

Geochronology and geochemistry of the Miocene volcanics from the Kütahya area: Constraints for post-collisional magmatism in western Anatolia, Turkey

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ABSTRACT

The first geochronological and geochemical data are presented for the Kütahya area volcanics in western Turkey to study mantle sources and magmatic processes. Petrographically, the studied volcanics are composed primarily of olivine augite basalt and augite basalt, with minor basaltic andesites/trachyandesites, and show porphyric, hyalo-microlithic porphyric and rarely glomeroporphyric textures. The rock samples contain plagioclase as phenocrysts and microlites, olivine, augite and biotite as phenocrysts, sanidine, opaques, and volcanic glass. Whole-rock K–Ar dating of the studied volcanics yielded cooling ages between 20.1 ± 0.7 and 17 ± 0.5 Ma (Early Miocene). The volcanics indicate magma evolution from shoshonitic to medium-high-K character. High contents of LILEs and LREEs, and low amounts of Nb, Ta, Zr and Ti indicate that fractional crystallization and assimilation processes had a role in the evolution of these volcanics. The studied volcanics also have moderate to high $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70719–0.70971), negative ϵNd values (–6.27 to –4.63), and high $^{206}\text{Pb}/^{204}\text{Pb}$ (18.93–19.05), $^{207}\text{Pb}/^{204}\text{Pb}$ (15.69–15.76) and $^{208}\text{Pb}/^{204}\text{Pb}$ (38.99–39.32) ratios. Integrated trace element geochemical and Sr–Nd–Pb–O isotopic data suggest that the Kütahya area volcanics evolved via AFC processes from parental magma (s) that originated from a subcontinental veined lithospheric mantle source metasomatized by subduction-related fluids and melts.

1. Introduction

Magmatic activity in western Anatolia (Turkey) developed as intrusions in the Eocene and Oligocene, and as extrusions in the Late Cenozoic (Miocene and Pliocene) and Quaternary (Fig. 1). This Late Cenozoic magmatism in western Anatolia resulted from the collision of the Eurasian and Afro-Arabian plates (Şengör and Yılmaz, 1981) with (i) subduction in the Aegean (Hellenic) Arc and following slab-break off (Altunkaynak, 2007), (ii) post-collisional NS stress-related grabenization (Prelević et al., 2015) and crustal thinning resultant magma generation, and (iii) the orogenic collapse of the Menderes Massif (Lister et al., 1984) being the main factors.

Western Anatolia contains many graben structures that are orientated north-south and east-west, and this grabenization is one of the causes of volcanism (e.g., Ersoy et al., 2010; Çoban et al., 2012; Prelević et al., 2012, 2015). The Edremit, Bakırçay, Kütahya, Simav, Gediz,

Küçükmenderes, Büyükenderes and Gökova grabens from north to south are some of the products of this extension system, and the east-west trending Gördes, Demirci, Selendi, Uşak, Güre, Seyitömer and Sabuncupınar grabens extend approximately NS (e.g., Yılmaz et al., 2000; Özburan and Güre, 2012). The geochemical features of basaltic volcanics in NE-SW trending basins suggest an enriched lithospheric mantle source (e.g., Ersoy et al., 2010; Karaoğlu et al., 2010; Çoban et al., 2012; Prelević et al., 2012; Ersoy and Palmer, 2013; Moghadam et al., 2014; Prelević et al., 2015; Semiz et al., 2015). In some cases, the volcanism is bimodal in these Early and Middle Miocene NE trending basins (Bigadiç, Foça, Selendi, Tunçbilek basins) (e.g., Ersoy et al., 2008; Altunkaynak et al., 2010; Ersoy and Helvacı, 2016), possibly due to a decrease in the effects of the subduction event and an increase in the intensity of the stress regime. In addition, the tectonics-volcanism connection is supported by the observation that the Miocene basins and volcanics are associated with N–S and NE-SW trending faults, and

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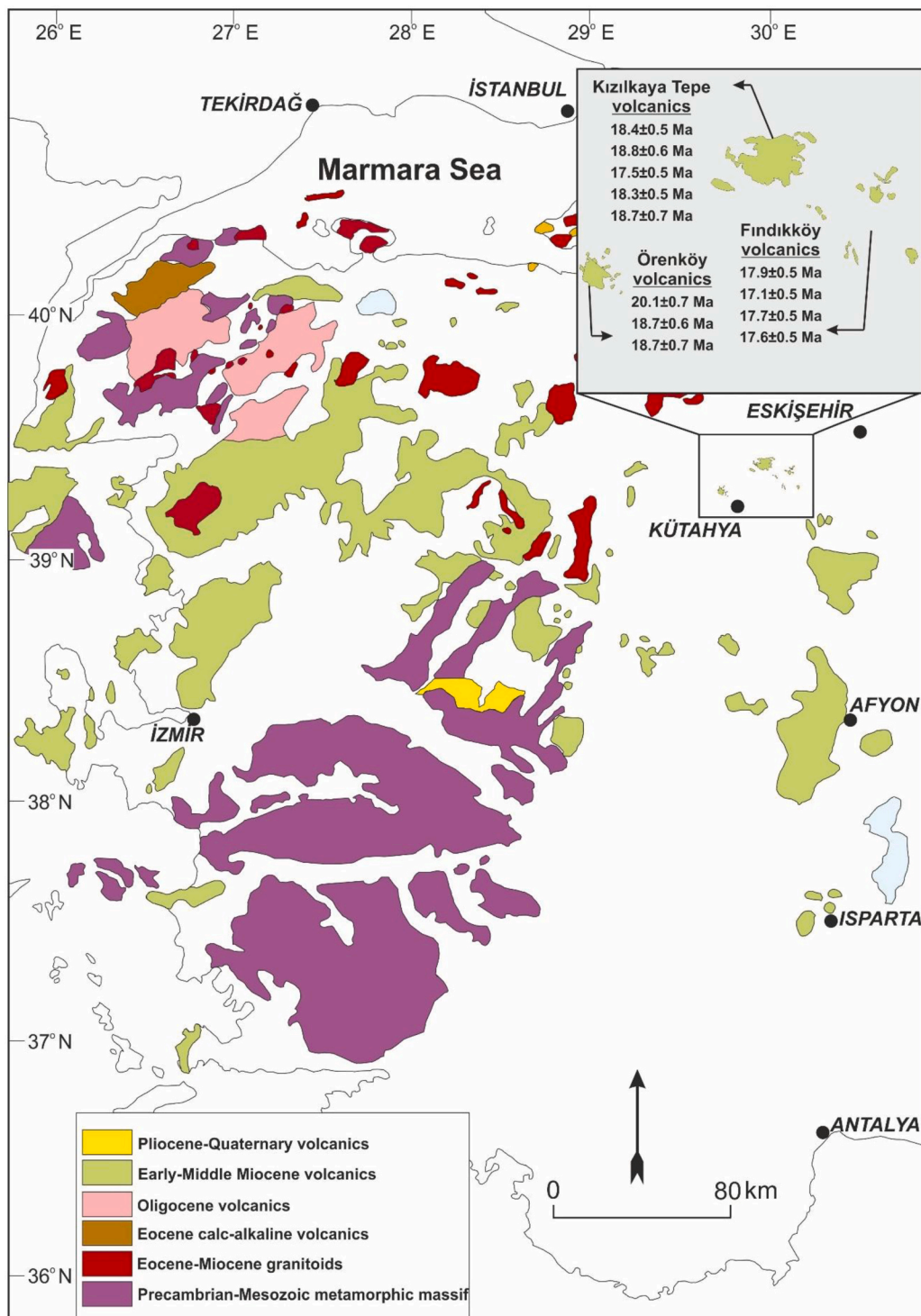


Fig. 1. The distribution of the volcanics and intrusions in western Anatolia (modified from Dilek and Altunkaynak, 2010) and age data of the studied Kütahya volcanics.

the Plio-Quaternary basins and volcanics are associated with NW-SE and E-W trending faults. Hence, the recent tectonic movements and volcanic activities are related in the Aegean Region. However, the volcanism is not only limited to the tectonic faults and grabens but is also controlled by other mechanisms.

The volcanics in the Kütahya area (Fig. 2) have mostly been dated stratigraphically, and their ages are reported as Lower-Middle Miocene to the Quaternary with a concentration in the Pliocene (e.g., Gürdal, 1990; Arık and Temur, 2003). However, radiometric dating of the

volcanics that cut the Neogene units, and the associated intermediate-acidic tuffs (e.g., Temel et al., 2011; Ersoy and Helvacı, 2016; Helvacı et al., 2017) yield ages of 21–17 Ma (Lower-Middle Miocene). Therefore, there is uncertainty regarding the absolute age and source of the Kütahya volcanics. In this study, we present the first petrographic and geochemical data, and K–Ar ages of the Kütahya area volcanics (Figs. 1 and 2), to study the origin and evolution of the parental magma(s) and to evaluate the magma chamber processes using major-trace element and Sr–Nd–Pb–O isotope compositions.

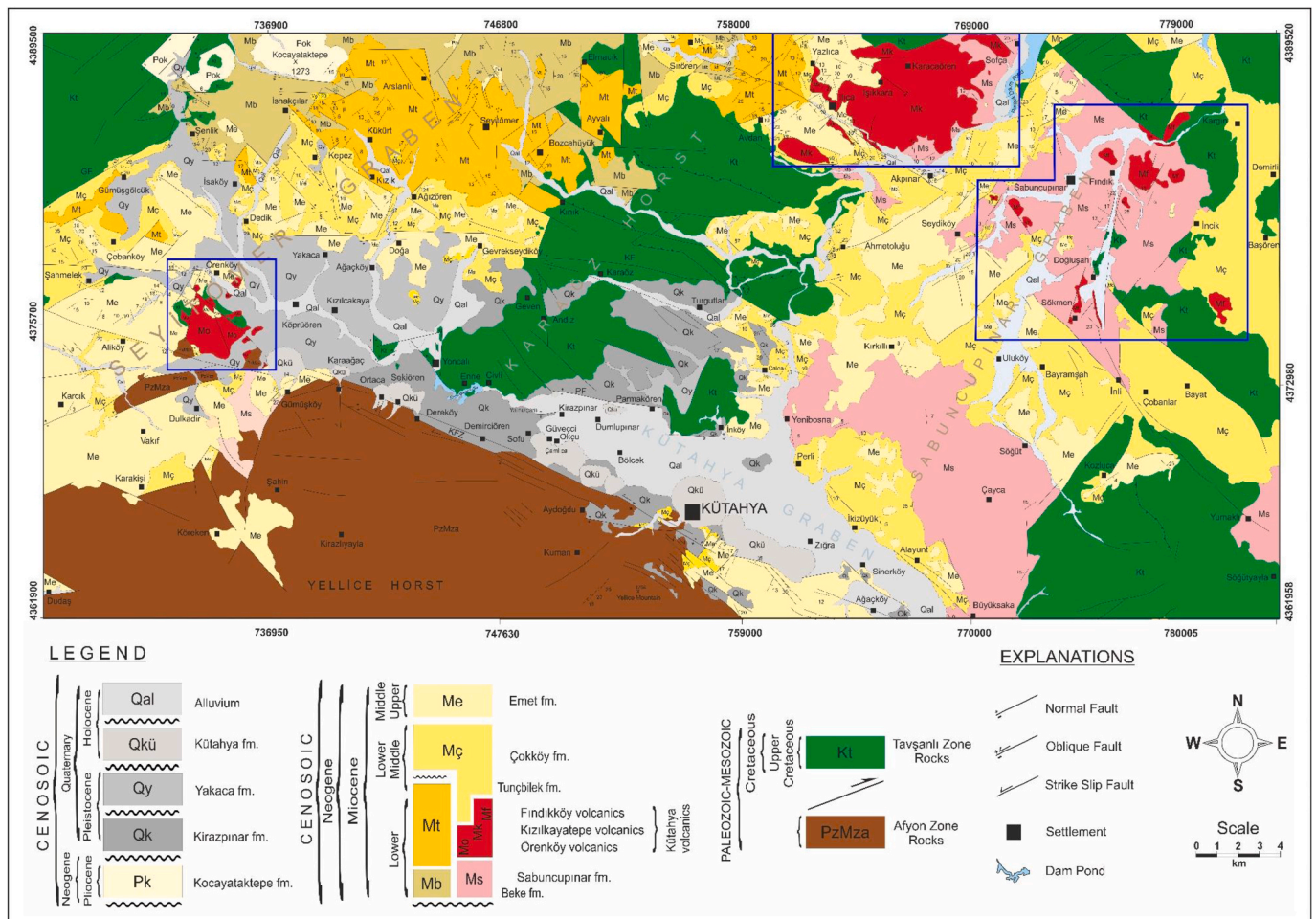


Fig. 2. Simplified geological map of the Kütahya area showing the studied volcanics and surrounding lithologies (modified from Özburan, 2009; Özburan and Gürer, 2012).

2. Volcanic outline

Western Anatolia of Turkey was shaped by crustal thickening and orogenic collapse after the continent-arc collision in Eocene time. The preliminary products of post-collisional volcanism in western Anatolia are andesitic volcanics that developed during the Middle Eocene (Genç and Yılmaz, 1997; Altunkaynak and Dilek, 2006). The Eocene volcanics in the region are represented by the Balıkcılaşme volcanics (Ercan et al., 1995). The secondary phase products of post-collisional volcanism were developed in the Oligo-Miocene period (Yılmaz, 1989). The Oligocene/Oligo-Miocene volcanics in the region are represented by the Sarıkaya/Çan volcanics (Ercan et al., 1995). In western Anatolia, especially in the Early Miocene, widespread volcanic activity occurred (Innocenti et al., 1982; Keller, 1983; Chen and Robertson, 2021). After widespread calc-alkaline volcanism during compression in the Early-Middle Miocene (e.g., Aldanmaz et al., 2000; Yılmaz et al., 2000, 2001), alkaline volcanism developed in the Middle-Late Miocene in an extensional tectonic regime (e.g., Yılmaz et al., 2000, 2001; Alıcı et al., 2002; Westaway et al., 2004; Aldanmaz et al., 2006; Çoban et al., 2012). Some studies also suggest that calc-alkaline and alkaline volcanism in the region occurred together as a result of the extensional tectonic regime (e.g., Seyitoğlu et al., 1992). It is also suggested that the rhyolitic volcanism was associated with crustal anatexis (e.g., Keller, 1983). The widespread Late Cenozoic intra-continental volcanism in western Anatolia has been the subject of many studies (e.g., Dilek and Altunkaynak, 2009; Temel et al., 2011; Prelević et al., 2012; Seghedi et al., 2013; Karaoğlu and Helvacı, 2014; Semiz et al., 2015; Ersoy and Helvacı,

2016; Helvacı et al., 2017; Demirbilek et al., 2018; Erkül et al., 2019; İskenderoğlu and Aysal, 2021).

3. Materials and methods

Whole-rock major-, trace and rare earth element analyses of the studied volcanics were performed from rock powders at ACME Analytical Laboratories Ltd. (Vancouver, Canada). Detailed analytical procedures and techniques for these analyses are given in Temizel et al. (2020). Whole-rock K–Ar dating analysis of the volcanics was conducted at Actlabs (Geochronology and Radiogenic Isotope Analysis Laboratories, Canada). Detailed analytical procedures and techniques for the K–Ar dating are given in Karacık et al. (2008). Sr and Nd isotope analysis of the volcanics were performed by using Thermo Scientific Triton TI Multi-Collector Thermal Ionisation mass spectrometer with static multi-collection at the Central Laboratory of Middle East Technical University (METU, Ankara, Turkey). Detailed analytical procedures and techniques for the Sr–Nd isotopes are reported in Temizel et al. (2020). Pb isotope analysis of the volcanics was carried out by using a Triton-MC mass-spectrometer at Actlabs (Geochronology and Radiogenic Isotope Analysis Laboratories, Canada). Whole-rock oxygen isotopes of the volcanics were measured by using a Finnigan MAT Delta, dual inlet, isotope ratio mass spectrometer at Actlabs (Geochronology and Radiogenic Isotope Analysis Laboratories, Canada). Detailed analytical procedures and techniques for the Pb–O isotopes are presented in Ersoy et al. (2012a).

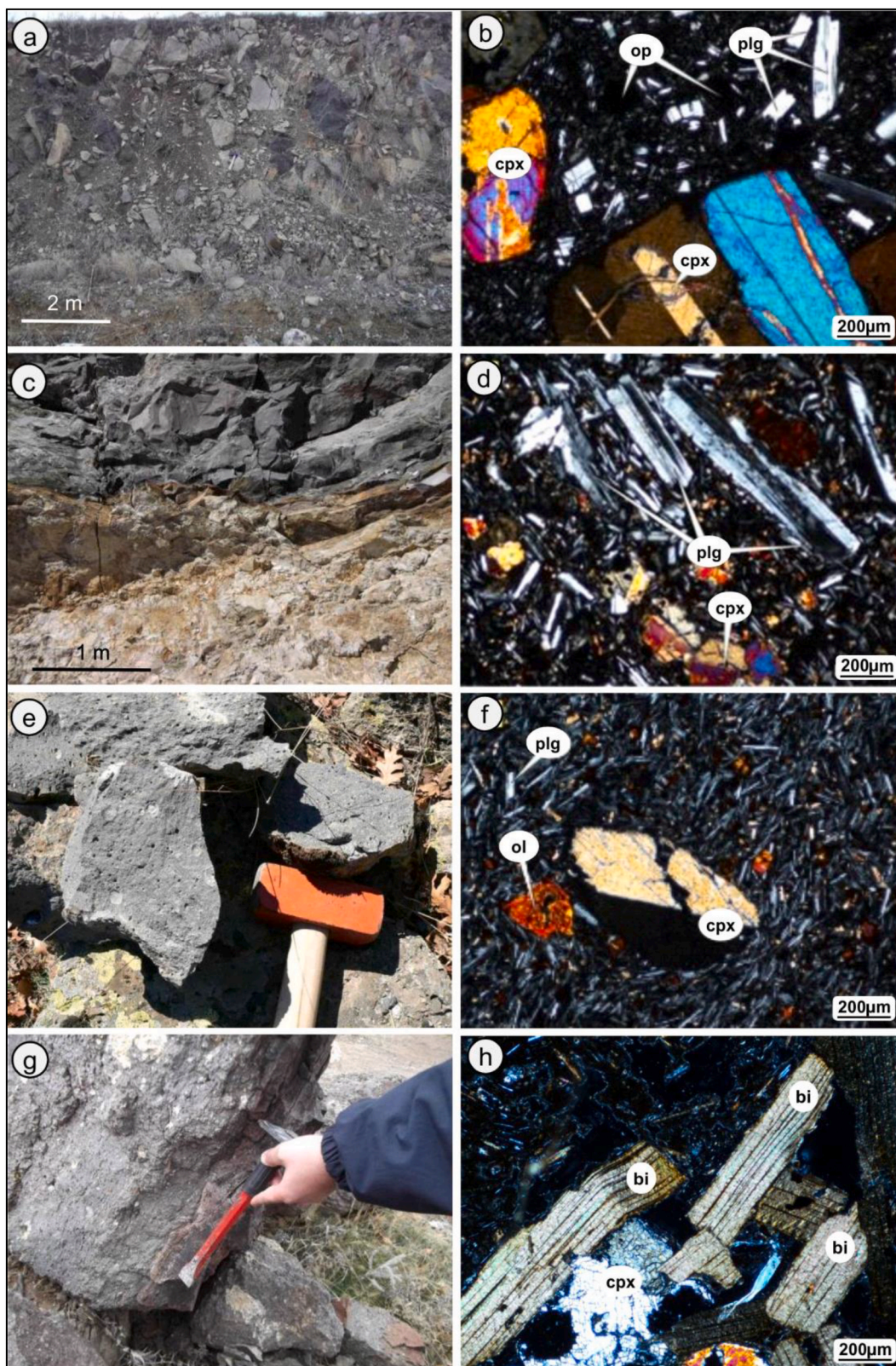


Fig. 3. Photographs showing field features and photomicrographs of the Kütahya volcanics (b, basalt; d and e, basaltic trachyandesite; h, biotite andesite; Cross-polarized light). (a–b) Örenköy, (c–d) Kızılkaaya Tepe, (e–h) Fındikköy volcanics (plg: plagioclase, cpx: clinopyroxene, ol: olivine, bi: biotite, op: opaque mineral).

Table 1
K–Ar dating data of the Kütahya volcanics.

Locality	Sample no	Rock name	%K	$^{40}\text{Ar}_{\text{rad}}$ (nl/g)	% $^{40}\text{Ar}_{\text{atm}}$	Age (Ma)
Örenköy volcanics	TS-8	Olivine augite basalt	1.19	0.912	84.1	20.1 ± 0.7
	TS-10	Augite basalt	1.79	1.283	62.7	18.7 ± 0.6
	TS-11	Olivine augite basalt	1.34	0.961	81.9	18.7 ± 0.7
Kızılkaya Tepe volcanics	KZ-6	Olivine augite basalt	1.67	1.176	56.1	18.4 ± 0.5
	KZ-12	Basaltic andesite	1.59	1.148	73.9	18.8 ± 0.6
	KZ-24	Basaltic andesite	2.03	1.363	48.5	17.5 ± 0.5
	KZ-31	Basaltic trachy-andesite	1.75	1.228	41.7	18.3 ± 0.5
	KZ-46	Augite basalt	1.87	1.345	83.5	18.7 ± 0.7
Fındıkköy volcanics	FN-6	Olivine augite basalt	3.15	2.159	40.4	17.9 ± 0.5
	FN-7	Olivine augite basalt	3.26	2.139	33.7	17.1 ± 0.5
	FN-11	Augite basalt	3.25	2.208	34.8	17.7 ± 0.5
	FN-16	Biotite trachy-andesite	4.06	2.746	27.9	17.6 ± 0.5

4. Results

4.1. Petrographic features of the volcanics

The studied Kütahya volcanics are spatially grouped into three localities as Örenköy, Kızılkaya and Fındıkköy areas.

The Örenköy volcanics (Fig. 2) are dark grey-black, mostly massive but fractured (Fig. 3a) and show a vesicular texture in places. Large plagioclase and augite crystals in the basaltic rocks show porphyric textures. Petrographically, these volcanics are composed of olivine-augite basalt, augite basalt and basaltic trachyandesite, with a texture of hyalo-porphyric, hyalo-microlithic porphyric and locally cumulo-phyrlic. They generally contain plagioclase, clinopyroxene, olivine and to a lesser extent sanidine and Fe–Ti oxide (Fig. 3b).

The Kızılkaya Tepe volcanics (Fig. 2) are brown-beige, and the freshly fractured surfaces are grey-black (Fig. 3c). Macroscopically, they contain augite phenocrysts. The lavas gain a very porous structure towards the upper parts, and these cavities are sometimes filled by calcite and zeolite. These volcanics are generally composed of olivine-augite basalt, augite basalt, augite basaltic andesite and glassy basaltic trachyandesite and show hyalo-porphyric, hyalo-microlithic porphyric, vesicular, intersertal and trachytic textures. They generally contain plagioclase, clinopyroxene, olivine, Fe–Ti oxide and occasionally sanidine (Fig. 3d). Calcite and chlorite accompany them as secondary minerals.

The Fındıkköy volcanics (Fig. 2) are dark grey-black and show a highly fractured structure. The weathered surfaces are brown-beige and freshly fractured surfaces are greyish-black (Fig. 3e, g). Augite phenocrysts in the rock can be seen macroscopically. The voids are partially filled by calcite. In general, the volcanics consist of olivine augite basalt, trachybasalt, augite basaltic trachyandesite, trachyandesite and biotitic andesite and show hyalo-porphyric, hyalo-microlithic porphyric, porous hyalo-microlithic porphyric, intersertal and cumulo-phyrlic textures. Basaltic rocks observed in the unit generally contain plagioclase,

clinopyroxene, olivine, sanidine and Fe–Ti oxide (Fig. 3f), while the intermediate rocks contain plagioclase, biotite and to a lesser extent clinopyroxene and Fe–Ti oxide (Fig. 3h). Calcite and chlorite accompany them as secondary minerals.

4.2. K–Ar dating

The K–Ar dating analysis of the Kütahya volcanics is presented in Table 1. K–Ar cooling ages are 18.8 ± 0.6 to 17.5 ± 0.5 Ma for the Kızılkaya Tepe volcanics, 17.9 ± 0.5 to 17.1 ± 0.5 Ma for the Fındıkköy volcanics, and 20.1 ± 0.7 to 18.7 ± 0.7 Ma for the Örenköy volcanics (Table 1). The K–Ar cooling ages correspond to Burdigalian (Early Miocene) age.

4.3. Major and trace element geochemistry

Major oxide, trace and rare earth element compositions of the Kütahya volcanics are given in Supplementary Table 1. According to the total alkali silicate classification scheme (Le Maitre, 2002), the Örenköy volcanic rock samples are mostly basaltic andesite and andesite, the Fındıkköy volcanics samples are basaltic trachyandesite and trachyandesite, and the Kızılkaya Tepe volcanic rock samples are basaltic andesite, basaltic trachyandesite, andesite and trachyandesite in composition (Fig. 4a). Based on the alkaline-subalkaline discrimination of Irvine and Baragar (1971), the Örenköy volcanics have subalkaline, the Kızılkaya Tepe volcanics have alkaline-subalkaline transition and the Fındıkköy volcanics have slightly alkaline affinities (Fig. 4a). In the Nb/Yb versus Zr/TiO₂*0.0001 nomenclature diagram of Pearce (1996), the Örenköy and Kızılkaya Tepe volcanics fall into the basalt field, and the Fındıkköy volcanics also mostly fall into the basalt field (Fig. 4b). In the total alkali-total iron-magnesium (AFM) diagram of Irvine and Baragar (1971), the volcanics generally are calc-alkaline in character (Fig. 4c). According to the SiO₂ versus K₂O diagram (Peccerillo and Taylor, 1976), the Örenköy volcanics are medium-high-K calc-alkaline transitional, the Kızılkaya Tepe volcanics are high-K calc-alkaline, and the Fındıkköy volcanics are shoshonitic in character (Fig. 4d).

The variations in most of the major oxides and trace elements against SiO₂ of the studied volcanics are related to the differentiation of the main phenocryst phases observed in the rocks (Fig. 5). The normal-type mid-ocean ridge basalt (N-MORB) normalized trace element distributions of the studied volcanics (Fig. 6a) are similar to each other, and there is an enrichment in large ion lithophile elements (LILEs) (Sr, K₂O, Rb and Ba), and depletion in Nb, Ta, Zr, TiO₂ and Y. The negative Nb–Ta anomalies in the volcanics probably indicate the presence of a crustal contribution in the evolution of magmas. Moreover, the observation that the Kızılkaya Tepe and Örenköy volcanics show relatively deeper negative Nb and Ta troughs than the Fındıkköy volcanics suggests that crustal contribution (or assimilation-fractional crystallization-AFC) was greater in the development of the Kızılkaya Tepe and Örenköy volcanics than in the Fındıkköy volcanics (Fig. 6a). The chondrite-normalized rare earth element (REE) distributions of the volcanics (Fig. 6b) are similar to each other and suggest that the volcanics are derived from a similar or the same source. The light rare earth elements (LREE) are generally enriched relative to the middle and heavy rare earth element (MREE–HREE) enrichment in the studied volcanics (Fig. 6b). This suggests that the parental magma(s) was formed by the low-degree partial melting of an enriched mantle source (e.g., Fitton et al., 1991; Barragan et al., 1998). The volcanics also show slightly negative Eu anomalies (Eu*/Eu = 0.71–0.97). In addition, the Kızılkaya Tepe, Fındıkköy and Örenköy volcanics have La_N/Lu_N ratios (10.9–14.4, 8.1–10.9 and 6.5–9.1, respectively) and La_N/Yb_N ratios (11.0–15.0, 8.2–11.7 and 6.8–9.5, respectively) (Fig. 6b).

4.4. Sr–Nd–Pb–O isotope composition

Sr, Nd, Pb and O isotope composition of the Kütahya volcanics are

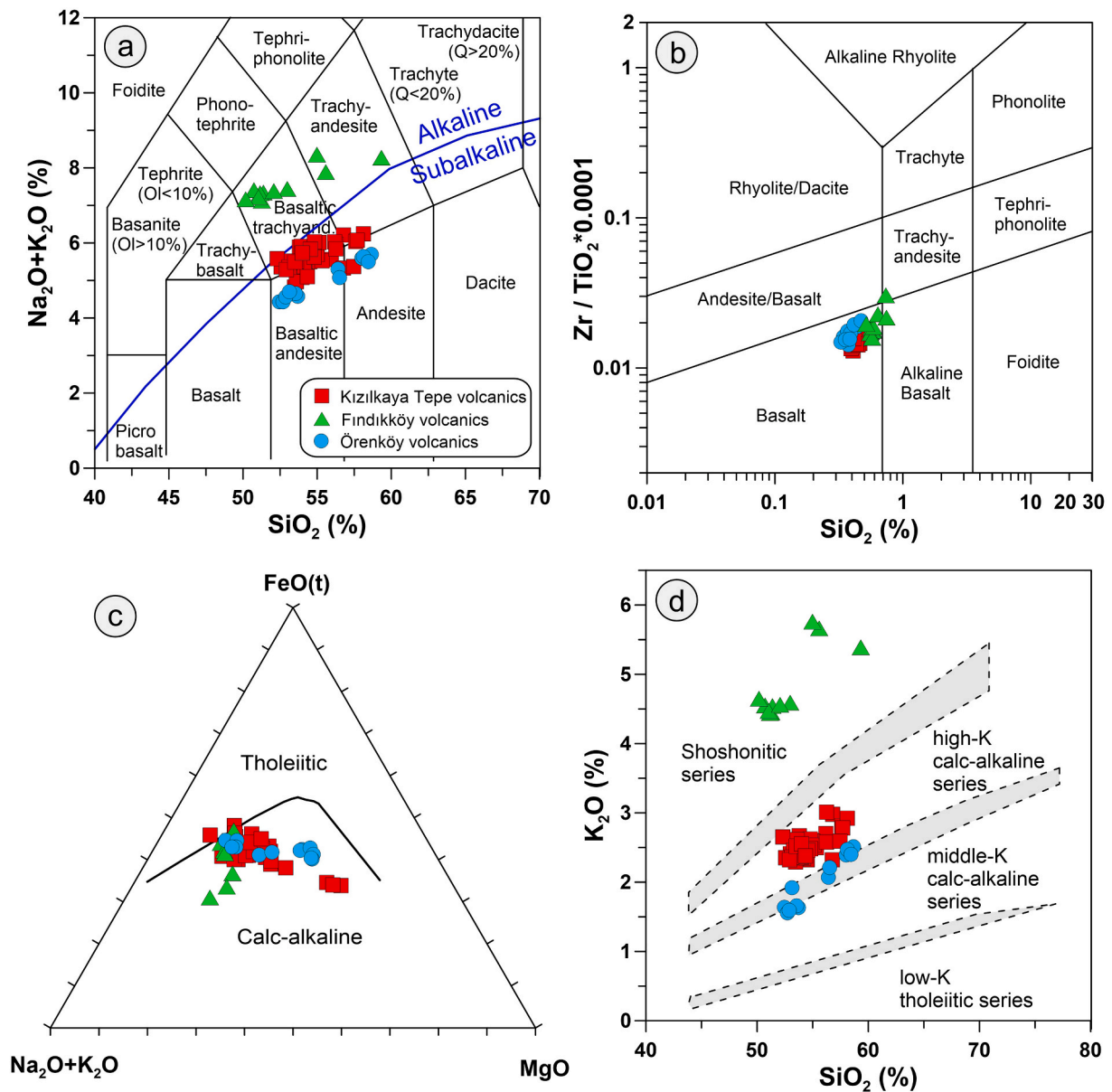


Fig. 4. Geochemical nomenclature and discrimination diagrams of the Kütahya volcanics. (a) the SiO_2 vs. $\text{NaO} + \text{K}_2\text{O}$ (Le Maitre, 2002), (b) Nb/Yb vs. $\text{Zr}/\text{TiO}_2 \cdot 0.0001$ (Pearce, 1996), (c) AFM ($\text{Na}_2\text{O} + \text{K}_2\text{O}$, $\text{FeO}(t)$, MgO) ternary, and (d) SiO_2 vs. K_2O (Peccerillo and Taylor, 1976) plots. Alkaline-subalkaline and tholeiitic-calcalkaline discriminations are from Irvine and Baragar (1971).

presented in Table 2. The $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $(^{143}\text{Nd}/^{144}\text{Nd})_i$ isotopic ratios and ϵNd_i values of studied volcanics are 0.70719–0.70849, 0.51237–0.51238 and (–4.85)–(–4.63) for the Kızilkaya Tepe volcanics, 0.70767–0.70821, 0.51232–0.51237 and (–5.70)–(–4.72) for the Örenköy volcanics and 0.70925–0.70971, 0.51231–0.51233 and (–6.27)–(–5.81) for the Fındikköy volcanics, respectively (Table 2). The observation that the Fındikköy volcanics show differences in Sr and Nd isotopic compositions from the Kızilkaya Tepe and Örenköy volcanics may indicate that these volcanics originate from an enriched mantle source area. Compared with other volcanics in western Anatolia, the studied Kütahya volcanics have similar characteristics to the Early-Middle Miocene high-K calc-alkaline and Middle Miocene shoshonitic-ultrapotassic volcanics (Fig. 7a).

The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ isotope ratios of the studied volcanics are 18.99–19.05 and 15.69–15.71 for the Kızilkaya Tepe volcanics, 18.95–19.00 and 15.73–15.76 for the Fındikköy volcanics and, 18.93–18.95 and 15.73–15.70 for the Örenköy volcanics, respectively (Table 2). In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ isotope diagram of the

studied volcanics, the positive correlation within each rock unit is seen (Fig. 7b). The isotopic ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ vary in a narrow range in all the studied volcanics. The Fındikköy volcanics have relatively higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than the Kızilkaya Tepe and Örenköy volcanics (Fig. 7b, Table 2). The $\delta^{18}\text{O}$ isotope values of the studied volcanics vary between 8.6 and 10.2‰ for the Kızilkaya Tepe, 8.6–9.3‰ for the Fındikköy and 8.3–10.4‰ for the Örenköy volcanics (Table 2). In the $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{18}\text{O}$ (‰) diagram (Fig. 7c), the Fındikköy volcanics, which have relatively higher Sr isotopic ratios than the Kızilkaya Tepe and Örenköy volcanics, have relatively lower $\delta^{18}\text{O}$ isotope values. In this diagram, the Kütahya volcanics are located on the mantle-crust mixing curves between 1:1 and 1:10, implying source and crustal contamination (Fig. 7c).

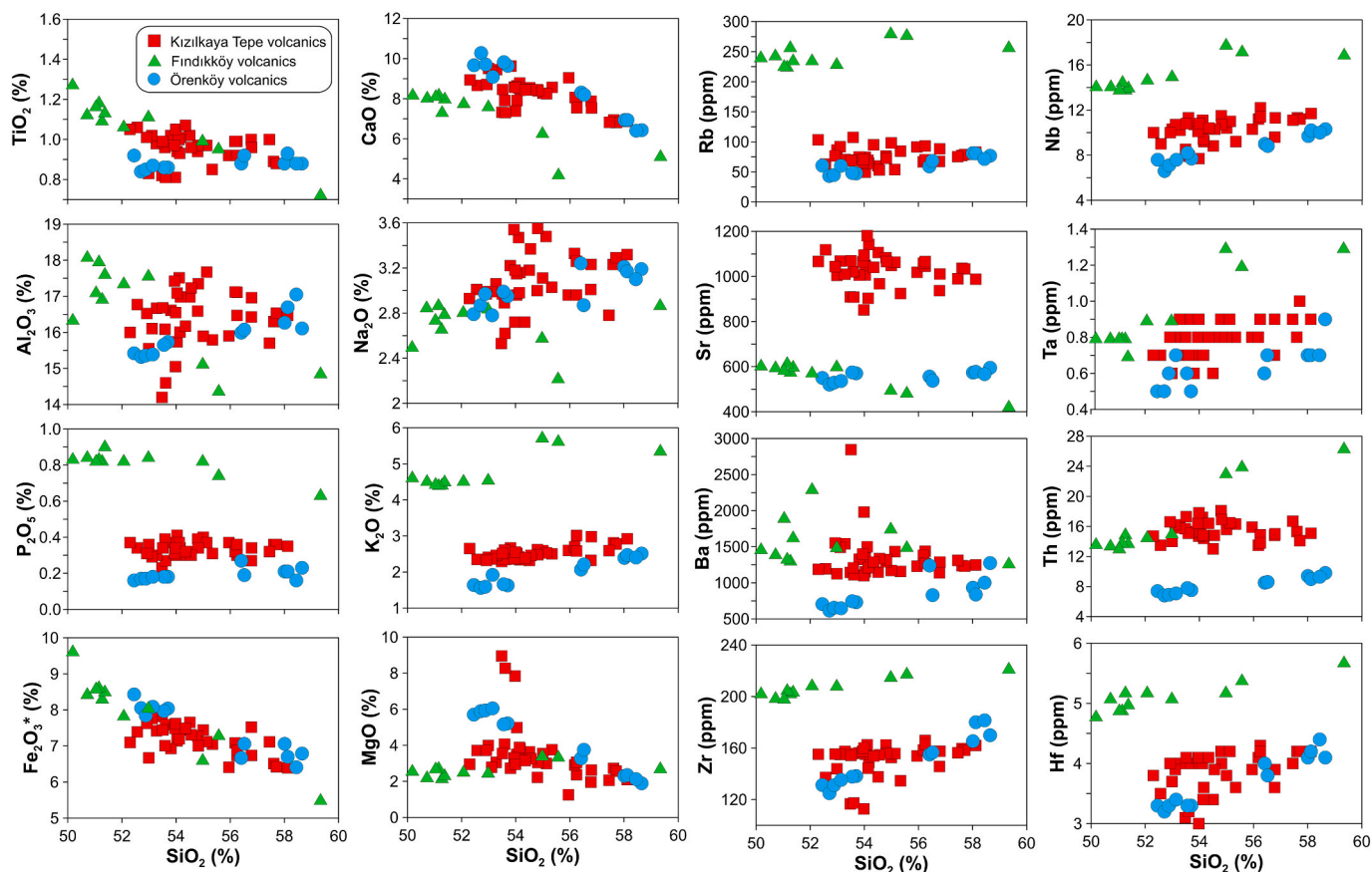


Fig. 5. SiO_2 (wt.%) vs. major oxide (wt.%) and trace element (ppm) plots of the Kütahya volcanics.

5. Discussion

5.1. Mantle source characteristics

The major-trace element and isotope geochemical features of the Kütahya volcanics are similar to those of volcanics formed by the active continental margin magmatism with high LREE/HREE ratios (e.g., Fitton et al., 1988; Wilson, 1989; Pearce et al., 1990; McCulloch and Gamble, 1991; Kerrich and Wyman, 1996). In the studied volcanics, the decreasing Nb, Zr, Y and TiO_2 contents compared to LILE, moderate LREE/HREE ratios (see Fig. 6b) and high Th/Yb ratios, relatively high ($^{87}\text{Sr}/^{86}\text{Sr}$)_i ratios and negative (ϵNd_i) values (Table 2) indicate that the parental magma(s) may have derived from an enriched lithospheric mantle that was previously metasomatized by the subduction fluids/sediments, in other words, a crustal component contribution at the mantle source (Faure and Mensing, 2005).

In general, HFSE and REE ratios (eg. Nb/Ta, Zr/Hf and Nb/Yb) can be used to identify different sources of the mantle in basaltic rocks (Pearce and Peate, 1995; Weyer et al., 2003). In this context, the studied volcanics show higher LREE and HFSE enrichment and Zr/Hf (35.47–53.17) ratios than chondritic values, which suggest they are derived from an enriched mantle source. In the Nb/Yb versus Th/Yb diagram (Fig. 8a), the studied volcanics in the field of continental arc volcanics. In the Nb/Yb versus TiO_2/Yb diagram (Fig. 8b), the studied volcanics have a composition close to an enriched mantle source (E-MORB) in the shallow mantle source field. In addition, DePaolo and Daley (2000) showed that the La/Nb ratio was generally greater than 1 for the lithospheric mantle source and ~ 0.7 for the asthenospheric mantle source. The La/Nb ratios (1.86–4.67) of the studied volcanics, therefore, suggest that their parental magma(s) originated from the lithospheric mantle source. This conclusion is also consistent with

previous studies on the petrogenesis of the other Miocene volcanics in western Anatolia (e.g., Aldanmaz et al., 2000; Ersoy et al., 2008, 2010, 2012a, b; Semiz et al., 2015; Prelević et al., 2015).

The enrichments of LILEs and LREEs in the Kütahya volcanics may be explained by fluid or melt metasomatism, crustal contamination and/or low-degree partial melting in the mantle sources. The enrichments in LREEs of these volcanics may suggest subduction derived fluid and/or melt metasomatism of their mantle source. The observation that LILEs (e.g., Rb, Sr, and Ba) are relatively higher than the neighbouring LREEs (La and Ce) and HFSE (Nb and Ta) (see Fig. 6) support a fluid enrichment process (e.g., Tatsumi and Takahashi, 2006). The mantle enrichment is likely related to the interaction between a depleted mantle source and fluids formed by the dehydration of subducted oceanic crust, sediments, or sediment-derived melts in the subduction zone (Elliott, 2004). Large ion lithophile elements (LILEs; Rb, Ba, Sr, K and U) are transported effectively with such fluid phases. Thorium (Th), LREEs, and HFSEs can be transported mainly by melts rather than fluid phases (e.g., Elliott et al., 1997; Hawkesworth et al., 1997; Turner and Hawkesworth, 1997; Class et al., 2000). Therefore, basaltic magmas showing high Ba/La and Ba/Th ratios are generally interpreted as resulting from the addition of aqueous fluids from the subducting plate to the overlying mantle wedge (e.g., Elliott et al., 1997; Pearce et al., 2005; Kirchenbaur et al., 2012), whereas basaltic magmas with high Th/La and Th/Yb ratios are thought to derive from a mantle source modified by subduction melts (e.g., Elliott et al., 1997; Johnson and Plank, 1999; Class et al., 2000; Brandl et al., 2017). The HFSE and REE element ratio plots of the studied Kütahya volcanics (Fig. 8a–f) all suggest that the parental magma(s) of the volcanics derived from a mantle source that was enriched by subduction-related fluids and lesser melts (e.g., Ersoy et al., 2010, 2012a, b).

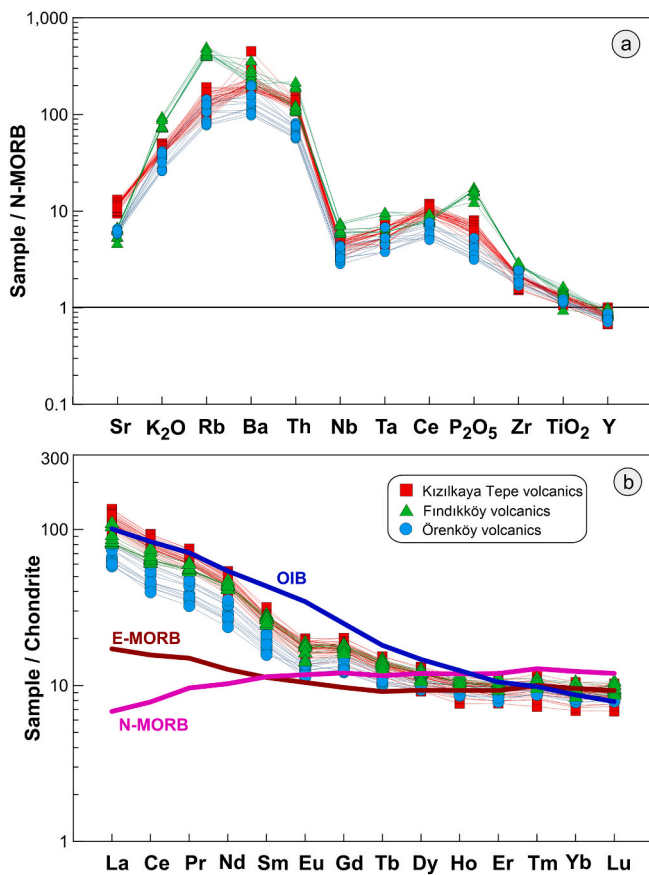


Fig. 6. (a) N-MORB (Sun and McDonough, 1989) normalized and (b) chondrite (Taylor and McLennan, 1985) normalized diagrams of the Kütahya volcanics. The compositions of enriched mid-ocean ridge basalt (E-MORB) and ocean island basalt (OIB) are from Sun and McDonough (1989).

5.2. Partial melting

The studied volcanics have high Zr/Y (5.8–9.6) and low Zr/Nb (12.1–18.9) ratios (Fig. 9a) that likely reflect low degree partial melting (e.g., Menzies and Kyle, 1990). The influence of the source mineralogy can be studied by plotting the concentration of a highly incompatible element versus the abundance ratios for incompatible elements. A constant abundance ratio over various incompatible element contents reflects the source ratio (Hofmann et al., 1986) whereas a systematic increase or decrease in the concentration ratio reflects the processes of melting (Yang et al., 2003). Tb is more incompatible in garnet than Yb (van Westrenen et al., 2000a). In the Tb_N/Yb_N versus Th diagram of the studied volcanics (Fig. 9b), all the samples are located below and near the horizontal line dividing the areas predicted for melting of garnet-bearing lherzolite (high Tb_N/Yb_N) and spinel-bearing lherzolite (low Tb_N/Yb_N) (e.g., Wang et al., 2002). The low-to-moderate Tb_N/Yb_N ratios observed in the studied volcanics suggest that the parental magma (s) was generated in the presence of residual spinel and to a lesser extent garnet. Fig. 9c shows the Sm/Yb versus Sm for partial melting of a garnet lherzolite and a spinel lherzolite enriched mantle source. These data suggest that the Örenköy volcanic were derived from higher degrees of partial melting (12–8%) than the Fındikköy (7–4.5%) and Kızilkaya Tepe volcanics (8–3.5%). Overall, the low-medium Tb_N/Yb_N (<1.8) and Sm/Yb (<3.2) ratios and partial melting modelling for the studied volcanics suggest that the parental magma(s) could be produced by relatively low-degree melting of a mantle region in the spinel + garnet (spinel > garnet) stability area at depths of less than about 60–70 km.

Table 2
Sr-Nd-Pb-O isotope compositions of the Kütahya volcanics.

Sample No	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr \pm 2\sigma_m$	$^{87}Sr/^{86}Sr_i$	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd \pm 2\sigma_m$	$(^{143}Nd/^{144}Nd)_i$	ϵNd_i	T_{DM} (Ma)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$\delta^{18}O$ (‰)
Örenköy volcanic	TS-8	0.240645	0.707738 ± 9	0.126403	0.512387 ± 2	0.512370	-4.72	1260	18.930	15.692	38.985	8.3
	TS-10	0.403972	0.708317 ± 12	0.116330	0.512336 ± 2	0.512322	-5.70	1210	18.953	15.725	39.102	9.5
	TS-11	0.324479	0.707962 ± 14	0.131501	0.512369 ± 2	0.512353	-5.09	1360	18.927	15.699	39.007	10.4
	KZ-6A	0.156069	0.707233 ± 6	0.110661	0.512380 ± 2	0.512367	-4.83	1080	18.989	15.686	38.969	9.3
Kızilkaya volcanics	KZ-12	0.219521	0.70855 ± 5	0.113847	0.512379 ± 2	0.512365	-4.85	1120	19.020	15.694	38.983	9.5
	KZ-24	0.181899	0.707294 ± 5	0.113516	0.512380 ± 1	0.512367	-4.85	1110	19.008	15.714	39.072	9.2
	KZ-31	0.146212	0.708359 ± 5	0.109327	0.512385 ± 1	0.512372	-4.73	1060	19.051	15.691	39.025	8.6
	KZ-46	0.186394	0.708307 ± 11	0.108549	0.512390 ± 2	0.512377	-4.63	1050	19.053	15.701	39.045	10.2
Fındikköy volcanics	FN-6	1.135966	0.709541 ± 7	0.126737	0.512332 ± 2	0.512317	-5.81	1350	18.957	15.728	39.218	8.6
	FN-7	1.059391	0.709606 ± 6	0.126008	0.512326 ± 2	0.512312	-5.93	1350	18.953	15.732	39.230	8.9
	FN-11	1.103697	0.709711 ± 7	0.120905	0.512322 ± 2	0.512308	-5.99	1290	18.977	15.743	39.272	8.6
	FN-16	1.753994	0.710151 ± 9	0.113079	0.512307 ± 2	0.512294	-6.27	1210	19.003	15.755	39.324	9.3

Uncertainties for the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios are $2\sigma_m$ errors in the last two digits. $\epsilon Nd_{(t)}$ values are calculated relative to CHUR with present-day values of $^{143}Nd/^{144}Nd = 0.512638$ (Jacobsen and Wasserburg, 1980). Nd single-stage model ages (T_{DM}) are calculated with a depleted-mantle reservoir and present-day values of $^{143}Nd/^{144}Nd = 0.51315$ and $^{147}Sm/^{149}Nd = 0.219$ (Liew and Hofmann, 1988).

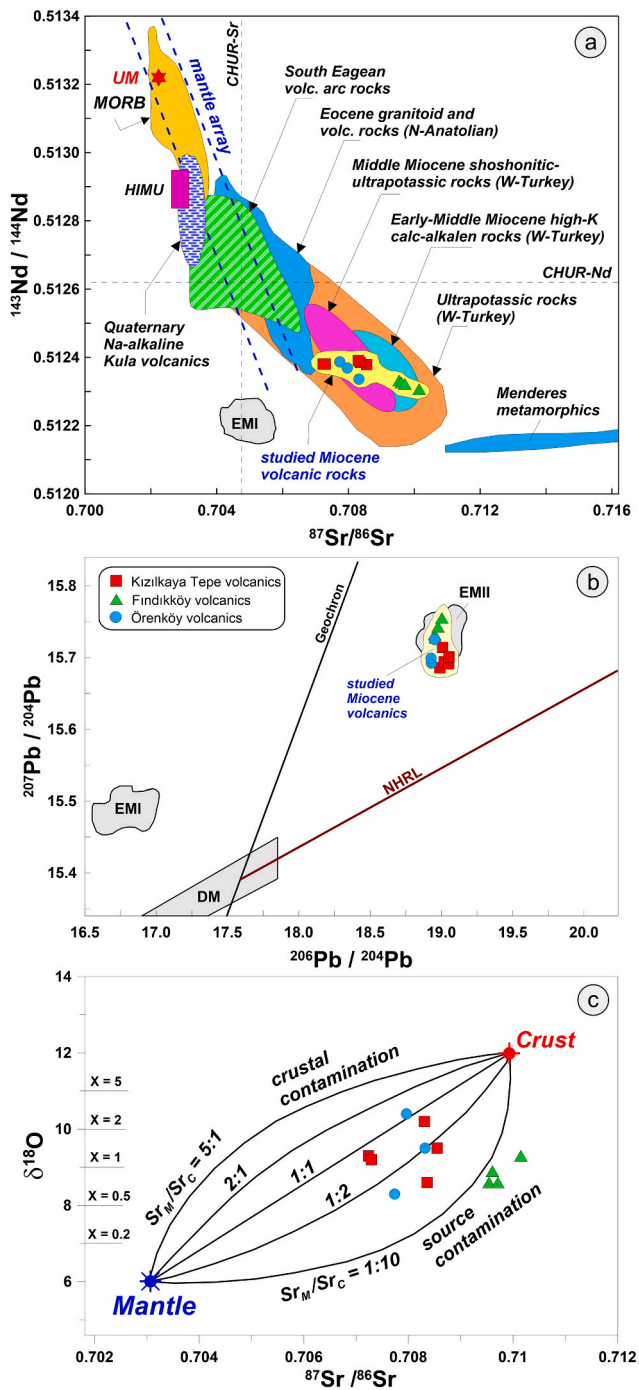


Fig. 7. (a) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$, (b) $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and (c) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\delta^{18}\text{O}$ (‰) diagrams for the studied Kütahya volcanics. The Quaternary Na-Alkaline Kula volcanics from western Turkey (Alıcı et al., 2002; Innocenti et al., 2005), South Aegean volcanic arc rocks (Zellmer et al., 2000; Buettner et al., 2005; Bailey et al., 2009; Ersoy and Palmer, 2013), Eocene granitoid and volcanics from north Anatolia (Kürkçüoğlu et al., 2008; Altunkaynak et al., 2012; Chakrabarti et al., 2012; Gülmez et al., 2012), Middle Miocene shoshonitic-ultrapotassic rocks from western Turkey (Aldanmaz et al., 2000; Innocenti et al., 2005; Ersoy et al., 2010, 2012b; Karaoğlu et al., 2010; Çoban et al., 2012; Prelević et al., 2012; Semiz et al., 2015), Early-Middle Miocene high-K calc-alkaline rocks from western Turkey (Karaoğlu et al., 2010; Ersoy et al., 2012b; Semiz et al., 2015), ultrapotassic rocks from western Turkey (Prelević et al., 2008), Menderes metamorphics (Prelević et al., 2012), MORB and mantle array from Wilson (1989), Gill (1981), Arculus and Powell (1986), McCulloch et al. (1994); Mantle reservoirs (EMI and II, HIMU, UM and DM) from Zindler and Hart (1986), Hart et al. (1992); NHRL from Hart (1984); crust and mantle compositions from James (1981).

5.3. Fractional crystallization

Linear-like correlations in the Harker diagrams of the studied volcanics (see Fig. 5) reveal the role of differentiation in the volcanics. With the increasing SiO_2 , the decrease in Fe_2O_3^* indicates the fractionation of clinopyroxene, and the decrease in CaO shows the fractionation of clinopyroxene and plagioclase. With the increasing SiO_2 , the decrease in Sr and the increase in K_2O indicate the fractionation of sanidine. With the increase of SiO_2 , the decrease in P_2O_5 , TiO_2 and Sr indicates apatite, magnetite and plagioclase fractionation, respectively; while the decrease in Fe_2O_3^* , MgO and MnO shows biotite fractionation. Generally, the positive correlation of K_2O with SiO_2 exhibits the fractionation of biotite and sanidine. The fact that the studied volcanics present concave-shaped REE patterns confirm that clinopyroxene fractionation (Thirlwall et al., 1994) was effective in their evolution. In addition, the slightly negative Eu anomalies with Eu_N/Eu^* : 0.75–0.97 for the Örenköy, Eu_N/Eu^* : 0.76–0.87 for the Kızılkağa Tepe and Eu_N/Eu^* : 0.71–0.84 for the Findikköy volcanics suggest that the fractionation of plagioclase and sanidine was probably less effective or that feldspar was retained at the source during the partial melting (See Fig. 6b).

The fractionation trends of the minerals and/or mineral assemblages that played a significant role during the evolution of the studied volcanics were studied using Rayleigh fractionation of trace element pairs and ratios. Minerals that participated in the fractionation and the extent of fractionation were determined separately for the basaltic and andesitic rocks (Fig. 10a–d). Based on the fractionation modelling, plagioclase \pm clinopyroxene \pm olivine fractionation was effective in the basaltic volcanics whereas plagioclase \pm biotite \pm clinopyroxene \pm sanidine \pm magnetite fractionation occurred in the andesitic volcanics (Fig. 10a–d). Overall, olivine, clinopyroxene, plagioclase, apatite and Fe–Ti oxide fractionation played an active role in the evolution of the basaltic rocks from the Örenköy, Kızılkağa Tepe and Findikköy areas. However, plagioclase, biotite, sanidine and Fe–Ti oxide fractionations have a significant role in the evolution of the andesitic rocks from the Findikköy area.

The studied volcanics show near-horizontal fractional crystallization (FC) trends with different La/Yb ratios remaining almost constant against the increasing Yb contents (Fig. 11a). The Th (ppm) versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram (Fig. 11b) suggests some role for crustal contamination in the Kütahya volcanics. So, it is difficult to explain the relations of some trace element ratios with SiO_2 with a simple mineral fractionation from a parental magma(s), because some of the major oxide and trace element ratios in the studied volcanics do not show smooth and linear correlations depending solely on fractionation. Hence, there appear to be varying amounts of crustal components added to the parental magma (s) during contamination (DePaolo, 1981; Powell, 1984), or changes in the source region or partial melting conditions (Altherr et al., 1995). In the studied volcanics, the near-horizontal trends and moderate/strong positive and/or negative trends observed in SiO_2 versus $^{87}\text{Sr}/^{86}\text{Sr}$, Sm/Nd versus $^{143}\text{Nd}/^{144}\text{Nd}$, $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ and Ce/Pb versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagrams suggests that in addition to fractional crystallization, the crustal assimilation (AFC) may also played an active role (Fig. 11c–f).

5.4. Crustal assimilation versus source contamination

The Kütahya volcanics show porphyric textures, suggesting residence in crustal magma chambers prior to the eruption and thus possible interaction with the continental crust through assimilation-fractional crystallization (AFC). In addition, the studied volcanics have high SiO_2 (%), La (ppm) and Ca (ppm) contents that may indicate that their parental magma(s) assimilated crustal material. In general, crustal contamination occurs by partial melting of the country rocks rather than complete melting and produces selective enrichment in certain incompatible elements (e.g., K, Ba, Th; Watson, 1982; Tindle and Pearce, 1983). The LILEs (K, Ba, Rb) enrichment relative to HFSEs (Nb, Ti) in the

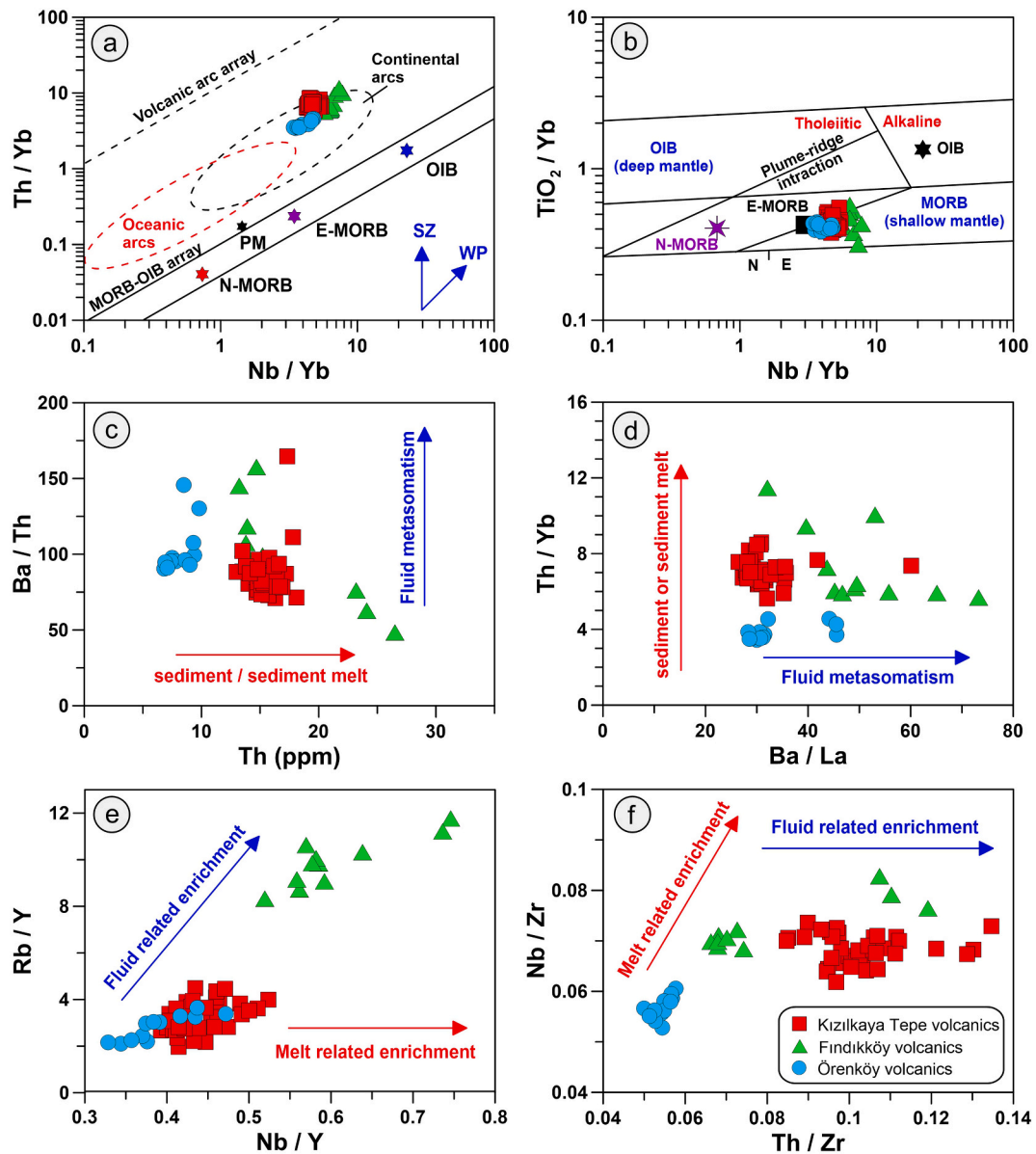


Fig. 8. (a) Nb/Yb vs. Th/Yb (Pearce, 2008), (b) Nb/Yb vs. TiO₂/Yb (Pearce, 2014), (c) Ba/Th vs. Th, (d) Th/Yb vs. Ba/La, (e) Rb/Y vs. Nb/Y and (f) Nb/Zr vs. Th/Zr diagrams for the Kütahya volcanics. For (a–b) fields of continental and oceanic arcs are from Pearce (2014); E-MORB, N-MORB, OIB and PM are from Sun and McDonough (1989); WP and SZ are vectors for within-plate evolution and subduction zone enrichment, respectively. Fluid- and melt-related enrichment vectors are from Kepezhinskias et al. (1996).

Kütahya volcanics may be associated with the subduction component and/or crustal contamination or the crystal fractionation. In addition, Nb_N/Ta_N ratios of the studied volcanics are <1.15, while the Zr_N/Hf_N ratios vary from 1.0 to 1.2 revealing an enriched mantle source. Pronounced Nb–Ta fractionation (most Nb_N/Ta_N < 1.15) may be due to mantle metasomatism with the subduction components. Assimilation-fractional crystallization (AFC; DePaolo, 1981; Powell, 1984) modelling using Rb/Sr ratios and initial ⁸⁷Sr/⁸⁶Sr compositions was performed in the Kütahya volcanics (Fig. 12a). In the AFC modelling diagrams (Fig. 12a), the studied volcanics are located above the “critical value” *r* (assimilation/fractional crystallization ratio) = 0.25 (Albarède,

1996) curve, indicating that the AFC processes played an important role in the evolution of the Kütahya volcanics. However, the distribution of the samples in Fig. 12a also suggests that the AFC evolution was controlled by a variety of factors, such as the distinct compositions of contaminants and variable fractionating mineral assemblages (e.g., Ersoy et al., 2012b).

The studied Kütahya volcanics also exhibit various disequilibrium textures such as sieve-patched-round and eroded plagioclase, deformations (bending) observed in euhedral biotite phenocrysts, partial melting and dissolution at the margins of augite phenocrysts, and resorption properties of ferromagnesian minerals (Hibbard, 1995).

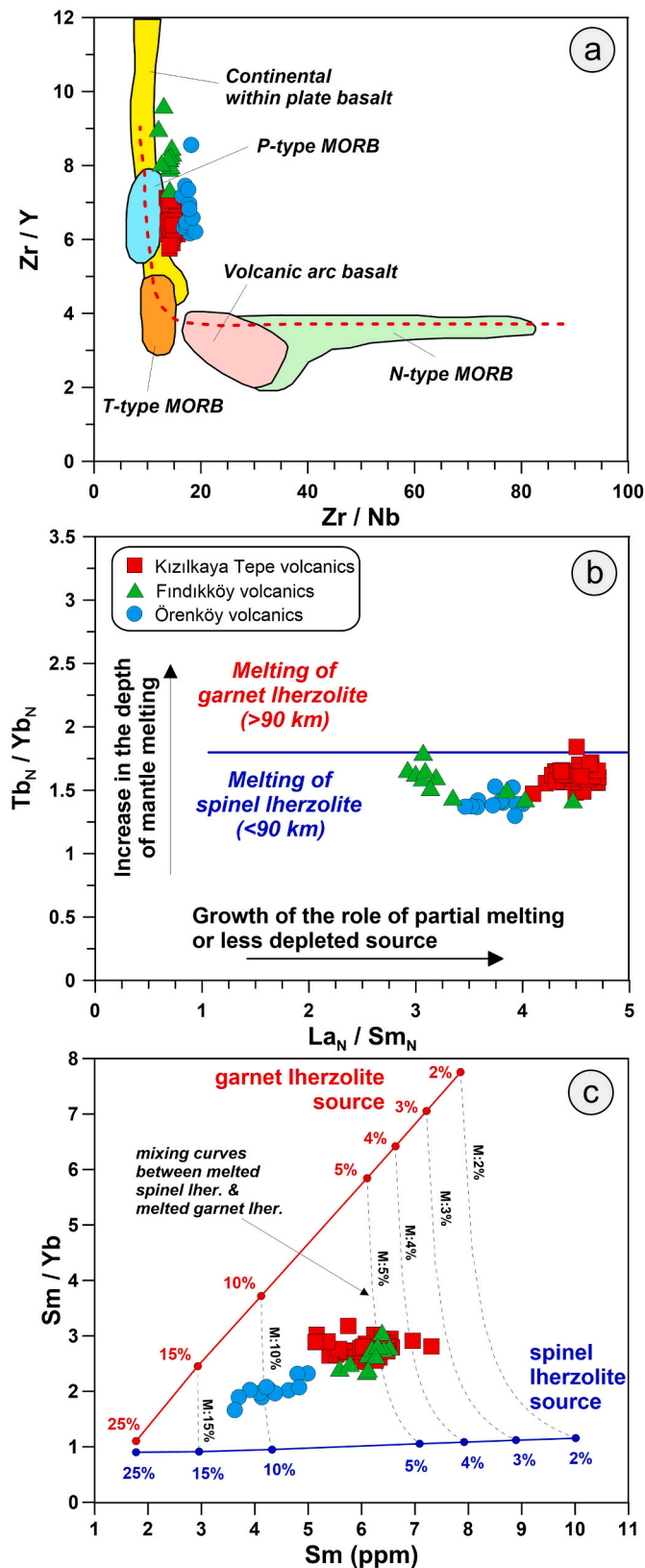


Fig. 9. (a) Zr/Nb vs. Zr/Y (Menzies ve Kyle, 1990), (b) La_N/Sm_N vs. Tb_N/Yb_N and (c) Sm (ppm) vs. Sm/Yb diagrams for the Kütahya volcanics. For (a) P: Plume, N: Normal ve T: Transition MORB fields from Le Roex (1987). The horizontal line in (b) divides the fields of garnet- and spinel-lherzolite melting (Wang et al., 2002). Partition coefficients, mode and melt mode for the melting model in (c) were adapted from Temizel et al. (2016).

Thus, taking into account the mineral textures of the studied volcanics, which show disequilibrium crystallization, a Sr–Nd isotopic mixing (e.g., DePaolo and Wasserburg, 1979) modelling was used to test the feasibility of the mantle-crust and mantle-subducting sediments (e.g., GLOSS) end members mixing in the evolution of the studied volcanics. In addition, the Sr–Nd isotopic-AFC (DePaolo, 1981) modelling (Fig. 12b) was performed between the parental magma(s) (IC_0) and upper continental crust (UCC). The Sr–Nd isotope end-member mixing modelling suggests that the parental magma(s) (IC_0) of the Kütahya volcanics assimilated 10–15% of the middle/lower continental crust and that subsequently, assimilation of the upper continental crust contributed to their evolution. (Fig. 12b). Thus, the studied Kütahya volcanics were probably derived from a parental magma(s), which is the product of mixing between the subduction-modified lithospheric mantle, the lower-middle crust and subduction-related melt components, and then evolved by fractional crystallization and assimilation processes in magma chambers in upper continental crust levels.

5.5. Implications for the geodynamic evolution

In recent years, post-collisional continental volcanism in extensional regions has been the subject of many studies (e.g., Seghedi et al., 2001; Cvetković et al., 2004; Marchev et al., 2004; Delibaş et al., 2017; Rabayrol et al., 2019; Chen and Robertson, 2021). An understanding of the geodynamic processes that control the volcanic activity of such regions is important for determining the mantle and crustal contributions. The geodynamic evolution of western Anatolia in Turkey contains subduction and collision-related events, each of which is followed by an extensional tectonic regime, and collectively these processes have played a major role during the development of Cenozoic volcanism in the region.

The Cenozoic volcanic activity and associated sedimentary basins in western Anatolia were formed as a result of compression-extension tectonics in the region. It has also been suggested that the Cenozoic volcanism is generally related to metasomatism of the subcontinental lithospheric mantle (e.g., Aldanmaz et al., 2000; Altunkaynak and Genç, 2008; Ersoy et al., 2010; Aldanmaz et al., 2015; Prelević et al., 2012, 2015). Considering the diversity and extent of the volcanics, the melting of the subcontinental lithospheric mantle (e.g., Seyitoğlu et al., 1997) is associated either with extensional thinning of the continental lithosphere and orogenic subsidence or by the partial removal of lithospheric roots in the post-collisional setting (e.g., Aldanmaz et al., 2000; Zhao et al., 2009; Ersoy et al., 2010, 2012a, b; Prelević et al., 2012, 2015). Thinning and transport of the subcontinental lithospheric mantle may also occur by the convective transport of lithospheric roots, delamination of the mantle lithosphere, or by thermal perturbation along with a tear of the subducting slab (e.g., Pe-Piper and Piper, 2007; Göğüş and Pysklywec, 2008; Ersoy et al., 2010; Prelević et al., 2012, 2015).

The Miocene volcanism in western Anatolia occurred under a post-collisional extensional regime. These calc-alkaline and shoshonitic volcanics likely formed by the melting of the metasomatized subcontinental lithospheric mantle associated with the previous subduction (e.g., Aldanmaz et al., 2000; Altunkaynak and Genç, 2008; Ersoy et al., 2010; Aldanmaz et al., 2015; Prelević et al., 2012, 2015). In addition, it is generally accepted that the lithospheric opening occurred due to the partial delamination of the lithosphere and that asymmetrical asthenospheric upwelling led to the potassic volcanism in western Anatolia, with the middle crustal units of the Menderes Massif ultimately emerging along successive detachment faults (e.g., Ersoy et al., 2010). Thus, this opening in the geodynamic regime allowed the multi-stage melting and melting percolation in the lithosphere that produced high concentrations of potassic (high-K, shoshonitic and ultrapotassic) magmas during detachment faulting (e.g., Ersoy et al., 2010; Aldanmaz et al., 2015; Prelević et al., 2012, 2015). In addition, potassium-rich volcanics formed by the melting of lithospheric mantle containing clinopyroxene/amphibole/phlogopite-rich metasomatic veins (e.g.,

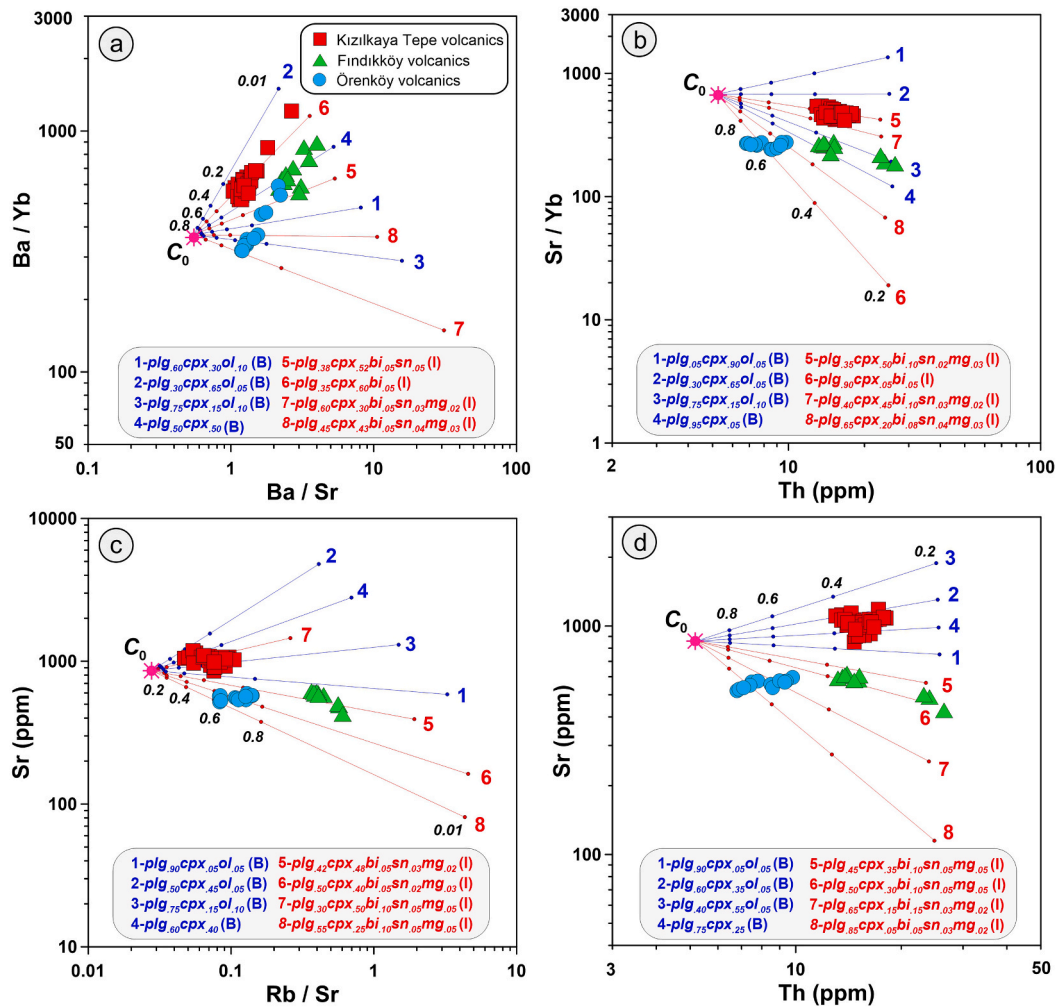


Fig. 10. (a–d) Rayleigh fractional crystallization (FC) models for the Kütahya volcanics. The starting melt composition (C_0) is Adikköy basalt from western Anatolia (Ersoy et al., 2012b) in (a–d). Numbers (0.01, 0.2, 0.4, 0.6 and 0.8) on the FC vectors (1–8) show the melt fraction remaining (F). Various mineral assemblages (for basaltic and andesitic rocks) used in the Rayleigh fractionation models are shown on each figure. Mineral-melt partition coefficients (K_d) values of plagioclase (plg), clinopyroxene (cpx), olivine, biotite, sanidine (sn) and magnetite (mg) for basic (B) and intermediate (I) rocks are from Keskin (1994).

Conticelli et al., 2009). Furthermore, the first volcanic products (ultrapotassic, shoshonitic) were mainly generated from the melts of metasomatic veins, and therefore were much more potassic than the late volcanic products (high-K, calc-alkaline) formed from the melts of residual peridotites. In this type of metasomatized lithospheric mantle, the K content of the melting column (and other incompatible elements) was higher because the metasomatized lithospheric mantle was thicker than that which produced the high-K volcanics (Ersoy et al., 2010; Semiz, 2011).

In the studied Kütahya area, the NE-SW trending oblique normal fault-controlled grabens developed on a Permian-Late Cretaceous basement (see Fig. 2). These grabens (Seyitömer and Sabuncupınar grabens; Özbüran, 2009; Özbüran and Gürer, 2012) are filled with Early-Middle Miocene fluvial/lacustrine sediments and volcanics. These fill products were folded by the periodic repetition of compression in the Miocene and were cut by reverse faults and thrusts. The units were thrust over the basement rocks by the last compressional phase (Özbüran, 2009; Özbüran and Gürer, 2012), and the development and

distribution of the Early Miocene volcanism are closely related to the NE-SW trending faults forming the grabens (see Fig. 2). The potassic (high-K, shoshonitic) parental magma(s) of the Örenköy, Kızilkaya Tepe and Fındikköy volcanics are widespread in the region and formed as a result of multi-stage low partial melting and melting percolation in the subcontinental lithospheric mantle. Furthermore, because the continental crust thickness increases from west to east (e.g., 50–55 km, Şengör et al., 1985), the temporal and spatial distribution from medium-high-K to shoshonitic composition is observed with decreasing partial melting degree and increasing AFC proportions in the studied volcanics (e.g., Ersoy et al., 2010, Fig. 13). The geochemical and petrological features of the studied volcanics suggest that the parental magma(s) were derived from an enriched subcontinental veined (amphibole and/or phlogopite) lithospheric mantle source with varying degrees of low partial melting, and then evolved by fractional crystallization + assimilation and lesser magma mixing events in deep and shallow magma chambers in the continental crust (Fig. 13).

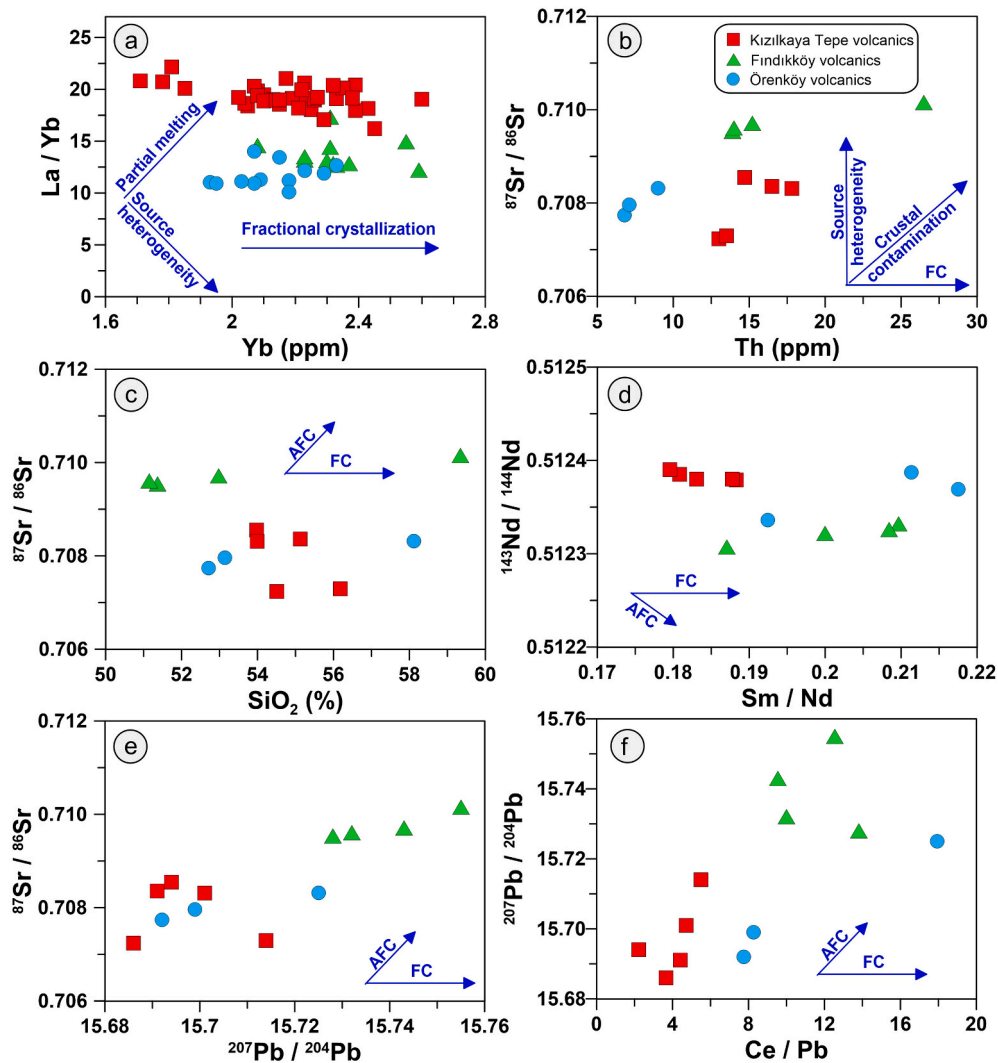


Fig. 11. (a) Yb (ppm) vs. La/Yb, (b) Th (ppm) vs. $^{87}\text{Sr}/^{86}\text{Sr}$, (c) SiO_2 (%) vs. $^{87}\text{Sr}/^{86}\text{Sr}$, (d) Sm/Nd vs. $^{143}\text{Nd}/^{144}\text{Nd}$, (e) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ and (f) Ce/Pb vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plots for the Kütahya volcanics.

6. Conclusions

New K–Ar dating, major-trace element and Sr–Nd–Pb–O isotope geochemical data are presented, and findings for the post-collisional Kütahya volcanics are also consistent with previous studies in Miocene volcanics of western Anatolia. So, this study summarises the following main points:

- (1) Petrographically, the Kütahya volcanics are composed primarily of olivine augite basalt and augite basalt, with minor basaltic andesites/trachyandesites, showing porphyric, hyalo-microclitic porphyric and rarely glomeroporphyric and sieve textures.
- (2) K–Ar dating of the Kütahya volcanics gave a cooling age between 20.1 ± 0.7 and 17 ± 0.5 Ma (Early Miocene). The studied volcanics indicate geochemical affinity from shoshonitic to medium-high-K characters. Depletion in Nb, Ta, Zr and Ti relative to LILE, moderate LREE/HREE ratios and high Th/Yb ratios in the studied volcanics indicate fractional crystallization with crustal assimilation and subduction signature.
- (3) The studied volcanics are characterized by moderate to high $^{87}\text{Sr}/^{86}\text{Sr}$ values from 0.70719 to 0.70971, negative ϵNd values from (-6.27) to (-4.63) , and high $^{206}\text{Pb}/^{204}\text{Pb}$ values from 18.93 to 19.05, and $^{207}\text{Pb}/^{204}\text{Pb}$ values from 15.69 to 15.76, moderate to high $\delta^{18}\text{O}$ isotope ratios from 8.3 to 10.4, suggesting enriched

lithospheric mantle-derived endmembers with a crustal contribution.

- (4) The parental magma(s) of the Kütahya volcanics may be generated by mixtures of melts derived from mainly spinel lherzolite and minor garnet-lherzolite mantle sources. Trace element and Sr–Nd isotope modelling show significant crustal assimilation during the evolution of the volcanics.
- (5) The petrological and Sr–Nd–Pb–O isotopic features and regional geology suggests that the parental magma(s) of the Kütahya volcanics were derived from a subcontinental veined lithospheric mantle source metasomatized by slab-derived fluids and melts, and then magma(s) developed by fractional crystallization + assimilation events in deep and shallow magma chambers in the continental crust.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has

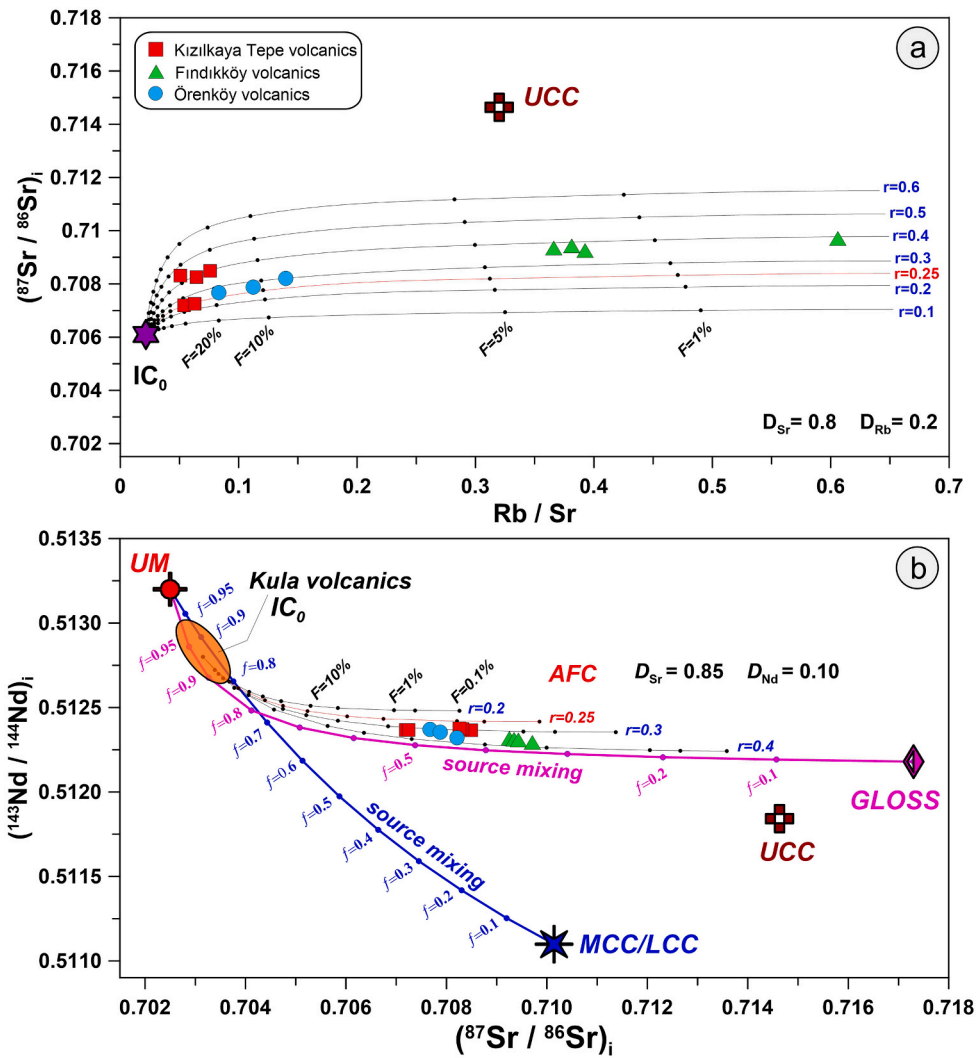


Fig. 12. (a) $(^{87}\text{Sr}/^{86}\text{Sr})_i$ vs. Rb/Sr , and (b) $(^{143}\text{Nd}/^{144}\text{Nd})_i$ vs. $(^{87}\text{Sr}/^{86}\text{Sr})_i$ diagrams for the studied Kütahya volcanics. For (a), parental magma composition (IC_0 ; Adilköy basalt) is from Ersoy et al. (2012b) and assimilated composition (UCC) is from Taylor and McLennan (1985). For (b), parental magma composition (IC_0 ; Kula volcanics) is from Alci et al. (2002), assimilated composition (UCC) is from Davies et al. (1985) and Taylor and McLennan (1985), Upper mantle composition (UM) is from Rehkamper and Hofmann (1997) and Zindler et al. (1984), Middle/lower continental crust composition (MCC/LCC) is from Ben Othman et al. (1984) and Rudnick and Fountain (1995), GLOSS (Global subducting sediments) composition is from Plank (2014).

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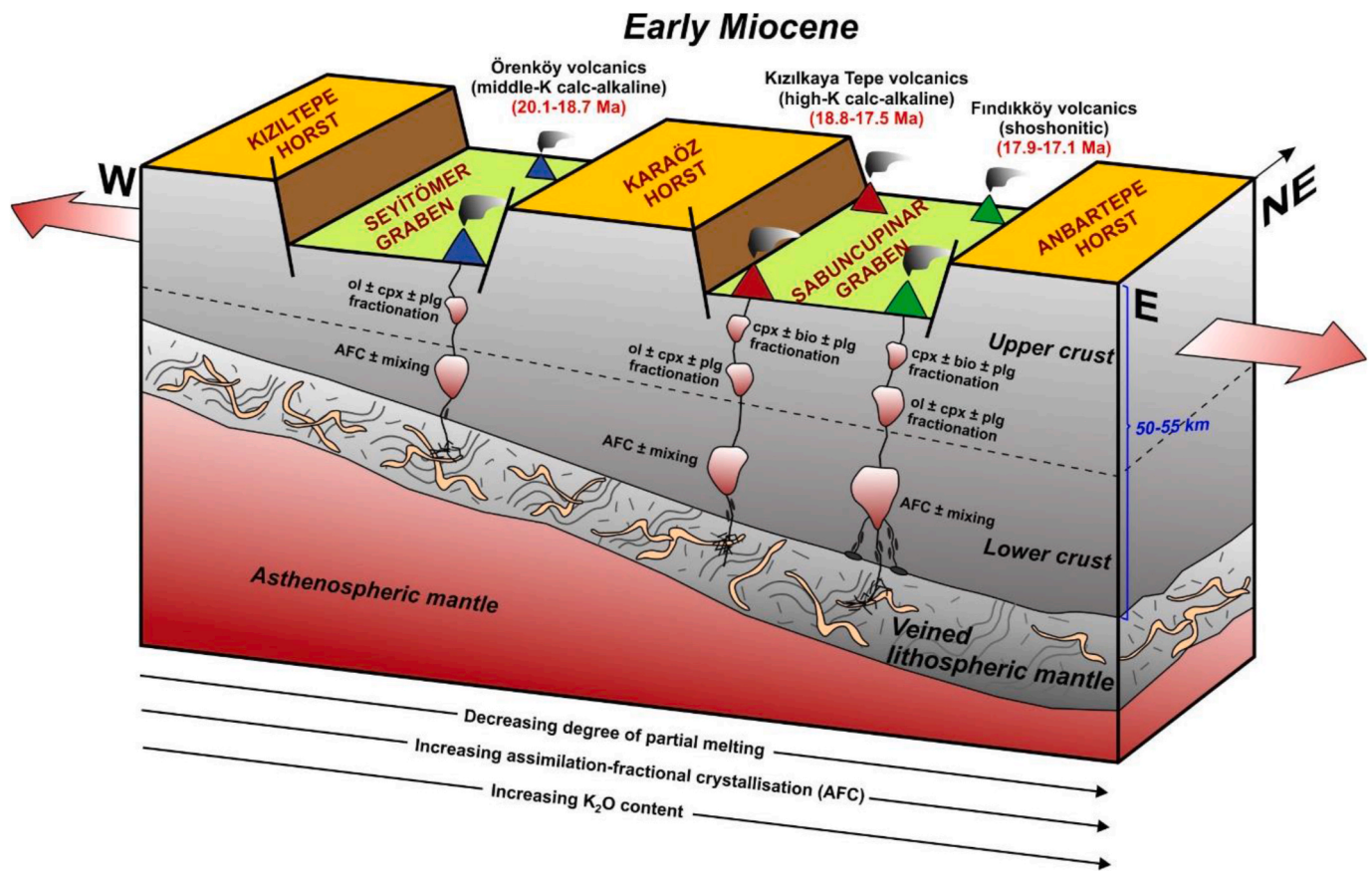


Fig. 13. Deduced geodynamic model showing extensional tectonics and the generation of the Early Miocene volcanism associated with normal faults controlled by Seyitömer and Sabuncupinar basins in the Kütahya area.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jafrearsci.2022.104679>.

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