	Feld/Tp	Kfs/T	Kfs/Tp	Kfs/T	Kfs/Ph
sample	AI	AN	AN	В	Ι	R		Vil1	988	Pap2	2008	Wh2003	Wo1983
Cs	0.07	0.08	0.07	0.04	0.03	0.03		0.08-0.12	0.04			0.04	
Rb	0.81	0.78	0.70	0.55	0.60	0.50		0.7-0.97	0.52			0.24-0.37	0.55-1.25
Ba	2.8	2.5	5.4	21	16	20		1.13-16.6	9.50	0.3-13	7.70	1.11-12.74	0.36-9.36
U				0.0001		0.0004		0.01-0.03	0.01				
Nb	0.002					0.001						0.03	
Та								0.01-0.03					0.008-0.009
La	0.08	0.10	0.07	0.05	0.06	0.05		0.08-0.10	0.09	0.13	0.05	0.03-0.06	0.058-0.132
Ce	0.03	0.04	0.03	0.02	0.02	0.02				0.04	0.02	0.02-0.06	0.009-0.050
Pb	0.47	0.57	0.54	0.42	0.45	0.34							
Sr	2.5	2.8	3.1	8.8	7.5	8.7		2-6.6		2.00	7.10	0.45-4.81	3.21-8.17
Pr	0.014	0.022	0.016	0.011	0.013	0.010						0.01-0.04	
Nd	0.006	0.012	0.006	0.004	0.007	0.005				0.01	0.005	0.01-0.04	0.090-0.130
Sm	0.009			0.003	0.005							0.01-0.04	0.004-0.015
Eu	0.87	1.2	0.93	1.2	1.3	1.4		0.85-1.06	1.17	0.90	0.80	2.04-2.10	0.46-0.991
Ti	0.13	0.24	0.13	0.13	0.13	0.11							
Y												0.01-0.06	
Sc	0.54	0.35		0.53	0.47			0.03-0.07	0.26				0.016-0.20
	Kfs/NaT	Kfs/Pnt	Kfs/Pnt	Kfs/Com		Kfs/Rhy		Kfs/	hsR				
	M&S	\$1990	Wh	2003	L&P1981	M&H1983	N&C1985	S&G1990	E&G1994				
Cs	0.0075-0.013	0.0004-0.0036	0.04-0.24	0.04-0.30	0.024	0.009-0.61	0.11-0.37	0.002-0.61					
Rb	0.11-0.26	0.25	0.21-0.37	0.22-0.51	0.4	0.31-0.74	1.2-2.4	0.28-0.74	0.11-0.72				
Ba	5.2-5.9	1.2-1.6	1.87-12.22	0.66-10.35	22	1.00-6.7	4.9-24	1.0-44	2.7-20.9				
U						0.008-0.037	0.04-0.07	0.002-0.037					
Nb			0.01-0.04	0.01-0.14					0.039-0.16				
Та					0.015	0.0045-0.029	0.001-0.02	0.0007-0.029					
La	0.042-0.0707	0.0007-0.0018	0.01-0.09	0.05-0.16	0.129	0.037-0.111	0.07-0.10	0.026-0.15					
Ce	0.0024-0.0349	0.0005-0.0018	0.01-0.06	0.05-0.14	0.065	0.031-0.095	0.02-0.06	0.017-0.095					
Pb			1.00	0.22			0.99-4.1		0.10-1.4				
Sr	3.6-10	0.9-1.24	0.40-4.06	0.53-2.79			4.5-7.3	2-6	2.11-22.1				
Pr			0.01-0.07	0.05-0.14									
Nd			0.02-0.07	0.05-0.12	0.054	0.013-0.093	0.03-0.04	0.009-0.093					
Sm	0.0018-0.0086	0.0004-0.0018	0.02-0.10	0.05-0.09	0.026	0.014-0.0458	0.03-0.04	0.0024-0.046					
Eu	0.439-2.50	0.0238-0.049	0.05-0.24	0.60-2.16	9.06	2-3.5	3.3-6.5	1.6-9.6					
Ti													
Y									0.015-0.067				
Sc	0.0051-0.0063	0.0067-0.0094			0.029	0.024-0.059	0.01-0.04						

Notes: Also shown are literature data for Campi Flegrei trachytes and trachyphonolites, for trachytes, phonolites (Kfs/Ph), sodic trachytes (Kfs/NaT), pantellerites (Kfs/Pnt), comendites (Kfs/Com), rhyolites (Pl/Rhy) and high-silica rhyolites (Pl/hsR). L&P1981 = Leeman and Phelps 1981. M&H1983 = Mahoood and Hildreth 1983. M&S1990 = Mahood and Stimac 1990. S&G1990 = Stix and Gorton 1990. Wh2003 = White et al. 2003. Other abbreviations as in Table 6 caption. Data from Villemant (1988) refer to feldspar/liquid equilibria (Feld/T and Feld/Tp), not taking into account whether plagioclase or alkali feldspar.

Table 8.	Calculat	ed Mt/L D	values fo	or the selected	l BM trac	chytes (Mt/T) a	nd trachypł	nonolites (M	t/Tp)			
	M	t/T	Mt/Tp	Mt/T	Mt/Tp	Mt/Ph	Mt	/NaT	Mt/	Rhy	Mt/l	hsR
sample	AI	AN	Ι	Vil19	88	Wo1983	Lem1987	M&S1990	N&C1985	B&D1988	M&H1983	E&G1994
Th		0.0033	0.0002	0.17-0.21	0.18	0.053-0.805	0.06	0.002-0.02	0.09-0.32	0.01	1.63-13.1	
U	0.0016	0.0031	0.0023	0.11-0.14	0.12	0.725	0.09		0.21-0.83		0.74	
Nb	0.23	0.27	0.37									
Та	0.24	0.26	0.37	0.47-0.55	0.42	0.164-0.90	1.13	1.36-2.35	2.3-4.5	1.2	0.74-2.73	
Pb			0.009									
Zr	0.097	0.10	0.086	0.21-0.25			0.62	0.17-0.29		0.24		0.37
Hf	0.11	0.13	0.13	0.27-0.31	0.20	0.032-0.13	0.51	0.10-0.29	0.95-2.9	0.24		
Ti	19	18	25									
Y	0.005	0.012	0.004									3.21
Yb			0.01			0.35-0.42		0.01-0.06	1.0-2.2	0.44	1.30	
Sc	1.7	1.7	0.96	3.8-7.95	9.70	2.85-5.38	10.42	1.88-3.33	1.5-15.6	5.0	8.9-12.4	
V	49	44	55									

Notes: Also shown are literature data for Campi Flegrei trachytes and trachyphonolites, for phonolites (Mt/Ph), sodic trachytes (Mt/NaT), rhyolites (Mt/Rhy) and high-silica rhyolites (Mt/hsR). N&C1985 = Nash and Crecraft 1985. Other abbreviations as in Tables 6 and 7 captions.

Table 9. Calculated D values for the selected Divi tracitytes (Di/T)									
	Bt/T		Bt/T	Bt/Ph	Bt/Rhy	Bt/hsR			
sample	AI	AI	Vill988	Wo1983	N&C1985	M&H1983	E&G1994		
Cs	0.32	0.32	0.56-0.79		1.2-4.4	1.2-3.1			
Rb	1.1	1.1	1.35-1.58	1.1-2.321	2.3-4.1	3.0-5.3	9.70		
Ba	5.7	10	1.04-21.5	10.1-11.2	5.6-36	3.7-7.0			
Th		0.002	0.09-0.11	0.08	0.27-2.0	0.511-1.74			
U	0.005	0.005	0.08	0.198	0.46-1.2	0.131-0.19			
Nb	1.3	1.1			4.0-9.5		9.10		
Та	1.0	0.93	0.74-1.02	0.26-0.325	1.2-1.9	1.31-1.36			
Pb	0.046	0.060			0.1-1.6		2.10		
Sr	0.15	0.20	0.20-0.78		0.29-0.53		7.20		
Zr	0.096	0.098	0.13-0.28		0.79-1.8		0.47		
Hf	0.11	0.12	0.13-0.15	0.047-0.10	0.44-0.84	0.47-0.68			
Ti	14	14							
Y	0.003	0.008			1.0-1.4		2.40		
Sc	2.2	2.3	2.81-5.56	23.20-26.8	4.9-20	13.1-18.1			
V	8.8	10.0							

Notes: ${}^{D'L}D_{Ti}$ was calculated on the basis of EMP data. Also shown are literature data for ${}^{Bt/L}D$ calculated for Campi Flegrei trachytes, for phonolites (Bt/Ph), rhyolites (Bt/Rhy) and high-silica rhyolites (Bt/hsR). Abbreviations for data sources as in Tables 6, 7 and 8 captions.

Table 9. Calculated ${}^{Bt/L}D$ values for the selected BM trachytes (Bt/T)

Table 10. Calculated $^{Ap/L}D$ values for the selected BM												
trachyphonolites (Ap/Tp)												
	Ap/Tp	Ap/Ph	Ap/NaT	Ap/Pnt	А	p/G						
sample	Ι	Wo1983	M&S	1990	Nag1970	W&G1981						
Ba	0.45		0.45									
Th	1.8	1.2	1.6									
U	0.75		2.6									
La	25	14.4	13-39	36-38		8.0-11.9						
Ce	27	24.3	28-46	40-43	29.6							
Pb	0.22											
Sr	3.3					2.1-2.4						
Pr	34											
Nd	39	54.3	23-38	35-38	57.1							
Sm	33	95.2	38		84.8	18.5-38.4						
Eu	29	102	30.2		9.22							
Gd	32											
Tb	25	41.4	30									
Ti	0.05											
Dy	23				246	15.9-30.7						
Но	21											
Y	23		20-21	11-12								
Er	17				275							
Tm	13											
Yb	9.6	8.81	10		232							
Lu	7.8	3.69	7.2		199	7.5-20.4						
V	2.0											

Lu 7.8 3.69 7.2 199 7.5-20.4 V 2.0 Notes: Also shown are literature data for $^{Ap/L}D$ calculated for phonolites (Ap/Ph), granites (Ap/G), sodic trachytes (Ap/NaT) and pantellerites (Ap/Pnt). Nag1970 = Nagasawa 1970. W&G1981 = Watson and Green 1981. Other abbreviations as in Tables 6, 7 and 8 captions.



Fig.1

















