

New insights into the ultrapotassic magmatism through xenoliths from the Eğirdir area, West Anatolia, Turkey

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Platevoet Bernard, Bardintzeff Jacques-Marie, Elitok Ömer, Noret Aurélie, Grégoire Michel, et al.. New insights into the ultrapotassic magmatism through xenoliths from the Eğirdir area, West Anatolia, Turkey. Arabian Journal of Geosciences, In press, 17 (1), pp.9. 10.1007/s12517-023-11766-7 . hal-04337266

HAL Id: hal-04337266 https://hal.science/hal-04337266

Submitted on 12 Dec 2023

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ORIGINAL PAPER

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New insights into the ultrapotassic magmatism through xenoliths from the Eğirdir area, West Anatolia, Turkey

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⁵ Received: 14 July 2023 / Accepted: 28 October 2023

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7 Abstract

AQ3 Plutonic xenoliths have been found within a pipe and a related phreatomagmatic leucitite deposit in the Eğirdir lake area, 9 belonging to the Potassic-Ultrapotassic Afyon volcanic Province, West Anatolia. They consist of kamafugite-type, feldspar-10 bearing svenite, pyroxenite, leucitolite, some small-sized melilitolite and garnet-rich xenoliths, and a carbonatite. A new 11 occurrence of kalsilite is described as either homogeneous acicular crystals or tabular two phases-exsolved crystals in the 12 kamafugite-type and melilitolite xenoliths. Rock textures and compositions indicate cumulates and near-liquid composition 13 rocks corresponding to relatively evolved magmas. All the rocks are strongly silica-undersaturated, Ca-, Mg-, and K-rich, and 14 Al-poor. The fractional crystallization model includes clinopyroxene, apatite, phlogopite, melilite and leucite. Fe-Ti oxides 15 and garnet may be also concerned. The $P_{\rm H2O}$ during crystallization and differentiation is not more than 0.8 GPa. Major ele-16 ments, trace elements, and REE patterns for xenoliths, which indicate near-liquid compositions, are typical of ultrapotassic 17 series in a post-collisional geodynamic context, as it is the case for the Roman and Central ultrapotassic Italian provinces. 18 The stable isotope ¹³C and ¹⁸O values of the calcio-carbonatite plot close to the primary carbonatite field, whereas the car-19 bonates of the feldspar-bearing syenite and the peperite matrix suggest a low-T extensive contamination process. The origin 20 of the carbonatite from kamafugite-type magmas by immiscibility or by fractional crystallization remains questionable; an 21 origin by fractionation-melting of a metasomatized mantle source should be tested in the future.

AG4 Keywords Ultrapotassic rock · Kamafugite · Leucitolite · Carbonatite · Turkey

Th sho	is work is dedicated to the late Dr. A. Poisson who have own the studied area to the first author many years ago.
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Introduction

New occurrence of strongly silica-undersaturated, potassic-ultrapotassic plutonic xenoliths

We report here the mineralogy and geochemical data for a new occurrence of melilite-, leucite-, kalsilite-bearing plutonic xenoliths found in the southern part of the Potassic-Ultrapotassic Afyon Province, Turkey. Some rare occurrences of such plutonic rocks have been previously found for example in the ejectas from Alban Hills and Montefiascone volcanism, Italy (Keller 1983; Peccerillo et al. 1984; Federico et al. 1994; Vollmer 1989; Beccaluva et al. 1991; Beccaluva et al. 2012; Peccerillo 1990, 1992, 1994; Di Battistini et al. 2001; Stoppa 2003; Stoppa et al. 2003a; Gaeta et al. 2006; Conticelli et al. 2013, 2015), and also in the ultrapotassic volcanic series from the East African rift (Bell and Powell 1969; Mitchell and Bell 1976; Pouclet 1980; Edgar and Arima 1981; Bergman 1987; Kampunzu and Lubala 1991; Laval and Hottin 1992; Bell and Tilton 2001; Stoppa

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41 et al. 2003b). For a long time, authors have paid attention to the distinctive mineralogy of potassic-ultrapotassic rocks 42 in relation with magma crystallization and differentiation 43 44 (Yoder 1986; Veksler et al. 1998) and their complex hypothetic mantle source and successive mantle metasomatism 45 events in relation with a post-collision, extensional geody-46 namical context (Savasçin et al. 1994; Yağmurlu et al. 1997). 47 However, there are few data regarding plutonic intracrustal 48 intrusions especially for the tertiary Potassic-Ultrapotassic 49 Afyon volcanic Province. Erosion processes did not allow 50 access to the plutonic level, and only scarce mafic-ultra-51 mafic xenoliths entrained during volcanic events have been 52 described and related to crustal intrusions (Akal 2003; 53 Prelević et al. 2015). 54

55 Geological background

As part of the Alpine-Himalayan orogenic belt, Turkey con-56 57 sists of an amalgamation of Gondwana-derived continental blocks associated with ophiolitic units. The Anatolide-Tau-58 ride block which occupies western and southern parts of 59 60 Turkey is subdivided into zones based on the type of metamorphism and age of deformation (Fig. 1a, b): Tavşanlı 61 Zone, Afyon Zone, Menderes Massif, Bornova Flysch Zone, 62 and Tauride Belt. The first four zones are characterized by 63 medium-high-pressure metamorphic rocks (Bornova Flysch 64 Zone). These zones are the low-grade metamorphic base-65 ment intruded by felsic igneous rocks (Tauride Belt, Gürsu 66 et al. 2004), Mesozoic to Cenozoic sedimentary sequences, 67 and stack of imbricated, ophiolite-bearing allochthonous 68 69 nappes. The western part of the Tauride carbonate axis forms a north-pointing cusp in the north of Eğirdir Lake, 70 the so-called Isparta Angle, and includes the study area. The 71 northeast-southwest trending Beydağları platform carbonate 72 separates allochthonous ophiolitic rock units with, from west 73 to east, the Lycian nappes, the Antalya complex, and the 74 Hoyran-Beyşehir-Hadım nappes. These four nappe systems 75 join around Eğirdir Lake (Fig. 1b). Southwestern Turkey has 76 been subjected to compressional and extensional tectonic 77 activities, ophiolite emplacements, block rotations, and vol-78 canic activities throughout Phanerozoic time. 79

Neotectonic structures developed in SW Turkey during the Late Miocene to Early Pliocene with local effects
at the end of Middle Oligocene in a transtensional regime
(Koçyiğit 1984a, b). They correspond to regional uplift, continental sedimentation (thick pile of molasse deposition),
syn-sedimentary volcanism, and block faulting.

86 Potassic-ultrapotassic volcanisms in West Anatolia

North–south trending volcanic rocks, named Kırka-AfyonIsparta Volcanic Province (Francalanci et al. 2000) or KırkaAfyon-Isparta Alkaline Volcanic assemblage (after Savaşçın

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and Oyman 1998), crop out from the apex of the Isparta 90 Angle to the north of Afyon, including the studied area, and 91 are characterized mainly by potassic-ultrapotassic volcanic 92 rocks (Fig. 1a, c) (Alici et al. 1998; Francalanci et al. 2000; 93 Akal 2003; Platevoet et al. 2008, 2014; Elitok 2019; Prelević 94 et al. 2012, 2015; Akal et al. 2013). In general, from north to AQ7 5 south in the Kırka-Afyon-Isparta volcanic Province, volcanic 96 activities get younger: 14.8 and 8.6 Ma around Kırka-Afyon 97 (Francalanci et al. 2000) in the north, from 4.7 ± 0.2 Ma 98 around Isparta (Lefèvre et al. 1983) to 24 ± 2 ka (Platevoet 99 et al. 2014) and 12.9 ± 0.4 ka (Schmitt et al. 2014; Guillou AQ8 of et al. 2017) in the south, corresponding to the last volcanic 101 events of the Gölcük volcano. The volcanic activities in SW 102 Turkey are in close relationship with the neotectonic evolu-103 tion of the region. 104

The Tertiary-Quaternary volcanic Province of West Ana-105 tolia is divided into a northern series named the Potassic-106 Ultrapotassic Afyon volcanic Province (Akal 2003; Akal 107 et al. 2013; Prelević et al. 2012, 2015) extending north to 108 south, from Afyon to Eğirdir Lake (Fig. 1b). It is formed by 109 three main series, including a strongly silica-undersaturated, 110 leucite-bearing volcanic series located at the southern part 111 where we found the xenoliths, the subject of the present 112 study. The Isparta potassic volcanic series is more recent, 113 with the Quaternary Gölcük volcano situated in the so-called 114 Isparta Angle (Lefèvre et al. 1983; Alici et al. 1998; Plat-115 evoet et al. 2014, 2015; Coban et al. 2019). AQ9 6

Field occurrence

Sample locations are in the NW Hoyran lake (N Eğirdir 118 lake), within a NE-SW trending horst structure bounded by 119 the Senirkent graben in the south (Fig. 1c) and the Haydarli 120 graben in the north. Mesozoic formations consisting mainly 121 of massive or bedded limestones form the basement (Fig. 1c, 122 d), locally unconformably overlain by Eocene flysch-type 123 deposit, or by Upper Miocene-Pliocene volcano-sedimentary 124 deposits (Elitok 2019, and references therein). Trachytic 125 domes are observed in the west of the studied area and leu-126 cite-bearing lava dome flows are observed to the NW close 127 to the Haydarli graben. 128

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Along the Afyon-Karahisar road, the Cretaceous lime-129 stones and Cenozoic lacustrine levels are cut by a volcanic 130 pipe 5 m wide (Fig. 1e). This pipe consists of a leucite-131 bearing brownish volcanic material including numerous 132 xenoliths of volcanic and plutonic types. At the contact 133 between the pipe and the limestone basement, the limestones 134 are brecciated and some blocks are incorporated in the vol-135 canoclastic breccia. The xenoliths and the enclosing matrix 136 are extensively hydrothermally altered by a CO₂-dominant 137 fluid phase, as evidenced by millimeter- to centimeter-size 138 calcite veins. 139



AQ6 Fig. 1 Geographic situation and geological map. Localization of the studied area and geological map from Isparta to Afyon northwest of Egirdir Lake, Anatolia: a volcanics in Anatolia; b structural scheme of West Anatolia; c main geological units from Afyon to Isparta; d

local geological units near the studied area; \mathbf{e} top, the leucitite pipe with limestone blocks and xenoliths; \mathbf{f} the volcanoclastic deposit, the peperite has a white calcitic matrix including black leucitite granules

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Near the pipe, towards the south, a volcanoclastic deposit 140 is formed by a brecciated leucitite, which also contains 141 numerous xenoliths. The lower part of this volcanoclastic 142 deposit is composed of a 50-cm-thick layer of a pulverized 143 leucitite lava in a calcitic-zeolitic matrix, similar to a pep-144 erite (Fig. 1e, f). The xenoliths (5 to 20 cm in size) were 145 collected in this volcanoclastic deposit. They are angular 146 or rounded and show a variety of textures from fine-grained 147 porphyric textures to equant coarse-grained textures (Fig. 2). 148

The xenoliths are leucocratic to melanocratic, depending on their mafic-felsic mineral assemblage. Small ultramafic xenoliths (no more than 5 cm in size) and a single coarsegrained carbonatite xenolith (10 cm in size) were also found. The xenoliths are relatively well preserved from hydrothermal alteration and provide a good opportunity for a petrological study in order to specify their possible connection with the Potassic Ultrapotassic Afyon volcanic Province.

Fig. 2 Rock textures: a pyroxenite with clinopyroxene, apatite, and garnet; b pyroxenite with clinopyroxene, apatite, and phlogopite; c microgranular texture of kamafugite with clinopyroxene, apatite, leucite, melilite, and kalsilite; d coarse-grained texture of kamafugite with clinopyroxene, apatite, leucite, garnet, kalsilite, and phlogopite; e melilitite with melilite, apatite, kalsilite, and garnet; f leucitolite with leucite, clinopyroxene, garnet (coarse-grained texture); g feldspar-bearing syenite with clinopyroxene, ghost of leucite, alkali feldspar, and calcite; h carbonatite with calcite, apatite, phlogopite, Feoxide, and vanadinite



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157 Analytical methods

Mineral compositions were determined at CAMPARIS 158 Lab. (Université Paris-Sorbonne, France), using the 159 Cameca SX 100 or Cameca SX Five electron probe 160 microanalyzers (with 4 or 5 wavelength-dispersive spec-161 trometers). Element calibrations were done using a set of 162 silicates, oxides, and REE-dopped glasses. Accelerating 163 voltage and beam current were U = 15 kV, I = 10 nA, with 164 a beam of 1–5 µm wide; the counting times for each ele-165 ment were 10 s and 5 s for background on each side of 166 the measured X-ray peak for each element. The mineral 167 compositions are calculated using a Z.A.F. iterative matrix 168 correction. Mineral structural formulae were calculated on 169 a classical stoichiometric basis chosen for each mineral 170 171 species.

¹⁸O and ¹³C stable isotope analyses were carried out 172 on calcite extracted from magmatic rocks and the lime-173 stone basement. Calcite powder was reacted with 100% 174 orthophosphoric acid at 25 °C and the derived CO₂ was 175 analyzed using a VG Sira 10 mass spectrometer to deter-176 mine O and C isotope composition at the GEOPS labora-177 tory (Université Paris-Saclay, France). All isotopic values 178 are reported in the standard δ -notation in per mil relative 179 to V-PDB (Vienna Pee Dee Belemnite) by assigning a δ^{13} C 180 value of + 1.95% and a δ^{18} O value of - 2.20% to NBS19. 181 Reproducibility was checked by a replicate analysis of 182 laboratory standards and was $\pm 0.1\%$ for carbon isotopes 183 and $\pm 0.2\%$ for oxygen isotopes. 184

185 Whole-rock major and trace element concentrations 186 of the samples were determined by inductively coupled 187 plasma optical emission spectrometry and inductively cou-188 pled plasma mass spectrometry, respectively at the Service 189 d'Analyse des Roches et des Minéraux (SARM, CRPG, 190 Nancy, France). CO_2 analyses of the fire loss on ignition 191 were carried out for each rock.

The volcanoclastic deposit: leucititeand peperite

The volcanoclastic deposit consists of a brecciated and 194 hydrothermally altered leucitite (Fig. 1e). At the base of 195 the deposit, there is a 50-cm-thick layer of a mixture of 196 dark leucitite granules enclosed in a white matrix com-197 posed essentially of calcite and zeolites. This 50-cm-thick 198 layer seems to be a peperite (Fig. 1f). Similar deposits are 199 commonly described during explosive phreatomagmatic 200 eruptive events occurring within lacustrine areas. The 201 gray-black leucitite granules contain phenocrysts of clino-202 pyroxene and leucite in an essentially dark microlithic 203

groundmass composed of opaque oxide, feldspar, clino-204 pyroxene, apatite, and glass. The granules are surrounded 205 by a matrix composed of calcite and zeolites. Some clino-206 pyroxenes are isolated during the granulation process of 207 leucitite. The volcanoclastic deposit also contains some 208 well-preserved angular to more rounded enclaves of leuci-209 tite, very similar in texture and mineral paragenesis to the 210 leucitite matrix of the volcanoclastic deposit. 211

Main petrological groups of xenoliths

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Forty xenoliths were investigated and divided into five
groups (Table 1), according to their mineral paragenesis
(Table 1): pyroxenites, plutonic kamafugite-type rocks, leu-
citolites, syenites, and only one carbonatite xenolith.213
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The pyroxenite xenoliths

Pyroxenites (Fig. 2a, b; Table 1) are ultramafic rocks with 218 more than 90 vol.% of mafic minerals (clinopyroxene, phlo-219 gopite) associated with numerous prismatic crystals of apa-220 tite and minor amounts of interstitial felsic minerals (<10 221 vol.%). Phlogopite, when present (0-20 vol. %), is typically 222 subhedral to anhedral, crystallizing after clinopyroxene 223 and apatite (Fig. 2b). Dark interstitial melanite-type garnet, 224 leucite, zeolites, and calcite are present in small amounts. 225 Leucite is commonly replaced by a mixture of zeolite, cal-226 cite, and phyllosilicate. These xenoliths are very similar to 227 ultramafic xenoliths from the Potassic Ultrapotassic Afyon 228 volcanic Province described by Prelević et al. (2015). 229

The kamafugite-type xenoliths

These xenoliths contain from 5 to 30 vol.% of kalsilite 231 (KAlSiO₄), 25–30 vol.% of leucite, nepheline, and no 232 feldspar. Kalsilite has never been described before in the 233 previous studies of the Potassic-Ultrapotassic Afyon vol-234 canic Province (Akal et al. 2013; Prelević et al. 2015; Elitok 235 2019). It also occurs in the Western Africa Rift ultrapotassic 236 magmatism and in the Italian Roman Province (Di Battistini 237 et al. 2001; Tappe et al. 2003; Stoppa et al. 2003a). Two 238 main textures of kamafugite-type xenolith are observed: 239 a microgranular porphyritic texture and a coarse-grained 240 texture. 241

The microgranular porphyritic xenoliths have variable 242 modal compositions (Fig. 2c, Table 1) with porphyrocrysts 243 of leucite, zoned clinopyroxene including tiny early Ti-244 magnetite, prismatic melilite, and later idiomorphic zoned 245 (black core to yellow rim) garnet and magnetite. Kalsilite is 246 typically the last major mineral to crystallize in these rocks, 247 after apatite, clinopyroxene, magnetite, melilite, and just 248 before garnet. Garnet includes other phases like melilite, 249

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 Table 1 Modal composition of

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 studied plutonic xenoliths and

 leucitite

Rock Nb	98-A	98,004	98,006	98,005	98,008	E-17	E8	E9	E12
	Melilitolite		Kamafug	ite group		Carbon	atite	Pyroxenite group	
Leucite		30	30	25	25		5	5	+
Melilite	45		10	15	7				
Kalsilite	30	5	15	25	15				
Nepheline		18	5		20				
Altered foide		5	10		5				
Feldspath					+				
Clinopyroxene				20	15		80	60	75
Garnet	20	15	10	10			5		
Calcite		3	10		3	90		2	5
Apatite	2	2	3		+	5	8	7	7
Mica		18			10	2		25	
Titanomagnetite		+		5	+	2			
Others (zeolites)	3	+	5		+	1	2	1	12
Groundmass									
Rock Nb	E11	E3	E4	E5	E6	E7	E10	E2	
	Leucititolite	e group					Syenite	Leucitite	
Leucite	70	45	65	70	60	60	10	30	
Melilite				l í					
Kalsilite		3				3			
Nepheline			$\mathcal{O}(\mathcal{A})$						
Altered foide	5	7			10	10	5	+	
Feldspath			3				65	+	
Clinopyroxene	10	35	20	10		5	5	20	
Garnet	10		10	15	12	10			
Calcite					5		10		
Apatite		5	2	2	2	3	2	+	
Mica	5		2	2	5		2		
Titanomagnetite								+	
Others (zeolites)	,	3					1	+	
Groundmass		_						50	

apatite, and thin elongate prisms of kalsilite, attesting of its
late nucleation and growth. Kalsilite exhibit clusters of very
elongated homogeneous prisms forming the micro-granular
groundmass of the rock (Fig. 2c).

254 The coarse-grained xenoliths (Fig. 2d, e) not only have the same mineralogy, with apatite, leucite, prismatic kalsi-255 lite, and zoned garnet but they also contain phlogopite. 256 257 Clinopyroxene is less abundant and melilite is rare or absent. In coarse-grained xenoliths, kalsilite and nepheline 258 crystallize as separate phases. Kalsilite forms euhedral, 259 tabular crystals (Fig. 2d) showing kalsilite-nepheline exso-260 lution intergrowths (Fig. 3), symptomatic of subsolidus 261 reequilibration. Such exsolution intergrowths have been 262 263 described in Mt Nyiragongo lava (Congo), in melilitolites, kalsilitites, and kamafugites from Roman Province and 264 Intramountain Ultra-alkaline Province, Italy (Aurisic-265 chio and Federico 1985; Federico et al. 1994, Stoppa and 266

Woolley 1997; Stoppa et al. 2003a). Melilite is associated 267 with variable amounts of clinopyroxene, garnet, apatite, 268 phlogopite, Ti-magnetite, and calcite, while olivine is not 269 present. Calcite and brown-yellowish phases (a mixt of 270 hydroxide amorphous phases and phyllosilicates) com-271 monly replace the core of melilite crystals. Intergrowth 272 features between garnet and leucite are common. Large 273 crystals of nepheline can be relatively abundant (5 to 274 20 vol.%) in these xenoliths and calcite is interstitial. 275 Two small (no more than 5 cm in size) mafic-ultramafic 276 xenoliths also belong to this group. The first xenolith is 277 extremely rich in melilite (45 vol.%, Table 1 sample 98-A), 278 and can be named melilitolite. The second xenolith is a 279 garnet-rich type; a similar garnet-bearing xenolith has 280 been also described in the leucitites from the Balç1khisar 281 volcanic area (Akal et al. 2013). 282

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Fig.3 Kalsilite and nepheline compositions. Microprobe backscattered picture of euhedral kalsilite, crystal showing exsolutions features: fine exsolutions lamellas of nepheline. Nepheline-kalsilite versus T°C diagram showing the position of kalsilite analyses in relation with solidus and solvus curves; the red curve is a more realistic

solidus position relative to temperature for the hypersolvus kalsilite. The blue line would be the solidus-solvus intersection given by the compositions of separate crystals of nepheline and exsolved kalsilite found in coarse-grained kamafugite-type xenolith (after Tuttle and Smith 1958; Zeng and MacKenzie 1984)

283 The leucitolite xenoliths

Leucitolites are the commonest and largest plutonic xeno-284 liths (10-15 cm in size). They are mostly coarse-grained 285 and their mineral parageneses differ only in the relative 286 mafic to felsic mineral ratio, in particular leucite, varying 287 from 45 to 70 vol.%, and giving mesocratic to leucocratic 288 type rocks (Fig. 2f). Adjacent crystals of leucite typically 289 show 180° triple joins, suggesting leucite crystal segrega-290 tion, followed by textural subsolidus re-equilibration and 291 crystal aging (Boudreau 1995; Marsh 1998, 2007; Laporte 292 and Provost 2000; McBirney 2007; McBirney et al. 2009). 293 This process of subsolidus re-equilibration can happen dur-294 ing slow cooling of magmatic intrusions, but it remains 295 controversial in particular for felsic intrusions (Holness and 296 Vernon 2014; Holness et al. 2017, 2018). Leucite is locally 297 partially replaced by a mixture of alkali feldspar and zeolite. 298 The other mineral phases are euhedral green clinopyroxene, 299 prismatic apatite, poikilitic garnet, Ti-Fe oxides, and phlo-300 gopite. Kalsilite is rare in leucitolite and occurs as poikilitic, 301 commonly altered crystals located between euhedral leucite 302 crystals. Textural features such as two-phase layering, with 303 304 pyroxene-rich thin layers and extremely rich leucite layers, are symptomatic of crystal segregation by a rheological pro-305 cess or by a density-driven cumulative process within the 306 307 magma intrusions.

308 Feldspar- and leucite-bearing syenite xenoliths

Their textures are fine-grained to coarse-grained (Fig. 2g). As for kamafugite-types and leucitolites, the mineral paragenesis consists of not only euhedral zoned (green core to dark green rim) clinopyroxene, prismatic apatite, and euhedral leucite but also rare euhedral kalsilite prism in some xenoliths, and 313 sometimes nepheline. Zoned garnet and poikilitic zoned alkali 314 feldspar are observed. Few sections of pale-brown mica and 315 Ti-Fe oxides are observed. The paragenesis variations from 316 one sample to one another are dependent upon the destabili-317 zation degree of leucite which is partially or totally replaced 318 by large, poikilitic feldspars. Calcite also crystallized as a pri-319 mary phase in some feldspar-bearing syenite, in relation to a 320 CO₂-enriched dissolved fluid phase. 321

The carbonatite xenolith

A single 10-cm-sized xenolith of carbonatite has been found, representing the first occurrence of coarse-grained carbonatite in this area. It consists of large crystals of calcite with clusters of prismatic apatite. Frequent pale-brown phlogopite exhibits sector zoned subhedral crystals. Magnetite and vanadinite have crystallized lately and are interstitial between calcite and apatite crystals (Fig. 2h).

At the apex of the so-called Isparta Angle, from the Senirkent area (Elitok 2019), inclusions and microscopic blobs of carbonatite have been also observed in a leucite-bearing phonolite. These small blobs and inclusions are mainly formed by carbonate with various amounts of phlogopite, clinopyroxene, leucite or nepheline, apatite, and garnet (Elitok 2019).

Mineral composition results

Leucite

Leucite compositions (Appendix 1A) are usually near the 338 ideal formulae with very small amounts of Na₂O, FeO, and 339

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BaO (< 0.8 wt.%). The leucite of pyroxenite and syenite 340 has undergone hydration. It has been partially replaced by 341 a mixture of feldspar, calcic zeolite, and calcite (see altered 342 leucite in Appendix 1A). Replacement of leucite by analcite 343 is not observed, probably due to very low sodium content. 344 The main feature that occurs in some syenite xenoliths is the 345 partial or almost total disappearance of leucite, replaced by 346 alkali feldspar and nepheline, corresponding to the subsoli-347 dus breakdown of leucite in the presence of water (Fudali 348 1963). 349

Kalsilite and nepheline 350

Homogeneous thin elongate prisms of kalsilite (Fig. 3; 351 Appendix 1B) are relatively Na₂O-rich with a maximum 352 of 21 mol% of nepheline, corresponding to the preserved 353 hypersolvus composition of kalsilite during rapid cooling. 354 Based on the experimental study of Tuttle and Smith (1958), 355 the crystallization temperature would be $\geq 1000 \,^{\circ}$ C (Fig. 3). 356 The kalsilite of the coarse-grained kamafugite-type con-357 tains 7-11 mol% of nepheline component, and the exsolved 358 nepheline lamellae have 25-26 mol% of kalsilite component, 359 indicating a solvus exsolution process during slow cool-360 ing, operating between 800 and 500 °C. In coarse-grained 361 kamafugite and feldspar-bearing syenite, crystals of nephe-362 line rim leucite form large anhedral crystals showing some 363 cancrinite-type alteration. Compared to the nepheline exso-364 lution lamellae from the exsolved kalsilite crystals, these 365 nepheline crystals are relatively potassic, with 35–39 mol% 366 of kalsilite component. This compositional range (Fig. 3) is 367

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consistent with the subsolvus kalsilite-nepheline pairs crys-368 tallizing as separate crystals, at about 800 °C under 0.5 GPa, 369 according to the experimental study of Zeng and MacKenzie 370 (1984), whereas the solvus exsolution process of kalsilite 371 has operated between 800 and 500 °C during slow cooling 372 (Fig. 3). 373

Alkali feldspar

The first feldspar to crystallize in syenite belongs to the hyal-375 ophane type (Appendix 1C). Crystals are strongly zoned; the 376 Ba-rich core has 12-13 wt.% BaO, giving 25 mol% of cel-377 sian component, and subsequent decrease of K₂O and Na₂O 378 wt.%. SrO reaches a maximum of 2.5 wt.% corresponding to 379 6 mol.% of the stronalsite component Na₂SrAl₄Si₄O₁₆ (see 380 Essene et al 2005). Crystal rims evolve to pure K-feldspar. 381 The feldspar of the leucitite lava is also Ba-rich (25 mol% of 382 celsian component) and is more Ca- and Sr-rich than those 383 of the syenite. This Ba-feldspar is plotted in the quartz-384 nepheline-kalsilite ternary system (Fig. 4). Ba, equivalent 385 of K and Na, is allocated to the calculated nepheline and 386 kalsilite components. The hyalophane feldspar plots in the 387 feldspathoid-bearing area of that diagram, due to Ba enrich-388 ment and coupled Si-Al substitution. When leucite was 389 replaced during the crystallization of silica-undersaturated, 390 Ba-rich, K-rich, and Na-poor magma, hyalophane feldspar 391 crystallized in place of kalsilite or nepheline, which are both 392 unable to incorporate large amounts of Ba and Sr in their 393 structures. In the Qz-Ne-Ks diagram, hyalophane feldspar 394 plays the same role as feldspathoid because of its strong 395

Fig. 4 Hyalophane and K-feldspar in the system nephelinekalsilite-quartz ternary diagram. Considering that Sr and Ba are equivalent to Na and K with equal repartition between the two poles. Blue dots: present study; pale-blue dots: analyses from Akal (2003)



SiO₂





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silica deficiency compared to typical K-feldspar. The E10 396 feldspar-bearing syenite (Table 2) illustrates this well: the 397 rock is strongly silica-deficient, Ba- and Sr-rich (11,000 ppm 398 of Ba, 2250 ppm of Sr), and Na-poor (0.25w.% Na₂O). Leu-399 cite was destabilized and was first replaced by hyalophane 400 feldspar instead of kalsilite or/and nepheline, followed by 401 K-feldspar crystallization. The control by Sr and Ba on feld-402 spar crystallization has been previously pointed out by Fer-403 guson and Cundari (1982) in leucite-bearing magmas. Ba 404 and Sr elements are important substitutes for K, Na, and Ca, 405 particularly in potassic-ultrapotassic silica-undersaturated 406 magmatism (Cundari 1979; Mitchell and Vladikin 1996; 407 Akal 2003; Platevoet et al. 2014; Caran 2016). To the best 408 of our knowledge, there seems to be no experimental system 409 that investigates the effect of Ba and Sr on the stability of 410 feldspar-feldspathoid phases in the Qz-Ne-Ks ternary sys-411 tem, and also in the more complex Qz-Ne-Ks-An quater-412 nary system (Carmichael et al. 1974). These systems would 413 probably show major changes if Ba and Sr elements were 414 considered instead of Na, in a K-rich, highly silica-deficient 415 experimental system. 416

417 Clinopyroxene

The composition of clinopyroxene (Appendix 1D) evolves 418 from diopside to augite and from augite to aegirine-augite 419 in the most evolved rocks. CaO and MgO contents are high, 420 especially in crystal cores of ultramafic and mafic xenoliths 421 (Fig. 5), but decrease from kamafugite-type to leucitolite, 422 syenite xenolith, and in leucitite lava. CaO and MgO con-423 tents decrease in the crystal rims together with SiO₂, while 424 FeOt, Al₂O₃ (< 4.60 wt.%), and TiO₂ (< 1.4 wt.%) contents 425 increase, probably due to the decrease of silica activity dur-426 ing the crystallization. The aegirine component rises in the 427 more evolved syenite xenoliths and in leucitite, a common 428 feature of the silica-undersaturated series evolving under 429 relative oxidizing conditions, and/or due to the alkali-ferric 430 effect in peralkaline magmas (Larsen 1976; Mitchell and 431 Platt 1978, 1982; Mitchell and Vladykin 1996). Tschermak 432 molecules, especially Fe-Tschermak mol., rise from core to 433 rim of crystals and from the less evolved ultramafic-mafic 434 groups (pyroxenite and kamafugite) to the more felsic 435 groups (leucitolite and syenite) and leucitite. In the Ti vs. 436 Al_t diagram (Fig. 5), the majority of clinopyroxene analy-437 ses plot in the transitional field and the HKS-KS field of 438 Perini and Conticelli (2002) and in the kamafugite field for 439 pyroxene depicted by Prelević et al. (2005, 2015). However, 440 some analyses of the kamafugite xenoliths are very poor in 441 TiO₂. This can be due to early crystallization of both Ti-442 magnetite and clinopyroxene (rock 98005, Fig. 2c), Ti being 443 prior incorporated in Ti-magnetite under relative elevated 444 fO₂. The clinopyroxene of melilite leucitite from Meşebaşi 445 described by Akal (2003) belongs to the lamproite field of 446

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Mitchell and Bergman (1991) and differs from clinopyroxene of the Eğirdir leucitite lava. 448

Melilite

Compositions of melilite (Appendix 1E) are plotted in the 450 Na-melilite/gehlenite/akermanite ternary system (Fig. 6). 451 They are poor in gehlenite and rich in akermanite compo-452 nents. They are relatively similar in composition to melilite 453 from Montefiascone pyroxenites of the Roman Province 454 and San Venanzo melilitolite (Stoppa et al. 2003a), but 455 they are lower in gehlenite than the melilites of the Alban 456 Hills ejecta (Stoppa et al. 2003a). Finally, they are more 457 Mg-rich, and Al- and Na-poor compared to the melilite of 458 the northern Mesebasi melilite-bearing leucitites from the 459 northern Potassic-Ultrapotassic Afyon volcanic Province 460 (Akal 2003). 461

Phlogopite

All mica can be classified as phlogopite (Appendix 1F) with 463 a Mg/Mg + Fe + Mn ratio ranging from 0.90 to 0.60. Their 464 Ti content is highly variable, being generally > 2.5 wt.% in 465 pyroxenite and decreasing through kamafugite and leuci-466 tolite groups, and is very low in phlogopite from syenite 467 and carbonatite xenoliths. F content is low to moderate in 468 pyroxenite, leucitolite, and kamafugite-type (from 0.3 to 469 1.13 cation pfu.), but more elevated in the feldspar-bear-470 ing syenite with 1.2 to 2.6 cations pfu., probably in rela-471 tion with a $[F+CO_2]$ -rich, H₂O-poor dissolved fluid phase. 472 BaO in phlogopite is high and increases from pyroxenite to 473 kamafugite and leucitolite, from around 1.0 up to 6.1 wt.%. 474 The main coupled substitution that governs Ba incorpora-475 tion involves Si, Al, and Ti, also Fe and Mg, in place of 476 Ti and K in the interlayer site (Wagner and Velde 1986; 477 Wagner et al. 1987; Edgar 1992; Seifert and Kämpf 1994). 478 The most barium-rich phlogopite occurs in the carbonatite 479 xenolith with a maximum of 13 wt.% BaO. The crystals 480 show obvious sector zoning (Fig. 7A) due to strong Ba vari-481 ations associated with coupled Al, Si, and K substitutions. 482 The correlation (Fig. 7B) observed between $[Ba + Al_{IV}]$ and 483 [Si+K] pointed out the main substitution: 484

$$Ba^{2+} + AI^{3+} = K^+ + Si^{4+}$$

Ba-rich phlogopite is frequent in potassic-ultrapotassic 487 magmatism. Such high BaO values, between 13 and 16 488 wt.%, have been observed in phlogopite (Fig. 7C) from the 489 Jacupiranga carbonatite, Brazil (Gaspar and Wyllie 1982), 490 and also in phlogopite of numerous nephelinites, ankara-491 trites, and kamafugites from various localities (Mansker 492 et al. 1979; Gaspar and Wyllie 1982; Edgar 1992; Seifer 493 and Kämp 1994; Stoppa et al. 2003c; Prelević et al. 494

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Whole-rock	Kamafu- gite-type rocks		~	Syenite	Leucitites		Pyroxen- ites			Leucito- lites						Carbonatite
analysis	Melilito- lite	Kalsilite rock	Kalsilite rock			* Most altered	Phlo. Leuc									
rock Nb	98,005	98-004	98-008	E10	E2	E1*	E9	E12	E8	E3	E4	E7	E5	E11	E6	E17
Si02	41.21	35.54	36.50	44.59	49.89	43.65	41.35	42.06	45.24	48.04	45.14	45.93	48.29	45.42	45.30	0.75
TiO2	1.42	2.63	2.13	0.79	0.85	1.36	0.86	0.69	0.81	0.53	0.95	1.57	0.72	3.19	0.79	0.12
A1203	13.64	11.97	13.68	14.03	15.69	12.34	5.56	3.08	6.45	14.43	14.70	15.06	15.98	16.76	17.20	0.40
Fe2O3	9.29	10.93	12.10	5.47	6.77	8.34	4.53	5.06	5.44	4.07	10.59	9.27	5.23	6.71	4.98	4.17
MnO	0.15	0.17	0.19	0.10	0.13	0.10	0.07	0.07	0.08	0.05	0.10	0.12	0.08	0.05	0.10	0.14
MgO	2.92	5.09	3.17	2.48	3.41	4.90	14.63	11.70	10.60	4.85	3.76	2.82	3.92	0.58	2.40	0.50
CaO	16.11	16.21	13.64	13.92	8.67	15.52	21.23	29.41	23.32	12.79	9.58	9.44	9.12	9.95	8.00	51.35
Na2O	1.17	0.40	1.14	0.25	1.48	0.16	0.13	0.13	0.22	0.18	0.17	0.39	0.25	0.19	1.04	0.02
K20	8.56	7.21	8.57	9.17	8.00	4.43	3.24	0.29	2.77	9.49	9.39	10.85	11.57	12.01	12.75	0.10
P205	0.80	0.88	0.48	0.53	0.65	06.0	4.80	5.89	3.78	1.39	0.68	0.48	0.72	0.18	0.47	2.58
Pf (F+H20)	3.64	3.07	3.25	1.36	3.19	7.67	1.44	1.06	1.85	3.32	4.48	3.11	3.61	4.36	2.78	0.37
C02	2.07	4.71	3.85	5.98	0.10	0.18	1.12	1.26	0.19	0.46	0.05	0.12	0.27	0.10	3.17	37.99
Total	100.98	98.81	98.70	98.65	98.82	99.56	98.95	100.70	100.75	09.60	99.58	99.18	77.66	99.49	98.96	98.48
mdd																
\mathbf{As}	3.87	2.21	3.19	15.69	3.05	<l.d< td=""><td><l.d< td=""><td>1.23</td><td>1.27</td><td><l.d< td=""><td><l.d< td=""><td>1.96</td><td><l.d< td=""><td><l.d< td=""><td>1.33</td><td>35.79</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>1.23</td><td>1.27</td><td><l.d< td=""><td><l.d< td=""><td>1.96</td><td><l.d< td=""><td><l.d< td=""><td>1.33</td><td>35.79</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	1.23	1.27	<l.d< td=""><td><l.d< td=""><td>1.96</td><td><l.d< td=""><td><l.d< td=""><td>1.33</td><td>35.79</td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>1.96</td><td><l.d< td=""><td><l.d< td=""><td>1.33</td><td>35.79</td></l.d<></td></l.d<></td></l.d<>	1.96	<l.d< td=""><td><l.d< td=""><td>1.33</td><td>35.79</td></l.d<></td></l.d<>	<l.d< td=""><td>1.33</td><td>35.79</td></l.d<>	1.33	35.79
Ba	1766.00	6945.00	6729.00	11,070.00	4515.00	2253.00	2506.00	360.30	1423.00	1826.00	2289.00	3761.00	3051.00	2048.00	5060.00	4160.00
Be	13.64	5.67	4.24	10.02	9.47	4.60	2.58	1.85	3.09	2.20	3.76	9.48	6.04	1.49	5.35	<l.d< td=""></l.d<>
Bi	0.66	0.43	0.15	<l.d< td=""><td><l.d< td=""><td>0.13</td><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.13</td><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	0.13	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.47</td><td><l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<></td></l.d<>	0.47	<l.d< td=""><td>0.15</td><td><l.d< td=""><td>8.48</td></l.d<></td></l.d<>	0.15	<l.d< td=""><td>8.48</td></l.d<>	8.48
Cd	0.37	0.79	0.66	0.40	0.28	0.32	0.12	0.14	0.10	<l.d< td=""><td>0.13</td><td>0.43</td><td>0.17</td><td>0.93</td><td>0.24</td><td>0.70</td></l.d<>	0.13	0.43	0.17	0.93	0.24	0.70
Ce	180.60	213.70	319.50	130.00	154.00	109.50	125.70	393.90	173.70	96.18	61.52	92.55	76.09	82.90	94.22	881.20
Co	29.55	32.94	28.07	10.78	16.85	28.48	34.67	30.46	30.47	17.55	33.28	24.30	18.02	6.87	15.32	3.60
Cr	72.22	59.30	<l.d< td=""><td>44.52</td><td>39.35</td><td>10.13</td><td>1566.00</td><td>413.50</td><td>574.60</td><td>17.69</td><td>6.50</td><td>4.44</td><td>9.59</td><td><l.d< td=""><td>12.63</td><td><l.d< td=""></l.d<></td></l.d<></td></l.d<>	44.52	39.35	10.13	1566.00	413.50	574.60	17.69	6.50	4.44	9.59	<l.d< td=""><td>12.63</td><td><l.d< td=""></l.d<></td></l.d<>	12.63	<l.d< td=""></l.d<>
Cs	20.17	15.67	13.74	5.67	24.64	5.31	5.01	0.78	9.86	34.83	20.43	49.67	27.97	31.58	56.74	0.09
Cu	189.30	211.60	156.70	55.19	42.58	61.54	7.74	12.25	27.41	7.96	12.96	73.74	32.44	67.35	40.74	<l.d< td=""></l.d<>
Dy	5.23	15.67	7.57	4.67	4.69	4.76	4.26	8.82	4.39	2.16	1.78	6.73	2.10	19.10	2.45	1.26
Er	1.98	7.15	3.35	2.11	2.09	1.95	1.31	2.66	1.42	0.70	0.65	2.94	0.77	8.73	1.01	0.41
Eu	4.03	7.50	4.82	2.57	2.60	2.91	3.42	8.03	3.51	1.77	1.23	3.48	1.38	8.50	1.63	1.40
Ga	20.84	19.72	22.04	21.71	17.77	11.46	8.05	8.15	9.17	11.66	14.04	17.28	14.23	15.18	18.03	6.28
Gd	10.24	22.44	12.44	7.49	7.35	8.12	9.59	20.83	9.56	4.75	3.42	10.14	3.89	25.62	4.43	3.62
Ge	1.35	2.16	1.98	1.29	1.37	1.46	1.66	2.15	1.86	1.07	1.05	1.34	1.10	1.98	0.97	0.41
Hf	8.00	34.28	18.46	12.46	10.19	14.18	3.00	7.12	6.65	4.79	4.60	18.27	5.76	51.16	7.88	0.12

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Journal : Large 12517 Article No :	11766 Pages : 26	MS Code : 11766
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Table 2 (con	tinued)															
Whole-rock	Kamafu- gite-type rocks			Syenite	Leucitites		Pyroxen- ites			Leucito- lites						Carbonatite
Но	0.79	2.72	1.23	0.78	0.79	0.76	0.59	1.22	0.62	0.31	0.27	1.14	0.32	3.38	0.38	0.13
In	<l.d< td=""><td>0.11</td><td>U.O.</td><td><l.d< td=""><td><l.d< td=""><td>0.09</td><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	0.11	U.O.	<l.d< td=""><td><l.d< td=""><td>0.09</td><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.09</td><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	0.09	<l.d< td=""><td>0.07</td><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	0.07	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.07</td><td><l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<>	0.07	<l.d< td=""><td>0.10</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<>	0.10	<l.d< td=""><td><l.d< td=""></l.d<></td></l.d<>	<l.d< td=""></l.d<>
La	84.84	94.96	135.90	70.09	81.02	45.48	57.25	202.40	88.64	47.69	30.25	41.66	37.17	18.87	48.99	662.00
Lu	0.25	0.91	0.50	0.30	0.28	0.24	0.12	0.21	0.14	0.07	0.08	0.38	60.0	1.07	0.15	0.03
Mo	0.74	0.81	2.16	13.32	0.71	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.63</td><td><l.d< td=""><td>1.13</td><td>0.56</td><td>0.61</td><td>1.38</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.63</td><td><l.d< td=""><td>1.13</td><td>0.56</td><td>0.61</td><td>1.38</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.63</td><td><l.d< td=""><td>1.13</td><td>0.56</td><td>0.61</td><td>1.38</td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td>0.63</td><td><l.d< td=""><td>1.13</td><td>0.56</td><td>0.61</td><td>1.38</td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.63</td><td><l.d< td=""><td>1.13</td><td>0.56</td><td>0.61</td><td>1.38</td></l.d<></td></l.d<>	0.63	<l.d< td=""><td>1.13</td><td>0.56</td><td>0.61</td><td>1.38</td></l.d<>	1.13	0.56	0.61	1.38
Nb	22.24	23.74	100.60	25.16	24.51	7.41	3.33	1.06	1.28	0.58	3.46	12.63	7.72	14.51	12.49	83.65
Nd	96.17	125.80	145.90	63.26	62.62	59.72	78.44	203.50	87.05	48.25	30.47	56.51	35.84	95.31	43.15	138.50
Ni	22.02	27.62	10.08	16.05	22.29	24.57	135.10	71.76	73.58	19.93	21.71	8.20	16.84	4.50	11.02	4.52
Pb	103.03	63.00	34.19	243.43	76.05	12.46	2.40	4.26	5.18	2.15	5.01	61.31	15.04	14.07	18.29	1618.68
Pr	23.11	27.91	38.10	15.74	17.29	13.05	17.83	48.47	21.28	11.65	7.40	12.29	9.15	15.95	10.95	62.68
Rb	363.20	345.30	275.80	238.60	962.50	386.90	202.90	30.34	232.00	836.70	873.70	749.20	721.80	800.40	850.10	3.93
Sc	<l.d< td=""><td>22.46</td><td><l.d< td=""><td><l.d< td=""><td>12.72</td><td>23.93</td><td>36.23</td><td>63.78</td><td>44.69</td><td>23.35</td><td>21.45</td><td>13.86</td><td>18.93</td><td>24.19</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	22.46	<l.d< td=""><td><l.d< td=""><td>12.72</td><td>23.93</td><td>36.23</td><td>63.78</td><td>44.69</td><td>23.35</td><td>21.45</td><td>13.86</td><td>18.93</td><td>24.19</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>12.72</td><td>23.93</td><td>36.23</td><td>63.78</td><td>44.69</td><td>23.35</td><td>21.45</td><td>13.86</td><td>18.93</td><td>24.19</td><td><l.d< td=""><td><l.d< td=""></l.d<></td></l.d<></td></l.d<>	12.72	23.93	36.23	63.78	44.69	23.35	21.45	13.86	18.93	24.19	<l.d< td=""><td><l.d< td=""></l.d<></td></l.d<>	<l.d< td=""></l.d<>
Sb	0.41	0.17	0.31	1.90	0.40	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.11</td><td><l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.11</td><td><l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.11</td><td><l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td><l.d< td=""><td>0.11</td><td><l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td><l.d< td=""><td>0.11</td><td><l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.11</td><td><l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<></td></l.d<>	0.11	<l.d< td=""><td><l.d< td=""><td>0.20</td><td>0.30</td></l.d<></td></l.d<>	<l.d< td=""><td>0.20</td><td>0.30</td></l.d<>	0.20	0.30
Sm	17.78	29.06	22.25	11.66	10.82	11.82	15.24	34.76	15.17	7.81	5.36	13.10	6.08	30.13	7.32	8.24
Sn	4.91	13.05	7.62	4.26	4.19	7.45	1.26	3.50	4.60	2.84	3.50	8.25	2.96	20.36	3.23	0.45
Sr	1626.00	740.20	423.60	2256.00	3592.00	1508.00	778.10	1517.00	1325.00	581.30	514.80	811.00	978.80	471.40	1046.00	11,960.00
Ta	2.66	3.61	8.09	1.61	1.83	1.03	0.34	0.37	0.36	0.06	0.33	1.24	0.68	3.19	1.11	0.04
Tb	1.19	3.05	1.59	0.94	0.95	1.00	1.01	2.18	1.03	0.52	0.40	1.33	0.46	3.60	0.53	0.37
Th	39.49	48.75	74.22	41.76	41.92	20.49	10.12	36.11	16.35	11.78	10.91	22.59	15.63	22.03	22.43	0.10
Tm	0.26	1.00	0.48	0.30	0.30	0.26	0.15	0.28	0.16	0.08	0.08	0.41	0.10	1.19	0.14	0.04
U	8.22	11.27	20.10	18.53	6.88	3.94	1.68	2.64	1.59	1.16	1.71	6.73	3.70	7.23	8.85	7.81
^	239.20	332.90	522.50	214.40	152.50	140.80	65.70	78.96	92.63	52.80	127.50	207.60	79.04	175.40	155.50	331.50
W	1.16	0.88	1.55	25.35	0.76	<l.d< td=""><td><l.d< td=""><td>0.12</td><td><l.d< td=""><td><l.d< td=""><td>0.13</td><td>0.21</td><td>0.16</td><td>0.21</td><td>0.14</td><td>0.30</td></l.d<></td></l.d<></td></l.d<></td></l.d<>	<l.d< td=""><td>0.12</td><td><l.d< td=""><td><l.d< td=""><td>0.13</td><td>0.21</td><td>0.16</td><td>0.21</td><td>0.14</td><td>0.30</td></l.d<></td></l.d<></td></l.d<>	0.12	<l.d< td=""><td><l.d< td=""><td>0.13</td><td>0.21</td><td>0.16</td><td>0.21</td><td>0.14</td><td>0.30</td></l.d<></td></l.d<>	<l.d< td=""><td>0.13</td><td>0.21</td><td>0.16</td><td>0.21</td><td>0.14</td><td>0.30</td></l.d<>	0.13	0.21	0.16	0.21	0.14	0.30
Υ	24.41	78.22	40.02	25.43	25.59	22.03	17.03	34.24	18.23	8.54	7.80	31.97	9.11	90.88	12.22	3.91
γb	1.65	6.40	3.29	2.00	1.93	1.65	0.83	1.55	0.94	0.48	0.52	2.63	0.61	7.44	0.93	0.22
Zn	118.90	108.70	43.73	59.34	80.97	47.61	41.12	27.94	34.76	19.09	58.40	87.97	37.84	26.25	59.29	41.58
Zr	495.30	1307.00	1000.00	00.609	414.40	463.10	97.79	163.00	172.20	104.10	132.70	580.40	177.80	1524.00	341.70	9.04
CIPW norm																
Quartz	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	00.0	0.00	0.00	
Plagioclase	5.96	6.74	4.18	5.58	11.63	18.96	4.00	7.85	6.82	9.81	10.67	6.50	7.07	8.57	2.57	
Orthoclase	0.00	00.00	0.00	17.92	36.24	4.68	0.00	0.00	0.00	2.54	0.00	0.00	0.00	0.00	1.63	
Nepheline	5.36	1.83	5.23	1.15	6.78	0.73	0.60	1.01	0.60	0.83	0.78	1.79	1.15	0.87	4.77	
Leucite	40.80	37.85	41.80	35.50	10.08	18.29	16.61	13.75	1.57	43.13	44.99	51.53	55.55	56.96	60.09	
Kalsilite	0.00	0.00	1.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

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Table 2 (con	tinued)															
Whole-rock	Kamafu-			Syenite	Leucitite	SS	Pyroxen-			Leucito-						Carbonatite
	gite-type rocks						ites			lites						
Corundum	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	0.00	0.00	
Diopside	13.94	3.54	0.00	18.87	22.15	40.58	41.77	58.32	66.93	33.45	25.60	22.92	24.83	7.98	11.75	
Hypersthene	0.00	00.0	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	
Wollastonite	0.00	00.0	0.00	0.00	0.00	0.71	0.00	0.00	0.00	0.03	0.00	0.00	0.00	9.62	0.00	
Olivine	6.66	14.27	13.90	1.53	3.13	0.00	14.59	2.75	1.67	0.00	5.53	2.92	1.98	0.00	3.54	
Larnite	12.20	10.54	11.19	0.00	0.00	0.00	3.10	2.73	2.16	0.00	0.45	2.84	0.44	2.05	0.00	
Acmite	0.00	00.0	0.00	0.00	00.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
K2SiO3	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	0.00	0.00	
Na2SiO3	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	0.00	0.00	
Rutile	0.00	00.0	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	
Ilmenite	2.70	4.99	4.05	1.50	1.61	2.58	1.63	1.54	1.31	1.01	1.80	2.98	1.37	6.06	1.50	
Magnetite	2.70	3.18	3.51	1.58	1.96	2.42	1.32	1.58	1.46	1.17	3.07	2.68	1.52	1.94	1.45	
Hematite	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	0.00	0.00	
Apatite	1.85	2.04	1.11	1.23	1.51	2.09	11.12	8.76	13.65	3.22	1.58	1.11	1.67	0.42	1.09	
Zircon	0.10	0.27	0.21	0.12	0.27	0.27	0.27	0.03	0.03	0.01	0.03	0.12	0.03	0.31	0.07	
Perovskite	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	0.00	0.00	
Chromite	0.01	0.01	0.00	0.01	0.00	0.00	0.34	0.12	0.09	0.00	0.00	0.00	0.00	0.00	0.00	
Calcite	4.71	10.71	8.76	13.60	0.23	0.41	2.55	0.43	2.87	1.05	0.11	0.27	0.61	0.23	7.21	
Total	96.99	95.97	95.52	98.59	95.59	91.72	97.90	98.87	99.16	96.25	94.61	95.66	96.22	95.01	96.57	
Fe3+/(Fe3+Fe2)	20.0	20.0	20.0	19.9	20.0	20.0	20.1	20.0	20.0	19.9	20.0	20.0	20.1	20.0	20.1	
Mg/ (Mg+Fet)	38.4	48.0	34.2	47.3	50.0	53.8	86.5	79.4	82.1	70.3	41.3	37.6	59.8	14.6	48.8	
DI	52.12	46.4	52.8	60.2	64.7	42.7	21.2	22.6	9.0	56.3	56.4	59.8	63.8	66.4	70.0	
agpa. Index	0.82	0.71	0.82	0.74	0.71	0.41	0.67	0.17	0.52	0.73	0.71	0.82	0.81	0.80	06.0	
EI*, hydroth	ermalized le	ucitite ma	atrix of the phre	eato-magm	atic deposit	<i>DI</i> , differe	ntiation index	x of Thornto	on and Tu	ttle (1960);	agpa. Inde	x, index of	f agpaicity			
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Fig. 5 A MgO versus CaO diagram (wt. %) for clinopyroxene. Arrow, evolution trend in pyroxenite xenoliths: the dotted fencing yellow field is for kamafugite from Prelević et al. (2005); the two other fields are for pyroxenite, kamafugite-type and leucitolites of the present study and leucitites of the present study. B Ti/Alt (a.p.f.u.) diagrams for clinopyroxene. L, lamproitic field after Mitchell and Bergman (1991); T and HK-K, transitional high-K and K series of Italian volcanic magmatism (after Perini and Conticelli 2002). Dotted fields: Cpx respectively from lamproites and kamafugites after Prelević et al. (2005)



2005; Caran 2016). Ba and Al-Si coupled substitution 495 occurred exclusively in phlogopite when it crystallized 496 before feldspar under high $P_{\rm H2O}$, and in strongly silica-497 deficient magmas, prohibiting feldspar crystallization. It 498 is also favored by a relatively high fO_2 and P_{H2O} (Edgar 499 and Arima 1981). This is true for kamafugite, nephelin-500 ite, ankaratrite, and carbonatite. On the other hand, when 501 alkali feldspar crystallizes, as it is in the feldspar-bearing 502 syenite of the present study, Ba is preferentially incorpo-503 rated into hyalophane and phlogopite remains Ba-poor. 504

Garnet

Garnet is strongly zoned from black core to brown-yellowish 506 rim. Andradite (81-87%) and almandine (5-15 wt.%) are 507 its main components (Appendix 1G). Black crystal cores 508 are composed of melanite with > 15 wt.% TiO₂. Yellowish 509 rims are Ti depleted and more Fe- and Ca-enriched with the 510 increase of Fe-andradite and almandine components. MgO 511 remains very low (<1.3 wt.%) and decreases from garnet of 512 kamafugite to those of syenite xenoliths. Melanite appears 513

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Fig. 6 Melilite compositions in the gehlenite–akermanite–Na melilite ternary diagram. Yellow dots, present study; SV field, San Venanzo volcanics, Intra-mountain Ultra-alkaline Province, Italy; AHE field, Alban Hill Ejecta, Roman Province, Italy; MVC, Montefiascone clinopyroxenite xenoliths, Roman Province, Italy; MLM, melilite-bearing leucitite, Meşebaşi area, Afyon K-UK Province Anatolia (after Stoppa et al. 2003a, b, c; Akal 2003)

514 to be a systematic phase in the Potassic-Ultrapotassic Afyon Province magmatism and has been also described in melilite 515 leucitites, melanite-bearing xenoliths from the Balç1khisar 516 area (Akal 2003; Akal et al. 2013), and in other localities 517 of the western Taurides ultrapotassic volcanism (Prelević 518 et al. 2015). Garnet is also present in leucitite and carbon-519 atite inclusions from the Senirkent area of the Isparta Angle 520 (Elitok 2019). Melanite has also been observed in other 521 Ultrapotassic Provinces, such as in xenoliths of the Alban 522 Hills ultrapotassic ejecta, Roman Province, Italy (Federico 523 et al. 1994). 524

525 **Other minerals**

Apatite is observed in all xenolith groups and in leucitite. 526 527 The composition variations (Appendix 2A, B) concern only SrO which varies between 0.3 and 1.2 wt.% but reaches up 528 to 6.5 wt.% in the syenite. Silica is in the range 0.6-1.9 529 wt.%, but reaches 2.8 wt% in the apatite of carbonatite. F is 530 relatively abundant with 1.5 to 2.4 wt.%, reaching 3.2-3.8 531 wt.% in the apatite of the syenite and leucitite. Apatite also 532 contains REE, particularly the apatite of the carbonatite, 533 with 1.2–1.3 wt.% of Ce₂O₃. 534

Magnetite has an ulvospinel component that varies widely from 39 to 4% (Appendix 2C). The Mn jacobsite and magnesioferrite components reach 9% and 15% respectively in the carbonatite magnetite. The early crystallization of magnetite in some leucitolites seems to be related to oxidising

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conditions. It would also be related to the $H_2O/CO_2/F$ ratio in the dissolved fluid phase, but we have no precise information on this ratio and its evolution. 542

Calcite forms the peperite matrix and is the major mineral of the carbonatite xenolith. Microprobe analysis results (Appendix 2D) show that it is almost pure calcite with very low MgO content even in the carbonatite. However, SrO can reach 2.2 wt.% in the calcite of the carbonatite. 547

Preliminary geochemical results

Major elements

All the studied felsic rocks belong to strongly silica-550 undersaturated series, and are foidite-foidolite type rocks 551 (Table 2). Many plutonic xenoliths found in the Eğirdir area 552 have cumulated characters such as the ultramafic pyroxenite 553 with one or two liquidus main phases (clinopyroxene and 554 phlogopite) and the leucitolite xenoliths with two main lay-555 ered phases (leucite and clinopyroxene). Kamafugite-type 556 xenoliths and feldspath-bearing syenite, exhibiting micro-557 granular or coarse-grained homogeneous textures, are closer 558 to liquid compositions. More appropriate specific classifica-559 tion schemes for ultrapotassic rocks than TAS diagram (Le 560 Maitre 2002) are usually used (Sahama 1974; Foley et al. 561 1987; Foley 1992b; Woolley et al. 1996). 562

The microgranular and texturally homogeneous coarse-563 grained xenoliths (Table 2, Figs. 8, 9) have MgO \geq 3 wt.%, 564 $K_2O > 7$ wt.%, and high CaO and are poor in Al₂O₃ and 565 Na_2O (<1.2 wt.%). They show the lowest value of SiO₂, 566 intermediate values of CaO and K2O, and are relatively rich 567 in FeOt and TiO₂. They are evolved with a DI (Thornton 568 and Tuttle 1960 > 45 and have no modal olivine like some 569 ultrapotassic plutonic rocks of the Roman Province, Italy 570 (Peccerillo et al. 1984; Peccerillo 1990). They belong to the 571 melilite-, leucite-, and kalsilite-bearing kamafugite group, 572 according to their major element characters (Table 2; Figs. 8, 573 9). These xenoliths are strongly silica-undersaturated (see 574 CIPW norms, Table 2) with normative leucite, nepheline, 575 and sometimes normative kalsilite. They are very calcic with 576 modal melilite, almost always with normative larnite (some-577 times > 10 wt.%) and normative calcite. 578

The pyroxenite xenoliths are the most enriched in MgO, $_{579}$ CaO, and P₂O₅ due to clinopyroxene and apatite (Figs. 8, $_{580}$ 9; Table 2). Their variable K₂O is essentially related to the occurrence of phlogopite. They are potentially silicaundersaturated but much less than kamafugite and leucitolite xenoliths (Table 2). $_{584}$

The leucitolite xenoliths plot in the leucitite field (Fig. 9). These rocks are relatively poor in MgO, and extremely rich in K_2O and Al_2O_3 , with a very high K_2O/Na_2O ratio (Fig. 9). The opposite variations between K_2O , Al_2O_3 , and FeOt, 588

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Fig. 7 Composition variations of phlogopite. A Sector zoning in phlogopite of the carbonatite xenolith, MEB back-scattered picture. B Ba-K substitution in phlogopite from Eğirdir xenoliths. C BaO versus FeO/FeO+MgO ratio in phlogopite of carbonatite xenolith and

other xenoliths compared to phlogopite of the Jacupiranga carbonatite and phlogopite of leucite lavas (after Gaspar and Wyllie 1982). Green dots, phlogopite of Montefiascone clinopyroxenite, Italy (after Stoppa et al. 2003a, b, c)

TiO₂, and MgO contents depend on the leucite/mafic phases (clinopyroxene, garnet, Fe-Ti oxides) ratio in this group, in relation with mineral segregation process. The leucitolite xenoliths (Fig. 9) are always very depleted in Na₂O by comparison to the melilite-bearing leucitites and other previously studied Afyon leucitites (Akal 2003; Prelević et al. 2015).

The observed gaps between the main xenolith groups 596 (Figs. 8, 9) can be related to cumulative processes involv-597 ing mainly clinopyroxene, apatite, and leucite, as indicated 598 by the textural characteristics of pyroxenites and leucito-599 600 lites. In almost all Harker diagrams (Fig. 8), the xenoliths from the Alban Hills ejecta, Italy (Peccerillo et al. 1984; 601 Federico et al. 1994) plot in the gap observed between 602 pyroxenite and leucitolite groups. They are P₂O₅-poor 603

compared to the pyroxenite group of Eğirdir. The KLT604kalsilitite from Alban Hills ejecta (Figs. 8, 9) plots close605to the kamafugite-type xenoliths of Eğirdir. The assumed606primary kamafugite "KAM" composition proposed by607Prelević et al. (2015) also plots between the pyroxenite608and leucitolite groups (Fig. 9).609

The hyalophane-bearing syenite and Eğirdir leucitite compositions are close to the leucitolite group, but with lower K_2O and $TiO_2 + FeOt$ values.

The carbonatite xenolith is very poor in Na_2O and MgO (Table 2) and belongs to the calcio-carbonatite type. The P_2O_5 is very high (2.58 wt.%) due to the presence of apatite clusters, which must be considered for the interpretation of REE and other trace elements in the rock. 617

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Fig. 8 Major elements versus MgO. Blue triangle, pyroxenite. Yellow triangle, leucitolite. Black square, kamafugite type. Red square, hyalophane-bearing syenite. Green dot, Egirdir leucitite. Open dot, plutonic xenoliths from the Alban Hills Ejecta, Italy



618 Trace elements

The spidergrams normalized to the primitive mantle 619 (Fig. 10A) for trace elements (Table 2) are used for the 620 621 feldspar-bearing syenite, leucitites, and kamafugite-type xenoliths that are close to liquid compositions. The syenite 622 and leucitite patterns are very similar, and show a rela-623 624 tively high LILE to HFSE ratio. The negative Ta, Nb, and Ti anomalies are present but are moderate (weak in the 625 case of Hf), while Zr displays a weak positive anomaly. 626 The kamafugite-types display the same negative anoma-627 lies. They are globally enriched in REE relative to the 628 syenite and leucitite. The negative Sr anomaly is particu-629 larly pronounced for two kamafugite-type xenoliths, prob-630 ably related to early apatite fractionation. All the rocks 631

have a prominent Pb positive peak. All these geochemical 632 features have been also noted for ultrapotassic magmatism 633 of the Roman Province, Italy (Conticelli et al. 2013, 2015). 634 They are related to an orogenic or post-orogenic signature 635 with a crustal material assimilation into the upper mantle 636 during a previous subduction process. However, there are 637 some discrepancies: Ba is not very depleted and there is 638 no clear positive Th and Cs peaks. The same geochemical 639 characters have been observed in the Ultrapotassic-Potas-640 sic Afyon volcanic Province (Prelević et al. 2015). The 641 trace element patterns of the studied xenoliths are very dif-642 ferent from those of intraplate ultrapotassic rocks, similar 643 to the Roman Province (Conticelli et al. 2015). Looking at 644 the REE patterns (Fig. 11), kamafugite-type xenoliths are 645 enriched in REE, especially HREE, compared to leucitite 646

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Fig. 9 Major element diagram with kamafugite, leucitite and lamproite fields after Foley (1987). Blue star, assumed primary kamafugite magma after Prelević et al. (2015). Open diamond, KLT kalsilitolite xenolith from Alban Hills ejecta (Federico et al. 1994). Afyon leucitites are from Prelević et al. (2015). Melilite leucitite are from Akal (2003), Akal et al. (2013)



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Fig. 10 Trace elements normalized to primordial mantle. A Patterns of kamafugite-type (M, black squares), syenite (Sy), leucitite (Leu), and carbonatite (Carbo) xenoliths. B Patterns of leucitolite (Leu) and clinopyroxenite (CPX) xenoliths. Normalizing values from Sun and McDonough (1989)



Fig. 11 REE/chondrite CI normalized patterns. Same rock references as Fig. 10

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and syenite (Figs. 10, 11). All the trends show no positive or negative Eu anomaly.

Spidergrams are less suited to xenoliths involving 649 cumulative processes (pyroxenite and leucitolite xeno-650 liths), but the patterns provide a simple overall view of the 651 main trace elements and can show the possible effects of 652 mineral fractionation on the parent liquids. The pyroxenite 653 xenoliths are depleted in HFSE, Pb, and LILE (including 654 Pb) relative to REE and have enriched HREE relative to 655 LREE, due to their high but variable modal apatite and 656 pyroxene fractions (Figs. 10B, 11). They are Th-enriched. 657 Rb and Ba are variable and enriched together with K in 658 two pyroxenites, due to the third mineral to crystallize 659 which is phlogopite. 660

The trace element patterns of the leucitolite xenoliths 661 are globally similar (Figs. 10B, 11) and characterized by a 662 global depletion in REE, Ta, Nb, and Ti when compared to 663 the patterns of leucitite and kamafugite type. The leucito-664 lites are globally enriched in LILE relative to pyroxenites, 665 and K. However, notable variations of HFSE troughs and 666 HREE/LREE ratio in this leucitolite group seem to be very 667 dependent upon the leucite/clinopyroxene ratio and garnet 668 content. Two garnet-rich leucitolites (Fig. 11) are strongly 669 enriched in HREE, Zr, and Hf relatively to LREE. The role 670 of garnet is probably crucial for these samples, and is con-671 sistent with the trace element patterns of garnet published 672 by Prelević et al. (2015). A prominent peak of Pb is always 673 seen for the most leucite- and garnet-enriched leucitolites, 674 which is a difference with the pyroxenite group. 675

The trace element pattern of the carbonatite (Figs. 10A, 676 11) shows a strong LREE/HREE fractionation pattern 677 and is very depleted in HFSE, except for Nb, and is also 678 depleted in K, Rb, and Th relative to U and Ba. It has the 679 most prominent Pb peak. This pattern has nothing to do 680 with that of intraplate carbonatites, but shows similari-681 ties with those of sandstones, pelites, and especially lime-682 stones of the past and present Mediterranean alpine area 683 (see the trends published by Conticelli et al. (2015 and 684 ref. wherein)), with very high peaks for U, Pb, and Sr and 685 deep troughs for K, Ta, Hf, Zr, and Ti. However, apatite, 686 which forms clusters in the carbonatite xenolith, is the 687 first mineral that can explain the LREE/HREE enrichment 688 of the carbonatite. Moreover, the spidergrams of apatite 689 from the Potassic Ultrapotassic Afyon volcanic Province 690 (Prelević et al. 2015) show the same LREE/HREE enrich-691 ment and deep troughs for Ti, Zr, Ta, and Rb. The only 692 discrepancy concerns Th, which is very low in this car-693 bonatite xenolith. This depletion eventually may be linked 694 to pneumatolytic reworking and escape of Th during the 695 phreatomagmatic event, a process that could be considered 696 as viable for a 10-cm-sized xenolith. 697

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698 Stable isotope data on calcite

¹⁸O and ¹³C stable isotope analyses have been carried out on 699 calcite extracted from the carbonatite xenolith, the peperite 700 matrix, the hyalophane-bearing syenite, and two limestones 701 from the surrounding basement that has been cut and cov-702 ered by the volcanoclastic deposit (Table 3, Fig. 12). Analy-703 ses are reported on the δ^{18} O versus δ^{13} C diagram (after Bell 704 2005; Doroshkevich et al. 2010). The δ^{13} C isotopic signa-705 tures of calcite from the carbonatite xenolith, the peperite 706 matrix, and the hvalophane-bearing svenite are negative and 707 are distinct from the δ^{13} C measured on the limestones from 708 the basement. The δ^{13} C and δ^{18} O values of the carbonatite 709 are close to the limit values for the primary carbonatite field 710 (PCF, Fig. 12). This means that a mantle signature, with 711



slight modification by fractionation or contamination, can be 712 considered for the carbonatite xenolith. Similarly, the δ^{13} C 713 of the calcite found in the syenite is also compatible with a 714 primary origin of the CO2-rich fluid component dissolved 715 in the magma parent and plots within the so-called Euro-716 pean carbonatite field. However, the δ^{18} O is significantly 717 higher, which can be ascribed to a contamination during a 718 low-temperature alteration process. The δ^{18} O of the peperite 719 matrix is much higher and disconnected from its δ^{13} C that 720 remains low, which can be ascribed to a main contamina-721 tion process at a low temperature involving meteoritic H₂O 722 during the volcanic event. A carbonatitic fluid interaction 723 has been proposed in some peperite belonging to the Ceno-724 zoic French Limagne phreatomagmatism (Bailey et al. 2006; 725 Chazot and Mergoil-Daniel 2012), which is an alternative 726

Rock sample	Processing	d13C/PDB	d18O/PBD	d180/SMOW*	Mineral specificity
E17 carbonatite	H3PO4 24 h à 25 °C	-4.60	-17.76	12.60	calcite
E17 carbonatite	H3PO4 15 Days at $T=25$ °C	-4.60	-17.82	12.54	calcite + Mg-carbonate
E10 syenite	H3PO4 15 Days at $T=25$ °C	-5.30	-13.81	16.67	calcite + Mg-carbonate
E10 syenite	H3PO4 24 h at T = $100 \degree C$	-5.55	-14.94	15.51	all carbonates
SE17 limestone	H3PO4 15 Days at $T = 25 $ °C	1.94	-2.34	28.50	calcite + Mg-carbonate
SE08 limestone	H3PO4 15 Days at $T=25$ °C	-0.83	-6.41	24.30	calcite + Mg-carbonate
PEP peperite matrix	H3PO4 15 Days at T=25 °C	-6,8	-9.65	20.96	calcite + Mg-carbonate

 δ^{18} O SMOW calculated after Coplen et al., 1983. Measure precisions: δ^{13} C/PDB ± 0.1; δ^{18} O/PBD ± 0.2

Fig. 12 δ^{13} C versus δ^{18} O stable isotope composition of calcite from xenoliths and limestones. Calcite has been extracted from two plutonic xenoliths (carbonatite and syenite), the peperite matrix at the bottom of the volcano-clastic deposit, and two limestones (Mesozoic limestone and Eocene lacustrine) of the surrounding basement. PCF, primordial carbonatite field



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from the classical origin of peperite. It is difficult to rule out 727 the prevalent low-T interaction process between the leuci-728 tite magma, meteoritic water, and limestones or lacustrine 729 that raises the δ^{18} O but not the δ^{13} C for the calcitic matrix 730 of the peperite. In the other hand, the low δ^{13} C can also be 731 explained by the presence of a juvenile CO₂-rich fluid in 732 relation with the leucitite lava or/and a separate carbonatitic 733 magma. 734

735 Discussion

736 Xenolith mineral parageneses and their origin

Textures and restricted mineral paragenesis of pyroxen-737 ites and leucitolites (one to three euhedral major phases), 738 and geochemical gaps existing between pyroxenites and 739 leucitolites on the one hand, and syenite, kamafugites, 740 and leucitites on the other hand, suggest that pyroxenites 741 and leucitolites are assumed to be cumulates derived from 742 underlying magma intrusions. The term of autolith would 743 be better than xenolith for these two groups of rocks as it 744 has been used for the autoliths from the Kilombe volcano, 745 Kenya Rift, and the Ilimaussaq autoliths, Greenland (Ridolfi 746 et al. 2006; Schönenberger et al. 2006). Cumulate-type rocks 747 are known in ultrapotassic provinces, such as the Malawi 748 ring complexes, in particular the ultrapotassic Mlindi ring 749 complex (Laval and Hottin 1992). Trace element patterns of 750 pyroxenite and leucitolite also show that their bulk composi-751 tions are a direct expression of the ratio of mafic and felsic 752 mineral. Apatite, clinopyroxene, phlogopite, and leucite are 753 the major mineral phases that crystallized in the magma at 754 depth, in good agreement with the differentiation process 755 suggested by Prelević et al. (2015). 756

Small xenoliths of kamafugite affinity are very enriched
in early melilite crystals and some leucitolite cumulates are
very garnet-enriched, which suggests that some garnet- or
melilite-enriched segregations or layers formed during their
crystallization.

Kamafugite-type and syenite xenoliths show homogeneous fine-grained porphyritic textures, a common feature
observed not only in small dykes, but also on the chilled
margins of intrusions. Coarse-grained kamafugite-type
xenoliths never show layering features or crystal segregation, indicating that they probably represent evolved liquids
injected and crystallized at depth in the crust.

769 Implications of experimental studies

The variable mineral paragenesis of the studied xenoliths is
relevant to the complex system kalsilite-forsterite-larnitequartz tetrahedron and related subtetrahedra (Yoder 1986;
Gupta 2015) and has been experimentally investigated for

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a long time (Gupta et al. 2006; Edgar et al. 1976; Gupta AQ11 74 and Yagi 1980; Veksler et al. 1998; Gupta 2015 and ref. 775 wherein). In the Eğirdir xenoliths, the presence of phlogo-776 pite and lack of olivine fit well in the phlogopite-kalsilite-777 clinopyroxene-leucite-melilite-feldspar sub-tetrahedra, 778 with mutual exclusion between melilite and feldspar, as it is 779 observed in melilite-bearing kamafugite-type and feldspar-780 bearing syenite xenoliths. However, the natural paragenesis 781 system is more complicated than the experimental system 782 because Fe and Ti were not considered. The later elements 783 probably complicated the paragenesis with crystallization 784 of FeTi-oxides and garnet. Heteromorphic relations with 785 incomplete reactions (Yoder 1986) in kamafugite magmas 786 can also complicate the paragenesis of the rocks during 787 crystallization. 788

Conditions of crystallization and fractionation processes

The modal variations depicted in the xenoliths show that791the early crystallizations of melilite, clinopyroxene, apatite,792and phlogopite, followed by leucite, play the major role in793the differentiation process, in good agreement with experi-794mental studies.795

Early crystallization of phlogopite rather than olivine in phlogopite-bearing pyroxenite cumulates, and early Ti-Fe oxides associated with clinopyroxene phenocrysts in subvolcanic kamafugite-type are symptomatic of relatively elevated partial $P_{\rm H2O}$ and oxidizing conditions during crystallization. 800

It is difficult to specify from which magmatic bodies 801 (depth and size) the rock samples have been extracted, when 802 they only consist of a set of xenoliths. The leucitite lava 803 was responsible for their extraction and we consider that 804 leucitite represents the last magma passing through the pre-805 vious crystallized intrusions and dykes, being the residual 806 magma coming from the crystallizing intrusions and lately 807 injected towards the surface. The stability field of leucite in 808 the presence of dissolved water is restricted when the pres-809 sure increases, leucite being finally removed beyond 0.8 GPa 810 (Fudali 1963; Gittins et al. 1980 and references therein). 811 The systematic occurrence of leucite in the xenoliths, even 812 in pyroxenite, indicates that the xenoliths have crystallized 813 under relatively low $P_{\rm H2O}$, not above the 0.3–0.8 GPa range, 814 i.e., at a maximum depth of 25 km. This maximum depth 815 corresponds to the xenoliths showing frequent and early 816 crystallization of phlogopite (Prelević et al. 2015). 817

Calcite crystallization depends not only on the composition and evolution of the dissolved fluid phase in magma, but also on the low-temperature alteration processes. This is true for the calcite-bearing syenite xenoliths and for the kamafugite-type xenoliths. In the CO_2 vs CaO diagram (Appendix 3), CO_2 is higher in the kamafugite and syenite xenoliths than in the pyroxenite and leucitolite cumulates B22 (see Table 2). The kamafugite and syenite evolved liquids appear to be enriched in CO_2 relative to H_2O . Early phlogopite fractionation may have increased the CO_2/H_2O ratio in the dissolved fluid phase.

As explained by Yoder (1986) and McBirney (1984) 829 for the Ultrapotassic Shonkin sag laccolith (Montana), it 830 is difficult to explain the relationships between all types of 831 rocks by a single fractional crystallization process from a 832 single primary magma; in addition, Eğirdir xenoliths are 833 not demonstrated to be all cogenetic. Other processes could 834 also operate during the crystallization of intrusions: (i) 835 percolation-reaction of the residual melt through the cumu-836 lates by infiltration metasomatism, as it is assumed in the 837 mafic-ultramafic cumulates of layered intrusions near the 838 solidus (Irvine 1980; Tait et al. 1984; Sparks et al. 1985; 839 Brandeis and Jaupart 1986; Boudreau 1995); (ii) volatile 840 transfer of Na relative to K explaining why the leucitolite 841 cumulates are very depleted in Na₂O (McBirney 1984; Pec-842 cerillo 1994); (iii) mobile pneumatophile elements such as 843 Th, during the hydrothermal activity at low pressure, and 844 percolation of a CO₂-rich fluid phase exsolved from the 845 residual magma. 846

The evolution trends may be illustrated in the CaO/K₂O/ 847 Fe_2O_3 ternary diagram (Fig. 13). The primary melts are 848 unknown. The less evolved KAM mafic magma assumed 849 by Prelević et al. (2015) is close to the intermediate and 850 salic ejecta found in the Alban Hill, Italy, especially the 851 KLT kalsilitite xenolith (Lacroix 1893, 1917; Conticelli and 852 Peccerillo 1992eccerillo 1992; Federico et al. 1994). The 853 Eğirdir kamafugite seems to be more evolved and may be 854 the result of efficient clinopyroxene and leucite fractionation, 855

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leading to iron enrichment relative to CaO and K₂O, being 856 thus related to the two main groups of Eğirdir cumulates 857 (pyroxenite and leucitolite). The evolution represented by 858 the leucitite lava is mainly controlled by leucite fractiona-859 tion, with iron content remaining globally constant, and is 860 related to the crystallization of garnet and Fe-Ti oxides. The 861 resulting liquid line of descent is questionable as not all 862 xenoliths are cogenetic, especially the kamafugite-type and 863 syenite xenoliths, which are most likely related to two dif-864 ferent magmas. If a reasonable liquid line of descent exists, 865 it should be restricted from kamafugite to leucitite magmas 866 in relation to the trend of assumed cumulates shown in this 867 ternary diagram. 868

Carbonatite xenolith significance and hypothetic origin

The association of carbonatite and kamafugite magmas is 871 known elsewhere in ultrapotassic magmatism, where blobs 872 of calcio-carbonatite and kamafugite can be intimately asso-873 ciated. This relationships between two contrasted carbon-874 ate-silicate conjugates have been described for example in 875 magmatic rocks of the Mahlber complex, Germany (Solo-876 vova et al. 2003), in the West Qinling Province, China (Yu 877 et al. 2003; Guo et al. 2014), in the Ruri Volcano, Kenya 878 (Stoppa et al. 2003b), and in the Roman Province and 879 Intra-mountain Ultra-alkaline Province, Italy (Stoppa and 880 Wooley 1997; Stoppa et al. 2003a). In the Potassic Ultra-881 potassic Afyon volcanic Province, this intimate association 882 has been observed in leucite-bearing phonolites (Elitok 883 2019). This close association between carbonatite and very 884



ternary diagram. Blue triangle, pyroxenites; yellow triangle, leucitolites; black square, kamafugite type; red square, hyalophane-bearing syenite; small green dots, leucitites of Afyon ultrapotassic series (after Prelević et al. 2015); large green dot, leucitite of Egirdir. Green star, KAM assumed primary kamafugite magma (Prelević et al. 2015); white cross, KLT kalsilitolite xenolith from Alban Hills ejecta (Federico et al. 1994); gray star, hypothetic primary mafic magma. Blue arrows trend of successive cumulates; blue broken arrows, hypothetic magma evolution trend. The fractionation process would be governed by the mineral phases in the successive boxes

Fig. 13 K₂O-Fe₂O₃-CaO

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silica-undersaturated rocks has been attributed to an immis-885 cibility process between carbonatite and silicate liquids. This 886 immiscibility model between two silicate-carbonate conju-887 gates has been experimentally tested at a relatively low pres-888 sure from < 0.1 to 0.5 GPa (Koster van Groos and Wyllie 889 1966; Wyllie 1987; Kjarsgaard and Hamilton 1988; Lee and 890 Wyllie 1998). Eğirdir xenoliths and their set of rock-forming 891 minerals are plotted in the silica-alkali-carbonate diagram 892 where the immiscibility fields are reported (Fig. 14) after 893 Kjarsgaard and Hamilton (1988). The two arrows drawn 894 from leucitolites and pyroxenites show that these cumulates 895 can lead to the Eğirdir kamafugite through immiscibility in 896 the 0.1-0.5-GPa pressure range. However, the theoretical 897 conjugate carbonatitic liquid does not fit with the calcio-car-898 bonatite xenolith found at Eğirdir: in this model, the compo-899 sition of the Eğirdir carbonatite would require an additional 900 process of accumulation of calcite and apatite crystals. 901

Another model for the genesis of the Eğirdir calciocarbonatite would be to consider a direct interaction of the leucitic magma with the limestone basement (Elitok 2019).

Phreatomagmatic interaction with limestone basement
or lacustrine carbonate during the explosive eruption
could explain the calcitic matrix of the breccia occurring
within the pipe and the peperite from the bottom of the
Eğirdir phreatomagmatic deposit. However, stable isotope



Fig. 14 Liquid immiscibility fields for Pt < 0.1 GPa and Pt=0.5 GPa, in the SiO₂+Al₂O₃+TiO₂ – Na₂O+K₂O – CaO+FeO+MgO ternary diagram. Blue stars, pyroxenite xenoliths; other stars, mineral phases. Black squares, kamafugite-type xenoliths; red square, hyalophane-bearing syenite; black dot, Egirdir leucitite; yellow dot, leucitolite xenoliths. Blue straight line, conjugate silicate-carbonate liquids at P < 0.1 GPa. Green dashed line, conjugate liquids at 0.5 GPa (after Kjarsgaard and Hamilton 1988). Blue and red dotted lines with arrows, effect of leucite and clinopyroxene during fractional crystallization; the two trends cross at the average cumulate

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compositions of calcite from the Eğirdir carbonatite indicate low crustal contamination. It seems that the origin of the Eğirdir carbonatite differs from the result of interaction between the leucitic magma with the limestone basement.

Globally, the composition of the Eğirdir calcio-carbonatite does not correspond to the intraplate carbonatite compositions related to HIMU and EM1 mantle components (Simonetti and Bell 1994; Woolley 2003; Tappe et al. 2003; AO12 AO13Bell and Simonetti 2009) or to a direct CO₂-enriched fluid produced during the asthenosphere upwelling after the breakoff of the slab. 916 917 918 918 920

The composition of the Eğirdir carbonatite xenolith is 921 more consistent with carbonatites found in an orogenic or 922 post-orogenic geodynamical setting. The coexistence of 923 ultrapotassic rocks and carbonatite has been a subject of 924 debate for a long time (Foley 1992a, 1992b; Peccerillo 1984, 925 1998; Vollmer 1989; Peccerillo and Foley 1992; Ersoy et al. 926 2010; Prelević et al. 2008, 2010a, 2010b, 2012, 2015; Con-927 ticelli 1998; Conticelli et al. 2007, 2013, 2015). In a post-928 collisional geodynamical situation, the carbonatite mantle 929 source would be phlogopite-bearing pyroxenite veins formed 930 in a moderately depleted lithospheric mantle metasomatized 931 by the fluid released by the sediments of the subducted slab. 932 There is also a possibility to produce a carbonatitic melt by 933 a fractionation-melting process of the metasomatized mantle 934 source: this origin for carbonatite was proposed by Mitchell 935 (2005). More extensive partial melting of the same source 936 may product primary lamproite or kamafugite magmas, with 937 high K/Na ratio, and high Ca, Mg, and CO₂ contents related 938 to the metasomatized source. The differentiation process can 939 also be at the origin of carbonatite: indeed, after extensive 940 differentiation of melilitite and nephelinite magmas, a car-941 bonatite residue may be produced (Mitchell 2005). 942

The mantle source of the UKAP magmatism and its com-943 plex metasomatization have been debated in the successive 944 papers of Prelević et al. (2008, 2010a, b, 2012, 2015). Future 945 isotopic studies of the Eğirdir xenoliths will be of great help 946 to better understand the origin and relationships of these 947 plutonic xenoliths with the Potassic Ultrapotassic Afyon 948 volcanic Province, and to clarify whether they have fully or 949 partially preserved their complex mantle geochemical signa-950 ture, despite contamination processes during crustal magma 951 injection and differentiation. 952

Concluding remarks

The plutonic xenoliths found in the Eğirdir phreatomagmatic954deposits have been extracted from dykes or/and plutonic955intrusions related to batches of magma injected at crustal956level.957

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Pyroxenite or leucitolite cumulates were formed during the differentiation of these crustal intrusions under a 959

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maximum P_{total} of 0.8 GPa corresponding to a maximum depth of 25 km. These rocks are assumed to be autoliths.

Eğirdir xenoliths are related to the strongly silica-depleted 962 ultrapotassic series of West Anatolia. Some of them have 963 kamafugite affinities and display the first occurrence of 964 kalsilite in this ultrapotassic series. Two forms of kalsilite 965 have been observed: a high-T hypersolvus homogeneous 966 form symptomatic of rapid cooling, and a subsolvus low-T 967 exsolved form associated with separate nepheline crystals 968 in slow-cooling intrusions. In syenite, feldspar crystallized 969 first as hyalophane, which played the same role of nepheline 970 during the leucite destabilization in K- and Ba-rich, and Na-971 poor magmas. 972

The mineral paragenesis that controlled the fractional 973 crystallization process was mainly composed of clinopyrox-974 ene apatite, melilite, phlogopite, and leucite, with additional 975 garnet and Fe-Ti oxides during the near-solidus evolution 976 of leucitolite cumulates. Phlogopite crystallization in some 977 pyroxenite indicates that partial P_{H2O} was high during their 978 crystallization, leading to an increase of the CO₂/H₂O ratio 979 in the dissolved fluid phase. 980

The trace elements of the investigated xenoliths corresponding to liquid compositions (kamafugite and syenite types) indicate an orogenic/post-orogenic geodynamical setting as assumed for the Potassic Ultrapotassic Afyon volcanic Province (Prelević et al. 2008, 2015) and the Roman Province, Italy (Peccerillo 1990; Conticelli et al. 2013).

A carbonatite xenolith has been found for the first time in 987 this area. There are no convincing petrographic arguments to 988 support an immiscibility process between two silicate-car-989 bonate conjugates. C and O stable isotopic compositions on 990 calcite indicate that the carbonatite has a mantle origin with 991 relatively limited crustal contamination. The origin of the 992 carbonatite by differentiation from a primitive kamafugite-993 type magma, or by a fractionation-melting process of a meta-994 somatized mantle source remains to be tested in the future. 995

New isotopic data on Eğirdir xenoliths, especially on
carbonatite- and kamafugite-type xenoliths, are needed to
better understand their origin, their possible cogenesis, and
mantle sources.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s12517-023-11766-7.

Acknowledgements Special thanks to E. Chassefière, past head of the 1002 GEOPS research team, N. Özgur, and F. Yağmurlu past dean of the 1003 Sûleyman Demirel University. M. Fialin and N. Rividi are thanked 1004 for microprobe analysis assistance at Camparis Lab., Université 1005 Paris-Sorbonne, also V. Godard for the excellent polish fine sections. 1006 L. Weinberg is thanked to improve the English language. An anony-1007 mous reviewer is thanked for his comments on an earlier version of 1008 the manuscript. J.P. Liégeois is warmly thanked for careful review of 1009 1010 the manuscript.

Funding This work was financially supported by the UMR CNRS 8148GEOPS, Dpt. Sciences de la Terre, Université Paris-Saclay, and the

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Sûleyman Demirel University, Isparta, Turkey for field work support and accommodations. 1014

Declarations

Conflict of interest The author(s) declare that they have no competing 1016 interests.

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fournal : Large 12517 Article No : 11766	Pages : 26	MS Code : 11766	Dispatch : 24-11-2023
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