### **ORIGINAL PAPER**



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

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### **Abstract**

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

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

This work is dedicated to the late Dr. A. Poisson who have shown the studied area to the frst 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 Montefascone volcanism, Italy (Keller [1983](#page-24-0); Peccerillo et al. [1984](#page-24-1); Federico et al. [1994](#page-23-0); Vollmer [1989](#page-25-0); Beccaluva et al. [1991](#page-22-0); Beccaluva et al. [2012](#page-22-1); Peccerillo [1990,](#page-24-2) [1992](#page-24-3), [1994;](#page-24-4) Di Battistini et al. [2001;](#page-23-1) Stoppa [2003;](#page-25-1) Stoppa et al. [2003a;](#page-25-2) Gaeta et al. [2006](#page-23-2); Conticelli et al. [2013,](#page-23-3) [2015](#page-23-4)), and also in the ultrapotassic volcanic series from the East African rift (Bell and Powell [1969;](#page-22-2) Mitchell and Bell [1976](#page-24-5); Pouclet [1980;](#page-24-6) Edgar and Arima [1981;](#page-23-5) Bergman [1987;](#page-22-3) Kampunzu and Lubala [1991](#page-23-6); Laval and Hottin [1992](#page-24-7); Bell and Tilton [2001](#page-22-4); Stoppa et al. [2003b\)](#page-25-3). For a long time, authors have paid attention to the distinctive mineralogy of potassic-ultrapotassic rocks in relation with magma crystallization and diferentiation (Yoder [1986;](#page-25-4) Veksler et al. [1998\)](#page-25-5) and their complex hypothetic mantle source and successive mantle metasomatism events in relation with a post-collision, extensional geodynamical context (Savasçin et al. [1994](#page-24-8); Yağmurlu et al. [1997](#page-25-6)). However, there are few data regarding plutonic intracrustal intrusions especially for the tertiary Potassic-Ultrapotassic Afyon volcanic Province. Erosion processes did not allow access to the plutonic level, and only scarce mafc–ultramafc xenoliths entrained during volcanic events have been described and related to crustal intrusions (Akal [2003](#page-22-5); Prelević et al. [2015\)](#page-24-9).

#### **Geological background**

As part of the Alpine-Himalayan orogenic belt, Turkey consists of an amalgamation of Gondwana-derived continental blocks associated with ophiolitic units. The Anatolide-Tauride block which occupies western and southern parts of Turkey is subdivided into zones based on the type of metamorphism and age of deformation (Fig. [1](#page-2-0)a, b): Tavşanlı Zone, Afyon Zone, Menderes Massif, Bornova Flysch Zone, and Tauride Belt. The frst four zones are characterized by medium–high-pressure metamorphic rocks (Bornova Flysch Zone). These zones are the low-grade metamorphic basement intruded by felsic igneous rocks (Tauride Belt, Gürsu et al. [2004](#page-23-7)), Mesozoic to Cenozoic sedimentary sequences, and stack of imbricated, ophiolite-bearing allochthonous nappes. The western part of the Tauride carbonate axis forms a north-pointing cusp in the north of Eğirdir Lake, the so-called Isparta Angle, and includes the study area. The northeast–southwest trending Beydağları platform carbonate separates allochthonous ophiolitic rock units with, from west to east, the Lycian nappes, the Antalya complex, and the Hoyran-Beyşehir-Hadım nappes. These four nappe systems join around Eğirdir Lake (Fig. [1](#page-2-0)b). Southwestern Turkey has been subjected to compressional and extensional tectonic activities, ophiolite emplacements, block rotations, and volcanic activities throughout Phanerozoic time.

Neotectonic structures developed in SW Turkey during the Late Miocene to Early Pliocene with local efects at the end of Middle Oligocene in a transtensional regime (Koçyiğit [1984a](#page-23-8), [b\)](#page-23-9). They correspond to regional uplift, continental sedimentation (thick pile of molasse deposition), syn-sedimentary volcanism, and block faulting.

#### **Potassic‑ultrapotassic volcanisms in West Anatolia**

North–south trending volcanic rocks, named Kırka-Afyon-Isparta Volcanic Province or Kırka-Afyon-Isparta Alkaline Volcanic assemblage (after Savaşçın and Oyman [1998\)](#page-24-10),

crop out from the apex of the Isparta Angle to the north of Afyon, including the studied area, and are characterized mainly by potassic–ultrapotassic volcanic rocks (Fig. [1](#page-2-0)a, c) (Alici et al. [1998;](#page-22-6) Akal [2003;](#page-22-5) Platevoet et al. [2008,](#page-24-11) [2014](#page-24-12); Elitok [2019;](#page-23-10) Prelević et al. [2012](#page-24-13), [2015](#page-24-9); Akal et al. [2013](#page-22-7)). In general, from north to south in the Kırka-Afyon-Isparta volcanic Province, volcanic activities get younger: 14.8 and 8.6 Ma around Kırka-Afyon in the north, from  $4.7 \pm 0.2$  Ma around Isparta (Lefèvre et al. [1983\)](#page-24-14) to  $24 \pm 2$  ka (Platevoet et al.  $2008$ ) and  $12.9 \pm 0.4$  ka (Guillou et al.  $2017$ ) in the south, corresponding to the last volcanic events of the Gölcük volcano. The volcanic activities in SW Turkey are in close relationship with the neotectonic evolution of the region.

The Tertiary-Quaternary volcanic Province of West Anatolia is divided into a northern series named the Potassic-Ultrapotassic Afyon volcanic Province (Akal [2003;](#page-22-5) Akal et al. [2013;](#page-22-7) Prelević et al. [2012](#page-24-13), [2015\)](#page-24-9) extending north to south, from Afyon to Eğirdir Lake (Fig. [1b](#page-2-0)). It is formed by three main series, including a strongly silica-undersaturated, leucite-bearing volcanic series located at the southern part where we found the xenoliths, the subject of the present study. The Isparta potassic volcanic series is more recent, with the Quaternary Gölcük volcano situated in the so-called Isparta Angle (Lefèvre et al. [1983;](#page-24-14) Alici et al. [1998](#page-22-6); Platevoet et al. [2008](#page-24-11); Ҫoban et al. [2019](#page-23-12)).

# **Field occurrence**

Sample locations are in the NW Hoyran lake (N Eğirdir lake), within a NE-SW trending horst structure bounded by the Senirkent graben in the south (Fig. [1](#page-2-0)c) and the Haydarli graben in the north. Mesozoic formations consisting mainly of massive or bedded limestones form the basement (Fig. [1](#page-2-0)c, d), locally unconformably overlain by Eocene fysch-type deposit, or by Upper Miocene-Pliocene volcano-sedimentary deposits (Elitok [2019,](#page-23-10) and references therein). Trachytic domes are observed in the west of the studied area and leucite-bearing lava dome flows are observed to the NW close to the Haydarli graben.

Along the Afyon-Karahisar road, the Cretaceous limestones and Cenozoic lacustrine levels are cut by a volcanic pipe 5 m wide (Fig. [1](#page-2-0)e). This pipe consists of a leucitebearing brownish volcanic material including numerous xenoliths of volcanic and plutonic types. At the contact between the pipe and the limestone basement, the limestones are brecciated and some blocks are incorporated in the volcanoclastic breccia. The xenoliths and the enclosing matrix are extensively hydrothermally altered by a  $CO<sub>2</sub>$ -dominant fuid phase, as evidenced by millimeter- to centimeter-size calcite veins.



<span id="page-2-0"></span>**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; **e** top, the leucitite pipe with limestone blocks and xenoliths; **f** the volcanoclastic deposit, the peperite has a white calcitic matrix including black leucitite granules

Near the pipe, towards the south, a volcanoclastic deposit is formed by a brecciated leucitite, which also contains numerous xenoliths. The lower part of this volcanoclastic deposit is composed of a 50-cm-thick layer of a pulverized leucitite lava in a calcitic-zeolitic matrix, similar to a peperite (Fig. [1e](#page-2-0), f). The xenoliths (5 to 20 cm in size) were collected in this volcanoclastic deposit. They are angular or rounded and show a variety of textures from fne-grained porphyric textures to equant coarse-grained textures (Fig. [2](#page-3-0)). The xenoliths are leucocratic to melanocratic, depending on their mafc-felsic mineral assemblage. Small ultramafc 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.

<span id="page-3-0"></span>**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



# **Analytical methods**

Mineral compositions were determined at CAMPARIS Lab. (Université Paris-Sorbonne, France), using the Cameca SX 100 or Cameca SX Five electron probe microanalyzers (with 4 or 5 wavelength-dispersive spectrometers). Element calibrations were done using a set of silicates, oxides, and REE-dopped glasses. Accelerating voltage and beam current were  $U=15$  kV,  $I=10$  nA, with a beam of 1–5  $\mu$ m wide; the counting times for each element were 10 s and 5 s for background on each side of the measured X-ray peak for each element. The mineral compositions are calculated using a Z.A.F. iterative matrix correction. Mineral structural formulae were calculated on a classical stoichiometric basis chosen for each mineral species.

 $18$ O and  $13$ C stable isotope analyses were carried out on calcite extracted from magmatic rocks and the limestone basement. Calcite powder was reacted with 100% orthophosphoric acid at 25 °C and the derived  $CO<sub>2</sub>$  was analyzed using a VG Sira 10 mass spectrometer to determine O and C isotope composition at the GEOPS laboratory (Université Paris-Saclay, France). All isotopic values are reported in the standard δ-notation in per mil relative to V-PDB (Vienna Pee Dee Belemnite) by assigning a  $\delta^{13}$ C value of + 1.95% and a  $\delta^{18}$ O value of−2.20‰ to NBS19. Reproducibility was checked by a replicate analysis of laboratory standards and was $±0.1\%$ for carbon isotopes and  $\pm 0.2\%$  for oxygen isotopes.

Whole-rock major and trace element concentrations of the samples were determined by inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry, respectively at the Service d'Analyse des Roches et des Minéraux (SARM, CRPG, Nancy, France).  $CO<sub>2</sub>$  analyses of the fire loss on ignition were carried out for each rock.

# **The volcanoclastic deposit: leucitite and peperite**

The volcanoclastic deposit consists of a brecciated and hydrothermally altered leucitite (Fig. [1](#page-2-0)e). At the base of the deposit, there is a 50-cm-thick layer of a mixture of dark leucitite granules enclosed in a white matrix composed essentially of calcite and zeolites. This 50-cm-thick layer seems to be a peperite (Fig. [1](#page-2-0)f). Similar deposits are commonly described during explosive phreatomagmatic eruptive events occurring within lacustrine areas. The gray-black leucitite granules contain phenocrysts of clinopyroxene and leucite in an essentially dark microlithic groundmass composed of opaque oxide, feldspar, clinopyroxene, apatite, and glass. The granules are surrounded by a matrix composed of calcite and zeolites. Some clinopyroxenes are isolated during the granulation process of leucitite. The volcanoclastic deposit also contains some well-preserved angular to more rounded enclaves of leucitite, very similar in texture and mineral paragenesis to the leucitite matrix of the volcanoclastic deposit.

# **Main petrological groups of xenoliths**

Forty xenoliths were investigated and divided into five groups (Table [1](#page-5-0)), according to their mineral paragenesis (Table [1](#page-5-0)): pyroxenites, plutonic kamafugite-type rocks, leucitolites, syenites, and only one carbonatite xenolith.

### **The pyroxenite xenoliths**

Pyroxenites (Fig. [2](#page-3-0)a, b; Table [1\)](#page-5-0) are ultramafic rocks with more than 90 vol.% of mafc minerals (clinopyroxene, phlogopite) associated with numerous prismatic crystals of apatite and minor amounts of interstitial felsic minerals  $\left($  < 10 vol.%). Phlogopite, when present (0–20 vol. %), is typically subhedral to anhedral, crystallizing after clinopyroxene and apatite (Fig. [2](#page-3-0)b). Dark interstitial melanite-type garnet, leucite, zeolites, and calcite are present in small amounts. Leucite is commonly replaced by a mixture of zeolite, calcite, and phyllosilicate. These xenoliths are very similar to ultramafc xenoliths from the Potassic Ultrapotassic Afyon volcanic Province described by Prelević et al. [\(2015](#page-24-9)).

### **The kamafugite‑type xenoliths**

These xenoliths contain from 5 to 30 vol.% of kalsilite  $(KAISiO<sub>4</sub>)$ , 25–30 vol.% of leucite, nepheline, and no feldspar. Kalsilite has never been described before in the previous studies of the Potassic-Ultrapotassic Afyon volcanic Province (Akal et al. [2013;](#page-22-7) Prelević et al. [2015;](#page-24-9) Elitok [2019](#page-23-10)). It also occurs in the Western Africa Rift ultrapotassic magmatism and in the Italian Roman Province (Di Battistini et al. [2001;](#page-23-1) Tappe et al. [2003](#page-25-7); Stoppa et al. [2003a](#page-25-2)). Two main textures of kamafugite-type xenolith are observed: a microgranular porphyritic texture and a coarse-grained texture.

The microgranular porphyritic xenoliths have variable modal compositions (Fig. [2](#page-3-0)c, Table [1](#page-5-0)) with porphyrocrysts of leucite, zoned clinopyroxene including tiny early Timagnetite, prismatic melilite, and later idiomorphic zoned (black core to yellow rim) garnet and magnetite. Kalsilite is typically the last major mineral to crystallize in these rocks, after apatite, clinopyroxene, magnetite, melilite, and just before garnet. Garnet includes other phases like melilite,

<span id="page-5-0"></span>**Table 1** Modal composition of studied plutonic xenoliths and leucitite



Altered foide  $5$  7  $10$  10  $5$  + Feldspath  $\frac{3}{3}$  65 + Clinopyroxene 10 35 20 10 5 5 20

Apatite 5 2 2 2 3 2 +

Titanomagnetite  $+$ Others (zeolites) 3 1 + Groundmass 50

Garnet 10 10 15 12 10 Calcite 5 10

Mica 5 2 2 5 2

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. [2](#page-3-0)c).

Nepheline Altered foide Feldspath Clinopyroxene

Titanomagnetite Others (zeolites) **Groundmass** 

Melilite

Nepheline

The coarse-grained xenoliths (Fig. [2d](#page-3-0), e) not only have the same mineralogy, with apatite, leucite, prismatic kalsilite, and zoned garnet but they also contain phlogopite. Clinopyroxene is less abundant and melilite is rare or absent. In coarse-grained xenoliths, kalsilite and nepheline crystallize as separate phases. Kalsilite forms euhedral, tabular crystals (Fig. [2](#page-3-0)d) showing kalsilite-nepheline exsolution intergrowths (Fig. [3\)](#page-6-0), symptomatic of subsolidus reequilibration. Such exsolution intergrowths have been described in Mt Nyiragongo lava (Congo), in melilitolites, kalsilitites, and kamafugites from Roman Province and Intramountain Ultra-alkaline Province, Italy (Aurisicchio and Federico [1985;](#page-22-8) Federico et al. [1994;](#page-23-0) Stoppa et al. [2003a\)](#page-25-2). Melilite is associated with variable amounts of clinopyroxene, garnet, apatite, phlogopite, Ti-magnetite, and calcite, while olivine is not present. Calcite and brown-yellowish phases (a mixt of hydroxide amorphous phases and phyllosilicates) commonly replace the core of melilite crystals. Intergrowth features between garnet and leucite are common. Large crystals of nepheline can be relatively abundant (5 to 20 vol.%) in these xenoliths and calcite is interstitial. Two small (no more than 5 cm in size) mafc–ultramafc xenoliths also belong to this group. The frst xenolith is extremely rich in melilite (45 vol.%, Table [1](#page-5-0) sample 98-A), and can be named melilitolite. The second xenolith is a garnet-rich type; a similar garnet-bearing xenolith has been also described in the leucitites from the Balç1khisar volcanic area (Akal et al. [2013](#page-22-7)).



<span id="page-6-0"></span>**Fig. 3** Kalsilite and nepheline compositions. Microprobe backscattered picture of euhedral kalsilite, crystal showing exsolutions features: fne 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;](#page-25-8) Zeng and MacKenzie [1984](#page-25-9))

### **The leucitolite xenoliths**

Leucitolites are the commonest and largest plutonic xenoliths (10–15 cm in size). They are mostly coarse-grained and their mineral parageneses difer only in the relative mafc to felsic mineral ratio, in particular leucite, varying from 45 to 70 vol.%, and giving mesocratic to leucocratic type rocks (Fig. [2f](#page-3-0)). Adjacent crystals of leucite typically show 180° triple joins, suggesting leucite crystal segregation, followed by textural subsolidus re-equilibration and crystal aging (Boudreau [1995;](#page-22-9) Marsh [1998,](#page-24-15) [2007;](#page-24-16) Laporte and Provost [2000;](#page-24-17) McBirney [2007;](#page-24-18) McBirney et al. [2009\)](#page-24-19). This process of subsolidus re-equilibration can happen during slow cooling of magmatic intrusions, but it remains controversial in particular for felsic intrusions (Holness and Vernon [2014](#page-23-13); Holness et al. [2017,](#page-23-14) [2018](#page-23-15)). Leucite is locally partially replaced by a mixture of alkali feldspar and zeolite. The other mineral phases are euhedral green clinopyroxene, prismatic apatite, poikilitic garnet, Ti-Fe oxides, and phlogopite. Kalsilite is rare in leucitolite and occurs as poikilitic, commonly altered crystals located between euhedral leucite crystals. Textural features such as two-phase layering, with pyroxene-rich thin layers and extremely rich leucite layers, are symptomatic of crystal segregation by a rheological process or by a densitydriven cumulative process within the magma intrusions.

#### **Feldspar‑ and leucite‑bearing syenite xenoliths**

Their textures are fne-grained to coarse-grained (Fig. [2](#page-3-0)g). 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 sometimes nepheline. Zoned garnet and poikilitic zoned alkali feldspar are observed. Few sections of pale-brown mica and Ti-Fe oxides are observed. The paragenesis variations from one sample to one another are dependent upon the destabilization degree of leucite which is partially or totally replaced by large, poikilitic feldspars. Calcite also crystallized as a primary phase in some feldspar-bearing syenite, in relation to a  $CO_2$ -enriched dissolved fluid phase.

### **The carbonatite xenolith**

A single 10-cm-sized xenolith of carbonatite has been found, representing the frst 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](#page-3-0)).

At the apex of the so-called Isparta Angle, from the Senirkent area (Elitok [2019\)](#page-23-10), 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](#page-23-10)).

### **Mineral composition results**

#### **Leucite**

Leucite compositions (Appendix 1A) are usually near the ideal formulae with very small amounts of  $Na<sub>2</sub>O$ , FeO, and BaO  $(< 0.8$  wt.%). The leucite of pyroxenite and syenite has undergone hydration. It has been partially replaced by a mixture of feldspar, calcic zeolite, and calcite (see altered leucite in Appendix 1A). Replacement of leucite by analcite is not observed, probably due to very low sodium content. The main feature that occurs in some syenite xenoliths is the partial or almost total disappearance of leucite, replaced by alkali feldspar and nepheline, corresponding to the subsolidus breakdown of leucite in the presence of water (Fudali [1963](#page-23-16)).

#### **Kalsilite and nepheline**

Homogeneous thin elongate prisms of kalsilite (Fig. [3](#page-6-0); Appendix 1B) are relatively  $Na<sub>2</sub>O$ -rich with a maximum of 21 mol% of nepheline, corresponding to the preserved hypersolvus composition of kalsilite during rapid cooling. Based on the experimental study of Tuttle and Smith [\(1958\)](#page-25-8), the crystallization temperature would be  $\geq 1000$  °C (Fig. [3\)](#page-6-0).

The kalsilite of the coarse-grained kamafugite-type contains 7–11 mol% of nepheline component, and the exsolved nepheline lamellae have 25–26 mol% of kalsilite component, indicating a solvus exsolution process during slow cooling, operating between 800 and 500 °C. In coarse-grained kamafugite and feldspar-bearing syenite, crystals of nepheline rim leucite form large anhedral crystals showing some cancrinite-type alteration. Compared to the nepheline exsolution lamellae from the exsolved

<span id="page-7-0"></span>**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](#page-22-5))

kalsilite crystals, these nepheline crystals are relatively potassic, with 35–39 mol% of kalsilite component. This compositional range (Fig. [3\)](#page-6-0) is consistent with the subsolvus kalsilite-nepheline pairs crystallizing as separate crystals, at about 800 °C under 0.5 GPa, according to the experimental study of Zeng and MacKenzie ([1984](#page-25-9)), whereas the solvus exsolution process of kalsilite has operated between 800 and 500 °C during slow cooling (Fig. [3](#page-6-0)).

# **Alkali feldspar**

The frst feldspar to crystallize in syenite belongs to the hyalophane type (Appendix 1C). Crystals are strongly zoned; the Ba-rich core has 12–13 wt.% BaO, giving 25 mol% of celsian component, and subsequent decrease of  $K_2O$  and  $Na_2O$ wt.%. SrO reaches a maximum of 2.5 wt.% corresponding to 6 mol.% of the stronalsite component  $Na<sub>2</sub>SrAl<sub>4</sub>Si<sub>4</sub>O<sub>16</sub>$  (see Essene et al [2005](#page-23-17)). Crystal rims evolve to pure K-feldspar. The feldspar of the leucitite lava is also Ba-rich (25 mol% of celsian component) and is more Ca- and Sr-rich than those of the syenite. This Ba-feldspar is plotted in the quartznepheline-kalsilite ternary system (Fig. [4](#page-7-0)). Ba, equivalent of K and Na, is allocated to the calculated nepheline and kalsilite components. The hyalophane feldspar plots in the feldspathoid-bearing area of that diagram, due to Ba enrichment and coupled Si-Al substitution. When leucite was replaced during the crystallization of silica-undersaturated, Ba-rich, K-rich, and Na-poor magma, hyalophane feldspar crystallized in place of kalsilite or nepheline, which are both unable to incorporate large amounts of Ba and Sr in their



structures. In the Qz-Ne-Ks diagram, hyalophane feldspar plays the same role as feldspathoid because of its strong silica deficiency compared to typical K-feldspar. The E10 feldspar-bearing syenite (Table [2\)](#page-9-0) illustrates this well: the rock is strongly silica-defcient, Ba- and Sr-rich (11,000 ppm of Ba, 2250 ppm of Sr), and Na-poor  $(0.25w\%$  Na<sub>2</sub>O). Leucite was destabilized and was frst replaced by hyalophane feldspar instead of kalsilite or/and nepheline, followed by K-feldspar crystallization. The control by Sr and Ba on feldspar crystallization has been previously pointed out by Ferguson and Cundari ([1982](#page-23-18)) in leucite-bearing magmas. Ba and Sr elements are important substitutes for K, Na, and Ca, particularly in potassic-ultrapotassic silica-undersaturated magmatism (Cundari [1979](#page-23-19); Mitchell and Vladikin [1996](#page-24-20); Akal [2003;](#page-22-5) Platevoet et al. [2014](#page-24-12); Caran [2016](#page-22-10)). To the best of our knowledge, there seems to be no experimental system that investigates the efect of Ba and Sr on the stability of feldspar-feldspathoid phases in the Qz-Ne-Ks ternary system, and also in the more complex Qz-Ne-Ks-An quaternary system (Carmichael et al. [1974\)](#page-22-11). These systems would probably show major changes if Ba and Sr elements were considered instead of Na, in a K-rich, highly silica-defcient experimental system.

### **Clinopyroxene**

The composition of clinopyroxene (Appendix 1D) evolves from diopside to augite and from augite to aegirine-augite in the most evolved rocks. CaO and MgO contents are high, especially in crystal cores of ultramafc and mafc xenoliths (Fig. [5\)](#page-12-0), but decrease from kamafugite-type to leucitolite, syenite xenolith, and in leucitite lava. CaO and MgO contents decrease in the crystal rims together with  $SiO<sub>2</sub>$ , while FeOt,  $Al_2O_3$  (<4.60 wt.%), and TiO<sub>2</sub> (<1.4 wt.%) contents increase, probably due to the decrease of silica activity during the crystallization. The aegirine component rises in the more evolved syenite xenoliths and in leucitite, a common feature of the silica-undersaturated series evolving under relative oxidizing conditions, and/or due to the alkali-ferric efect in peralkaline magmas (Larsen [1976](#page-24-21); Mitchell and Platt [1978](#page-24-22), [1982](#page-24-23); Mitchell and Vladykin [1996](#page-24-20)). Tschermak molecules, especially Fe-Tschermak mol., rise from core to rim of crystals and from the less evolved ultramafc–mafc groups (pyroxenite and kamafugite) to the more felsic groups (leucitolite and syenite) and leucitite. In the Ti vs.  $Al<sub>t</sub>$  diagram (Fig. [5](#page-12-0)), the majority of clinopyroxene analyses plot in the transitional feld and the HKS-KS feld of Perini and Conticelli ([2002\)](#page-24-24) and in the kamafugite feld for pyroxene depicted by Prelević et al. ([2005](#page-24-25), [2015\)](#page-24-9). However, some analyses of the kamafugite xenoliths are very poor in  $TiO<sub>2</sub>$ . This can be due to early crystallization of both Timagnetite and clinopyroxene (rock 98005, Fig. [2](#page-3-0)c), Ti being prior incorporated in Ti-magnetite under relative elevated  $fO<sub>2</sub>$ . The clinopyroxene of melilite leucitite from Mesebasi described by Akal ([2003\)](#page-22-5) belongs to the lamproite feld of Mitchell and Bergman [\(1991](#page-24-26)) and difers from clinopyroxene of the Eğirdir leucitite lava.

### **Melilite**

Compositions of melilite (Appendix 1E) are plotted in the Na-melilite/gehlenite/akermanite ternary system (Fig. [6](#page-13-0)). They are poor in gehlenite and rich in akermanite components. They are relatively similar in composition to melilite from Montefascone pyroxenites of the Roman Province and San Venanzo melilitolite (Stoppa et al. [2003a](#page-25-2)), but they are lower in gehlenite than the melilites of the Alban Hills ejecta (Stoppa et al. [2003a](#page-25-2)). Finally, they are more Mg-rich, and Al- and Na-poor compared to the melilite of the northern Meşebaşi melilite-bearing leucitites from the northern Potassic-Ultrapotassic Afyon volcanic Province (Akal [2003\)](#page-22-5).

#### **Phlogopite**

All mica can be classifed as phlogopite (Appendix 1F) with a Mg/Mg+Fe+Mn ratio ranging from 0.90 to 0.60. Their Ti content is highly variable, being generally  $> 2.5$  wt.% in pyroxenite and decreasing through kamafugite and leucitolite groups, and is very low in phlogopite from syenite and carbonatite xenoliths. F content is low to moderate in pyroxenite, leucitolite, and kamafugite-type (from 0.3 to 1.13 cation pfu.), but more elevated in the feldspar-bearing syenite with 1.2 to 2.6 cations pfu., probably in relation with a  $[F + CO<sub>2</sub>]$ -rich, H<sub>2</sub>O-poor dissolved fluid phase. BaO in phlogopite is high and increases from pyroxenite to kamafugite and leucitolite, from around 1.0 up to 6.1 wt.%. The main coupled substitution that governs Ba incorporation involves Si, Al, and Ti, also Fe and Mg, in place of Ti and K in the interlayer site (Wagner and Velde [1986](#page-25-10); Wagner et al. [1987;](#page-25-11) Edgar [1992](#page-23-20); Seifert and Kämpf [1994](#page-24-27)). The most barium-rich phlogopite occurs in the carbonatite xenolith with a maximum of 13 wt.% BaO. The crystals show obvious sector zoning (Fig. [7](#page-14-0)A) due to strong Ba variations associated with coupled Al, Si, and K substitutions. The correlation (Fig. [7B](#page-14-0)) observed between  $[Ba + Al_{IV}]$  and  $[Si+K]$  pointed out the main substitution:

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

Ba-rich phlogopite is frequent in potassic-ultrapotassic magmatism. Such high BaO values, between 13 and 16 wt.%, have been observed in phlogopite (Fig. [7](#page-14-0)C) from the Jacupiranga carbonatite, Brazil (Gaspar and Wyllie [1982\)](#page-23-21), and also in phlogopite of numerous nephelinites,



 $\overline{a}$ 

<span id="page-9-0"></span> $\underline{\textcircled{\tiny 2}}$  Springer





<span id="page-12-0"></span>**Fig. 5 A** MgO versus CaO diagram (wt. %) for clinopyroxene. Arrow, evolution trend in pyroxenite xenoliths: the dotted fencing yellow feld is for kamafugite from Prelević et al. ([2005\)](#page-24-25); the two other felds 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 feld after Mitchell and Bergman [\(1991](#page-24-26)); T and HK-K, transitional high-K and K series of Italian volcanic magmatism (after Perini and Conticelli [2002\)](#page-24-24). Dotted felds: Cpx respectively from lamproites and kamafugites after Prelević et al. [\(2005](#page-24-25))



ankaratrites, and kamafugites from various localities (Mansker et al. [1979](#page-24-28); Gaspar and Wyllie [1982](#page-23-21); Edgar [1992;](#page-23-20) Seifer and Kämp [1994;](#page-24-27) Stoppa et al. [2003c](#page-25-13); Prelević et al. [2005](#page-24-25); Caran [2016](#page-22-10)). Ba and Al-Si coupled substitution occurred exclusively in phlogopite when it crystallized before feldspar under high  $P_{H2O}$ , and in strongly silica-deficient magmas, prohibiting feldspar crystallization. It is also favored by a relatively high fO<sub>2</sub> and  $P_{\text{H2O}}$  (Edgar and Arima [1981\)](#page-23-5). This is true for kamafugite, nephelinite, ankaratrite, and carbonatite. On the other hand, when alkali feldspar crystallizes, as it is in the feldspar-bearing syenite of the present study, Ba is preferentially incorporated into hyalophane and phlogopite remains Ba-poor.

### **Garnet**

Garnet is strongly zoned from black core to brown-yellowish rim. Andradite (81–87%) and almandine (5–15 wt.%) are its main components (Appendix 1G). Black crystal cores are composed of melanite with > 15 wt.% TiO<sub>2</sub>. Yellowish rims are Ti depleted and more Fe- and Ca-enriched with the increase of Fe-andradite and almandine components. MgO remains very low  $\left($ <1.3 wt.%) and decreases from garnet of kamafugite to those of syenite xenoliths. Melanite appears to be a systematic phase in the Potassic-Ultrapotassic Afyon Province magmatism and has been also described in melilite leucitites, melanite-bearing xenoliths from the Balç1khisar



<span id="page-13-0"></span>**Fig. 6** Melilite compositions in the gehlenite–akermanite–Na melilite ternary diagram. Yellow dots, present study; SV feld, San Venanzo volcanics, Intra-mountain Ultra-alkaline Province, Italy; AHE feld, Alban Hill Ejecta, Roman Province, Italy; MVC, Montefascone clinopyroxenite xenoliths, Roman Province, Italy; MLM, melilitebearing leucitite, Meşebaşi area, Afyon K-UK Province Anatolia (after Stoppa et al. [2003a,](#page-25-2) [b](#page-25-3), [c](#page-25-13); Akal [2003](#page-22-5))

area (Akal [2003;](#page-22-5) Akal et al. [2013](#page-22-7)), and in other localities of the western Taurides ultrapotassic volcanism (Prelević et al. [2015](#page-24-9)). Garnet is also present in leucitite and carbonatite inclusions from the Senirkent area of the Isparta Angle (Elitok [2019](#page-23-10)). Melanite has also been observed in other Ultrapotassic Provinces, such as in xenoliths of the Alban Hills ultrapotassic ejecta, Roman Province, Italy (Federico et al. [1994](#page-23-0)).

### **Other minerals**

Apatite is observed in all xenolith groups and in leucitite. The composition variations (Appendix 2A, B) concern only SrO which varies between 0.3 and 1.2 wt.% but reaches up to 6.5 wt.% in the syenite. Silica is in the range 0.6–1.9 wt.%, but reaches 2.8 wt% in the apatite of carbonatite. F is relatively abundant with 1.5 to 2.4 wt.%, reaching 3.2–3.8 wt.% in the apatite of the syenite and leucitite. Apatite also contains REE, particularly the apatite of the carbonatite, with 1.2–1.3 wt.% of  $Ce_2O_3$ .

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

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.

### **Preliminary geochemical results**

#### **Major elements**

All the studied felsic rocks belong to strongly silicaundersaturated series, and are foidite-foidolite type rocks (Table [2\)](#page-9-0). Many plutonic xenoliths found in the Eğirdir area have cumulated characters such as the ultramafc pyroxenite with one or two liquidus main phases (clinopyroxene and phlogopite) and the leucitolite xenoliths with two main layered phases (leucite and clinopyroxene). Kamafugite-type xenoliths and feldspath-bearing syenite, exhibiting microgranular or coarse-grained homogeneous textures, are closer to liquid compositions. More appropriate specifc classifcation schemes for ultrapotassic rocks than TAS diagram (Le Maitre [2002\)](#page-24-29) are usually used (Sahama [1974;](#page-24-30) Foley et al. [1987](#page-23-22); Foley [1992b](#page-23-23); Woolley et al. [1996\)](#page-25-14).

The microgranular and texturally homogeneous coarse-grained xenoliths (Table [2](#page-9-0), Figs. [8,](#page-15-0) [9\)](#page-16-0) have  $MgO \ge 3$  wt.%,  $K_2O > 7$  wt.%, and high CaO and are poor in Al<sub>2</sub>O<sub>3</sub> and  $\text{Na}_2\text{O}$  (<1.2 wt.%). They show the lowest value of SiO<sub>2</sub>, intermediate values of CaO and  $K_2O$ , and are relatively rich in FeOt and TiO<sub>2</sub>. They are evolved with a DI (Thornton and Tuttle  $1960$ ) > 45 and have no modal olivine like some ultrapotassic plutonic rocks of the Roman Province, Italy (Peccerillo et al. [1984](#page-24-1); Peccerillo [1990](#page-24-2)). They belong to the melilite-, leucite-, and kalsilite-bearing kamafugite group, according to their major element characters (Table [2](#page-9-0); Figs. [8](#page-15-0), [9](#page-16-0)). These xenoliths are strongly silicaundersaturated (see CIPW norms, Table [2](#page-9-0)) with normative leucite, nepheline, and sometimes normative kalsilite. They are very calcic with modal melilite, almost always with normative larnite (sometimes  $> 10$  wt.%) and normative calcite.

The pyroxenite xenoliths are the most enriched in MgO, CaO, and  $P_2O_5$  due to clinopyroxene and apatite (Figs. [8,](#page-15-0) [9](#page-16-0); Table [2](#page-9-0)). Their variable  $K_2O$  is essentially related to the occurrence of phlogopite. They are potentially silicaundersaturated but much less than kamafugite and leucitolite xenoliths (Table [2](#page-9-0)).

The leucitolite xenoliths plot in the leucitite field (Fig. [9](#page-16-0)). 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](#page-16-0)). The opposite variations between  $K_2O$ ,  $Al_2O_3$ , and FeOt,  $TiO<sub>2</sub>$ , and MgO contents depend on the leucite/mafic phases



<span id="page-14-0"></span>**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](#page-23-21)). Green dots, phlogopite of Montefascone clinopyroxenite, Italy (after Stoppa et al. [2003a](#page-25-2), [b,](#page-25-3) [c](#page-25-13))

(clinopyroxene, garnet, Fe-Ti oxides) ratio in this group, in relation with mineral segregation process. The leucitolite xenoliths (Fig. [9](#page-16-0)) are always very depleted in Na<sub>2</sub>O by comparison to the melilite-bearing leucitites and other previously studied Afyon leucitites (Akal [2003;](#page-22-5) Prelević et al. [2015](#page-24-9)).

The observed gaps between the main xenolith groups (Figs. [8,](#page-15-0) [9](#page-16-0)) can be related to cumulative processes involving mainly clinopyroxene, apatite, and leucite, as indicated by the textural characteristics of pyroxenites and leucitolites. In almost all Harker diagrams (Fig. [8\)](#page-15-0), the xenoliths from the Alban Hills ejecta, Italy (Peccerillo et al. [1984;](#page-24-1) Federico et al. [1994](#page-23-0)) plot in the gap observed between pyroxenite and leucitolite groups. They are  $P_2O_5$ -poor compared to the pyroxenite group of Eğirdir. The KLT kalsilitite from Alban Hills ejecta (Figs. [8,](#page-15-0) [9\)](#page-16-0) plots close to the kamafugite-type xenoliths of Eğirdir. The assumed primary kamafugite "KAM" composition proposed by Prelević et al. ([2015](#page-24-9)) also plots between the pyroxenite and leucitolite groups (Fig. [9](#page-16-0)).

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  $Na<sub>2</sub>O$  and  $MgO$ (Table [2\)](#page-9-0) 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.

<span id="page-15-0"></span>**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



#### **Trace elements**

The spidergrams normalized to the primitive mantle (Fig. [10](#page-17-0)A) for trace elements (Table [2\)](#page-9-0) are used for the feldspar-bearing syenite, leucitites, and kamafugite-type xenoliths that are close to liquid compositions. The syenite and leucitite patterns are very similar, and show a relatively high LILE to HFSE ratio. The negative Ta, Nb, and Ti anomalies are present but are moderate (weak in the case of Hf), while Zr displays a weak positive anomaly. The kamafugitetypes display the same negative anomalies. They are globally enriched in REE relative to the syenite and leucitite. The negative Sr anomaly is particularly pronounced for two kamafugite-type xenoliths, probably related to early apatite fractionation. All the rocks have a prominent Pb positive peak. All these geochemical features have been also noted for ultrapotassic magmatism of the Roman Province, Italy (Conticelli et al. [2013](#page-23-3), [2015](#page-23-4)). They are related to an orogenic or post-orogenic signature with a crustal material assimilation into the upper mantle during a previous subduction process. However, there are some discrepancies: Ba is not very depleted and there is no clear positive Th and Cs peaks. The same geochemical characters have been observed in the Ultrapotassic-Potassic Afyon volcanic Province (Prelević et al. [2015\)](#page-24-9). The trace element patterns of the studied xenoliths are very diferent from those of intraplate ultrapotassic rocks, similar to the Roman Province (Conticelli et al. [2015](#page-23-4)). Looking at the REE patterns (Fig. [11](#page-17-1)), kamafugite-type

<span id="page-16-0"></span>**Fig. 9** Major element diagram with kamafugite, leucitite and lamproite felds after Foley (1987). Blue star, assumed pri mary kamafugite magma after Prelević et al. [\(2015](#page-24-9)). Open diamond, KLT kalsilitolite xenolith from Alban Hills ejecta (Federico et al. [1994](#page-23-0)). Afyon<br>leucitites are from Prelević et al.  $(2015)$  $(2015)$ . Melilite l[euciti](#page-24-9)te are f[rom A](#page-22-7)kal [\(2003](#page-22-5)), Akal et al. ([2013\)](#page-22-7)



**KAMAFUGITE** 

73

**LAMPROITE** 

**FIELD** 

 $\overline{9}$ 

 $11$ 

 $13$ 

**FIELD** 

 $\overline{7}$ 

5

Kamafugite rocks

Apyroxenite

 $\Delta$  leucitolite

 $\overline{3}$ 

● A fy on leucitites o melilite leucitites

n hyalophane syenite o Egirdir leucitite

15.00

 $10.00$ 

 $5.00$ 

 $0.00$ 

19

 $Al2O3$ 

 $17$ 

 $15$ 

**FELDSPAR** 

**LEUCITITE** 

**FIELD** 



<span id="page-17-0"></span>**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\)](#page-25-15)



<span id="page-17-1"></span>**Fig. 11** REE/chondrite CI normalized patterns. Same rock references as Fig. [10](#page-17-0)

xenoliths are enriched in REE, especially HREE, compared to leucitite and syenite (Figs. [10](#page-17-0), [11](#page-17-1)). All the trends show no positive or negative Eu anomaly.

Spidergrams are less suited to xenoliths involving cumulative processes (pyroxenite and leucitolite xenoliths), but the patterns provide a simple overall view of the main trace elements and can show the possible efects of mineral fractionation on the parent liquids. The pyroxenite xenoliths are depleted in HFSE, Pb, and LILE (including Pb) relative to REE and have enriched HREE relative to LREE, due to their high but variable modal apatite and pyroxene fractions (Figs. [10](#page-17-0)B, [11](#page-17-1)). They are Th-enriched. Rb and Ba are variable and enriched together with K in two pyroxenites, due to the third mineral to crystallize which is phlogopite.

The trace element patterns of the leucitolite xenoliths are globally similar (Figs. [10](#page-17-0)B, [11\)](#page-17-1) and characterized by a global depletion in REE, Ta, Nb, and Ti when compared to the patterns of leucitite and kamafugite type. The leucitolites are globally enriched in LILE relative to pyroxenites, and K. However, notable variations of HFSE troughs and HREE/ LREE ratio in this leucitolite group seem to be very dependent upon the leucite/clinopyroxene ratio and garnet content. Two garnet-rich leucitolites (Fig. [11\)](#page-17-1) are strongly enriched in HREE, Zr, and Hf relatively to LREE. The role of garnet is probably crucial for these samples, and is consistent with the trace element patterns of garnet published by Prelević et al. [\(2015\)](#page-24-9). A prominent peak of Pb is always seen for the most leucite- and garnet-enriched leucitolites, which is a diference with the pyroxenite group.

The trace element pattern of the carbonatite (Figs. [10A](#page-17-0), [11](#page-17-1)) shows a strong LREE/HREE fractionation pattern and is very depleted in HFSE, except for Nb, and is also depleted in K, Rb, and Th relative to U and Ba. It has the most prominent Pb peak. This pattern has nothing to do with that of intraplate carbonatites, but shows similarities with those of sandstones, pelites, and especially limestones of the past and present Mediterranean alpine area (see the trends published by Conticelli et al. ([2015](#page-23-4) and ref. wherein)), with very high peaks for U, Pb, and Sr and deep troughs for K, Ta, Hf, Zr, and Ti. However, apatite, which forms clusters in the carbonatite xenolith, is the frst mineral that can explain the LREE/ HREE enrichment of the carbonatite. Moreover, the spidergrams of apatite from the Potassic Ultrapotassic Afyon volcanic Province (Prelević et al. [2015\)](#page-24-9) show the same LREE/ HREE enrichment and deep troughs for Ti, Zr, Ta, and Rb. The only discrepancy concerns Th, which is very low in this carbonatite xenolith. This depletion eventually may be linked to pneumatolytic reworking and escape of Th during the phreatomagmatic event, a process that could be considered as viable for a 10-cm-sized xenolith.

 $18$ O and  $13$ C stable isotope analyses have been carried out on calcite extracted from the carbonatite xenolith, the peperite matrix, the hyalophane-bearing syenite, and two limestones from the surrounding basement that has been cut and covered by the volcanoclastic deposit (Table [3,](#page-18-0) Fig. [12\)](#page-18-1). Analyses are reported on the  $\delta^{18}$ O versus  $\delta^{13}$ C diagram (after Bell [2005](#page-22-12); Doroshkevich et al. [2010\)](#page-23-24). The **δ**13C isotopic signatures of calcite from the carbonatite xenolith, the peperite matrix, and the hyalophane-bearing syenite are negative and are distinct from the  $\delta^{13}$ C measured on the limestones from the basement. The  $\delta^{13}$ C and  $\delta^{18}$ O values of the carbonatite are close to the limit values for the primary carbonatite feld (PCF, Fig. [12](#page-18-1)). This means that a mantle signature, with

<span id="page-18-0"></span>**Table 3**  $\delta$ 1<sup>3</sup>C and  $\delta$ <sup>18</sup>O stable isotope measures on carbonates

slight modifcation by fractionation or contamination, can be considered for the carbonatite xenolith. Similarly, the **δ** 13C of the calcite found in the syenite is also compatible with a primary origin of the  $CO<sub>2</sub>$ -rich fluid component dissolved in the magma parent and plots within the so-called European carbonatite field. However, the  $\delta^{18}$ O is significantly higher, which can be ascribed to a contamination during a low-temperature alteration process. The  $\delta^{18}$ O of the peperite matrix is much higher and disconnected from its  $\delta^{13}$ C that remains low, which can be ascribed to a main contamination process at a low temperature involving meteoritic  $H_2O$ during the volcanic event. A carbonatitic fuid interaction has been proposed in some peperite belonging to the Cenozoic French Limagne phreatomagmatism (Bailey et al. [2006](#page-22-13); Chazot and Mergoil-Daniel [2012](#page-23-25)), which is an alternative



**δ**<sup>18</sup>O SMOW calculated after Coplen et al., 1983. Measure precisions:  $\delta$ <sup>13</sup>C/PDB  $\pm$  0.1;  $\delta$ <sup>18</sup>O/PBD  $\pm$  0.2

<span id="page-18-1"></span>**Fig.** 12  $\delta^{13}$ C versus  $\delta^{18}$ 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 feld



from the classical origin of peperite. It is difficult to rule out the prevalent low-T interaction process between the leucitite magma, meteoritic water, and limestones or lacustrine that raises the  $\delta^{18}$ O but not the  $\delta^{13}$ C for the calcitic matrix of the peperite. In the other hand, the low  $\delta^{13}$ C can also be explained by the presence of a juvenile  $CO_2$ -rich fluid in relation with the leucitite lava or/and a separate carbonatitic magma.

# **Discussion**

#### **Xenolith mineral parageneses and their origin**

Textures and restricted mineral paragenesis of pyroxenites and leucitolites (one to three euhedral major phases), and geochemical gaps existing between pyroxenites and leucitolites on the one hand, and syenite, kamafugites, and leucitites on the other hand, suggest that pyroxenites and leucitolites are assumed to be cumulates derived from underlying magma intrusions. The term of autolith would be better than xenolith for these two groups of rocks as it has been used for the autoliths from the Kilombe volcano, Kenya Rift, and the Ilimaussaq autoliths, Greenland (Ridolf et al. [2006;](#page-24-31) Schönenberger et al. [2006\)](#page-24-32). Cumulate-type rocks are known in ultrapotassic provinces, such as the Malawi ring complexes, in particular the ultrapotassic Mlindi ring complex (Laval and Hottin [1992\)](#page-24-7). Trace element patterns of pyroxenite and leucitolite also show that their bulk compositions are a direct expression of the ratio of mafc and felsic mineral. Apatite, clinopyroxene, phlogopite, and leucite are the major mineral phases that crystallized in the magma at depth, in good agreement with the diferentiation process suggested by Prelević et al. [\(2015](#page-24-9)).

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 fne-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.

### **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](#page-25-4); Gupta [2015](#page-23-26)) and has been experimentally investigated for a long time (Gupta et al. [2006](#page-23-27); Edgar et al. 1976; Gupta and Yagi [1980;](#page-23-28) Veksler et al. [1998](#page-25-5); Gupta [2015](#page-23-26) and ref. wherein). In the Eğirdir xenoliths, the presence of phlogopite and lack of olivine ft well in the phlogopite-kalsiliteclinopyroxene-leucite-melilite-feldspar sub-tetrahedra, with mutual exclusion between melilite and feldspar, as it is observed in melilite-bearing kamafugite-type and feldsparbearing syenite xenoliths. However, the natural paragenesis system is more complicated than the experimental system because Fe and Ti were not considered. The later elements probably complicated the paragenesis with crystallization of FeTi-oxides and garnet. Heteromorphic relations with incomplete reactions (Yoder [1986](#page-25-4)) in kamafugite magmas can also complicate the paragenesis of the rocks during crystallization.

# **Conditions of crystallization and fractionation processes**

The modal variations depicted in the xenoliths show that the early crystallizations of melilite, clinopyroxene, apatite, and phlogopite, followed by leucite, play the major role in the diferentiation process, in good agreement with experimental studies.

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  $P_{\text{H2O}}$  and oxidizing conditions during crystallization.

It is difficult to specify from which magmatic bodies (depth and size) the rock samples have been extracted, when they only consist of a set of xenoliths. The leucitite lava was responsible for their extraction and we consider that leucitite represents the last magma passing through the previous crystallized intrusions and dykes, being the residual magma coming from the crystallizing intrusions and lately injected towards the surface. The stability feld of leucite in the presence of dissolved water is restricted when the pressure increases, leucite being fnally removed beyond 0.8 GPa (Fudali [1963](#page-23-16); Gittins et al. [1980](#page-23-29) and references therein). The systematic occurrence of leucite in the xenoliths, even in pyroxenite, indicates that the xenoliths have crystallized under relatively low  $P_{\text{H2O}}$ , not above the 0.3–0.8 GPa range, i.e., at a maximum depth of 25 km. This maximum depth corresponds to the xenoliths showing frequent and early crystallization of phlogopite (Prelević et al. [2015\)](#page-24-9).

Calcite crystallization depends not only on the composition and evolution of the dissolved fuid 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  $CO<sub>2</sub>$  vs CaO diagram (Appendix 3),  $CO<sub>2</sub>$  is higher in the kamafugite and syenite xenoliths than in the pyroxenite and leucitolite cumulates (see Table [2](#page-9-0)). The kamafugite and syenite evolved liquids appear to be enriched in  $CO<sub>2</sub>$  relative to H<sub>2</sub>O. Early phlogopite fractionation may have increased the  $CO<sub>2</sub>/H<sub>2</sub>O$  ratio in the dissolved fuid phase.

As explained by Yoder [\(1986](#page-25-4)) and McBirney ([1984\)](#page-24-33) for the Ultrapotassic Shonkin sag laccolith (Montana), it is difficult to explain the relationships between all types of rocks by a single fractional crystallization process from a single primary magma; in addition, Eğirdir xenoliths are not demonstrated to be all cogenetic. Other processes could also operate during the crystallization of intrusions: (i) percolation-reaction of the residual melt through the cumulates by infltration metasomatism, as it is assumed in the mafc–ultramafc cumulates of layered intrusions near the solidus (Irvine [1980;](#page-23-30) Tait et al. [1984](#page-25-16); Sparks et al. [1985](#page-25-17); Brandeis and Jaupart [1986;](#page-22-14) Boudreau [1995\)](#page-22-9); (ii) volatile transfer of Na relative to K explaining why the leucitolite cumulates are very depleted in  $Na<sub>2</sub>O$  (McBirney [1984](#page-24-33); Peccerillo [1994](#page-24-4)); (iii) mobile pneumatophile elements such as Th, during the hydrothermal activity at low pressure, and percolation of a  $CO<sub>2</sub>$ -rich fluid phase exsolved from the residual magma.

The evolution trends may be illustrated in the CaO/K<sub>2</sub>O/  $Fe<sub>2</sub>O<sub>3</sub>$  ternary diagram (Fig. [13\)](#page-20-0). The primary melts are unknown. The less evolved KAM mafc magma assumed by Prelević et al. [\(2015\)](#page-24-9) is close to the intermediate and salic ejecta found in the Alban Hill, Italy, especially the KLT kalsilitite xenolith (Lacroix [1893,](#page-24-34) [1917;](#page-24-35) Conticelli and Peccerillo [1992;](#page-23-31) Federico et al. [1994\)](#page-23-0). The Eğirdir kamafugite seems to be more evolved and may be the result of efficient clinopyroxene and leucite fractionation, leading to iron enrichment relative to CaO and  $K_2O$ , being thus related to the two main groups of Eğirdir cumulates (pyroxenite and leucitolite). The evolution represented by the leucitite lava is mainly controlled by leucite fractionation, with iron content remaining globally constant, and is related to the crystallization of garnet and Fe-Ti oxides. The resulting liquid line of descent is questionable as not all xenoliths are cogenetic, especially the kamafugite-type and syenite xenoliths, which are most likely related to two diferent magmas. If a reasonable liquid line of descent exists, it should be restricted from kamafugite to leucitite magmas in relation to the trend of assumed cumulates shown in this ternary diagram.

# **Carbonatite xenolith signifcance and hypothetic origin**

The association of carbonatite and kamafugite magmas is known elsewhere in ultrapotassic magmatism, where blobs of calcio-carbonatite and kamafugite can be intimately associated. This relationships between two contrasted carbonate–silicate conjugates have been described for example in magmatic rocks of the Mahlber complex, Germany (Solovova et al. [2003](#page-25-18)), in the West Qinling Province, China (Yu et al. 2003; Guo et al. [2014](#page-23-32)), in the Ruri Volcano, Kenya (Stoppa et al. [2003b\)](#page-25-3), and in the Roman Province and Intra-mountain Ultra-alkaline Province, Italy (Stoppa et al. [2003a\)](#page-25-2). In the Potassic Ultrapotassic Afyon volcanic Province, this intimate association has been observed in leucite-bearing phonolites (Elitok [2019\)](#page-23-10). This close association between carbonatite and

<span id="page-20-0"></span>**Fig. 13**  $K_2O$ -Fe<sub>2</sub>O<sub>3</sub>-CaO 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](#page-24-9)); large green dot, leucitite of Egirdir. Green star, KAM assumed primary kamafugite magma (Prelević et al. [2015\)](#page-24-9); white cross, KLT kalsilitolite xenolith from Alban Hills ejecta (Federico et al. [1994](#page-23-0)); gray star, hypothetic primary mafc 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



very silica-undersaturated rocks has been attributed to an immiscibility process between carbonatite and silicate liquids. This immiscibility model between two silicatecarbonate conjugates has been experimentally tested at a relatively low pressure from < 0.1 to 0.5 GPa (Koster van Groos and Wyllie 1966; Wyllie 1987; Kjarsgaard and Hamilton 1988; Lee and Wyllie [1998\)](#page-24-36). Eğirdir xenoliths and their set of rock-forming minerals are plotted in the silica-alkali-carbonate diagram where the immiscibility felds are reported (Fig. [14](#page-21-0)) after Kjarsgaard and Hamilton (1988). The two arrows drawn from leucitolites and pyroxenites show that these cumulates can lead to the Eğirdir kamafugite through immiscibility in the 0.1–0.5- GPa pressure range. However, the theoretical conjugate carbonatitic liquid does not ft with the calcio-carbonatite xenolith found at Eğirdir: in this model, the composition of the Eğirdir carbonatite would require an additional process of accumulation of calcite and apatite crystals.

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](#page-23-10)).

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



<span id="page-21-0"></span>**Fig. 14** Liquid immiscibility fields for  $Pt < 0.1$  GPa and  $Pt = 0.5$  GPa, in the  $SiO_2 + Al_2O_3 + TiO_2 - Na_2O + K_2O - CaO + FeO + MgO$  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, efect of leucite and clinopyroxene during fractional crystallization; the two trends cross at the average cumulate

phreatomagmatic deposit. However, stable isotope compositions of calcite from the Eğirdir carbonatite indicate low crustal contamination. It seems that the origin of the Eğirdir carbonatite difers 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;](#page-24-37) Woolley [2003;](#page-25-19) Tappe et al. [2003](#page-25-7); Bell and Simonetti  $2009$ ) or to a direct  $CO_2$ -enriched fluid produced during the asthenosphere upwelling after the breakoff of the slab.

The composition of the Eğirdir carbonatite xenolith is more consistent with carbonatites found in an orogenic or post-orogenic geodynamical setting. The coexistence of ultrapotassic rocks and carbonatite has been a subject of debate for a long time (Foley [1992a,](#page-23-33) [1992b](#page-23-23); Peccerillo [1984,](#page-24-1) 1998; Vollmer [1989;](#page-25-0) Peccerillo and Foley [1992;](#page-24-38) Ersoy et al. [2010](#page-23-34); Prelević et al. [2008,](#page-24-39) [2010a,](#page-24-40) [2010b,](#page-24-41) [2012,](#page-24-13) [2015;](#page-24-9) Conticelli [1998;](#page-23-35) Conticelli et al. [2007,](#page-23-36) [2013,](#page-23-3) [2015](#page-23-4)). In a postcollisional geodynamical situation, the carbonatite mantle source would be phlogopite-bearing pyroxenite veins formed in a moderately depleted lithospheric mantle metasomatized by the fuid released by the sediments of the subducted slab. There is also a possibility to produce a carbonatitic melt by a fractionation-melting process of the metasomatized mantle source: this origin for carbonatite was proposed by Mitchell ([2005\)](#page-24-42). More extensive partial melting of the same source may product primary lamproite or kamafugite magmas, with high K/Na ratio, and high Ca, Mg, and  $CO<sub>2</sub>$  contents related to the metasomatized source. The diferentiation process can also be at the origin of carbonatite: indeed, after extensive diferentiation of melilitite and nephelinite magmas, a carbonatite residue may be produced (Mitchell [2005](#page-24-42)).

The mantle source of the UKAP magmatism and its complex metasomatization have been debated in the successive papers of Prelević et al. [\(2008](#page-24-39), [2010a,](#page-24-40) [b,](#page-24-41) [2012](#page-24-13), [2015](#page-24-9)). Future isotopic studies of the Eğirdir xenoliths will be of great help to better understand the origin and relationships of these plutonic xenoliths with the Potassic Ultrapotassic Afyon volcanic Province, and to clarify whether they have fully or partially preserved their complex mantle geochemical signature, despite contamination processes during crustal magma injection and diferentiation.

### **Concluding remarks**

The plutonic xenoliths found in the Eğirdir phreatomagmatic deposits have been extracted from dykes or/and plutonic intrusions related to batches of magma injected at crustal level.

Pyroxenite or leucitolite cumulates were formed during the diferentiation of these crustal intrusions under a 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 ultrapotassic series of West Anatolia. Some of them have kamafugite afnities and display the frst occurrence of kalsilite in this ultrapotassic series. Two forms of kalsilite have been observed: a high-T hypersolvus homogeneous form symptomatic of rapid cooling, and a subsolvus low-T exsolved form associated with separate nepheline crystals in slow-cooling intrusions. In syenite, feldspar crystallized frst as hyalophane, which played the same role of nepheline during the leucite destabilization in K- and Ba-rich, and Napoor magmas.

The mineral paragenesis that controlled the fractional crystallization process was mainly composed of clinopyroxene apatite, melilite, phlogopite, and leucite, with additional garnet and Fe-Ti oxides during the near-solidus evolution of leucitolite cumulates. Phlogopite crystallization in some pyroxenite indicates that partial  $P_{H2O}$  was high during their crystallization, leading to an increase of the  $CO<sub>2</sub>/H<sub>2</sub>O$  ratio in the dissolved fuid phase.

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](#page-24-39), [2015\)](#page-24-9) and the Roman Province, Italy (Peccerillo [1990;](#page-24-2) Conticelli et al. [2013\)](#page-23-3).

A carbonatite xenolith has been found for the frst time in this area. There are no convincing petrographic arguments to support an immiscibility process between two silicate-carbonate conjugates. C and O stable isotopic compositions on calcite indicate that the carbonatite has a mantle origin with relatively limited crustal contamination. The origin of the carbonatite by diferentiation from a primitive kamafugitetype magma, or by a fractionation-melting process of a metasomatized mantle source remains to be tested in the future.

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.

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#### **Declarations**

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

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