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Mineral chemistry and P-T conditions of the Karakaya volcanites at Kırka-Afyon-Isparta volcanic province, Afyon, Turkey

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ABSTRACT

The Kırka-Afyon-Isparta Volcanic Province (KAIVP) is one of the best known regions in Turkey for the origin and petrological evolution of the high potassium volcanic activity. The temporal and spatial variability of volcanic rocks in the region exerts significant control over their geochemical diversity. Alkaline and ultrapotassic volcanic rocks of the Afyon volcanism are the first products of asthenospheric origin after the orogenesis in western Anatolia. We have determined the mineralogical and petrographic properties of the Karakaya volcanites surrounding Afyon with the help of microprobe analyses. Estimated thermobarometers are calculated. The Karakaya volcanites have been grouped into four different units according to their their mineralogical, petrographic and geochemical characteristics: Seydiler ignimbirite, basaltic trachyandesite, trachyandesite, trachyte and lamproite. Most samples display hypocrystalline porphyritic texture, whereas samples of lamproite unit have a holocrystalline texture. Generally, volcanic units also exhibit some textural evidence of disequilibrium crystallisation, such as sieve texture and corrosion in plagioclase phenocrysts, zoning and inclusions in clinopyroxene phenocrysts. Mineral thermobarometric estimations in all suites were tested on clinopyroxene and feldspar compositions, considering different authors' approaches. Values of temperatures and pressure range from 1105 to 1273°C and 5.6 to 12.2kbar, respectively. The temperature and pressure values calculated from the mineral-melt associations in the volcanics suggest that the Afyon Volcanites were affected by magma mixing processes and crystallised at different depths during the transport of magma.

KEYWORDS **Mineral Chemistry. Thermobarometry. KAIVP. Karakaya volcanites. Western Turkey..**

INTRODUCTION

Western Anatolia is divided into five tectonic zones related to the closure of Neotethys Ocean, from north to south the Tavşanlı Zone, the Afyon Zone, the Menderes Massif, the Lycian Nappes and the Taurides (Okay and Tüysüz, 1999). Basal units of these tectonic zones were intruded in some regions by volcanic activity at different ages. These regions are West Anatolian Volcanic Province (WAVP), Kırka-Afyon-Isparta Volcanic Province (KAIVP) with N-S extension and Central Anatolia Volcanic Province (CAVP) (Fig. 1) (Akal, 2003, 2008; Aydar *et al.*, 1998; Besang *et al.*, 1977; Çoban and Flower, 2006; Dilek and Altunkaynak, 2009; Elitok *et al.*, 2010; Francalanci *et al.*, 2000; Keller, 1983; Keller and Villari, 1972; Prelević *et al.*, 2010, 2012, 2015; Savaşçın and Oyman, 1998; Sunder, 1982; Yağmurlu *et al.*, 1997).

The KAIVP extents from Kırka (Eskişehir) in the north to the south of Isparta (Fig. 1). It is approximately 250km long, it has a N-S trend, and developed during the early Miocene through Pliocene times. The volcanic rocks exposed along the KAIVP are more alkaline (K-rich) than the Miocene rocks in the WAVP (Akal, 2003, 2008; Alıcı *et al.*, 1998; Aydar, 1998; Besang *et al.*, 1977; Çoban and Flower, 2006; Dilek and Altunkaynak, 2009; Elitok *et al.*, 2010; Floyd *et al.*, 1998; Francalanci *et al.*, 2000; Helvacı

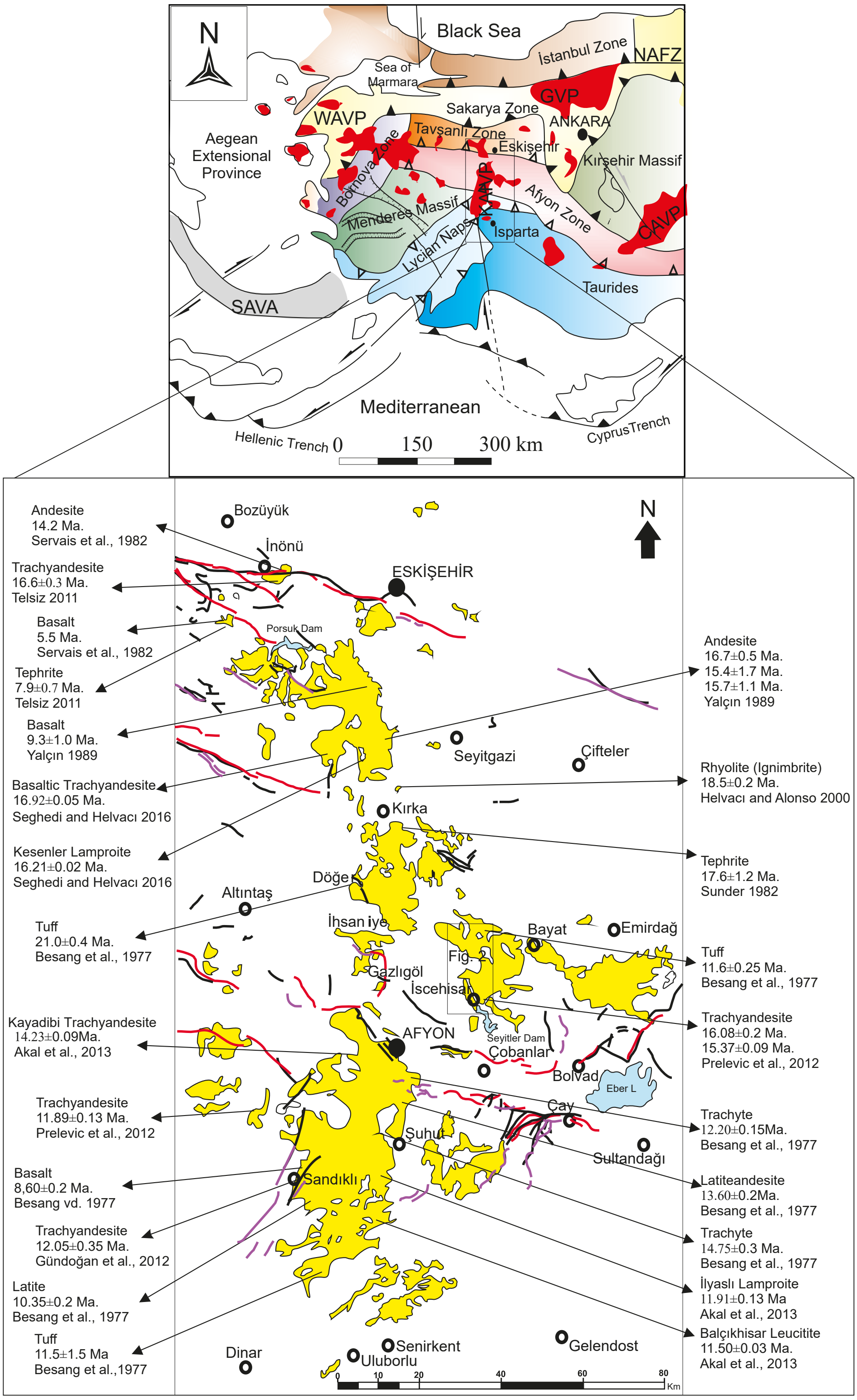

FIGURE 1. Simplified tectonic map (upper) of western Anatolia (Turkey) with the distribution of early-middle Miocene volcanic rocks (modified from Ersoy *et al.*, 2012; Okay and Tüysüz, 1999), and distribution of volcanic rocks (lower) in the Kırka-Afyon-Isparta Volcanic Province (KAIVP) indicating their ages and references, (Akal *et al.*, 2013; Besang *et al.*, 1977; Gündogan *et al.*, 2012; Helvacı and Alonso, 2000; Prelević *et al.*, 2012; Seghedi and Helvacı, 2016; Servais, 1982; Telsiz, 2011; Yalçın, 1989). SAVA: South Aegean Volcanic Arc, WAVP: West Anatolia Volcanic Province, KAIVP: Kırka-Afyon-Isparta Volcanic Province, GVB: Galatian Volcanic Province, CAVP: Central Anatolia Volcanic Province. (for lower figure yellow areas - Neogene volcanic rocks; black lines - possible Quaternary faults and lineations; red lines - Holocene faults; purple lines - Quaternary faults).

and Alonso, 2000; Keller, 1983; Keller and Villari, 1972; Platevoet *et al.*, 2008; Prelević *et al.*, 2010, 2012, 2015; Savaşçın and Oyman, 1998; Sunder, 1982; Yağmurlu *et al.*, 1997).

Volcanic units exposed along the KAIVP have extremely variable chemical compositions. Calc-alkaline, ultra-potassic and shoshonitic volcanic units in Kırka consist of rhyolites, trachytes, basalts, and associated pyroclastic rocks emplaced at 21.0-16.1Ma (Besang *et al.*, 1977; Francalanci *et al.*, 2000; Seghedi and Helvacı, 2016). They become more potassic towards the south. Alkaline-rhyolitic, latitic and trachytic lavas, domes and ultrapotassic volcanism in the Afyon area formed between 14 and 8Ma (Dilek and Altunkaynak, 2010; Prelević *et al.*, 2012). Phonolitic tephrites, tephritic-phonolites and lamproitic rocks developed at about 4,70- 4,07My and are located south of Isparta (Savaşçın and Oyman, 1998) (Fig. 1).

The southward increase in volcanism is linked to different amounts of K enrichment, levels of Si saturation, and isotope and trace element compositions (Dilek and Altunkaynak, 2007; Francalanci *et al.*, 2000; Prelević *et al.*, 2012). Prelević *et al.* (2015) emphasised the asthenosphere-lithosphere interaction using new Pb, Sr, and Nd radiogenic isotope and trace element data. The Cenozoic magmatism in the KAIVP represents a geological phenomenon with a complex evolution, intricately shaped by a variety of processes, including accretionary tectonics and collisional events, extensional tectonics, subduction-zone processes, and collision-induced mantle dynamics, such as slab breakoff and delamination, alongside asthenospheric upwelling.

In this context, understanding the interplay of these geological processes is crucial for elucidating the magmatic history of the region. By examining the geochemical signatures and temporal patterns of magmatism, we can gain insights into the tectonic evolution and dynamics of the KAIVP. This study focuses on the mineralogical and petrographic characteristics of the Karakaya volcanites, in the north-eastern region of Afyon in the KAIVP. The mineral chemistry data are utilised to ascertain the physicochemical conditions, specifically parameters such as Pressure (P) and Temperature (T), aiming to elucidate the magma emplacement and crystallisation conditions. Furthermore, a generic evolutionary model is presented to delineate the plausible processes within the magma chambers.

Geological Setting

The origin, formation and evolution of the Oligo-Miocene volcanism that developed under the post-collision extensional regime in western Anatolia are still under debate (Akal, 2003, 2008; Alıcı *et al.*, 1998; Aydar, 1998; Besang *et al.*, 1977; Çoban and Flower, 2006; Dilek and Altunkaynak, 2009; Elitok *et al.*, 2010; Floyd *et al.*, 1998; Francalanci *et al.*, 2000; Helvacı and Alonso, 2000; Keller, 1983; Keller and Villari, 1972; Platevoet *et al.*, 2008; Prelević *et al.*, 2010, 2012, 2015; Savaşçın and Oyman, 1998; Sunder, 1982; Yağmurlu *et al.*, 1997). It is accepted that the region has considerable mantle heterogeneity (Akal, 2008; Akal *et al.*, 2013; Aydar *et al.*, 2003; Güleç, 1991; Savaşçın and Güleç, 1990). Neogene volcanics in the area should be studied more systematically to evaluate the models discussed.

These areas affected by extensional tectonic regimes are commonly observed in plutonic and volcanic regions with orogenic geochemical characteristics. It is considered that the orogenic character of these magmatic and volcanic formations is the result of the convergence that had previously occurred along the Hellenic arc (Savaşçın and Güleç, 1990; Yilmaz, 1989). While western Turkey experienced an extensional regime, alkaline and ultrapotassic volcanic units with an asthenospheric geochemical signature in the Afyon area already occurred along the Kırka-Afyon-Isparta Province (Akal *et al.* 2013; Pe-Piper and Piper 2001; Savaşçın and Oyman 1998; Yagmurlu *et al.* 1997).

The study area is located in the Afyon Zone of Okay (1984), the Bolkardağı Union of Özgül (1976) and the Anatolid-Torid Platform of Şengör and Yılmaz (1981). The Afyon Zone is represented by a Paleozoic-Mesozoic shelf-type sequence of the Taurides (Okay, 1984). Volcanic units forming the main subject of this study are exposed in various areas of Afyon. The Paleozoic and Cenozoic rock units are located around İscehisar in the north-northeast of Afyon (Fig. 2). The Afyon metamorphics (Doğanlar schist, İscehisar marble, and Deliktaştepe metakonglomera) described by Metin *et al.* (1987) form the basement and are covered by the lower Miocene Yeniköy Formation (Saraç, 2003) with an angular unconformity. The Seydiler ignimbrite rests unconformably on the Yenikoy Formation. The Seydiler ignimbrite forms the pyroclastic base of the Karakaya volcanites.

The Karakaya volcanites, first defined by Metin *et al.* (1987) as 'Karakaya basalt', represent the product of Afyon volcanism, which continues intermittently throughout the lower-middle Miocene, with lava compositions of trachybasalt, basaltic trachyandesite, and trachyandesite. Erkan *et al.* (1996) named the volcanic rocks located north of Afyon as 'northern volcanics' and interpreted these volcanics as lava spills. Aydar (1998) indicated that these lavas are the products of lamproitic magma and explained their formation as lava flows and dikes. The age of the unit was determined as 11.60Ma by Besang *et al.* (1977) and 15.37–16.08Ma by Prelević *et al.* (2012).

Effusive volcanism products formed the lower-middle Miocene Karakaya volcanites over the Seydiler ignimbrite, which can be subdivided into four units according to their mineralogical, petrographic and geochemical properties (Aksoy, 2019).

The Karakaya volcanites include basaltic trachyandesite, trachyandesite, trachyte and lamproite units (Fig. 3). They grade laterally and vertically with the Miocene lacustrine deposits of the Gebeceler Formation (Akpınar Limestone). The Erdemir Formation, consisting of an irregular alternation of conglomerate, sandstone and mudstone, rests on the lacustrine sediments of the Gebeceler Formation. Alluvium blankets all the units mentioned above.

ANALYTICAL METHODS

Fresh samples of most typical volcanic rocks from each volcanic unit were chosen to classify the rocks and determine their mineralogical and petrographic properties, and mineral proportions. After determining the rock composition in the Karakaya volcanites, samples of basaltic trachyandesite, trachyandesite, trachyte and lamproite were

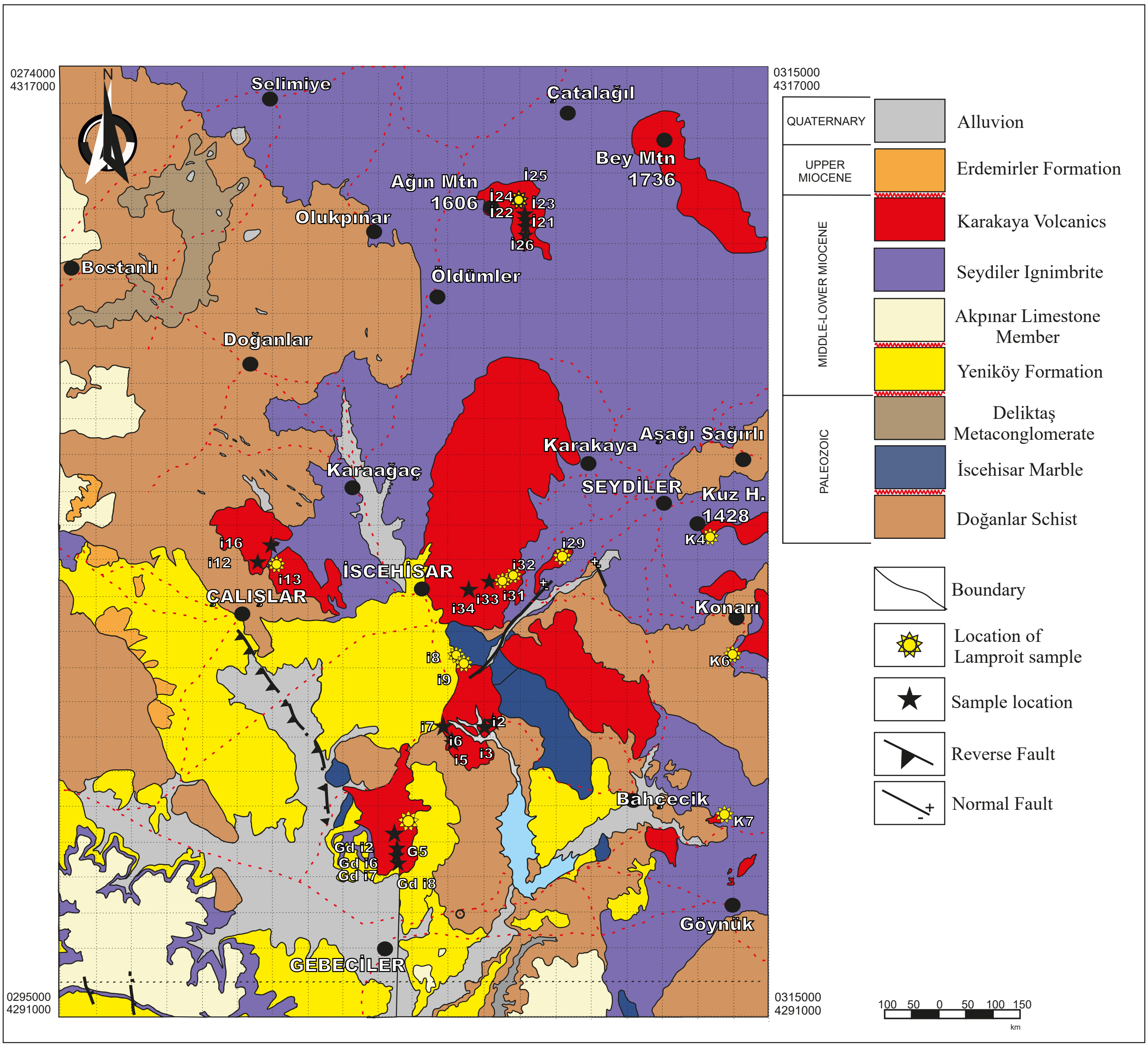

FIGURE 2. Geological map of the study area (modified from the General Directorate of Mineral Research and Exploration (MTA) 1:100,000 scale geological map of Turkey).

selected to analyse mineral phases. Thin sections were examined in detail under a Nikon Eclipse LV100POL polarised microscope at the Optical Microscope Laboratory of the Geological Engineering Department of Kütahya Dumlupınar University, and photomicrographs were taken with an OLYMPUS E-330 camera.

Whole-rock major element compositions of representative volcanic rock samples were determined by an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) following lithium metaborate/tetraborate fusion and dilute nitric acid digestion at ACME analytical laboratories (Canada).

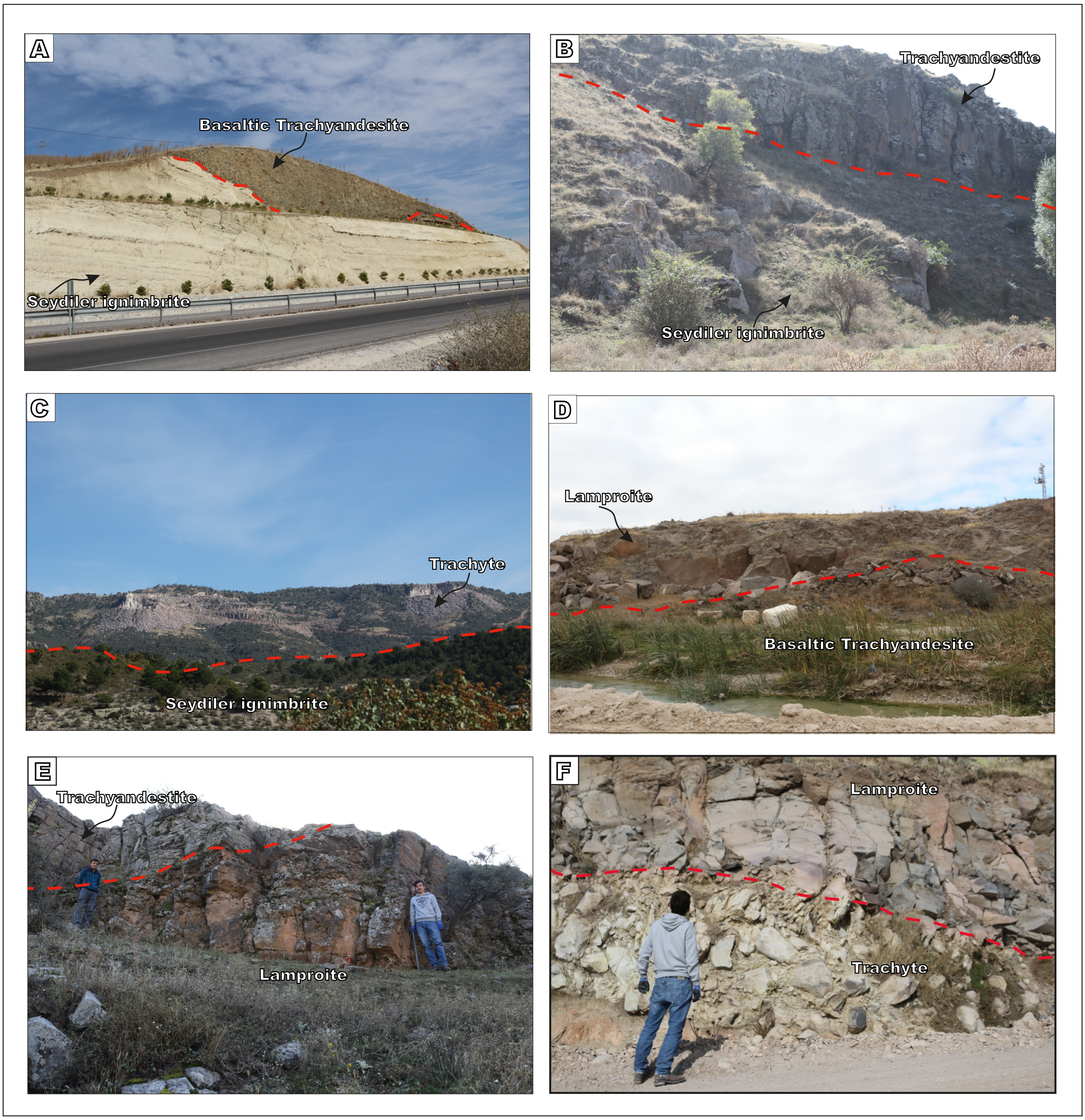

FIGURE 3. Field photographs of lower-middle Miocene Karakaya volcanites. A) Basaltic trachyandesite overlying the Seydiler Ignimbrite, B) Trachyandesite overlying the Seydiler Ignimbrite. C) Tachyte. overlying the Seydiler Ignimbrite. D) Lamproite on top of basaltic trachyandesite. E) Trachyandesite on top of lamproite. F) Lamproite on top of tachyte.

Scanning electron microscopy was done using an FEI NanoSEM 650 scanning electron microscope with integrated EDAX energy-dispersion spectrometer device at Kütahya Dumlupınar University Advanced Technologies Center (ILTEM). For qualitative mineral chemistry analysis, beam properties were set to 20kV and 20nA$^{\circ}$. Moreover, electron microprobe (EPMA) analyses were performed on polished thin sections at the Ankara University Earth Sciences Application and Research Center (YEBİM) using a JEOL brand JXA – 8230 model device containing 5 Wavelength Dispersive Spectrometers (WDS). Operating conditions were 20kV acceleration voltage, 10Na$^{\circ}$ electrode and dot size. Detection limits for Na, Mg, Al, Si, Fe, Mn, K, Ca and Ti were below 0.04%. Natural oxide and mineral reference materials were used for calibration and measurements. Matrix effects were corrected using the ZAF software provided by JEOL. The carbon coating of polished sections was made using the Quorum Q150T ES machine in YEBIM.

RESULTS

Mineralogy and Petrography of the Karakaya volcanites

The lavas in the Karakaya volcanic region exhibit a great array of mineralogical and petrographic characteristics. To classify and categorise these lavas, we followed the classification scheme proposed by the International Union of Geological Sciences (IUGS) as outlined in Le Maitre *et al.* (2002). Additionally, we used the systematics specifically designed for potassic rocks and lamproites by Mitchell and Bergman (1991) and Woolley *et al.* (1996). These classification frameworks provided a comprehensive and standardised approach for characterising the various types of lavas encountered in the Karakaya volcanic region, facilitating a systematic analysis of their geological features and formation processes. The textural and mineralogical characteristics of representative samples from these types of lavas are summarised in Supplementary field IA-H.

The Karakaya volcanites were previously identified and mapped as a single unit of aphyric lavas (Dedeoglu and Yilmaz, 2016). Recently, they have been grouped into four volcanic units based on mineralogical, petrographic and geochemical characteristics. These are basaltic trachyandesite, trachyandesite, trachyte and lamproite units (Aksoy, 2019). Except for the lamproite unit, which overlies the Seydiler Ignimbrite, the contacts between the units could not be determined due to surface alterations and the high-speed train road excavations.

The Basaltic Trachyandesite unit:

The representative rocks of The Basaltic Trachyandesite unit occur as horizontal lava flows, forming a wide plateau extending N-S across the study area, including Iscehisar. These rocks are thought to be the earliest, first-generation “lava flow” in the evolution of Köroğlu Caldera, defined by Aydar *et al.* (1998). They are spheroidally altered to reddish black in many areas, and have a dense vesicular texture that indicates flow direction. All samples from this unit have a hypocrystalline porphyritic texture (Fig. 4A). The unit includes two different phenocryst mineral combinations reflected in olivine content. One mineral association consists mainly of feldspar + clinopyroxene + olivine ± Fe-Ti oxides ± accessory ilmenite, while the other contains feldspar ± clinopyroxene ± Fe-Ti oxides ± accessory ilmenite. Groundmass mineralogy is plagioclase + pyroxene ± opaque minerals and transparent glass. The most important characteristic of this unit is that all elongate microlites in the glass, such as feldspar, are oriented in the direction of flow (trachytic texture).

Feldspars, occurring as phenocrysts (1.0-2.4vol%) and microlites (43.70-55vol%), are alkali feldspars (sanidine) and plagioclase. Euhedral to subhedral plagioclase crystals generally occur as phenocrysts and microlites in the groundmass. Some phenocrysts show albite twinning, zoning, sieve texture and embayment. Clinopyroxenes are usually present as euhedral phenocrysts (5.10-9.10vol%), showing predominantly zoned texture and Carlsbad twinning. Most of them have sieve and corrosion textures. Clinopyroxene and plagioclase phenocrysts also display typical glomeroporphyritic textures. Fe-Ti oxides such as ilmenite and magnetite were observed as microphenocrysts (0.2-5.4vol%).

The Trachyandesite unit:

The trachyandesite unit is the product of lava flows, is exposed in the northeast of Çalışlar village and oriented approximately NW-SE. This unit has blackish and dark grey colours and spheroidal alteration without vesiculation in many areas. The mineral assemblage and texture (hypocrystalline porphyritic texture) of trachyandesitic rocks are similar to those of the basaltic trachyandesites (Fig. 4B). However, they have a higher content of transparent glass (14.80-19.70vol%) and thinner, smaller microlites (63.30-67.80vol%) (hyalopilitic texture). Samples are characterised by a subhedral to euhedral phenocryst assemblage of feldspar + clinopyroxene + olivine ± Fe-Ti oxides ± accessory ilmenite embedded in a microcrystalline matrix composed mainly of plagioclase + pyroxene ± opaque minerals and transparent glass. Clinopyroxene (10.5-12.60vol%) and plagioclase (2vol%) phenocrysts display typical glomeroporphyritic textures.

The Trachyte unit:

The Trachyte unit rocks are exposed in a few areas of small lava flows found in the mountains of Ağın and Bey, close to Çatalağıl village (Fig. 4C). The colour of this unit range from grey to dark grey and textures are primarily massive. The trachyte unit is composed of microphenocrysts of clinopyroxene + phlogopite + Fe-Ti oxides + accessory apatite embedded in a pilotaxitic groundmass exhibit porphyritic textures (Fig. 4C). The groundmass contains clinopyroxene microlites (9.60-22.30vol%), K felspar microlites (33.60-48.40vol%) and glass (13.40-15.80vol%). Clinopyroxene generally occurs as euhedral phenocrysts (13.0-18.70vol%), most of them exhibiting sieve and corrosion textures. Phlogopite typically appears as euhedral phenocrysts (7.10-10.70vol%), although it also occurs as altered anhedral grains without cleavage, grains with distinct cleavage, and grains that have become wholly turned opaque.

The Lamproite unit:

The Lamproite unit represents according to Aydar *et al.* (1998) a second-generation lava flow (extra-caldera extrusions). This unit differs from the other units by having reddish and brown to dark brown colours, flow structure and occasional vesicular magmatic enclaves (which have not been studied) ranging up to 3 and 7cm in size. Dense alteration is pervasive and does not permit us to examine the enclaves. Combined optical microscopic and Back-Scattered Electron (BSE) imaging revealed that this unit has typical lamproitic texture. It is represented by mainly clinopyroxene (14.50-17.90vol%) + olivine (5.70-10.90vol%) + phlogopite (0.70-7.10vol%) + Fe-Ti oxides (2.7-3.9vol%) phenocrysts, which are enclosed in mainly holocrystalline groundmass sanidine (Fig. 4D).

Whole-Rock Major Elements and Classification

Chemical analyses of samples from the Karakaya volcanites provided representative whole-rock major oxide compositions and CIPW norm values (See supplementary field IB). The concentrations of major elements were recalculated on an anhydrous basis normalised to 100 percent by weight, and these values were used in the classifications. Petrographic investigations are consistent with specific basaltic samples having high Loss On Ignition (LOI) values up to 6.10wt%, which are probably connected to iddingsitation and serpentinization as well as to partial alteration of feldspars to clay minerals. These high values of LOI imply that Karakaya volcanites are variably affected by weathering or secondary alteration processes. We have therefore tested whether or not the element abundances of the rocks reflect their primary characteristics by applying the Weathering Index of Parker (WIP; Parker, 1970), Chemical Index of Alteration (CIA; Nesbitt and Young, 1982), and

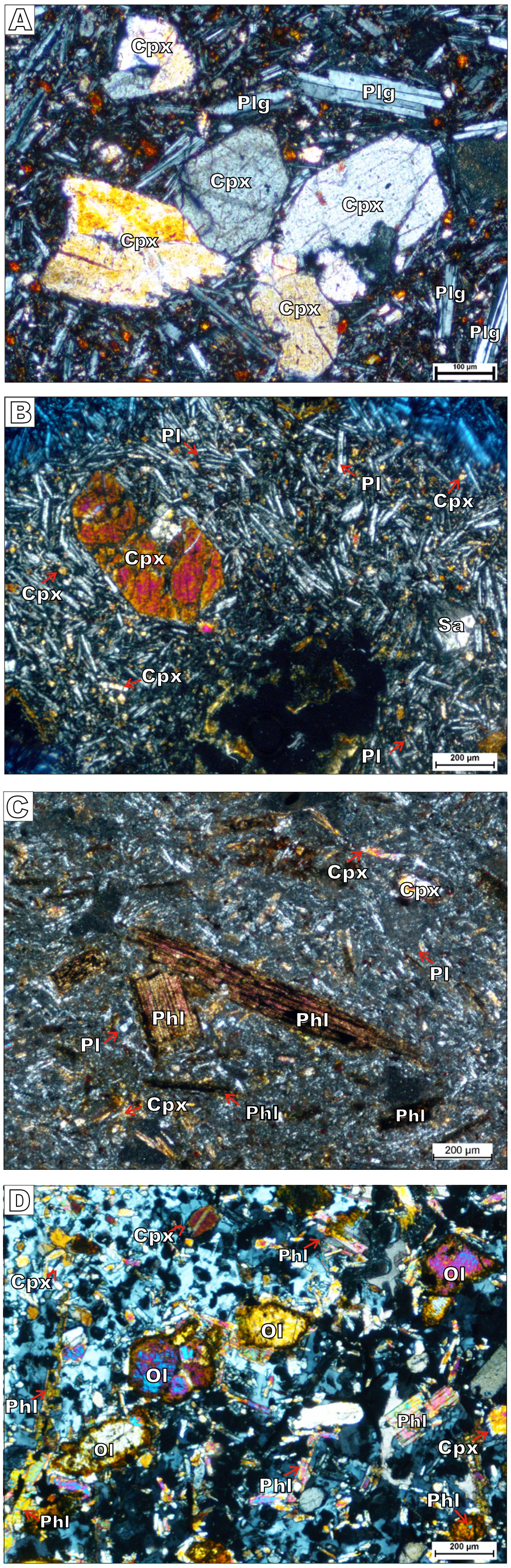

FIGURE 4. Thin section photomicrographs of some representative samples of Karakaya volcanites (in cross-polarised light). A) Hypocrystalline porphyritic texture in the basaltic trachyandesite. B) Hypocrystalline porphyritic texture in the trachyandesite. C) Small crystals embedded in a pilotaxitic groundmass in the trachyte. D) Lamproitic texture in the lamproite. cpx: clinopyroxene; pl: plagioclase; ol: olivine; phl: phlogopite, sa: sanidine.

Plagioclase Index of Alteration (PIA; Fedo *et al.*, 1995; an alternative to CIA). The values of the CIA and PIA from the basaltic to andesitic rocks are less than 50 (Supplementary field IB). WIP values of these samples vary between 85.27 and 121.02. The WIP and CIA values are above 80 and below 55, respectively, indicating that most lavas are fresh and have not suffered notable alteration or weathering (Fig. 5A). Fresh magmatic rocks follow a "magmatic trend" on the FMW ternary plot of Ohta and Arai (2007), and all the Karakaya volcanites analysed extend in this trend (Fig. 5B). Thus, overall, these alteration indices, together with the petrographic observations, suggest that the whole rock geochemical data can be used with confidence in the following discussion.

The volcanic rocks show a wide compositional range from basaltic trachyandesite to rhyolite with SiO_2 contents of 51.56–63.12wt% and MgO contents of 1.71–12.13 wt% (the rhyolites representing the Seydiler ignimbrite are not mentioned in this study, but only included in the classification diagram) (Supplementary field IB). The Karakaya volcanites have been categorised on the Total Alkali-Silica diagram (TAS) (after Le Bas *et al.*, 1986) (Fig. 6A).

According to the TAS diagram, the samples from the Karakaya volcanites predominantly fall within the basaltic trachyandesite, trachyandesite and trachyte fields (Fig. 6A). Furthermore, these volcanic samples exhibit an alkaline chemistry based on the alkaline-sub-alkaline separation line determined by Miyashiro (1978). The K_2O content of Karakaya volcanites increases from the trachyandesite unit to the lamproite unit (Fig. 6B). This observed increase in K_2O is further highlighted when examining the K_2O vs. Na_2O graph presented in Figure 6C. While the basaltic trachyandesite unit and the trachyandesite unit show shoshonitic characteristics, the lamproite unit stands out with ultrapotassic characteristics, indicating an even more pronounced potassium content enrichment than the other units.

Volcanic rocks with MgO>3, K_2O>3 and K_2O/Na_2O>2 were defined as ultrapotassic (Foley *et al.*, 1987). Samples from Karakaya volcanic units were assessed according to the criteria recommended by Foley et al. (1987). Major element analyses of lamproite unit in Karakaya volcanites indicate 3.03<MgO<12.13%, 5.38<K_2O<9.44%, 2.04<K_2O/Na_2O<7.52. The mentioned element contents and ratios show that samples from the lamproite unit in the Karakaya volcanites can be classified as ultrapotassic. The samples exhibit lamproite features, taking into consideration mineralogical descriptions, mineral chemistry and geochemical data. Calculated CIPW norm values of the samples (Supplementary field IB) reflect the chemical trends noted above. Normative quartz and nepheline were calculated in most Karakaya volcanites, whereas normative plagioclase was determined in Karakaya lamproites. Moreover, all samples contain diopside, hypersthene and accessory

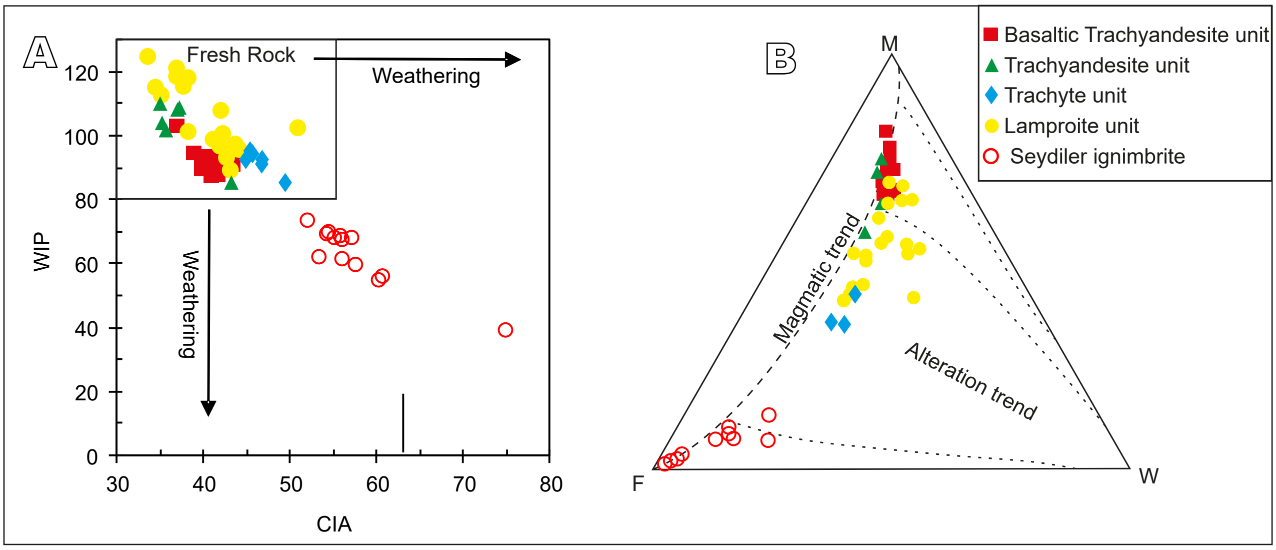

FIGURE 5. Alteration indexes and related plots for the samples. A) Chemical Index of Alteration (CIA) vs Plagioclase Index of Alteration (WIP) plot. B) FMW ternary plot of Ohta and Arai (2007). [$M= -0.395 \times \ln(SiO_2) + 0.206 \times \ln(TiO_2) - 0.316 \times \ln(Al_2O_3) + 0.160 \times \ln(Fe_2O_3) + 0.246 \times \ln(MgO) + 0.368 \times \ln(CaO) + 0.073 \times \ln(Na_2O) - 0.342 \times \ln(K_2O) + 2.266$; $F= 0.191 \times \ln(SiO_2) - 0.397 \times \ln(TiO_2) + 0.020 \times \ln(Al_2O_3) - 0.375 \times \ln(Fe_2O_3) - 0.243 \times \ln(MgO) + 0.079 \times \ln(CaO) + 0.392 \times \ln(Na_2O) + 0.333 \times \ln(K_2O) - 0.892$; $W= 0.203 \times \ln(SiO_2) + 0.191 \times \ln(TiO_2) + 0.296 \times \ln(Al_2O_3) + 0.215 \times \ln(Fe_2O_3) - 0.002 \times \ln(MgO) - 0.448 \times \ln(CaO) - 0.464 \times \ln(Na_2O) + 0.008 \times \ln(K_2O) - 1.374$].

minerals (apatite, magnetite and ilmenite).

The samples belonging to the lamproite unit fall in Roman province-type ultrapotassic rocks (Fig. 7). The lamproite unit in the Karakaya volcanites reflects an active orogenic province with low content of TiO_2 (1.22-2.18wt%) relative to the stable continental area based on the ratios of P_2O_5/TiO_2 vs. TiO_2 to characterise the geological setting of ultrapotassic rocks (Foley *et al.*, 1987). Previous researchers also identified rocks with alkali lamprophyre and lamproite compositions in the regions further south of the area (Akal, 2008; Aydar *et al.*, 2003; Prelević *et al.*, 2012, 2015). This consistency in classifying these rocks as ultrapotassic and the presence of analogous rock types in neighbouring regions further validates the findings of this study.

Figure 8A shows primitive mantle-normalised multi-element spider diagrams (Sun and McDonough, 1989). The Karakaya volcanites have a discernible depletion in elements such as Nb, Pb and Ti, but they display an enrichment in elements such as U, K and Zr. Figure 8B illustrates the chondrite-normalised rare earth element spider diagrams (Boynton, 1984). All observed samples exhibit a decrease in abundance from light rare earth elements to heavy rare earth elements.

Mineral chemistry

Pyroxene, feldspars, olivine, micas and Fe-Ti oxides (magnetite and ilmenite) were analysed by scanning electron microscopy (SEM-EDS). A summary of representative analyses is given in Supplementary field IC. Six oxygen atoms for pyroxene, 8 oxygen atoms for feldspars, 4 oxygen atoms for olivine, 11 oxygen atoms for micas, 4 oxygen atoms for magnetite, 3 oxygen atoms for ilmenite are used in stoichiometric calculations for mineral type.

Pyroxene

Clinopyroxenes commonly occur in almost all units as phenocrysts and groundmass phase. Phenocrysts are euhedral

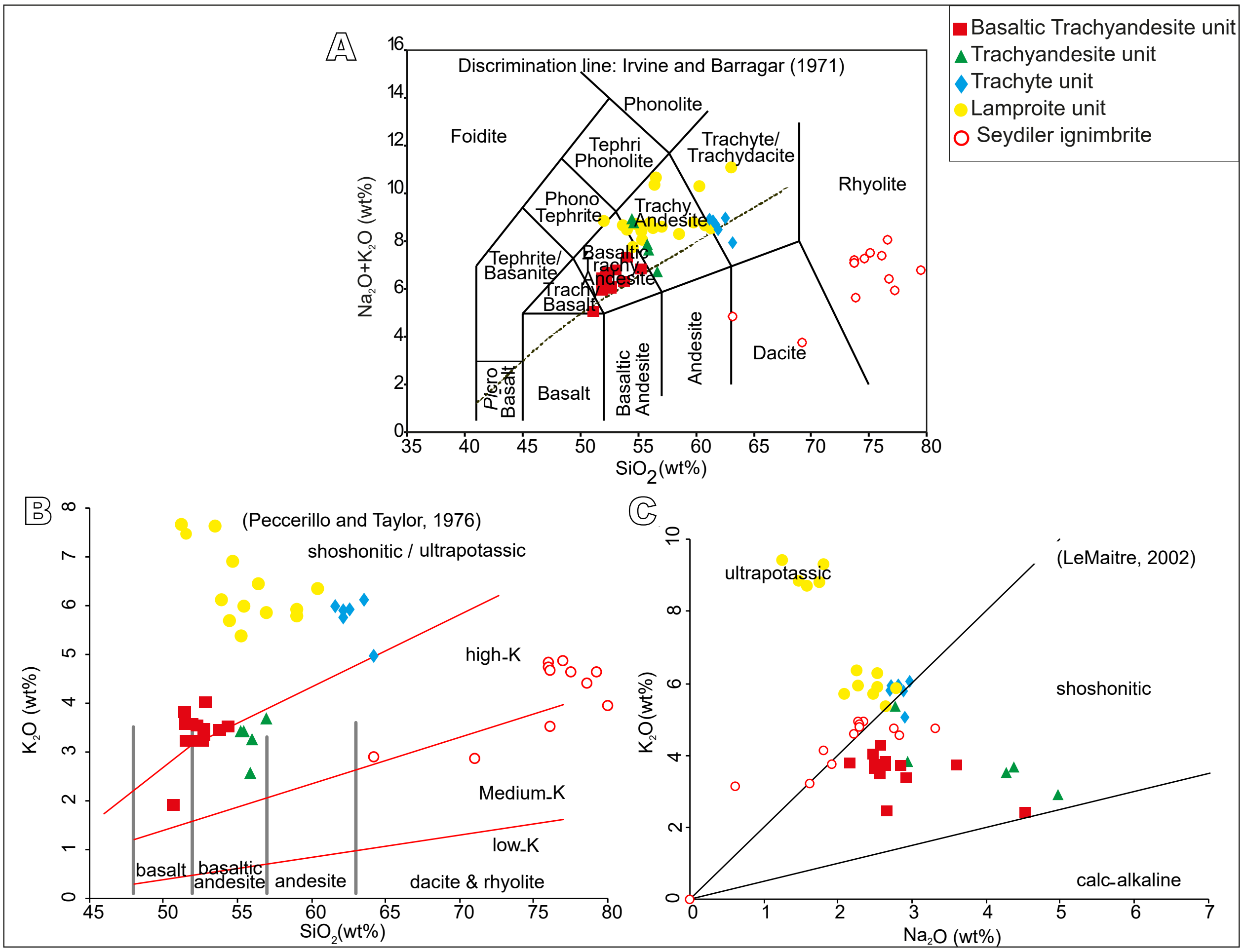

FIGURE 6. Whole-rock classification and discrimination plots of the studied rock groups. A) Classification diagram of Total Alkali-Silica (TAS). Alkaline-sub-alkaline discrimination line by Irvine and Baragar (1971). B) K_2O vs. SiO_2 plot (Peccerillo and Taylor, 1976). C) K_2O vs. Na_2O diagram (Le Maitre *et al.*, 2002).

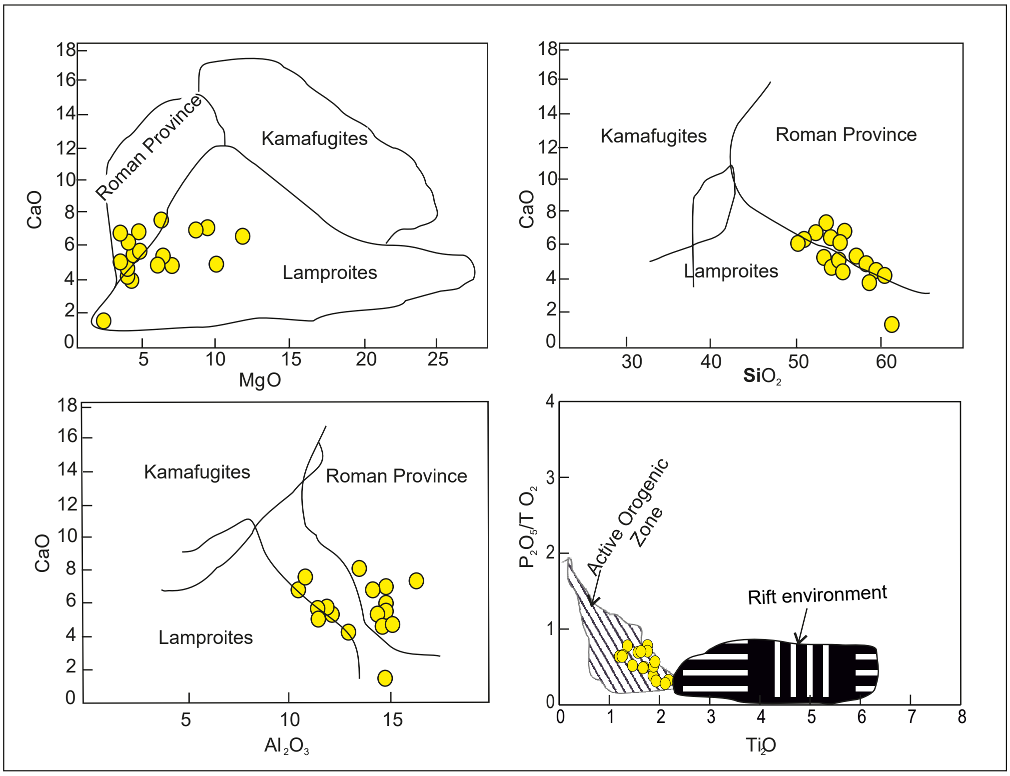

FIGURE 7. Lamproite plots on diagrams of ultrapotassic rock classification of Foley *et al.*, 1987. (Italian lamproite fields are from Conticelli, 1998; Conticelli *et al.*, 1992, 2002; Peccerillo *et al.*, 1988. Fields are from Duggen *et al.* 2005 and Prelević *et al.* 2005 for Spanish and Serbian lamproites, respectively).

to subhedral, rounded and broken, unzoned or weakly zoned. Data from core to rim of the clinopyroxenes indicate only minor compositional variation in the rock groups identified. Compositional ternary Wo-En-Fs diagrams (Morimoto, 1989) (Fig. 9) indicate that clinopyroxenes are augite and diopside types according to the classification of the International Mineralogical Association (IMA). Based on ternary components normalised to 100 percent,

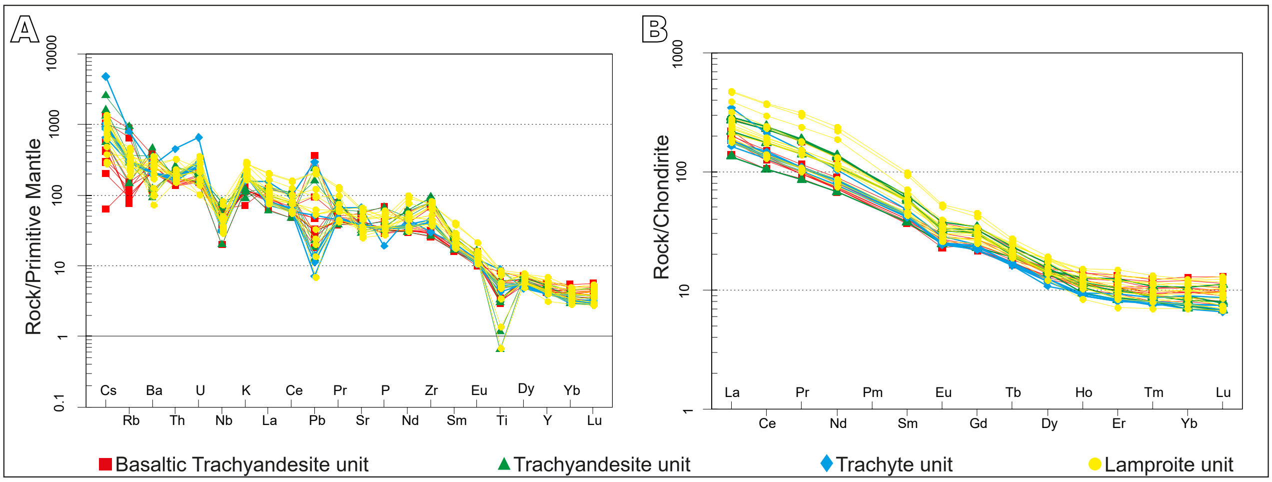

FIGURE 8. A) Primitive mantle-normalised multi-element abundances. The Primitive Mantle values are from Sun and McDonough (1989). B) Chondrite-normalised rare earth element patterns. Chondrite values are from Boynton (1984).0.243 × ln(MgO) + 0.079 × ln(CaO) + 0.392 × ln(Na_2O) + 0.333 × ln(K_2O) – 0.892; W= 0.203 × ln(SiO_2) + 0.191 × ln(TiO_2) + 0.296 × ln(Al_2O_3) + 0.215 × ln(Fe_2O_3) – 0.002 × ln(MgO) – 0.448 × ln(CaO) – 0.464 × ln(Na_2O) + 0.008 × ln(K_2O) – 1.374].

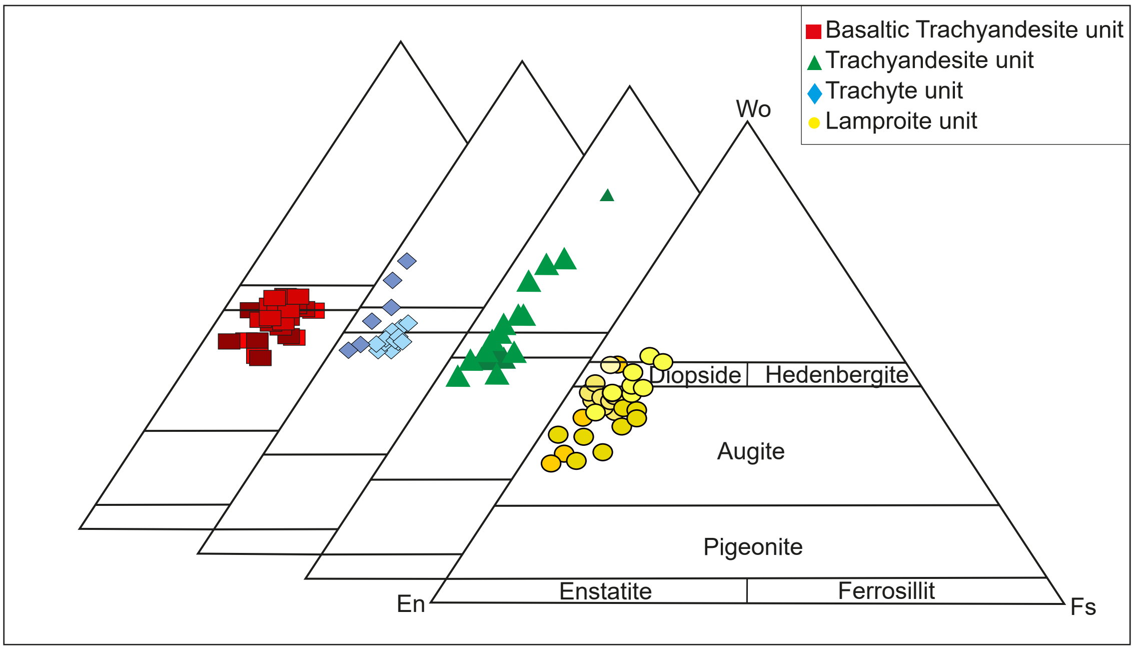

FIGURE 9. Schematic characterisation of the clinopyroxene compositions of Karakaya volcanites (Morimoto, 1989). Variably shaded colored symbols (insets) depict samples used in multiple analyses.

the composition of clinopyroxene is $Wo_{35–48}En_{41–57}Fs_{4–13}$ in the basaltic trachyandesite unit, $Wo_{45–54}En_{19–50}Fs_{3–9}$ in the trachyandesite unit, $Wo_{43–65}En_{30-54}Fs_{1-8}$ in trachyte unit and $Wo_{31-52}En_{36-67}Fs_{3–13}$ in lamproite unit.

Feldspar

Feldspars occur as phenocrysts and microlites in the basaltic trachyandesite and trachyandesite units, whereas they exist as only microlites in the trachyte and lamproite units. The feldspar phenocrysts have a wide composition range from albite to labradorite (Fig. 10). A limited number of microlites have sanidine compositions. Microlites in the trachyte and lamproite units range from $An_1Ab_9Or_{90}$ to $An_{28}Ab_{55}Or_{36}$, which are plotted in the sanidine classification of Deer *et al.* (1992).

Olivine

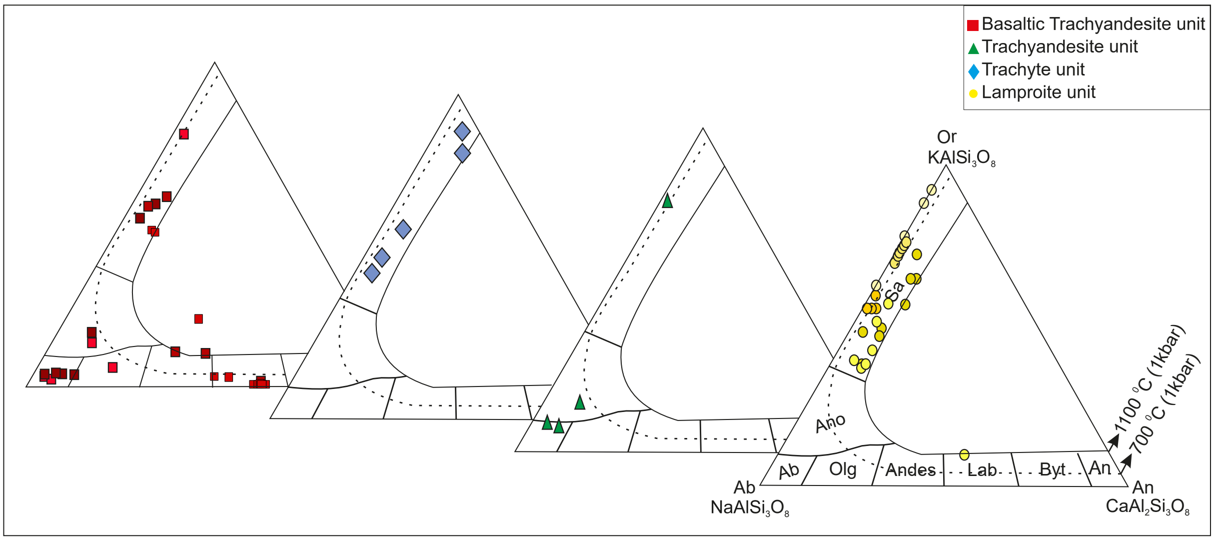

FIGURE 10. Ternary An-Ab-Or diagrams of the feldspar classification with compositions of analysed samples of Karakaya volcanites (Deer *et al.* 1992). (Ab: Albite, An: Anorthite, Ano: Anorthoclase, Andes: Andesine, Byt: Bytownite, Lab: Labradorite, Olg: Oligoclase, Or Orthoclase).

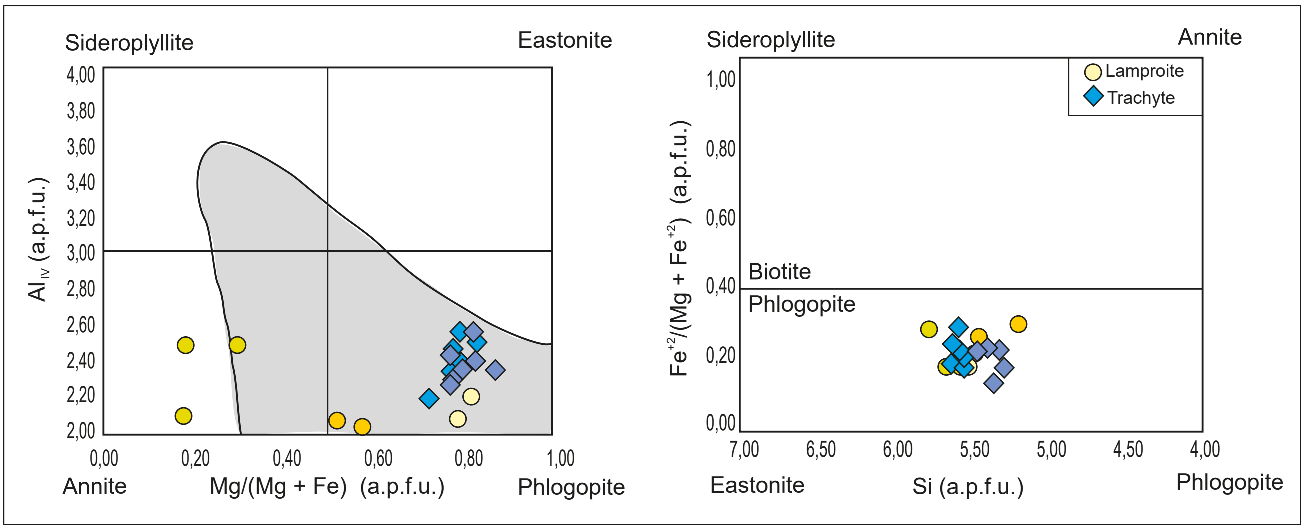

FIGURE 11. Nomenclature diagrams for mica minerals (Deer *et al.*, 1963).

Olivine phenocrysts in the basaltic trachyandesite, trachyandesite and lamproite units indicate heterogeneous compositions (Fo76–93). A common trend observed in most of the studied rocks is the systematic decrease in the Fo content of olivine from its core to the outer rim. This pattern suggests typical growth zoning, where variations in Fo content occur as the phenocrysts crystallise and evolve. Such zoning is often a result of changes in the surrounding magma composition or temperature during crystal growth.

Brown Micas

The nomenclature of brown micas from the trachyte and lamproite units was determined based on their mineral formula. The Mg# of brown micas varies from 0.72 to 0.87 for the trachyte unit and from 0.60 to 0.82 for the lamproite unit. The annite–siderophyllite–phlogopite–eastonite quadrilateral is generally used to exhibit the Al_{tot} (apfu) and Mg# compositional relations of trioctahedral micas in magmatic rocks (Deer *et al.*, 1963). Brown micas are the product of the solid solution between phlogopite and annite end members and are close to the magnesium-rich phlogopite end (Fig. 11).

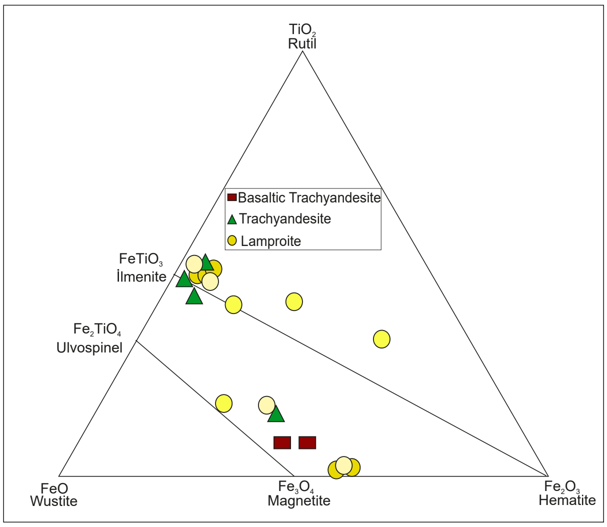

FIGURE 12. Plot of Fe-Ti oxides in the ternary TiO$_2$-FeO-Fe$_2$O$_3$ diagram (Bacon and Hirschmann, 1988)

Fe-Ti Oxides

Analyses of Fe-Ti oxides, given in Supplementary field IH, indicate they are mainly ilmenite with lesser amounts of magnetite. The magnetite is actually a solid solution of ulvospinel and magnetite, and mostly compositions plot close to the magnetite end (Fig. 12). Ilmenite compositions generally fall close to the ilmenite end, along the tie-line of the ilmenite-hematite solid solution (Fig. 12).

INTENSIVE PARAMETERS

Clinopyroxene thermobarometry

Clinopyroxene-melt couples were used for geothermobarometric calculations in the Karakaya volcanites. Temperature, pressure and depth of crystallisation of volcanic rocks can be determined using clinopyroxene composition alone (Nimis, 1995; Nimis and Ulmer, 1998; Nimis and Taylor, 2000) and clinopyroxene-liquid experimental equilibria (Putirka, 2008; Putirka *et al.*, 1996, 2003). Base on the clinopyroxene barometric (Equation 32a) and thermometric (Equation 32d) equations of Putirka (2008), quantitative pressure and temperature values were calculated for the examined volcanics. Also, pressure is converted to depth using the relation Depth(km) = 3.02P(kbar) + 5 (Scarrow and Cox, 1995).

Results indicate that the lamproite unit has higher mean temperature, pressure and depth values than the other units (Table 1). We have converted to the clinopyroxene-melt couples geothermobarometric datasets because pyroxenes only represent the earliest crystallising phases and reflect the upper pressure and temperature limitations of magma storage.

Feldspar–liquid thermometry

Plagioclase–liquid thermometry has attracted much attention after being presented by Kudo and Weill (1970). An equilibrium test was designed by Putirka (2008). The following values were reported in two temperature intervals based on the An–Ab exchange between plagioclase and liquid phases: KD. $(An\text{–}Ab)^{plg\text{–}liq}$=0.10±0.5 at T< 1,050°C and 0.27±0.11 at T>1,050°C.

Considering Putirka's equilibrium test, we have extended our thermodynamic calculations to natural plagioclases, presumably representing the final crystallisation stage. Hence, the data obtained can be compared with the magma storage equilibrium conditions just before the magma ascent. Geothermobarometric estimations of plagioclases exhibit lower average temperatures than temperatures for clinopyroxenes (Table 2).

Disequilibrium parameters

Plagioclase, clinopyroxene, olivine, phlogopite and opaque minerals commonly occur in the Karakaya volcanites and offer many petrographic data indicating unbalanced crystallisation of magma mixture (Fig. 13). Disequilibrium textures are generally associated with magmatic events that occur during the crystallisation and development of magma. These textures may be in response to disequilibrium resulting from changes in pressure and temperature that occur as a result of changes in the composition of the magma (Dobosi and Fodor, 1992; L'heureux and Fowler, 1994; Nixon, 1988; Ortoleva, 1990; Rutherford *et al.*, 1993; Simonetti *et al.*, 1996). The fluctuation in rock chemistry may be related to the mixture of mafic and felsic magmas. The mafic end member may come from the mantle, whereas the felsic end member is most likely derived from crustal contamination and magma

TABLE 1. Temperature and pressure calculation of clinopyroxene for Karakaya volcanites

Clinopyroxene-liquid thermobarometer (Putirka, 2008)				
KD(Fe-Mg)$^{cpx\text{-}liq}$ =0.27±0.03		Eqn 32d* (°C)	Eqn 32a** (kbar)	Depth (km)
Basaltic Trachyandesite unit (n=9)	Max	1188.4	5.1	20.402
	Min	1161.1	2.1	11.342
	Mean	1174.3	3.6	15.872
Trachyandesite unit (n=11)	Max	1216.3	4.2	17.684
	Min	1132.3	0.2	5.604
	Mean	1189.2	2.0	11.04
Trachyte unit (n=3)	Max	1170.2	4.1	17.382
	Min	1150.3	2.3	11.946
	Mean	1161.7	3.1	14.362
Lamproite unit (n=3)	Max	1320.2	18.5	60.87
	Min	1271.4	5.9	22.818
	Mean	1264.2	13.7	46.374

*Eqn 32d: $T\,K = 93100 + 544P\,(kbar)/(61.1 + 36.6(X_{Ti}^{cpx}) + 10.9(X_{Fe}^{cpx}) - 0.95(X_{Al}^{cpx} + X_{Cr}^{cpx} - X_{Na}^{cpx} - X_{K}^{cpx}) + 0.395[\ln(a_{En}^{cpx}]^{2})$

**Eqn32a: $P(kbar) = 3205 + 0.384T(K) - 518lnT(K) - 5.62(X_{Mg}^{cpx}) + 83.2(X_{Na}^{cpx}) + 68.2(X_{DiHd}^{cpx}) + 2.52ln(X_{Al(VI)}^{cpx}) - 51.1(X_{DiHd}^{cpx})^{2} + 34.8(X_{EnFs}^{cpx})^{2}$

segregation (Grove and Donnelly-Nolan, 1986).

Spongy texture is present in the plagioclases in the rocks forming the basaltic trachyandesite and trachyandesite units of the Karakaya volcanites (Fig. 13A, B), and the re-growth envelopes at the edges are the disequilibrium textures indicating the magma mixture.

The clinopyroxene phenocrysts and microphenocrysts in the lamproite unit are fragmented and eroded. The central parts of some euhedral clinopyroxene phenocrysts ultimately became opaque due to having a cavity structure. The abundant volcanic glass inclusions seen in the euhedral clinopyroxene phenocrysts, whose edges are serrated and partially surrounded by opaque minerals, indicate a dense magma mixing (Fig. 13B, C). In most of the Karakaya lamproites, a reaction texture formed by needle-like clinopyroxene microphenocrystals enveloping the quartz xenocrysts is observed (Fig. 13D). This quartz texture indicates that it is xenocrystic and develops due to a reaction of quartz xenocrysts with magma (Vernon, 2014). This property can be explained by magma mixing and disequilibrium crystallisation. The presence of clinopyroxene, plagioclase and opaque minerals (glomeroporphyritic texture) (Fig. 13E) in the Karakaya volcanites suggest disequilibrium textures (Vernon, 2014).

DISCUSSION

TABLE 2. Plagioclase-liquid thermometer for Karakaya volcanites

Temperature T (ºC) Putirka, 2008			
	Eqn 23*	Eqn 24a**	Mean T(˚C)
Basaltic Trachyandesite unit	1105.2	1105.6	1105.4
	1163.0	1189.8	1176.4
Trachyte unit	1140.0	1160.8	1150.4
			1163.4
Lamproite unit	1136.6	1139.6	1138.1

*Eqn23: $10^4/T(K): 6.12 + 0.257\ln\left(X_{An}^{pl}/(X_{CaO}^{liq}(X_{AlO_{1.5}}^{liq}{}^{2})(X_{SiO_2}^{liq})^2\right) - 3.166\left(X_{CaO}^{liq}\right) - 3.137(X_{AlO_{1.5}}^{liq}/(X_{AlO_{1.5}}^{liq} + X_{SiO_2}^{liq}) + 1.216(X_{Ab}^{pl})^2 - 2.475 \times 10^{-2}\left(P(kbar)\right) + 0.2166(H2O^{liq})$

**Eqn24a: $10^4/T(K): 6.4706 + 0.3128 ln\left(X_{An}^{pl}/(X_{CaO}^{liq}(X_{AlO_{1.5}}^{liq}{}^{2})(X_{SiO_2}^{liq})^2\right) - 8.103\left(X_{SiO_2}^{liq}\right) + 4.872(X_{KO_{0.5}}^{liq}) + +1.5346(X_{Ab}^{pl})^2 + 8.661(X_{SiO_2}^{liq})^2 - 3.341 \times 10^{-2}\left(P(kbar)\right) + 0.18047(H2O^{liq})$

Recent publications on the geology of western Anatolia have focused on topics such as geodynamic developments, P-wave tomography, geochronology, isotope geochemistry, mineralogy-petrography and geochemistry (*e.g.* Akal *et al.*, 2012, 2013; Doğan-Külahci *et al.*, 2015; Erkül *et al.*, 2019; Ersoy *et al.*, 2017; Karaoğlu and Helvaci, 2014; Karaoğlu *et al.*, 2010; Portner *et al.*, 2018; Prelević *et al.*, 2012, 2015; Uzel *et al.*, 2020).

The Origins of Magma

Karakaya volcanites are represented by alkaline basaltic trachyandesites, trachyandesites, trachytes and lamproites together with calcalkaline pyroclastics in mineralogical composition within the rock assemblages belonging to the middle-late Miocene volcanism occurring in the Eskişehir, KAIVP. The varying mineralogical and geochemical characteristics of Karakaya Volcanites indicate that the units were affected by fractional crystallisation and contamination processes. There is no significant correlation between La/Sm and Th/Nb in the Karakaya volcanic units. Increasing La/Sm with almost constant Th/Nb indicates the important role of fractional crystallisation (Fig. 14A). This crystallisation and/or different degrees of partial melting processes give Karakaya volcanites a composition ranging from basaltic trachyandesite to trachyte. The positive trend observed in the La/Nb vs. SiO_2 diagram suggests that crustal contamination and fractional crystallisation are effective in

Karakaya Volcanites (Fig. 14B). Increasing Th/Yb ratios point toward a mantle source progressively metasomatized by subduction-related fluids. The high Th/Nb ratios imply a substantial subduction-related contribution during magma formation (Fig. 14C).

In general, negative Nb-Ta-Ti and positive Pb-U patterns in the normalised multi-element diagrams of the volcanites suggest that the magma source may have been affected by both crustal contamination and subduction-related enrichment to different degrees. In addition to Pb enrichment, enrichment of large ion lithophile elements is expected in subduction-related volcanic rocks. In the Karakaya volcanic units, both the enrichment in Pb content identical to the subduction environment and the depletion of Pb in some samples, support this situation in multi-element spider diagrams. Although a negative Pb anomaly indicates an asthenospheric mantle source, the behaviour of the elements in the volcanic units clearly shows the addition of subduction-related metasomatic solutions infiltrating an enriched mantle source in the Karakaya volcanites. High Mg# values in the Karakaya volcanic units indicate more mantle input during formation. The La/Yb vs Dy/Yb diagram (Fig.14D) shows that melt production is predominantly close to the spinel stability field, with a decreasing contribution from the garnet stability field. The data indicate the development of a mixing mechanism between the units and reflect polybaric melting of the mantle source.

Magma Chamber Attributes in the Context of

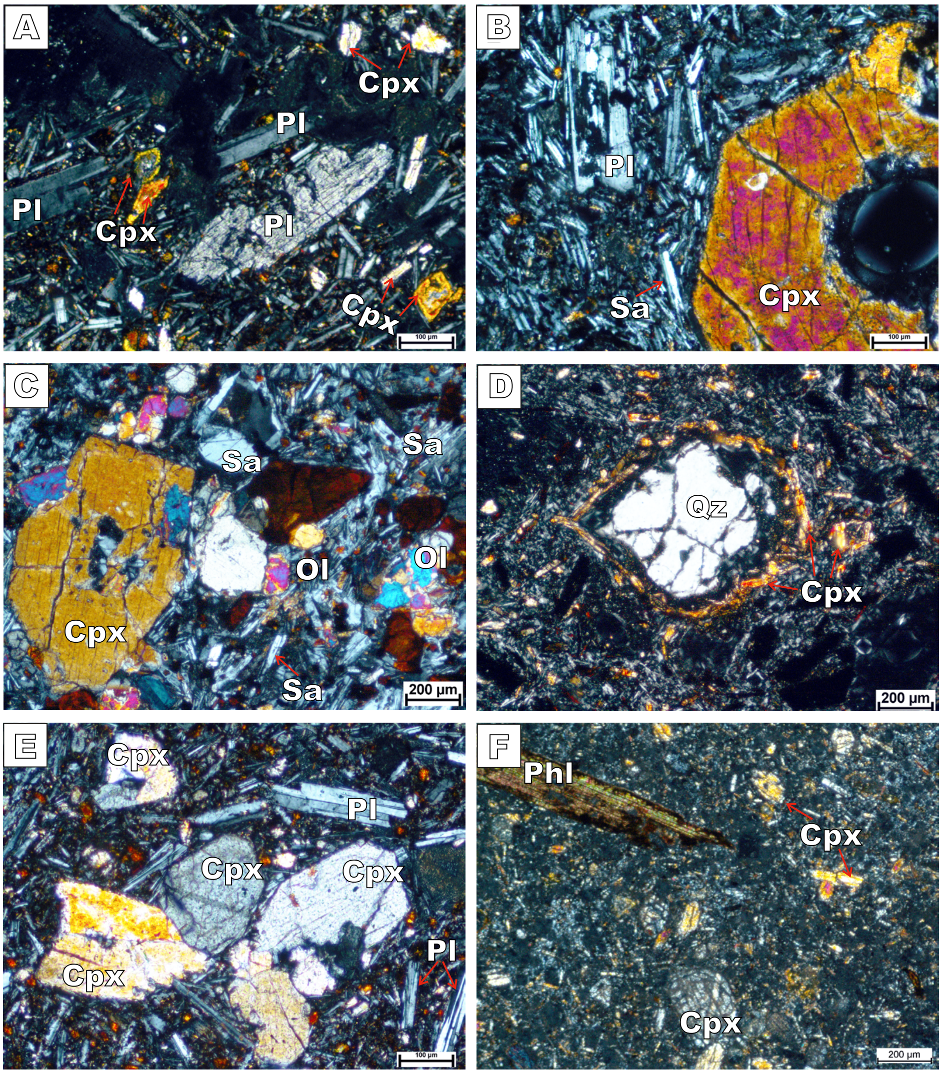

FIGURE 13. Photomicrographs of textures indicating disequilibrium crystallisation of the Karakaya volcanites (in crossed polarised light). A-B) Corroded margins and cores of plagioclase (spongy texture). B-C) Abraded margins and cores of clinopyroxenes. D) Small quartz crystal surrounded by a needle-like clinopyroxene microphenocrysts reaction belt. E) Clinopyroxene phenocrysts in the form of cumulate (glomeroporphyritic texture). F) Disequilibrium textures indicating magma mixing observed in phlogopites. (cpx: clinopyroxene; pl: plagioclase; ol: olivine; phl: phlogopite, sa: sanidine, Qz: quartz).

Tectono-Magmatic Evolution

Given the limited isotopic data available (*e.g.* Akal *et al.*, 2013; Besang *et al.*, 1977; Prelević *et al.*, 2015), field observations and mineralogical-petrographic characteristics of the samples described in this study suggest an early volcanic stage. The comprehensive petrographic, mineral chemistry and thermobarometric data point to complex polybaric evolutionary pathways in the Karakaya volcanites units, reflecting multiple petrogenetic processes. Based on all available data, the basaltic trachyandesite and trachyte compositions of Karakaya volcanites represent a last stage of orogenic volcanism. In contrast, trachyandesite and lamproite compositions indicates a first stage of anorogenic volcanism, with evidence of asthenospheric input. Variable crystallisation pressure and compositional variations of phenocrysts indicate a polybaric evolutionary development.

Four different magma storage levels were determined for the Karakaya volcanites. Basaltic trachyandesites, arising from shoshonitic volcanism originating in lithospheric mantle and crustal source materials in the Iscehisar region, constitute the final phase of orogenic volcanic activity. These findings indicate that deep crustal magma chambers (at an average pressure of 3.6kbar), situated at approximately 15km, were the starting point for the development of basaltic trachyandesites. This development may have been significantly influenced by open-system processes similar to melting, assimilation, storage and homogenisation. The subducting slab's rollback resulted in the asthenosphere's upwelling, acting as a heat source in the overlying mantle wedge, leading to crustal uplift and expansion. This process potentially involved partial melting of the metasomatized mantle wedge by the ascending asthenosphere and, concurrently, partial melting of the lower crust due to the ascent of the asthenosphere. The magmas derived from lithospheric mantle and crustal partial melting may have subsequently mixed in varying proportions, indicating the presence of a magma chamber responsible for the trachyte unit at an average depth of approximately 14km and a mean pressure of 3.1kbar. However, it can be argued that the extension of the Seydiler Ignimbrite due to a caldera system was formed by the accumulation of the melts that emerged in the continental crust in an early period in the upper crust. This extension regime, which evolved with the late mixing of magmas of lithospheric mantle and lower crustal origin, suggests that it may have preceded the tear of the subducting oceanic slab. The geochemical transition from orogenic to anorogenic is due to the increased role of the lithosphere-asthenosphere interaction of the Afyon lavas. At the same time, volcanism is directly related to the location of the slab tearing as heat transfer from the uplifted asthenosphere triggers magmatism (Prelević *et al.*,

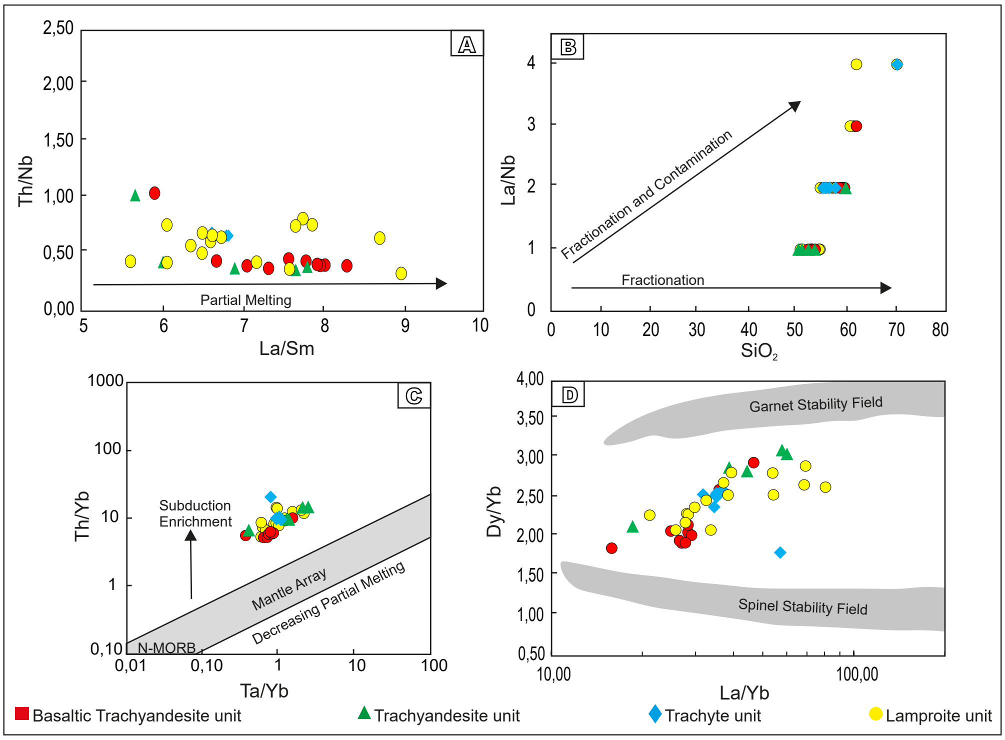

FIGURE 14. Variation diagrams for A) Th/Nb vs. La/Sm. B) La/Nb vs. SiO_2. C) Th/Yb vs. Ta/Yb. D) La/Yb vs Dy/Yb. Fields of melt compositions for melting in the garnet and spinel peridotite stability fields are from Prelević *et al.* (2012).

2015). The trachyandesite and lamproite units are probably related to the slab tearing that developed in the later period and were predominantly produced by melting in the mantle source. This suggests that the magma chamber that produced the lamproite unit was formed at an average pressure of 13.7kbar at a depth of approximately 46km. After magma ascent, the formation of a trachyandesite-producing magma chamber at a mean pressure of 2kbar and a depth of about 11km may have been caused by processes such as assimilation, fractional crystallisation and contamination or mixing with basaltic trachyandesite-producing magma. Alkaline volcanic rocks of different compositions in the Afyon volcanic complex indicate a slab-tearing event (Bilgiç Gencer *et al.*, 2020).

The data provided in this work suggest that, consistent with Prelević *et al.* (2015), the Karakaya volcanic units developed as separate volcanic units with distinct compositions not affiliated with a shared parental magma by fractional crystallisation. The role of assimilation of crustal rocks is of limited importance, and most of the geochemical diversity of lavas is due to mantle processes. Karakaya Volcanites developed along multiple differentiation pathways from different parental magmas.

CONCLUSION

The Karakaya volcanites have been grouped according to their mineralogical, petrographic and geochemical properties. They comprise basaltic trachyandesite, trachyandesite, trachyte and lamproite units. According to geochemical data the basaltic trachyandesite and trachyandesite units are shoshonitic in character, whereas the trachyte and lamproite units are ultrapotassic. All the pyroclastic rocks of the Seyitler ignimbrite are in the rhyolitic and high-potassium calc-alkaline series.

In the investigated volcanic rocks, melting along and corrosion at crystal edges and opaque mineral inclusions are detected in clinopyroxene crystals. In contrast, textural features such as sieve texture and abrading are evident in plagioclase crystals, indicating a disequilibrium between minerals and melts. In light of data from textural and mineral chemistry, it can be said that more than one petrogenetic event played an essential role in developing volcanic rocks.

The olivines in the Karakaya volcanites are forsteritic, and the pyroxenes found in the basaltic trachyandesite samples are augitic. However, both augite and diopside structures were detected in the pyroxenes of the trachyandesite samples. Biotites are classified only as phlogopite in mica minerals of the basaltic trachyandesite and trachyandesite samples. The composition of albite and sanidine was discovered in mineral chemistry studies on feldspars.

Based on the values of temperature and pressure calculated from the mineral-melt associations in the investigated volcanics, it is concluded that different types of mineral associations (magma mixture) may have crystallised into varying depths during the magma transport.

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