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Eocene magmatism related to postcollisional extension in the Eastern Pontides (NE Türkiye): 40Ar-39Ar geochronology, geochemistry, and whole-rock Sr-Nd-Pb-Hf isotopes

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Abstract: The mineral chemistry, whole-rock geochemistry, ^{40}Ar / ^{39}Ar dating and Sr-Nd-Pb-Hf isotopes of the Eocene Narman (Erzurum) Volcanic rocks in the southeast of the Eastern Pontides Orogenic Belt (EPOB, NE Türkiye) were investigated. The Narman Volcanites consist of basaltic dyke, basaltic lava, and basaltic volcanic breccia facies. Volcanites contain plagioclase (An_{34-80}), clinopyroxene ($Wo_{38-47}En_{41-50}Fs_{5-18}$), and olivine ($Fo_{68-90}$) as phenocrystals with magnetite/titanomagnetite microphenocrysts. New ^{40}Ar-^{39}Ar ages suggest that these volcanic rocks erupted between 44.5 ± 0.1 and 43.4 ± 0.1 Ma, within the Middle Eocene (Lutetian). Narman Volcanites have calc-alkaline character, with medium-high K content. Volcanites are enriched in large ion lithophile elements (LILE) and light rare earth elements (LREE), while they are depleted in terms of high field strength elements (HFSE). Chondrite-normalized rare earth element distributions have concave shape with moderate enrichment (La_N/Lu_N = 2.78–7.99), leading to consideration that the magmas forming the volcanics derived from similar sources. Isotopically, the rocks in the Narman Volcanites have low-medium initial $^{87}Sr/^{86}Sr$ values (0.70405–0.70485), initial $^{143}Nd/^{144}Nd$ values (0.512606–0.512848) and positive εNd_i (+0.5 – +5.2). Depleted mantle Nd model ages were T_{DM1} = 0.29–0.62 Ga and T_{DM2} =0.43–0.83 Ga. $(^{206}Pb/^{204}Pb)_i$, $(^{207}Pb/^{204}Pb)_i$, and $(^{208}Pb/^{204}Pb)_i$ values vary in the ranges of 18.246–18.709, 15.578–15.616, and 38.225–38.791, respectively. The initial $(^{176}Hf/^{177}Hf)_i$ ratios for the volcanites are between 0.282770 and 0.283013, while the εHf values range from +7.6 to +9.

All the evidence supports the conclusion that the parental magma for the rocks probably derived from an enriched lithospheric mantle, previously metasomatized by fluids derived from subducted slab during asthenospheric upwelling, due to fragmented asymmetric delamination in a postcollisional extensional tectonic environment.

Key words: ^{40}Ar-^{39}Ar thermochronology, mineral chemistry, postcollisional setting, delamination, Eastern Pontides, Türkiye

1. Introduction

The Eastern Pontides Orogenic Belt (EPOB) is located east of the Sakarya Zone (northern Türkiye, Figure 1a) and is considered one of the most complicated and important sections of the Alpine-Himalayan system due to sequential subduction and collision events (Şengör and Yilmaz, 1981; Okay and Sahinturk, 1997; Yilmaz et al., 1997). The Eastern Pontides formed when the Neo-Tethys Ocean was subducted under the Eurasian plate to the north and is accepted as being a well-preserved arc system in the Early Jurassic and Late Cretaceous (Figure 1a). From the past to the present, numerous authors have studied the geodynamic evolution of the EPOB (Şengör and Yilmaz, 1981; Okay and Sahinturk, 1997; Yilmaz et al., 1997; Okay and Tüysüz, 1999; Altunkaynak, 2007; Keskin et al., 2008; Dilek et al., 2010; Temizel et al., 2012; Ustaömer et al., 2013; Arslan et al., 2013, 2022; Aydınçakır and Şen, 2013; Aydınçakır et al., 2022; Ersoy et al., 2017; Özdamar et al., 2017; Yücel et al., 2017; Göçmengil et al., 2018; Dokuz et al., 2019; Aydin et al., 2020; Kaygusuz et al., 2022). Understanding the features of Eocene magmatism is very important in terms of interpreting the geodynamic

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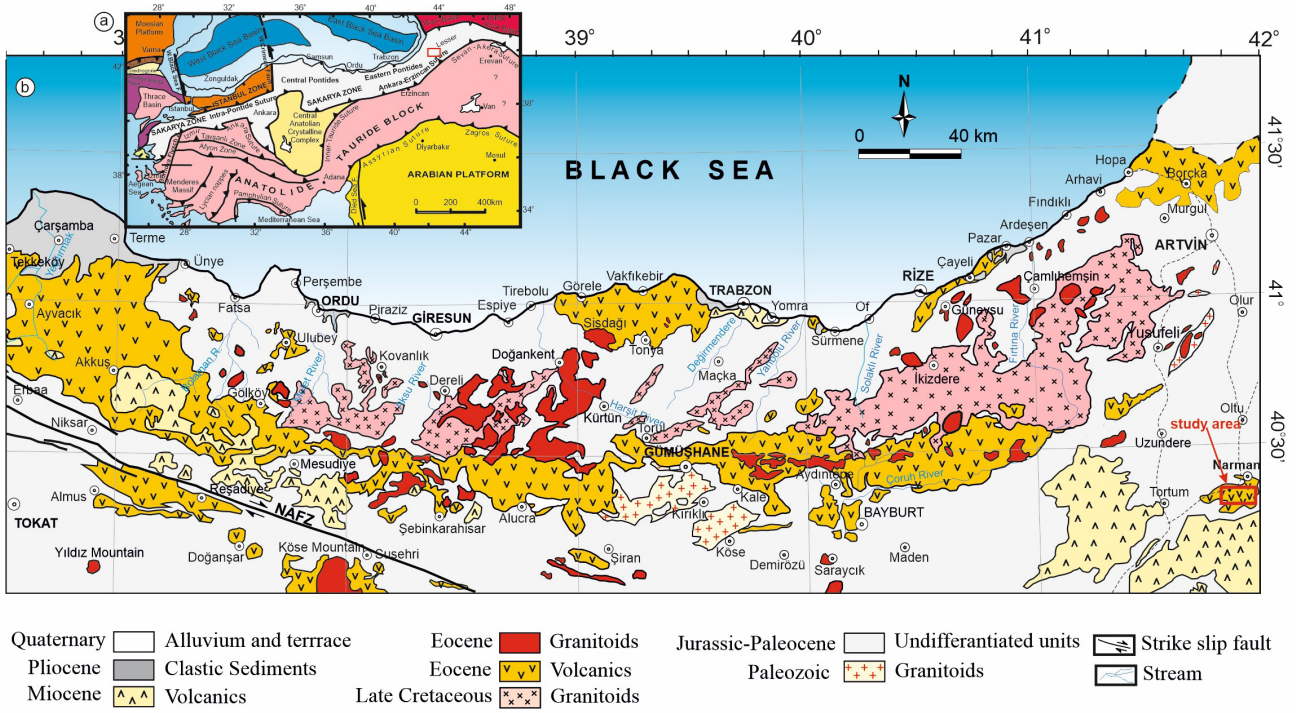

Figure 1. (a) The tectonic units and the main suture zones of Türkiye (after Okay and Tüysüz 1999); (b) the simplified geological map of the Eastern Pontides showing distribution of the Eocene and Miocene–Quaternary volcanic rocks. Modified after Güven (1993)[1], Arslan et al. (2013), Aydınçakır and Şen (2013), Temizel et al. (2016), Yücel (2019), and Kaygusuz et al. (2022).

[1]Güven IH (1993). Doğu Pontidler'in 1:25000 ölçekli jeolojisi ve kompilasyonu [1:25000 scale geology and compilation of the Eastern Pontide] (unpublished). Ankara, Türkiye: General Directorate of Mineral Research and Exploration (MTA).

evolution of the region. There are ongoing debates about whether the Eocene magmatism, which covers a very wide area in the EPOB, is subduction-related or postcollisional, resulting from the collision of the Anatolide-Tauride block with the Pontides during the closure of the northern branch of the Neo-Tethys Ocean (Robertson et al., 2006; Eyuboglu et al., 2011; Temizel et al., 2012; Arslan et al., 2013, 2022; Aydınçakır and Şen, 2013; Aydınçakır et al., 2022; Yücel et al., 2017; Göçmengil et al., 2018; Kaygusuz et al., 2022, 2024). Eocene volcano-sedimentary and intrusive rocks cover a large area of Türkiye (Robertson et al., 2006; Keskin et al., 2008; Aydınçakır and Şen, 2013; Gülmez et al., 2013; Arslan et al., 2013; Yücel et al., 2017; Ersoy et al., 2017; Özdamar et al., 2017; Göçmengil et al., 2018; Aydınçakır et al., 2022; Arslan et al., 2022) and Iran (Stern et al., 2021). Some models related to widespread Eocene magmatism were proposed: (1) collisional slab breakoff under the İzmir–Ankara–Erzincan Suture Zone (İAESZ, Altunkaynak, 2007; Dilek et al., 2010), (2) back-arc expansion events related to northward subduction along the Bitlis Zagros Suture Zone (BZSZ, Robertson et al., 2006), (3) postcollisional crustal thickening and delamination of thickened crust along the IAES (Karsli et al., 2011; Aydınçakır and Şen, 2013; Aydınçakır et al., 2020; 2022), and (4) slab window-related processes (Eyuboglu et al., 2011).

This study provides important clues to understanding petrogenetic processes for Eocene volcanic rocks in the Narman (Erzurum) region at the easternmost point of the EPOB. This article presents new ^{40}Ar-^{39}Ar dating, Sr-Nd-Pb-Hf isotopes, and whole-rock geochemical data for Middle Eocene volcanic rocks at the southeastern end of the Eastern Pontides (Figure 1b). Our objectives are to clarify the petrogenesis and tectonomagmatic evolution of the volcanic rocks in the region and to characterize the geodynamic evolution of the Eastern Pontides during the Eocene.

2. Regional and local geology

The Eastern Pontides are a subset of the Sakarya zone, which is one of the major tectonic units in Türkiye (Figure 1a, Okay and Tüysüz, 1999). The Sakarya Zone is a strip-like continent that extends from the Biga Peninsula to the Lesser Caucasus located in the north of Türkiye. This region is surrounded by Rhodope-Istranca to the northwest, İstanbul and Zonguldak regions and the Central and Eastern Pontides. This tectonic unit comprises a chain of mountains that are 200 km width and 500 km length, and

it is accepted as part of the Alpine orogenic system. The basement rocks of the Sakarya Zone comprise pre-Variscan gneiss and schists (Topuz et al., 2004) and metasediments that accumulated in Cadomian sedimentary basins (Dokuz et al., 2022). These units are intruded by Ordovician, Early Cambrian and Silurian-Devonian metagranites (Karsli et al., 2020a), and Middle-Late Carboniferous granitoid (Topuz et al., 2010; Dokuz, 2011; Kaygusuz et al., 2012). This basement is unconformably overlain by Permo-Carboniferous shallow marine-terrestrial sedimentary rocks observed around Pulur (Okay and Leven, 1996). Early-Middle Jurassic volcanoclastic and sedimentary rocks unconformably overlie basement rocks (Şen, 2007; Kandemir and Yılmaz, 2009). The pre-Jurassic basement rocks are cut by Early and Middle Jurassic intrusive rocks (Eyuboglu et al., 2016; Dokuz et al., 2017; Karsli et al., 2017; Saydam Eker and Arı, 2020; Aydınçakır et al., 2020, 2023). The Late Jurassic-Early Cretaceous period passed very calmly in terms of tectonic movements and magmatic activity. In Late Cretaceous time, the Eastern Pontides represented a magmatic arc developing with northward subduction of the Neo-Tethys along the Sakarya Zone (Okay and Sahinturk, 1997; Yilmaz et al., 1997). The subduction direction and geotectonic evolution of the Eastern Pontides in the Cretaceous is controversial. Numerous researchers proposed that the Eastern Pontides are a magmatic arc resulting from northward subduction of the Neo-Tethys along the south margin of the Sakarya Zone (Okay and Sahinturk, 1997; Yilmaz et al., 1997; Kaygusuz and Aydınçakır, 2009; Uysal et al., 2014; Aydınçakır, 2016; Özdamar, 2016; Temizel et al., 2019; Aydin et al., 2020; Kaygusuz et al., 2021; Yücel et al., 2024). Conversely, others proposed southward subduction that continued uninterruptedly from the Paleozoic period until the end of the Eocene period (Dewey et al., 1973; Eyuboglu et al., 2011). The Eastern Pontides are dominated by plutonic and volcanic rocks with facies variations in north-south direction (Karsli et al., 2012; Arslan et al., 2013; Yücel et al., 2017; Dokuz et al., 2019; Temizel et al., 2020; Aydınçakır et al., 2022). From the Paleocene to Early Eocene, the Eastern Pontides was above sea level, probably because of the collision between the Pontides magmatic arc and the Tauride-Anatolide Platform (TAP, Okay and Sahinturk 1997; Boztuğ et al., 2004). This caused common compression, crustal elevation and thickening, and flysch accumulation. Adakitic and nonadakitic rocks with Early Eocene age (54–48 My) occurred in the final stage of arc-continent collision (Eyuboglu et al., 2011; Topuz et al., 2011; Karsli et al., 2011; Aydınçakır, 2014; Gücer, 2021). During the Middle Eocene, postcollisional volcano-sedimentary rocks and calc-alkaline shoshonitic plutons developed (Karsli et al., 2012; Arslan et al., 2013; Yücel et al., 2017; Kaygusuz et al., 2018, 2022; Dokuz et al., 2019; Temizel et al., 2020; Aydınçakır et al., 2022). Miocene-Pliocene-Quaternary volcanic rocks, mostly alkali with lower rates of calc-alkali composition, are the youngest representatives of magmatic activity in the Eastern Pontides (Karsli et al., 2008, 2020b; Kaygusuz, 2009; Eyuboglu et al., 2012; Dokuz et al., 2013; Yücel et al., 2017; Yücel, 2019).

The study area is in the east part of the EPOB (Figures 1b and 2). The basement for units in the study area comprises volcanoclastic rocks representing andesitic, basaltic, trachytic lava, and pyroclastic units, defined as the Karataş Formation (Bozkuş, 1992, as cited in Konak and Hakyemez, 2008). The unit is covered above an angular unconformity by the Narman volcanic rocks comprising olivine basalt and pyroclastic rocks (Konak and Hakyemez, 2001). Due to its location above and below the Narman Volcanics, the Oltu Formation is considered to be the lateral transition of this unit. The Oltu Formation comprises white gypsum and limestone interlayers containing coal seams, and yellow-red-green pebblestone, sandstone and mudstone. The age of the unit was given as Late Oligocene-Early Miocene by Benda (1971). The Early Miocene Alabalık Formation occurs above the Oltu Formation with conformable transition and is represented by yellow-green tuff, agglomerate and epiclastic levels (Figure 2, Bayraktutan, 1994).

3. Analytical methods

3.1. Electron microprobe analysis

Based on petrographic observations and photomicrography, the newest and most representative volcanic rock samples from volcanic rocks were chosen to determine the mineral composition. The major element composition of the minerals (feldspar, hornblende, brown mica, clinopyroxene, and Fe–Ti oxides) from carbon-coated polished sections were analyzed using a CAMECA SX100 instrument from the IFREMER EPMA Laboratories (Brest, France) with accelerating voltage of 15 kV and a sample current of 15 nA. The peak and background counting times ranged from 10 to 20 s and from 5 to 10 s, respectively. Natural minerals and synthetic/compounds were used as standards. The matrix effects were corrected by using Phi (r) z Peak Sight software from CAMECA. Typical standard deviations (1σ) ranged from 0.1 to 0.3 wt.% for Si, Ca, Na, and Al and from 0.03 to 0.1 wt.% for Fe, Cr, K, Ti, Mg, and Mn.

3.2. Whole-rock major and trace element analysis

Twenty-five samples were selected for major and trace element analysis. To prepare the rock powders, 0.5–1 kg of the fresh samples was crushed in a steel crusher, and then, the samples were ground in an agate mill to obtain grain sizes of <200 mesh. The major and trace element contents were determined at the commercial ACME Laboratories Ltd. in Vancouver, Canada. The major element oxides of

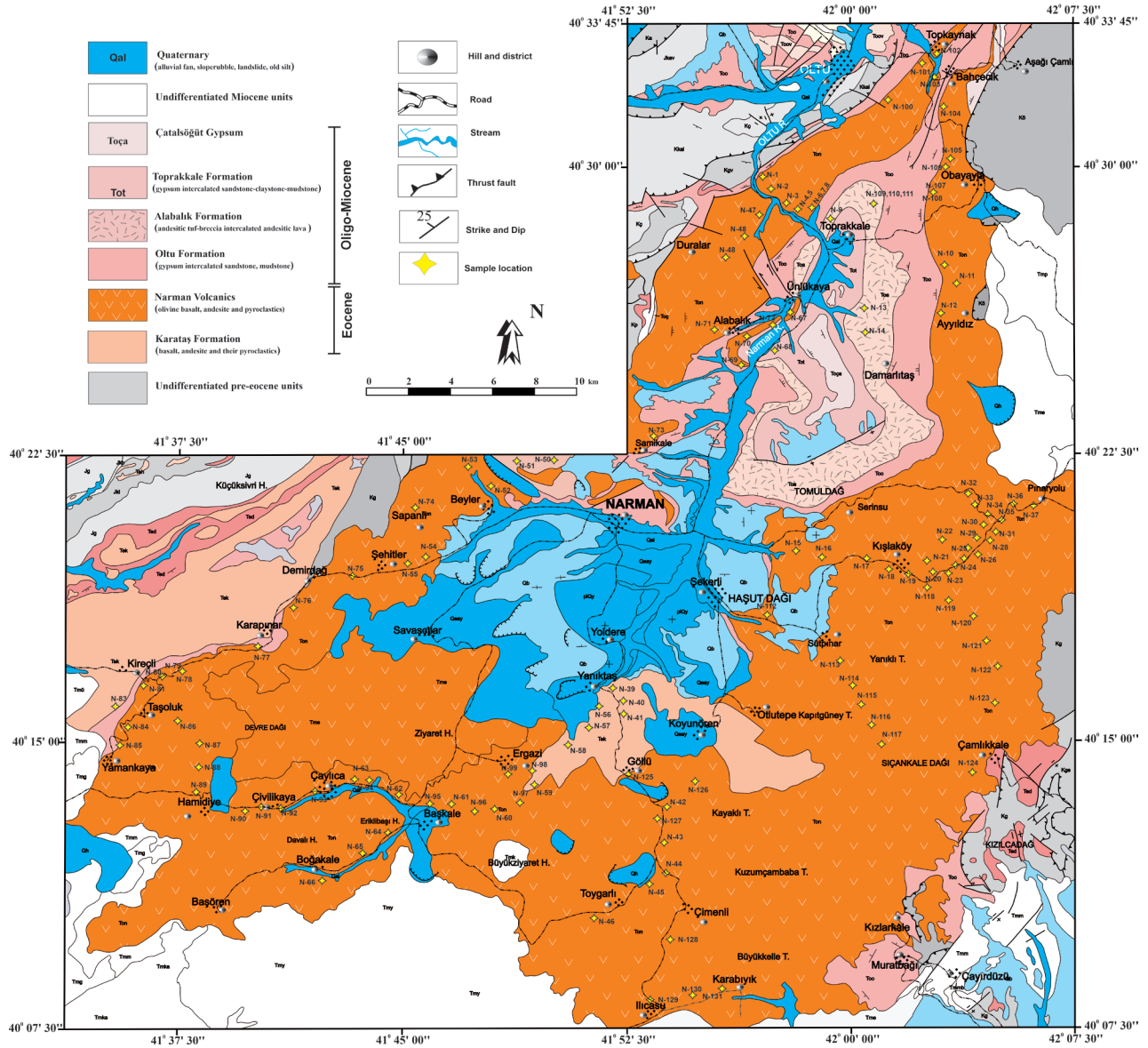

Figure 2. (a) The geological map of the Narman (Erzurum) area, and the sample locations.

the samples were measured by ICP-ES for major oxides (0.2 g pulp sample by $LiBO_2$ fusion). The detection limits are approximately 0.001–0.1 wt.%. For the trace elements, 0.2 g of the sample powder and 1.5 g of $LiBO_2$ flux were mixed in a graphite crucible and subsequently heated to 1050 °C for 15 min in a muffle furnace. The molten sample was then dissolved in 100 mL of %5 HNO_3. Sample solutions were shaken for 2 h, and then, an aliquot was poured into a polypropylene test tube and aspirated into the Perkin-Elmer Elan 600 ICP mass spectrometer. Calibration and verification standards (STD-SO-19), together with reagent blanks, were added to the sample sequence. The detection limits determine the range from 0.01 to 0.5 ppm for most trace elements.

3.3. Sr–Nd–Pb-Hf isotope analysis

Sr, Nd, and Pb isotope compositions of selected samples from the plutons were performed at the Department of Geological Sciences, New Mexico State University. All isotopic measurements were conducted using TIMS on a VG Sector 30 mass spectrometer. Samples were loaded onto rhenium filaments either on the cathode bead of a single filament or on the side filament of a triple-filament assembly. The reproducibility of $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ ratios is within 0.3%, and $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios are within ±0.000025 and ±0.00003, respectively. NBS 987 standard analyses yielded values of 0.710226 (11), 0.710213 (13), 0.710219 (10), and 0.710260 (11). Pb isotopes were analyzed using the middle filament position

of a Cathodeon bead assembly. Samples were loaded using 5% HNO_3 in a matrix composed of silica gel and phosphoric acid. Approximately 2 µL of silica gel was positioned on the filament, and 1 µL of phosphoric acid was added. Standards were also loaded and analyzed using the same procedures. The mean values of the standards were $^{206}Pb/^{204}Pb = 16.844$, $^{207}Pb/^{204}Pb = 15.379$, and $^{208}Pb/^{204}Pb = 36.199$. Deviations from standards are within 0.2%. Detailed analytical procedures for Sr, Nd, and Pb isotopic measurements are provided by Ramos (1992).

3.4. Ar-Ar dating

Three single groundmass fragments from the studied dikes were analyzed by the continuous laser probe (CO_2 Synrad) stepwise heating ^{39}Ar-^{40}Ar technique at Geosciences Rennes (France).

The samples were wrapped in Al foil to form small packets (11 ´ 11 mm) that were stacked up to form columns within which packets of fluence monitors were inserted every 10 samples. Irradiation was performed at the McMaster Nuclear Reactor (Hamilton, Canada) and used 5C high flux location without Cd shielding. It lasted 13.42 h ($J/h \approx 3.71 \times 10^{-4}\ h^{-1}$). The irradiation standard was sanidine TCRs (28.608 ± 0.033 Ma; according to Renne et al., 1998, 2010, 2011). The sample arrangement in the irradiation allowed us to monitor the flux gradient with a precision of ± 0.2%.

Heating steps were performed with a CO_2 laser probe. All experiments concerned single grains. The experimental procedure was described by Ruffet et al. (1991, 1995). The five argon isotopes and the background baselines were measured in 11 cycles in peak-jumping mode. Blanks were performed routinely every first or third/fourth run and subtracted from subsequent sample gas fractions. All isotopic measurements are corrected for K, Ca, and Cl isotopic interferences, mass discrimination and atmospheric argon contamination.

Apparent age errors are plotted at the 2s level and do not include the errors on the $^{40}Ar^*/^{39}Ar_K$ ratio and age of the monitor and decay constant. The errors on the $^{40}Ar^*/^{39}Ar_K$ ratio and age of the monitor and decay constant are included in the final calculation of the (pseudo-) plateau age error margins or for apparent ages individually cited. The analyses were performed on a Map215 mass spectrometer.

4. Results

4.1. Field and petrographic content

The unit crops out in the study area, mainly in an area containing Oltu and Narman districts in the north, Ilıcasu in the south, Çamlıkaya in the east and Başören in the west. The studied Eocene volcanic rocks are generally observed as pyroclastics, lava flows, and dikes.

Pyroclastic rocks comprise angular rock fragments with diameters varying from 2 cm to block size (Figures 3a and 3b). The groundmass for breccia fragments within the rock is generally tuff, with the breccia-pebble ratio reaching nearly 70%. Fresh fractured surfaces are dark gray-black color. They contain abundant amounts of mafic mineral phenocrysts.

Basaltic volcanic breccia: These generally have hyalomicrolithic, porphyritic, and glomeroporphyritic texture with modal mineralogy comprising plagioclase, clinopyroxene, olivine phenocrystals, and Fe-Ti oxides.

Basaltic dykes: These were emplaced by cutting basaltic lava and pyroclastics. Most dykes have fresh appearance, while weathered surfaces generally have light brown-beige color, and fresh surfaces have dark gray-black color (Figure 3c). Dykes have massive structures and strikes are generally NE-SW. The width of dykes varies from 30 cm to 2–3 m. Basaltic dyke samples comprise clinopyroxene, olivine, plagioclase, and Fe-Ti oxide minerals. They generally display microlithic, porphyritic, poikilitic, intersertal, and occasionally glomerophyritic textures (Figures 4a and 4b). Clinopyroxene is generally euhedral to anhedral and is observed as mega and phenocrystals and anhedral micrograins in the groundmass. This crystal is corroded by groundmass, has sieve texture, and contains mostly opaque and olivine inclusions with remnant centers (Figure 4a). Olivine is generally euhedral and subhedral. They are partly and fully iddingsitized along fractures and edges (Figure 4b). Olivine sometimes occurs as inclusions within clinopyroxenes or displays cumulophyric texture with clinopyroxenes. Plagioclase generally forms euhedral phenocrystals and microcrystals and displays albite twinning. Fe-Ti oxide minerals are generally found as subhedral and anhedral crystals around ferromagnesian minerals, as inclusions within clinopyroxenes, and as micrograins in the groundmass. Secondary minerals generally comprise zeolite minerals developing as cavity fill and chlorites developed from ferromagnesian minerals.

Basaltic lava: Massive basalts are present around Narman and Kışlaköy. In the study area, they represent very steep sections of topography above the sedimentary sequence of the Oltu Formation. Massive basalts have macroscopic porphyritic texture, with large augite and plagioclase phenocrystals easily recognized. There are abundant gas cavities, and these cavities are filled with carbonate and silica. Basalts are generally black-purple in color and form thick lava levels. Basalts contain clinopyroxene, plagioclase, and olivine phenocrystals, as well as Fe-Ti oxide minerals and generally have microlithic porphyritic, hyalomicrolithic porphyritic, sieve texture, and glomerophyritic textures (Figures 4c and 4d). Clinopyroxene minerals are observed as megacrystals and phenocrystals and are found as

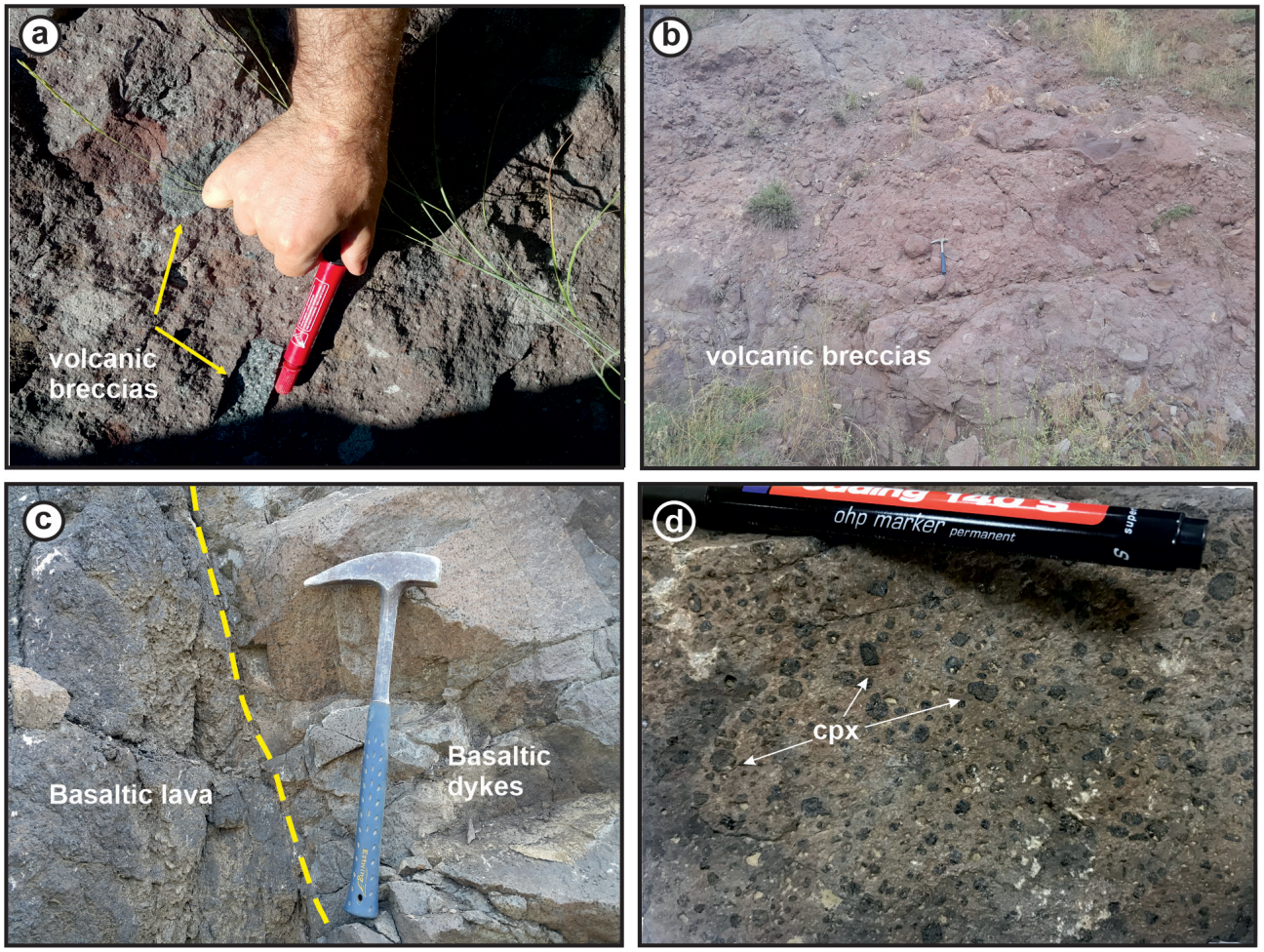

Figure 3. General view (a) of the contact between basaltic lava and basaltic dykes, (b) one hand specimen sampled from the basaltic lava with large clinopyroxene phenocryst, (c, d) various-sized breccia fragments constituting pyroclastic rocks and volcanic breccias.

microliths in the groundmass (Figures 4e and 4f). They contain abundant plagioclase, opaque minerals, and olivine inclusions. Zoning is commonly observed in clinopyroxene. Additionally, some clinopyroxenes affected the groundmass and display rough sieve texture (Figures 4e and 4f). Glomerophyritic texture was observed to form where the main clinopyroxene and opaque minerals occur together. Plagioclases are observed as subhedral phenocrystals and as microphenocrystals in groundmass. Generally, they display albite twinning. Sponge-like texture and dissolution by groundmass are very common. Cavities in the sponge-like texture are filled with glass. Some crystals contain both twinning and zoning, while others have a regrowth envelope at the outermost section. Olivine is generally euhedral and found as phenocrystals. Fe-Ti oxide minerals are occasionally found as inclusions and phenocrystals and vary from euhedral to anhedral. They are observed as micrograins in groundmass, and as enclosures within some clinopyroxene and olivine minerals.

4.2. Mineral chemistry

Mineral chemistry analysis for basaltic lava and basaltic dyke samples from the Narman volcanic rocks are presented in Supplementary information. Analyses represent core-mantle-edge compositions for zoned plagioclase and/or at least core and edge analyses for the other minerals. Clinopyroxene in basaltic lava samples consists of diopside and augite with $Wo_{39-47}En_{41-50}Fs_{5-18}$ composition and $Mg/(Mg+Fe^{+2})$ ratio of 0.70–0.87 (Figure 5a). Normal and inverse zoning was common in samples. Clinopyroxene in basaltic dyke samples consists of diopside and augite with $Wo_{38-46}En_{41-50}Fs_{5-18}$ composition and $Mg/(Mg+Fe^{+2})$ ratio of 0.72–0.89 (Figure 5a). Plagioclase in basaltic lava samples has labradorite ($An_{51-68}Ab_{29-42}Or_{2-4}$) composition, while plagioclase in basaltic dyke samples has labradorite ($An_{64-69}Ab_{29-33}Or_{2-3}$) and bytownite ($An_{70-80}Ab_{18-28}Or_{1-6}$) composition (Figure 5b). Olivine in basaltic lava samples has hyalosiderite and chrysolite (Fo_{67-90}) composition, while olivine in basaltic dyke samples has hyalosiderite

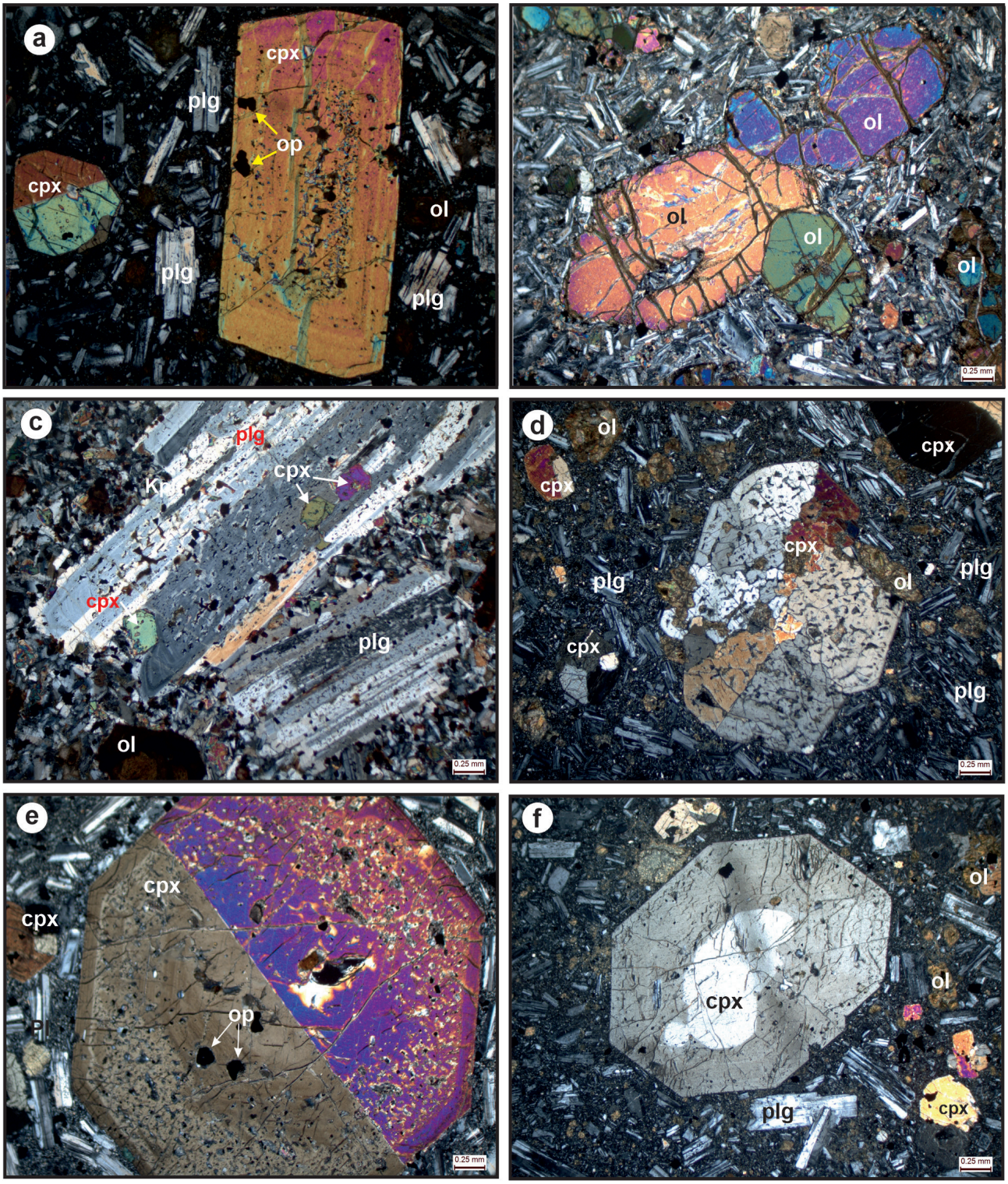

Figure 4. Photomicrograph showing textural relationships of the Narman volcanic rocks, (a) clinopyroxene mineral showing zoning and sieve texture in basaltic dykes, (b) euhedral olivine phenocrysts and glomerophyric texture of the basaltic dykes, (c) albite-twinned plagioclase phenocrysts containing clinopyroxene inclusions and sieve texture of the basaltic lava, (d) clinopyroxene phenocryst showing sieve texture in rocks with microlithic-porphyritic texture, (e) euhedral and zoning mega clinopyroxene mineral of basaltic lava, (f) clinopyroxene phenocryst with a sieve texture on the edge and containing a residual center and iddingsitized olivine minerals (plg, plagioclase, cpx, clinopyroxene, ol, olivine, op, opaque mineral).

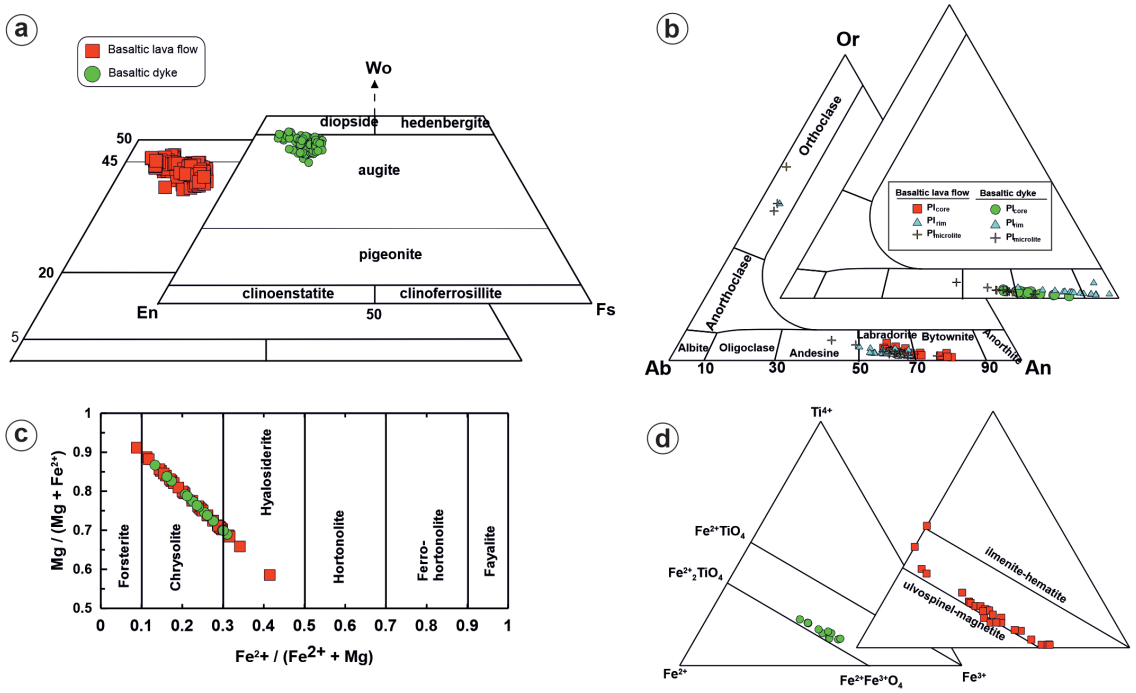

Figure 5. (a) Wo-En-Fs ternary plot of pyroxenes (Morimoto et al., 1988), (b) Or-Ab-An ternary plot of plagioclase, (c) olivine classification diagram, and (d) Ti^{4+}-Fe^{3+}-Fe^{2+} ternary plot of Fe-Ti oxides (Bacon and Hirschmann, 1988) for the volcanic rock samples from the Narman volcanic.

and chrysolite (Fo_{68-86}) composition (Figure 5c). Opaque minerals observed as eu-subhedral enclosures within clinopyroxene minerals and within groundmass of basaltic rocks are generally magnetite and titano-magnetite with one ilmenite found. Fe-Ti oxides in basaltic dyke samples had magnetite and titano-magnetite composition (Figure 5d).

4.3. ^{40}Ar-^{39}Ar dating

The ^{40}Ar-^{39}Ar age determination for the whole-rock of the three volcanic samples are presented in Supplementary information. A summary of ^{40}Ar-^{39}Ar age determination for volcanic rock samples is also given in Table 1. The step heating experiment results are given as age spectra in Figure 6 and the age spectra and their inverse isochronous calculation results are presented in Supplementary information. The ^{40}Ar-^{39}Ar plateau ages for basaltic lavas within the Narman Volcanites varied from 43.4 ± 0.1 My (N-53) to 44.5± 0.1 My (N-33), while 43.6 ± 0.1 My (N-38) was determined to be the age of the basaltic dyke. The ages from 43.4 ± 0.1 to 44.5± 0.1 My obtained with ^{40}Ar-^{39}Ar dating indicate the Narman volcanic rocks are Middle Eocene (Lutetian).

4.4. Whole-rock geochemistry

Whole-rock major and trace element analyses for the Narman Volcanics are given in Table 2. According to the SiO_2 versus Na_2O+K_2O (TAS) diagram by Le Maitre et al. (1989), basaltic dyke samples plotted in the basalt field, with one sample in the trachybasalt field; basaltic lava samples plotted in the basalt field; and basaltic volcanic breccia plotted in the basaltic andesite field (Figure 7a). Additionally, according to the alkali-subalkali differentiations of Irvine and Baragar (1971), on this diagram, nearly all the samples had subalkali affinity. The SiO_2 composition of Narman volcanic rock samples varies from 46 to 56 wt.%, with Mg numbers from 43 to 71. On the Nb/Y versus Zr/TiO_2*0.0001 diagram by Winchester and Floyd (1976), samples from the basaltic dyke fall within the andesite/basalt field, while samples from basaltic lava also fall within the andesite/basalt field. Two samples fall within the alkali-basalt and trachyandesite areas, and samples of basaltic volcanic breccia plot in the andesite field (Figure 7b). Nearly all samples plot in the calc-alkali field on the Th versus Co diagram with basaltic dyke and basaltic lava samples in the basalt field and basaltic volcanic breccia samples in the basaltic andesite field (Figure 7c). On the K_2O versus SiO_2 diagram (Ewart, 1982), basaltic dyke and basaltic lava samples plot in the medium-high K calk-alkali series, while basaltic volcanic breccia samples plot in the low-medium K calc-alkali series (Figure 7d).

The samples of the basaltic dyke and basaltic lava contain variation of 46–51% SiO_2 content (Table 2). The trends on the SiO_2 versus major oxide and trace element

Table 1. A summary of ^{40}Ar-^{39}Ar dating results for the Narman volcanic rocks.

Sample no	Material	Lithology	Rock name	Plateau age (Ma)
N-38	Whole-rock	Basaltic dyke	Basalt	43.6 ± 0.1
N-33	Whole-rock	Basaltic lava flow	Basalt	44.5± 0.1
N-53	Whole-rock	Basaltic lava flow	Basalt	43.4 ± 0.1

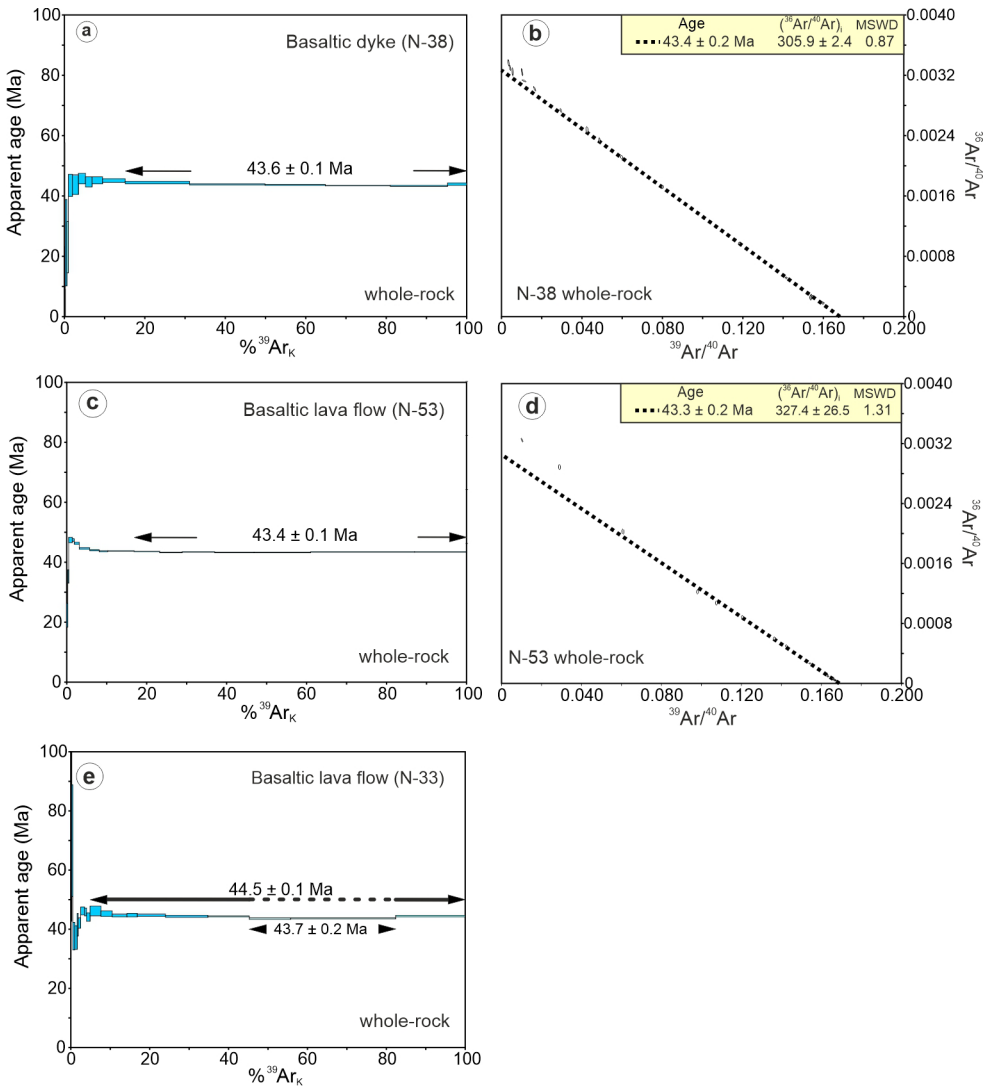

Figure 6. (a) ^{40}Ar-^{39}Ar ages of the Narman volcanics, (a-b) basaltic dyke (N-38), (c-d-e) basaltic lava flow (N-53, N-33).

variation diagrams (Figure 8) are very clear, with Fe_2O_3*, CaO, MnO, MgO, Sr, Co, and Ni displaying negative correlations and reducing with increasing SiO_2, while K_2O, Na_2O, P_2O_5, TiO_2, Al_2O_3, Ba, Hf, Zr, Rb, Th, Nb, and Y have positive correlations and increase with increasing SiO_2. The clear negative trends in the variations of MgO, Fe_2O_3*, Co, and Ni show that olivine fractionation may have been effective in these rocks. The negative trends on CaO and MgO diagrams indicate clinopyroxene fractionation, while negative Fe_2O_3* and MnO trends indicate fractionation of Fe-Ti oxides (Figure 8). The SiO_2 content of rocks forming basaltic volcanic breccia varies from 53% to 56%. Trends on SiO_2 versus major oxide and trace element variation diagrams are very clear. With increasing SiO_2, CaO, MgO, K_2O, Al_2O_3, P_2O_5, MnO and Rb have negative correlations and reduce, while Fe_2O_3*, Na_2O, TiO_2, Ba, Hf, Zr, Th, Sr, Nb, Y, and Ni have positive correlations and increase (Figure 8).

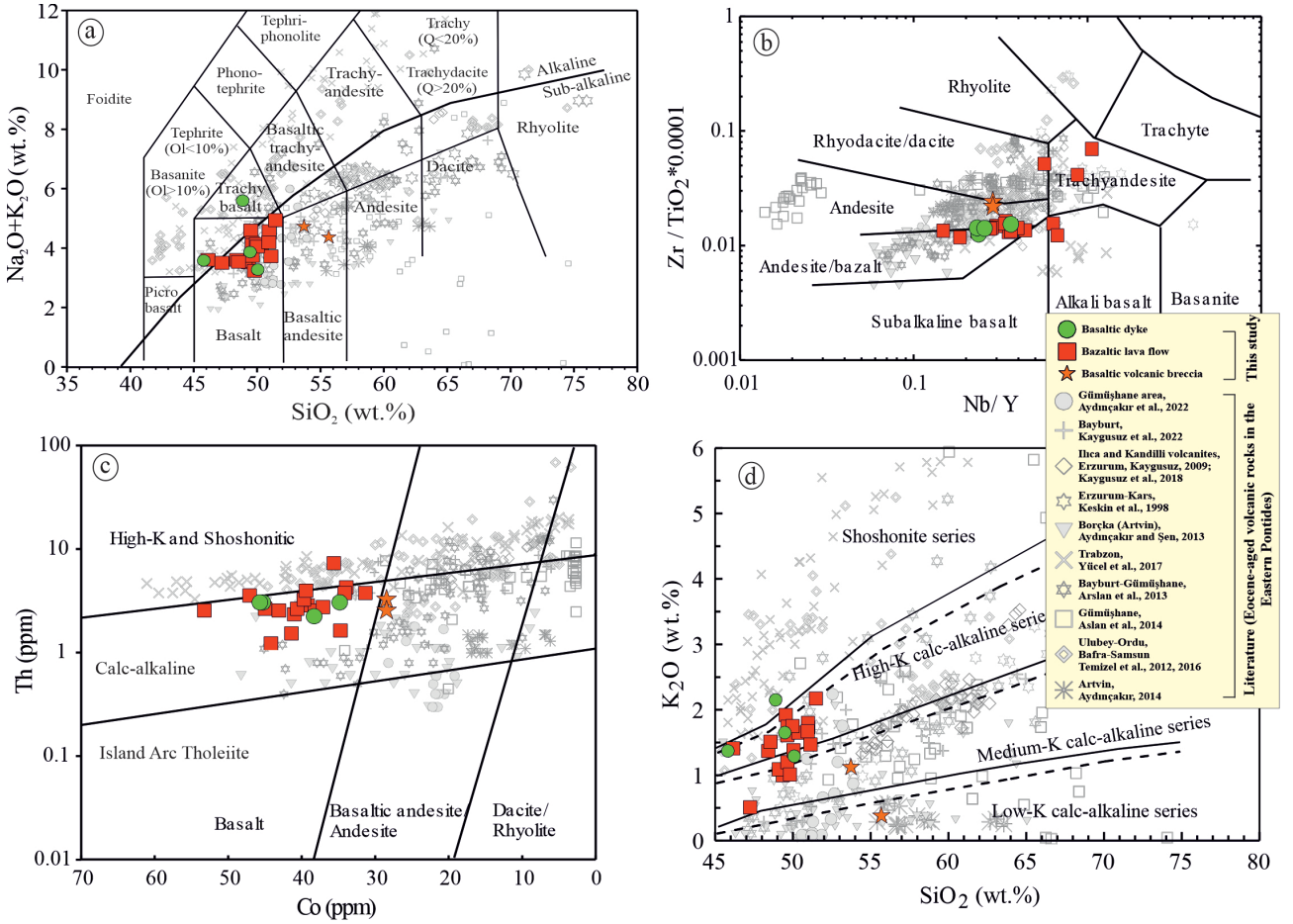

Figure 7. Chemical classification and nomenclature plots for the studied volcanic rocks, using (a) the total alkalis versus silica (TAS) diagram (after Le Maitre et al., 1989) (the alkaline and subalkaline discrimination line after Irvine and Baragar, 1971), (b) Zr/TiO_2*0.0001 versus Nb/Y diagram (after Winchester and Floyd, 1976), (c) Th versus Co diagram (after Hastie et al., 2007), (d) SiO_2 versus K_2O plot (after Ewart, 1982). Other data sources for comparison are Middle Eocene volcanic rocks (Keskin et al., 1998; Kaygusuz, 2009; Kaygusuz et al., 2018, 2022; Aslan et al., 2014; Arslan et al., 2013; Aydınçakır and Şen, 2013, Aydınçakır et al., 2022; Aydınçakır, 2014; Temizel et al., 2012, 2016; Yücel et al., 2017).

When trace element diagrams normalized to primitive mantle (Sun and McDonough, 1989) are examined, the studied volcanic rocks generally show pattern of enriched in large ion lithophile elements (LILE: Sr, K_2O, Rb and Ba), Th and Ce and depleted in high field strength elements (HFSE; Zr, TiO_2 and Y), Nb and Ta content (Figures 9a and 9d). These features in the trace elements in the studied rocks have similar patterns to other Eocene aged volcanic rocks in the region (Figure 9d).

The LILE and HFSE enrichment observed in the Narman volcanic rocks and clear Nb-Ta depletion indicates that these rocks derived from an enriched source rather than a depleted source (Condie et al., 2002). The reason for clear Nb-Ta reduction in melts derived from mantle compared to the primitive mantle (PM) is generally explained by crustal contamination during magma rise and metasomatism associated with subduction (Pearce et al., 1990).

The rare earth element (REE) distributions normalized to chondrite (Taylor and McLennan, 1985) for the studied volcanic rocks are generally similar (Figures 9e and 9h). This situation confirms that the rock assemblage forming the Narman Volcanics derived from the same source. Basaltic lava especially and basaltic volcanic breccia samples display moderate degree of enrichment, while basaltic dyke samples have more enriched distribution compared to the others. Samples from basaltic dykes had $(La/Lu)_N$ ratio of 5.06–6.47, basaltic lava samples had $(La/Lu)_N$ ratio of 2.78–7.99, and basaltic volcanic breccia had $(La/Lu)_N$ ratio of 4.26–5.98. The enrichment in light REE in basaltic lava samples compared to basaltic dyke and basaltic volcanic breccia samples indicates the source of the magma forming basaltic lava was more enriched compared to the source of magma forming the other rocks (Table 2, Figures 9e and 9h). Compared with other

Table 2. Whole-rock major (wt.%), trace and rare earth element (ppm) analyses from Eocene-aged Narman volcanic rocks.

Sample		Basaltic dyke				Basaltic lava flow																			Basaltic volcanic breccia	
No	MDL	N-5	N-7	N-8	N-38	N-20	N-25	N-26	N-27	N-30	N-36	N-33	N-53	N-71	N-87	N-89	N-103	N-105	N-107	N-108	N-120	N-122	N-124	N-131	N-65	N-66
Coordinate		37T 07°51'12.7"E 44°85'72.9"N	37T 07°52'19.9"E 44°85'61.1"N	37T 07°52'18.8"E 44°85'44.6"N	37T 07°54'38.0"E 44°06'70.9"N	38T 02°47'77.0"E 44°68'01.4"N	38T 02°48'88.0"E 44°67'60.1"N	38T 02°49'27.2"E 44°68'09.3"N	38T 02°49'76.4"E 44°68'19.8"N	38T 02°51'24.9"E 44°69'36.5"N	38T 02°52'75.2"E 44°71'20.8"N	38T 02°51'63.7"E 44°70'06.1"N	37T 07°37'21.4"E 44°72'00.7"N	37T 07°48'71.2"E 44°79'87.9"N	37T 07°24'97.5"E 44°59'09.6"N	37T 07°24'68.2"E 44°55'81.2"N	38T 02°49'94.3"E 44°92'79.9"N	38T 02°50'78.1"E 44°87'67.6"N	38T 02°50'10.4"E 44°87'17.8"N	38T 02°49'83.7"E 44°88'93.5"N	38T 02°49'74.7"E 44°65'93.9"N	38T 02°52'87.2"E 44°63'07.3"N	38T 02°50'94.0"E 44°58'09.0"N	37T 07°4 8'69.	37T 07°31'78 .9"E	37T 07°31'27 .5"E
SiO_2	0.01	45.80	48.87	50.06	49.46	49.52	49.33	49.07	49.64	49.62	50.34	48.4	49.96	46.14	47.23	49.63	51.11	50.02	50.97	50.96	49.79	51.46	48.54	50.9	55.67	53.71
TiO_2	0.01	0.69	0.90	0.76	0.86	1.17	1.07	1.04	0.87	0.89	0.86	0.92	1.04	0.74	1.08	0.7	0.9	1.01	1.09	1.04	0.93	1.36	0.76	0.82	0.92	0.91
Al_2O_3	0.01	13.57	17.01	12.96	14.22	15.2	15.84	15.4	15	15.26	14.85	12.67	14.74	15.57	16.56	16.22	14.86	15.97	16.69	16.4	14.15	15.07	13.32	14.9	18.29	19.44
$Fe_2O_3^*$	0.04	8.94	10.56	9.57	9.24	11.01	10.2	10.68	9.24	9.63	9.49	9.83	10.15	9.51	9.31	8.33	7.79	10.49	9.21	9.87	9.28	9.06	8.85	9.58	7.43	7.14
MnO	0.01	0.17	0.18	0.21	0.16	0.18	0.17	0.17	0.16	0.15	0.16	0.15	0.2	0.25	0.17	0.13	0.14	0.15	0.16	0.11	0.14	0.12	0.15	0.16	0.13	0.13
MgO	0.01	6.20	4.43	8.26	9.84	6.77	5.77	5.83	8.04	6.98	7.05	11.43	6.75	4.23	7.04	4.58	6.64	5.24	4.42	4.66	7.96	5.79	10.83	7.65	2.8	3.54
CaO	0.01	14.54	8.10	11.63	9.65	10.3	10.43	10.25	10.14	9.49	10.34	9.93	10.11	12.61	10.05	10.15	10.5	9.6	9.32	9.31	11.5	8.3	10.06	9.72	7.19	8.15
Na_2O	0.01	2.20	3.43	1.97	2.20	2.66	2.5	2.46	2.43	2.48	2.41	2.22	2.37	2.18	2.98	2.53	2.24	2.66	2.77	2.76	2.21	2.76	2.01	2.51	3.97	3.59
K_2O	0.01	1.38	2.16	1.30	1.66	1.93	1.01	1.1	1.75	1.62	1.66	1.38	1.76	1.42	0.52	1.21	1.48	1.39	1.74	1.81	1.02	2.18	1.52	1.68	0.39	1.13
P_2O_5	0.01	0.21	0.24	0.19	0.19	0.3	0.19	0.2	0.18	0.19	0.19	0.2	0.23	0.17	0.14	0.13	0.17	0.24	0.26	0.25	0.14	0.41	0.16	0.18	0.19	0.18
LOI		6.0	3.8	2.6	2.1	0.7	3.3	3.5	2.1	3.3	2.3	2.3	2.3	6.9	4.6	6.1	3.8	2.9	3.1	2.5	2.5	3.1	3.3	1.5	2.7	1.8
Total		99.75	99.76	99.68	99.69	99.8	99.82	99.81	99.71	99.73	99.73	99.67	99.71	99.79	99.77	99.79	99.76	99.76	99.77	99.77	99.75	99.72	99.69	99.7	99.78	99.8
Ni	0.1	49.9	22.3	73.9	158.9	77.4	41.7	80	67.2	33.4	57	223.4	64.1	29.9	85.9	89.7	42.1	45.9	32.5	41.8	60.4	101.8	148	70.1	55.7	30.9
Sc	1.0	32.0	19.0	34.0	30	35	38	36	30	31	32	30	33	28	26	27	33	29	29	29	36	25	31	30	13	18
Ba	1.0	341.0	373.0	294	401	362	355	349	431	378	344	331	374	277	122	325	361	343	389	349	221	440	461	369	236	224
Co	0.2	38.4	34.9	45.4	45.8	47.2	39.3	41.1	39.8	38.3	40.7	53.4	39.8	45.1	44.3	34.8	31.4	39.5	34	34.2	41.5	35.7	43.2	37.2	28.5	28.5
Hf	0.1	1.40	2.10	1.70	2.1	2.8	2.3	2.2	2.3	2.1	2.1	2	2.4	1.5	2	1.5	2.3	2.2	2.6	2.4	2	4.4	1.6	2	3.3	2.7
Nb	0.1	3.50	4.80	4.40	6.3	13	7.6	7.3	6.2	6.7	5.8	7	7.4	3.2	2.9	2.6	6.1	5.5	6.1	5.5	6.2	16.8	4	5.9	6.3	5.6
Rb	0.1	22.40	46.90	28.60	36.1	41.4	19.9	24.6	36	28.4	36.2	30.3	29	24.9	11.2	18.7	30.8	25.2	31.9	51	15.5	57.8	24.6	36.1	6.8	22.7
Sr	0.5	475	453	473	407.1	471.8	358.1	375.4	421.8	415	417.6	385.5	493	410.6	330.1	440.8	387.5	421.3	430.7	405.2	274.7	325.4	407.5	401	680.2	392.9
Ta	0.1	0.2	0.3	0.2	0.4	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.2	0.2	0.1	0.3	0.4	0.3	0.4	0.4	1	0.3	0.4	0.5	0.4
Th	0.2	2.20	3.00	3.00	3	3.5	2.8	2.3	3.2	2.5	2.6	2.5	3.2	2.6	1.2	1.6	3.7	3.9	4.2	3.7	1.5	7.2	2.5	2.7	3.2	2.5
U	0.1	1.10	0.90	0.90	1	0.9	0.7	0.8	1.1	0.9	0.8	0.9	1.1	0.8	0.2	0.3	0.8	1.1	1.4	1	0.5	2.2	0.8	0.8	1.2	0.8
V	8	258	283	354	241	264	289	285	241	249	253	222	282	262	162	224	242	289	295	301	276	261	237	232	165	177
Zr	0.1	51.2	75.7	63.4	77.9	108.7	86.9	81.8	85.2	79.4	76.2	74.8	88.6	59.1	86.9	49.3	83.8	86.7	93.2	87.2	74.2	100	63.8	73.8	130.5	117.1
Y	0.1	14.9	20.9	17.3	17.5	20.6	20.9	20.9	18.4	18.5	19.5	16	18.8	13.9	19.8	14.2	18.4	21	21.8	20.6	17.2	25.1	14.6	17.5	22.2	19.7
Cu	0.1	100.6	129.1	80.3	106.6	22.4	43.4	104.9	91.6	88.9	75.9	85.2	105.1	41.9	48.6	42.5	39.6	115.3	101.3	84	55.8	189	95.4	37.5	31.4	45.2
Pb	0.1	1.90	2.6	2.60	2.7	1.2	2.5	2.1	1.5	2.5	2.5	1.9	1.5	3.4	1.8	1.7	3	3.3	1.7	2.1	1.6	2.2	2.7	1.3	4.1	2.1
Zn	1	54.0	74.0	48.0	50	52	82	54	52	44	62	56	57	63	50	33	65	71	79	61	49	71	52	53	48	42
La	0.1	11.40	15.60	14.3	14.5	21.2	13.2	13.4	16.4	13.6	13.8	12.5	17.2	11.1	8.3	8.4	13.5	16.3	16.7	15.7	8.8	27.7	11	13.6	15.2	13
Ce	0.1	23.00	35.80	39.6	30.8	49.5	31.8	28.4	33	35.2	30.7	34.1	36.1	22.2	18.9	16.6	27	31.5	32.2	31	18.2	53.7	20.7	26.1	35.4	58.8
Pr	0.02	3.31	5.36	6.84	4.96	10.21	8.75	6.12	4.78	6.31	5.03	8.16	5.48	2.77	2.48	2.16	3.28	3.81	4.12	3.89	2.48	6.16	2.64	3.23	7.63	14.31
Nd	0.3	14.00	21.70	26.1	19.7	38.3	31.5	24.1	18.7	24.6	20.8	29.2	21.7	11.4	10.9	9.2	13.6	16.2	17.5	16.2	11	24	10.3	13.5	28.2	52.3
Sm	0.05	2.81	3.67	3.23	3	4.34	3.73	3.6	3.24	3.01	3.21	2.99	4.24	2.61	2.59	2.3	3.01	3.49	3.78	3.55	2.49	4.76	2.42	2.87	3.48	2.95
Eu	0.02	0.90	1.18	1	0.98	1.41	1.14	1.14	1	1.02	0.98	0.95	1.29	0.85	1	0.83	0.95	1.13	1.25	1.14	0.89	1.31	0.81	0.94	1.11	1.08
Gd	0.05	3.49	5.51	7.14	4.63	7.04	6.25	4.95	4.54	6.14	5.45	6.71	5.01	2.81	3.33	2.78	3.56	4.03	4.17	4.03	3.33	4.95	2.78	3.47	5.92	13.54
Tb	0.01	0.45	0.61	0.52	0.51	0.68	0.65	0.65	0.53	0.56	0.56	0.49	0.62	0.44	0.55	0.42	0.55	0.61	0.65	0.62	0.51	0.75	0.43	0.53	0.62	0.56
Dy	0.05	2.71	3.93	3.42	3.32	4.51	4.63	4.27	3.28	3.57	3.51	3.51	3.77	2.57	3.39	2.56	3.25	3.7	3.73	3.77	3.08	4.55	2.53	3.09	4.3	4.23
Ho	0.02	0.57	0.81	0.65	0.67	0.8	0.89	0.79	0.66	0.74	0.73	0.64	0.74	0.52	0.77	0.54	0.7	0.81	0.84	0.75	0.66	0.91	0.54	0.63	0.84	0.77
Er	0.03	1.60	2.34	1.83	1.76	2.46	2.6	2.37	1.9	2.19	2.04	1.68	2.06	1.59	2.2	1.53	2.08	2.23	2.46	2.24	1.87	2.54	1.52	2.02	2.46	2.15
Tm	0.01	0.24	0.32	0.25	0.26	0.34	0.34	0.33	0.26	0.29	0.29	0.23	0.27	0.22	0.31	0.22	0.29	0.33	0.33	0.32	0.27	0.37	0.22	0.27	0.34	0.3
Yb	0.05	1.54	2.17	1.63	1.8	2.25	2.05	2.14	1.71	1.93	1.96	1.49	1.83	1.43	1.95	1.47	1.89	2.06	2.25	2.12	1.69	2.46	1.38	1.79	2.29	2.17
Lu	0.01	0.23	0.32	0.26	0.26	0.28	0.3	0.31	0.27	0.29	0.3	0.24	0.27	0.22	0.31	0.21	0.3	0.31	0.36	0.33	0.25	0.36	0.21	0.28	0.37	0.31
Eu_N/Eu^*		0.88	0.80	0.62	0.80	0.78	0.72	0.83	0.80	0.71	0.71	0.63	0.85	0.95	1.04	1.00	0.89	0.92	0.96	0.92	0.94	0.82	0.95	0.91	0.74	0.44
La_N/Yb_N		5.00	4.86	5.93	5.44	6.37	4.35	4.23	6.48	4.76	4.76	5.67	6.35	5.25	2.88	3.86	4.83	5.35	5.02	5.00	3.52	7.61	5.39	5.13	4.49	4.05
Mg#		58	45	63	68	55	53	52	63	59	60	70	57	47	60	52	63	50	49	48	63	56	71	61	43	50

$Fe_2O_3^*$ is total iron as Fe_2O_3, LOI = loss on ignition, $Eu/Eu^* = (Eu_N) / (1/2\ (Sm_N + Gd_N))$ and Mg# (Mg-number)= 100 × MgO / ($MgO+0.9Fe_2O_3^{tot}$)

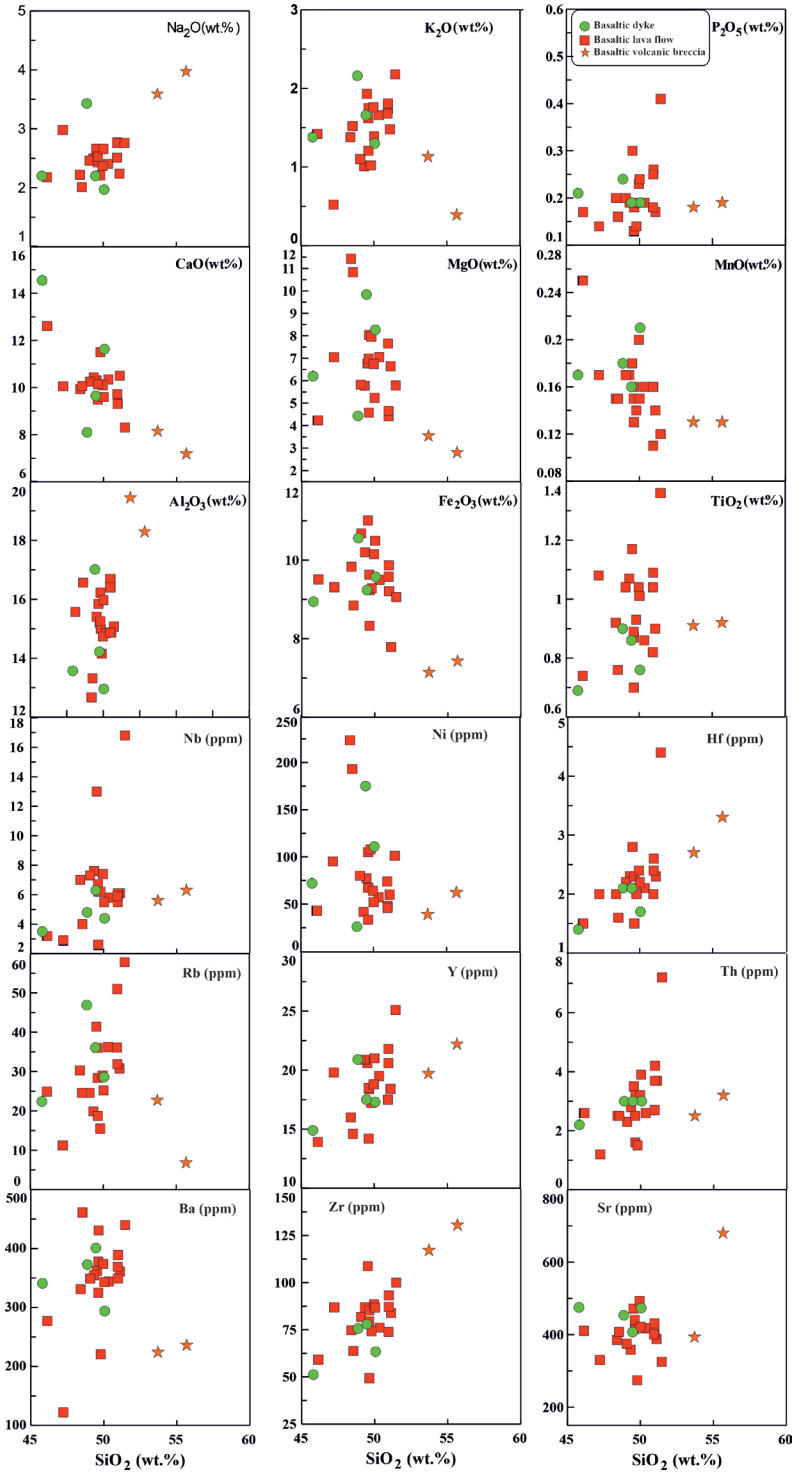

Figure 8. SiO_2(wt.%) versus major oxide (wt.%), trace element (ppm) variation plots of the Narman volcanic rocks.

Eocene volcanic rocks from the EPOB (e.g., Keskin et al., 1998; Kaygusuz, 2009; Temizel et al., 2012, 2016; Arslan et al., 2013; Aydınçakır and Şen, 2013; Aydınçakır et al., 2022; Aslan et al., 2014; Aydınçakır, 2014; Yücel et al., 2017; Kaygusuz et al., 2018; 2022), the general geochemical features of the studied volcanic rocks are similar to those of the Eocene volcanic rocks from the EPOB (Figure 9h).

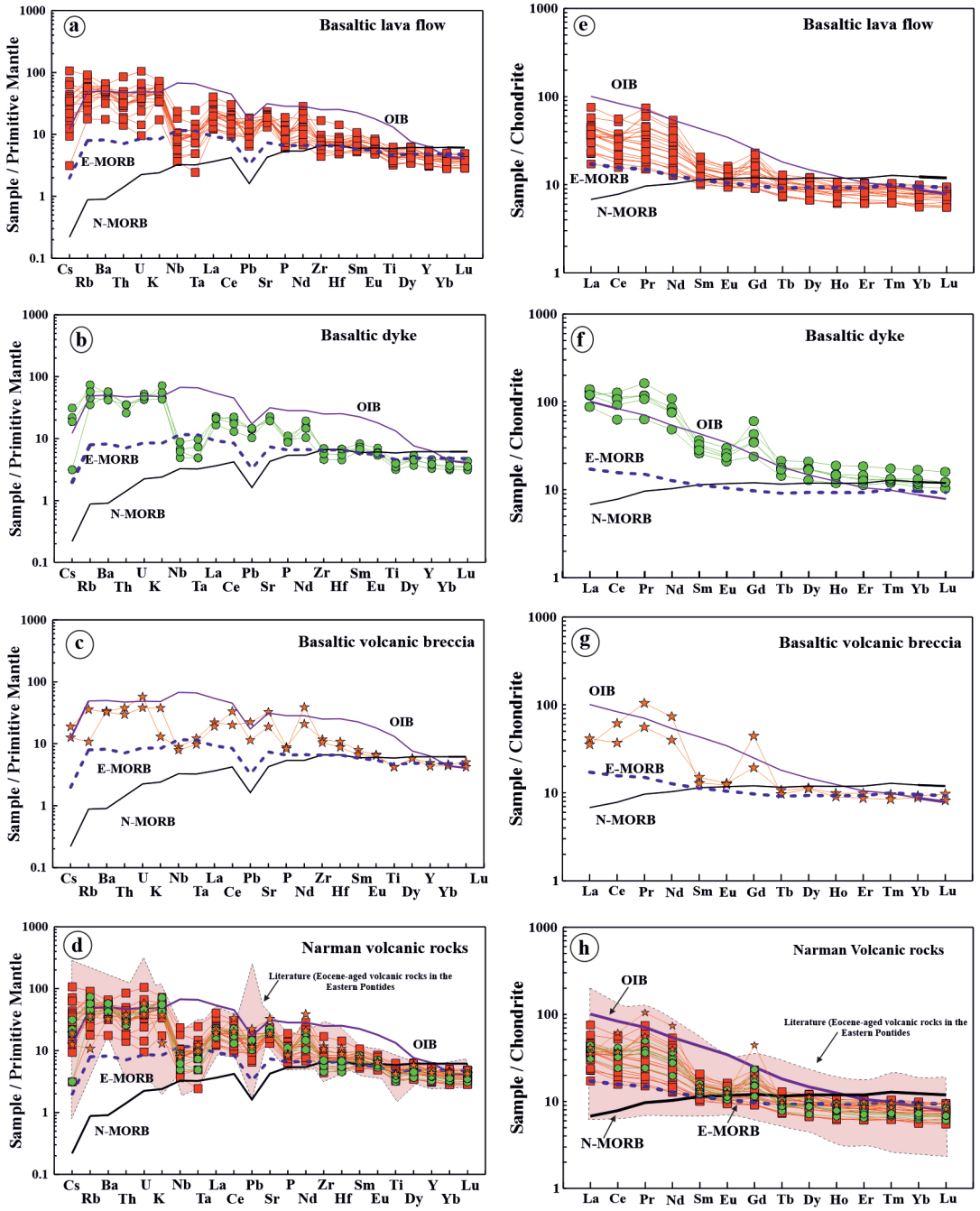

Figure 9. (a-d) Primitive mantle-normalized (Sun and McDonough, 1989) spider plots and (e-h) chondrite-normalized (Taylor and McLennan, 1985) rare earth element plots of the Narman volcanic rocks, OIB, N-MORB and E-MORB compositions from Sun and McDonough (1989). Data sources for comparison of other Eocene volcanic rocks are as in Figure 7d.

The REE distributions normalized to chondrite for the volcanic rocks indicated the magmas forming the rocks did not have a significant Eu anomaly, suggesting that plagioclase fractionation did not have much effect in these rocks, or there was high oxygen fugacity (Gill, 1981). The $(Eu/Eu^{*})_{N}$ ratio varied from 0.62 to 0.88 for basaltic dykes, 0.63 to 1.04 for basaltic lavas, and 0.44 to 1.00 for basaltic volcanic breccia. Generally, the chondrite-normalized REE distributions for the rocks showed more enrichment in LREE compared to MREE and HREE. The REE distribution diagrams had a concave shape, indicating that clinopyroxene fractionation was effective during the

evolution of volcanic rocks (Thirlwall et al., 1994). All volcanic rocks had $(Yb)_N < 10$. This value indicates that garnet was a remnant phase in the mantle source.

4.5. Sr-Nd-Pb-Hf isotope geochemistry

The basaltic lava samples from the Narman Volcanics had initial $^{87}Sr/^{86}Sr_{(i)}$ ratios from 0.70404 to 0.70445, $^{143}Nd/^{144}Nd_{(i)}$ ratios varied from 0.512636 to 0.512847, and $\varepsilon Nd_{(45)}$ values were between 1.1 and 5.2 (Table 3). The model age (T_{DM}) values calculated for the basaltic lavas varied from 410 to 510 Ma (Table 3). For basaltic dyke samples, initial $^{87}Sr/^{86}Sr_{(i)}$ ratios were from 0.70476 to 0.70485, $^{143}Nd/^{144}Nd_{(i)}$ ratios varied from 0.512606 to 0.512706, and $\varepsilon Nd_{(45)}$ values were between 0.5 and 2.43 (Table 3). The T_{DM} values calculated for the basaltic dyke samples varied from 450 to 620 Ma (Table 3). On the initial Sr and Nd comparison diagrams, they were located in the mantle interval between depleted mantle (DM) and enriched mantle (EMI, EMII) regions (Figure 10a). The $(^{87}Sr/^{86}Sr)_i$ ratios varying in a narrow interval and the εNd_i values indicate a depleted mantle source region enriched by subducting plate components. On the Sr-Nd diagram (Figure 10a), rocks forming the Narman Volcanics appear to plot between the Eastern Pontide calc-alkali volcanic rocks and the Central Anatolia calc-alkali volcanic rocks on a regional scale.

The basaltic lavas samples of the studied volcanic rocks had $^{206}Pb/^{204}Pb$ isotope ratios from 18.845 to 18.918, $^{207}Pb/^{204}Pb$ isotope ratios from 15.607 to 15.621, and $^{208}Pb/^{204}Pb$ isotope ratios from 38.870 to 38.900 (Table 4). The basaltic dyke samples had $^{206}Pb/^{204}Pb$ isotope ratios varying from 18.830 to 18.838, $^{207}Pb/^{204}Pb$ isotope ratios from 15.617 to 15.624, and $^{208}Pb/^{204}Pb$ isotope ratios from 38.852 to 38.955. On $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ isotope diagrams for the Eocene volcanic rocks, a positive correlation is clearly observed (Figures 10b and 10c). The samples from the investigated rocks are very clearly located in the upper section of the Northern Hemisphere Reference Line (NHRL) (Figures 10b and 10c). Additionally, samples plot between the Enriched Mantle I (EMI) and Enriched Mantle II (EMII) reservoir fields and are closer to the EMII reservoir field. As the EMII reservoir has typical composition for the upper continental crust, while EMI has typical composition for the lower continental crust, enrichment of these mantle reservoirs may be explained by a cycle of upper and lower crustal material mixing in the mantle in subduction zones.

The basaltic lava of the Eocene Narman Volcanics had $^{176}Lu/^{177}Hf$ ratios ranging from 0.0119 to 0.3332, initial $^{176}Hf/^{177}Hf$ ratios from 0.282770 to 0.282998, and ε_{Hf} values varying from +7.6 to +9.2. The rocks forming the basaltic dykes had $^{176}Lu/^{177}Hf$ ratios of 0.0217 to 0.0176, initial $^{176}Hf/^{177}Hf$ ratios between 0.282991 and 0.283013, and ε_{Hf} values varying from +7.9 to +8.6 (Table 5). The Hf isotope values for the Narman Volcanics are similar to those of mid-oceanic ridge basalts (MORB) and oceanic island basalts (OIB), similar to the Sr-Nd isotope ratios (Figure 10d).

5. Discussion

5.1. Age

Considering reliable geochronological data, the ages of Eocene volcanic rocks within the Eastern Pontides vary from 37 Ma to 46 Ma (Arslan et al., 2013; Aydınçakır and Şen, 2013; Aslan et al., 2014; Yücel et al., 2017; Aydınçakır et al., 2022; Kaygusuz et al., 2022). In previous studies, the age relations of volcanic rocks were based on volcano-stratigraphic criteria, contact relationships and geochronological studies (Konak and Hakyemez, 2001). The Narman Volcanics were given a Late Oligocene-Early Miocene (?) age based on their position above the Oligocene-Early Miocene Sütkans coals and lateral transition from the Oltu Formation with the same age. Keskin et al. (1998) proposed an age of 38.5 ± 0.7 Ma based on K-Ar dating of one sample from within the volcano-sedimentary unit. In this study, new ^{40}Ar-^{39}Ar dating of Narman volcanic rocks found that the age ranges from 43.4 ± 0.1 Ma to 44.5± 0.1 Ma (Lutetian).

5.2. Fractional crystallization (FC) and assimilation-fractional crystallization (AFC)

Major and trace element variation diagrams show that fractionation was effective in formation of the volcanic rocks (Figure 8). The reduction in TiO_2 and Fe_2O_3* contents with increasing SiO_2 content in the Narman Volcanics shows Fe-Ti oxide fractionation, while negative relationships between SiO_2 versus CaO, Fe_2O_3* and MgO indicate fractionation of clinopyroxene phases from the main magma. Chondrite-normalized REE distributions for the volcanic rocks show no clear negative anomaly for Eu values, indicating that plagioclase fractionation was not very effective during the evolution of the rocks (Figures 9e and 9h). Major and trace element distribution diagrams show that clinopyroxene, olivine, plagioclase, Fe-Ti oxide, and apatite fractionation played important roles in the evolution of the studied rocks.

Binary diagrams were prepared using pairs of compatible-incompatible elements to determine the mineral phases affecting fractional crystallization (Figure 11). On these diagrams, the negative trend for increasing Zr versus TiO_2 content indicates Fe-Ti oxide fractionation, while a positive trend indicates clinopyroxene, olivine, plagioclase and apatite fractionation (Figure 11a). The increasing Zr versus positive Y and Nb variations show olivine, clinopyroxene, Fe-Ti oxide, plagioclase and apatite fractionation (Figures 11b and 11c). The negative correlation for Zr versus Ni indicates olivine fractionation (Figure 11d). The positive Sr variation versus Zr represents

Table 3. Sr and Nd isotope compositions of samples from the Narman Volcanics.

Sample	Rb(ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	2sm	$(^{87}Sr/^{86}Sr)_i$	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	$(^{143}Nd/^{144}Nd)_i$	2sm	$e_{Nd}(t)$	T_{DM1} (Ga)
Basaltic dyke (44 Ma)														
N-8	0.06	473.2	0.1748	0.704874	10	0.70476	3.23	26.1	0.0751	0.512728	0.512706	3	2.4	0.4
N-38	0.09	407.1	0.2565	0.705012	10	0.70485	3.00	19.7	0.0925	0.512633	0.512606	4	0.5	0.6
Basaltic lava (45 Ma)														
N36	0.21	503	0.6002	0.704425	10	0.70404	4.62	28.2	0.0367	0.512801	0.512772	3	3.7	0.4
N20	0.09	472	0.2538	0.704615	10	0.70445	4.34	38.3	0.0688	0.512656	0.512636	3	1.1	0.5
N33	0.08	386	0.2273	0.704501	11	0.70436	2.99	29.2	0.0622	0.512779	0.512761	3	3.5	0.4
N53	0.06	493	0.1701	0.704533	10	0.70442	4.24	21.7	0.1187	0.512882	0.512847	3	5.2	0.4

Note: $e_{Nd} = ((^{143}Nd/^{144}Nd)_s/(^{143}Nd/^{144}Nd)_{CHUR} -1) \times 10000$, $(^{143}Nd/^{144}Nd)_{CHUR} = 0.512638$, and $(^{147}Sm/^{144}Sm)_{CHUR} = 0.1967$ (Jacobsen and Wasserburg, 1980).

Nd model ages (T_{DM}) are calculated with a depleted-mantle reservoir and present-day values of $^{143}Nd/^{144}Nd = 0.513151$ and $^{147}Sm/^{144}Sm = 0.219$ (Liew and Hofmann, 1988). The model ages were calculated using a linear isotopic ratio growth equation: $TDM = 1/l \times \ln(1 + ((^{143}Nd/^{144}Nd)s - 0.51315)/((^{147}Sm/^{144}Nd)s - 0.2137))$.

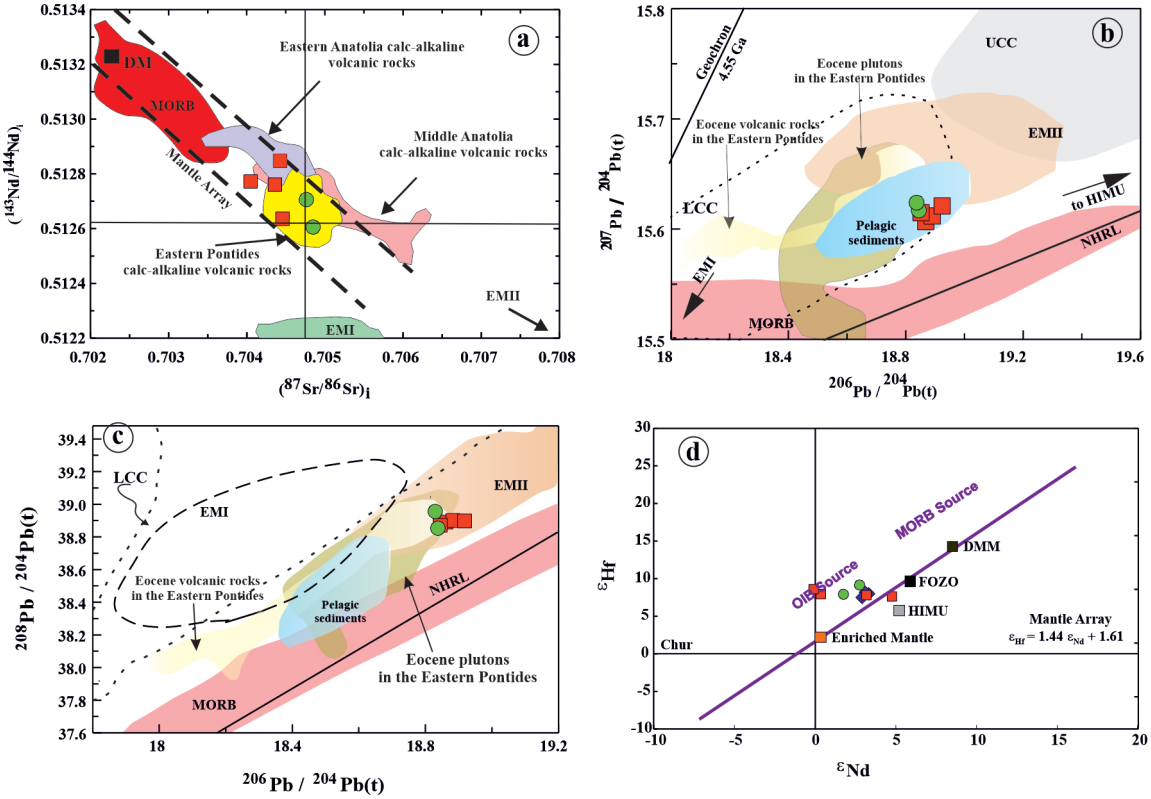

Figure 10. (a) $(^{143}Nd/^{144}Nd)_i$ versus $(^{87}Sr/^{86}Sr)_i$ plot to show the Narman Volcanics. Data for lithospheric mantle array from Davies and von Blanckenburg (1995). Compositions of MORB (mid-ocean ridge basalt) and mantle array from Wilson (1989), Gill (1981) and McCulloch et al. (1994); EMI (enriched mantle type I) and EMII (enriched mantle type II), HIMU (high μv: mantle with high U/Th ratio), DM (Depleted Mantle) fields and CHUR (Chondritic Uniform Reservoir)-Sr and -Nd reference lines after Zindler and Hart (1986), Eastern Anatolia calc-alkaline volcanic rocks (Pearce et al., 1990; Buket and Temel, 1998; Keskin et al., 2006), Middle Anatolia calc-alkaline volcanic rocks (Temel et al., 1998; Varol et al., 2007), Eastern Pontides calc-alkaline vaolcanic rocks (Arslan et al., 2013; Aydınçakır and Şen, 2013; Yücel et al., 2017; Dokuz et al., 2019; Göçmengil et al., 2019; Aydınçakır et al., 2022; Kaygusuz et al., 2022), (b, c) $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ diagrams for the samples of the Narman Volcanics. the composition of the mantle components EM-1 and EM-2 are from (Zindler and Hart, 1986), whereas the composition of subducted sediments is from (Plank and Langmuir, 1998), MORB and crust data are from (Chauvel and Blichert-Toft, 2001). NHRL is after (Vervoort and Blichert-Torft, 1999). Literature data of the Eocene volcanic and plutonic rocks in the Eastern Pontides (Aydınçakır and Şen, 2013; Aydınçakır, 2014; Arslan et al., 2013; Yücel et al., 2017; Aydınçakır et al., 2022; Kaygusuz et al., 2020, 2022), (d) ε_{Nd} versus ε_{Hf} diagram (the data of EM, DM and μ (HIMU) from the study of Stracke (2012); terrestrial range, Vervoort et al. (2011) (symbols are as in Figure 4). Data sources for comparison of other Eocene volcanic rocks are as in Figure 7d.

Table 4. Pb isotope compositions of samples from the Narman Volcanics.

Sample	Pb (ppm)	U (ppm)	Th (ppm)	$^{206}Pb/^{204}Pb$	$(^{206}Pb/^{204}Pb)i$	$^{207}Pb/^{204}Pb$	$(^{207}Pb/^{204}Pb)i$	$^{208}Pb/^{204}Pb$	$(^{208}Pb/^{204}Pb)i$
Basaltic dyke (44 Ma)									
N-8	2.60	0.90	3.00	18.838	18.686	15.617	15.610	38.852	38.685
N-38	2.70	1.00	3.00	18.830	18.667	15.624	15.616	38.955	38.794
Basaltic lava (45 Ma)									
N36	2.00	2.80	9.20	18.862	18.232	15.607	15.577	38.890	38.210
N20	1.20	0.90	3.50	18.883	18.546	15.612	15.596	38.900	38.468
N33	1.90	0.90	2.50	18.918	18.705	15.621	15.611	38.896	38.701
N53	1.50	1.10	3.20	18.845	18.515	15.615	15.600	38.870	38.555

Table 5. Hf isotope compositions of samples from the Narman Volcanics.

Sample	Lu (ppm)	Hf (ppm)	$^{176}Hf/^{177}Hf$	$^{176}Lu/^{177}Hf$	$(^{176}Hf/^{177}Hf)i$	ε_{Hf}
Basaltic dyke (44 Ma)						
N-8	0.26	1.70	0.283009	0.021692	0.282991	7.9
N-38	0.26	2.10	0.283028	0.017560	0.283013	8.6
Basaltic lava (45 Ma)	-					
N36	0.37	4.40	0.283006	0.011927	0.282996	7.8
N20	0.28	2.80	0.283010	0.014183	0.282998	8.0
N33	4.70	2.00	0.283044	0.333163	0.282770	9.2
N53	4.04	2.40	0.283001	0.238968	0.282805	7.6

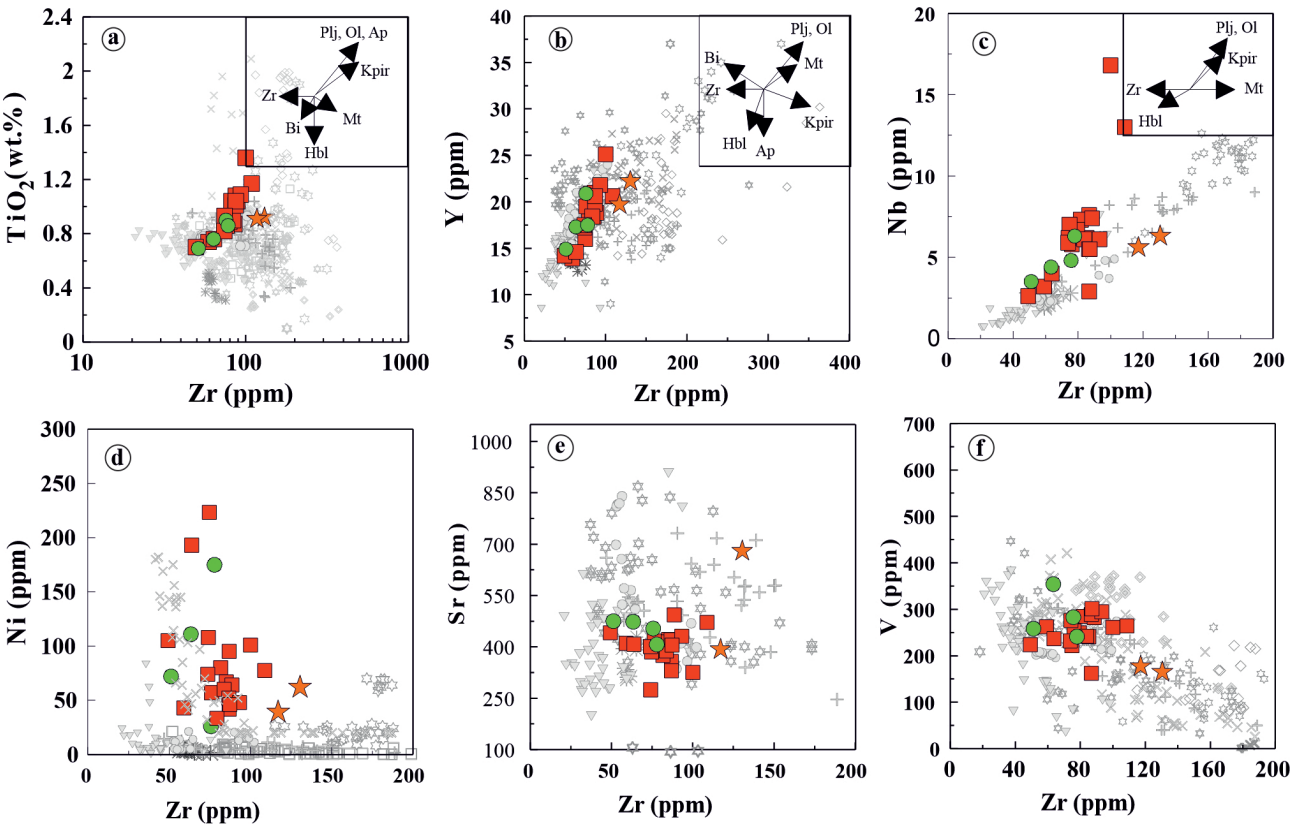

Figure 11. Zr (ppm) versus TiO_2 (wt. %), Y (ppm), Nb (ppm), Ni (ppm), Sr (ppm) and V (ppm) diagrams demonstrating the fractional crystallization (FC) and accumulation of the Narman volcanic rocks (vectors show fractional crystallization and accumulation, according to Pearce and Norry (1979), symbols are as in Figure 4). Data sources for comparison of other Eocene volcanic rocks are as in Figure 7d.

plagioclase fractionation (Figure 11e). The clear negative trends on the diagram for Zr versus the compatible element V (Figure 11f) indicate Fe-Ti oxide fractionation.

The trends in the vertical direction on the Nb/Y versus Rb/Y diagram for the studied volcanic rocks suggest subduction zone enrichment and/or crustal contamination occurred, while positive trends around Rb/Nb = 1 and high Nb/Y values indicate within-plate enrichment. For the samples of the Narman Volcanics, subduction enrichment, crustal assimilation, and within-plate enrichment played an effective role (Figure 12).

To determine the role of fractionation and crustal assimilation in samples from the Narman volcanic rocks, the SiO_2 versus Sr and Nd isotope ratios and Th diagrams were drawn (Figures 13a–13d). Positive and negative trends indicate that magma was affected by crustal assimilation with fractional crystallization (AFC) processes, while a flat trend shows that fractionation was effective. According to the variation diagrams, fractional crystallization (FC) and/or AFC are suggested by changes in primitive source fields. The variations occurring in horizontal and close to horizontal directions in Figures 13a–13d indicate FC,

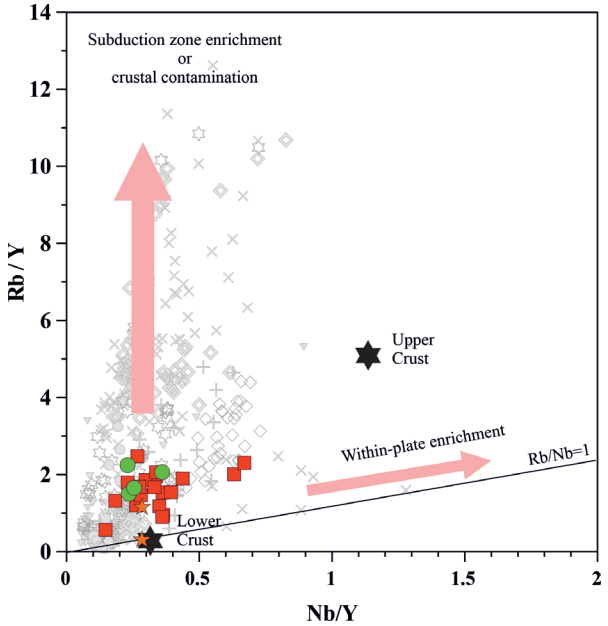

Figure 12. Nb/Y versus Rb/Y plots of the Narman Volcanites (diagram are taken from Pearce et al., 1990; compositions of the upper and lower crusts after Taylor and McLennan, 1985) (symbols are as in Figure 4). Data sources for comparison of other Eocene volcanic rocks are as in Figure 7d.

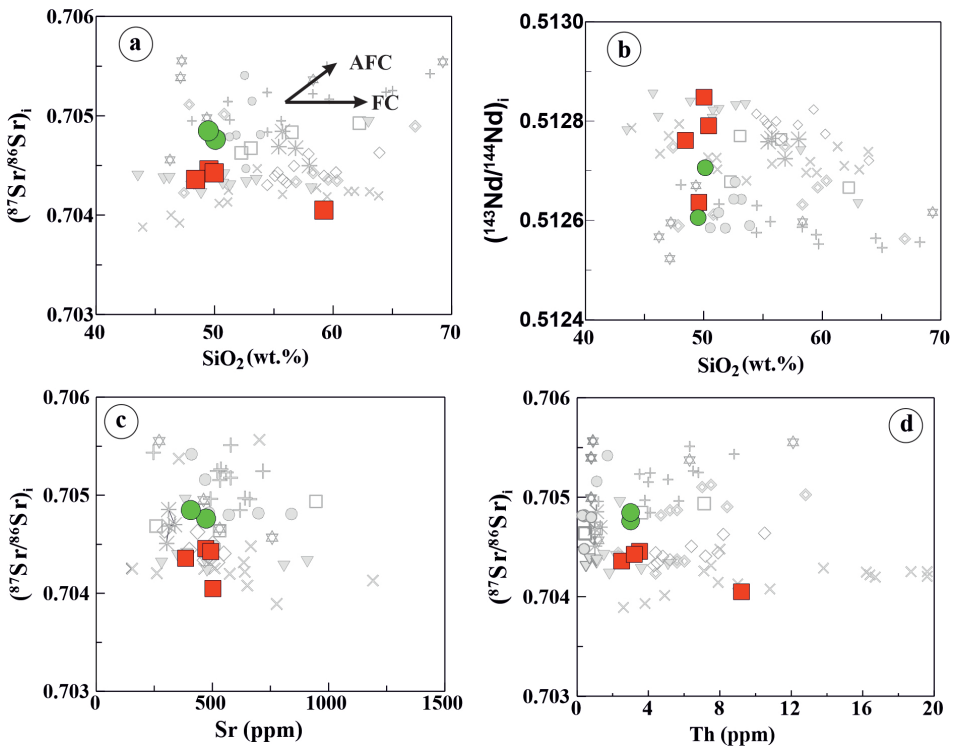

Figure 13. (a) SiO_2 versus $(^{87}Sr/^{86}Sr)_i$, (b) SiO_2 versus $(^{143}Nd/^{144}Nd)_i$, (c) Sr versus $(^{87}Sr/^{86}Sr)_i$, and (d) Th versus $(^{87}Sr/^{86}Sr)_i$ plots showing possible fractional crystallization (FC) and/or assimilation-fractional crystallization (AFC) trends for the Narman volcanic rocks (symbols are as in Figure 4). Data sources for comparison of other Eocene volcanic rocks are as in Figure 7d.

while positive or negative trends indicate AFC. During the formation of the basaltic dyke and basaltic lava rocks comprising the Narman volcanic rocks, AFC can be generally said to play a more effective role.

5.3. Source nature

The trace element variation diagrams for the Narman volcanic rocks have features of typical subduction zone volcanic rocks with depletion of HFSE elements such as Nb, Zr, and Ta, enrichment of LILE such as Sr, K, Rb, and Ba, and high Ba/La ratios (Figures 8a–8d; Ewart, 1982; Pearce, 1983).

As is known, enrichment in HFSE compared to LILE, enrichment in HREE compared to LREE and negative Nb, Ta, Zr, Hf, and Ti anomalies are characteristic of subduction-related continental arc magmas (McCulloch and Gamble, 1991; Thirlwall et al., 1994; Kelemen et al., 2003). Contrarily, the presence of positive Nb, Ta, and Ti anomalies (Figures 9a–9d) differentiates ocean island basalts (OIB) from subduction zone arc volcanics (Hofmann, 1997). Enrichments in LILE and LREE (Figures 9a–9h) show that the main magma was derived from a source region (probably lithospheric mantle) enriched by fluids emerging from subducting oceanic lithosphere and/or sediments on the subducting lithosphere (metasomatism) (Cameron et al., 2003; Münker et al., 2004). On the Sr/Th versus $^{87}Sr/^{86}Sr$ diagram (Figure 14a), high Sr/Th ratio indicates fluid phases. The Sr isotope ratio varies depending on whether there is interaction with altered basaltic crust (≥0.704; Bickle and Teagle, 1992; Staudigel et al., 1995) with fluids or with subducting sediments (>0.709).

Hawkesworth et al. (1997) stated that rocks with high Sr/Th ratio and low $^{87}Sr/^{86}Sr$ (approximately 0.704) value develop in several volcanic arcs based on the correlation of $^{87}Sr/^{86}Sr$ versus Sr/Th. Based on this, low $^{87}Sr/^{86}Sr$ value was proposed to support fluid composition while high $^{87}Sr/^{86}Sr$ value was proposed to support sediment composition. The $^{87}Sr/^{86}Sr$ versus Sr/Th diagram for rocks in depleted and enriched arcs have a trend with hyperbolic shape (Figure 14a). The Narman volcanic rocks are like rocks forming in depleted arcs with low Sr/Th (<200) ratio and low $^{87}Sr/^{86}Sr$ (<0.705) value (Macdonald et al., 2000). Again, the Ba/La versus Th/Yb diagram is used to show fluid or sediment input in subduction zones (Figure 14b). The vertical trend on the diagram indicates mantle enriched by metasomatism with subducting fluids, while the horizontal trend indicates mantle source enriched by metasomatism related to subducting sediments. The basaltic dyke, basaltic lava, and basaltic volcanic breccia samples from the Narman Volcanics display enrichment trends associated with fluids (Figure 14b). The Ta/Yb versus Th/Yb diagram (Figure 14c) provides the opportunity to interpret whether variations in source composition and crustal contamination were effective in evolution of magma or not. The vertical trend toward higher Th/Yb ratios on this diagram (Figure 14c) shows the effect of subduction-derived fluids and/or melts, while high Th/Yb and parallel or subparallel trends to the mantle series show FC and AFC. As seen on this diagram, fractionation in addition to crustal assimilation appears to be effective on the evolution of the Eocene volcanic rocks.

According to Smith et al. (1999), the lithospheric mantle is more depleted in LREE compared to HFSE (such as Nb and Ta). The high Nb/La ratio (approximately >1) for basaltic magma shows an asthenospheric mantle source, while a low ratio (approximately >0.5) shows a lithospheric mantle source. The most basic samples from the Narman volcanic rocks had Nb/La ratio from 0.29 to 0.70, while the La/Yb ratio ranged from 4.26 to 17.14, and these values indicate lithospheric mantle source (Figure 14d).

Petrological models based on trace element content may be used to determine source mineralogy, scope, depth, and degree of partial melt. Shaw (1970) proposed a model to determine the mineralogic and geochemical composition of the source area and partial melt conditions for magmas. The almost flat HREE patterns for the studied volcanic rock samples indicate mantle mineralogy containing spinel, probably shallower than 85 km (McKenzie and O'Nions, 1991; Klemme, 2004). Mantle mineralogy containing garnet, indicating a deeper source generally, produces melts with higher Dy/Yb_N ratios (>2.5, Yang et al., 2012), while a source containing spinel has lower Dy/Yb_N ratios (<1.5). The Dy/Yb ratios for basaltic dyke, basaltic lava, and basaltic volcanic breccia samples from the Narman volcanic rocks vary from 1.15 to 1.30, 1.22 to 2.27, and 1.08 to 1.47, respectively. To estimate the source mineralogy and degree of partial melting, La/Yb_N versus Dy/Yb_N and Th versus $(Tb/Yb)_N$ are used (Figures 14e and 14f). The Dy/Yb_N ratios of the studied rocks are similar to other Eocene volcanic rocks in the EPOB, indicating that mostly melting of spinel peridotite (approximately 1-3 partial melt) could produce the melts for the Narman volcanic rocks.

5.4. Geodynamic implications

Tertiary volcanic rocks in the Eastern Pontides have been investigated by several researchers and much data was obtained about the evolution of Tertiary volcanism because of these investigations. This study for the Eocene volcanic rocks from the Narman area was compared with other studies of volcanics outcropping in the Eastern Pontides to collate information about the evolution of Tertiary volcanism in the region. Middle Eocene volcanic and sedimentary units commonly outcrop in the Central Pontides in Hamamözü (Amasya), Almus (Tokat) and Yıldızeli (Sivas) and in the Eastern Pontides in Artvin and

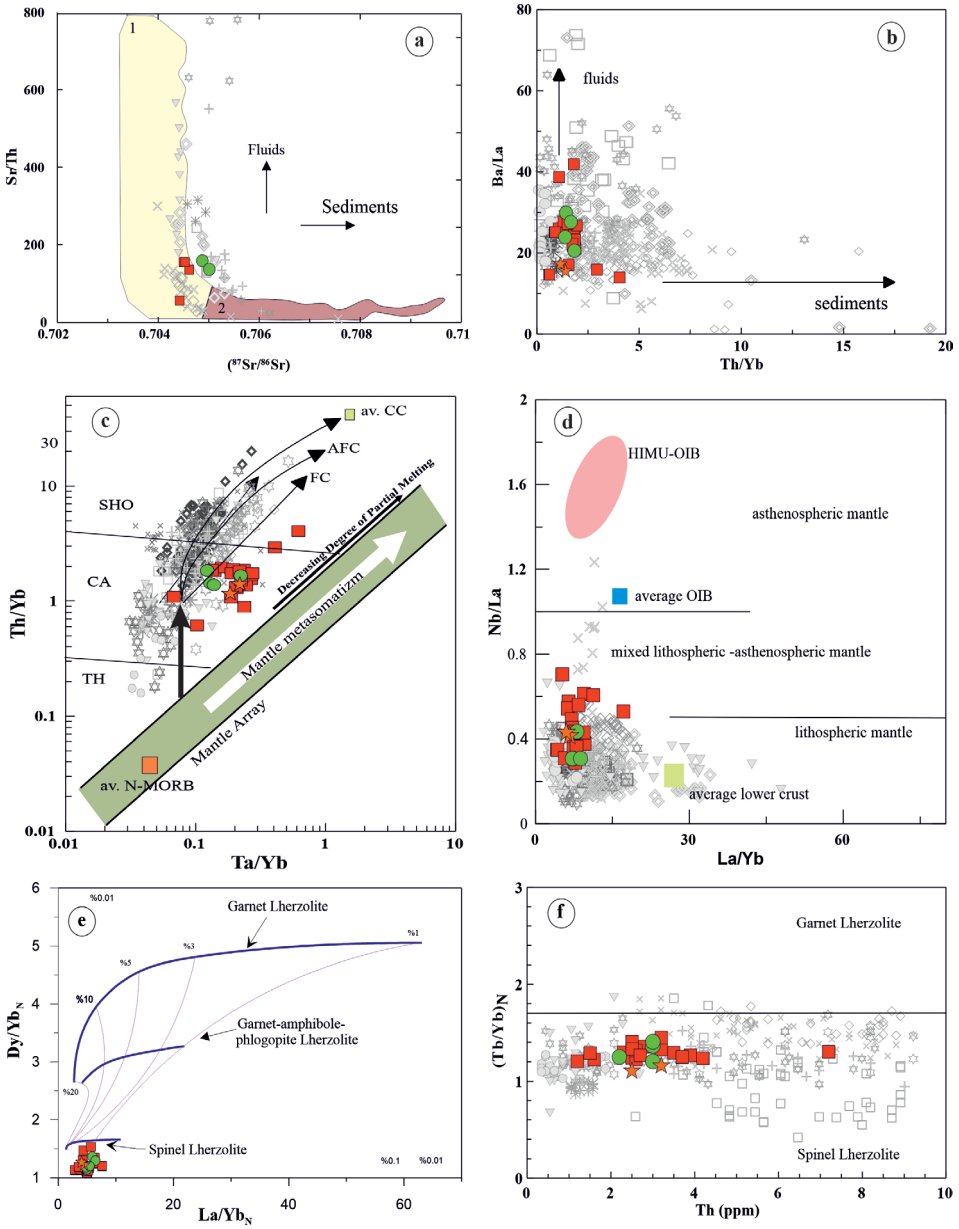

Figure 14. (a) $^{87}Sr/^{86}Sr$ versus Sr/Th variations in Narman volcanic rocks. Fields 1 and 2 enclose data from arcs considered incompatible element depleted and enriched, respectively, by Hawkesworth et al. (1997). The arrows show the sense of enrichment predicted from addition of fluid and sedimentary components to the mantle wedge, (b) Th/Yb versus Ba/La diagram (Woodhead et al., 2001), (c) Th/Yb versus Ta/Yb diagram (after Pearce et al., 1990) for the Narman Volcanics. Average N-MORB composition and average CC (Continental Crust) are from Sun and McDonough (1989) and Taylor and McLennan (1985), respectively. Vectors showing inferred effects of fractional crystallization (FC), assimilation-fractional crystallization (AFC), subduction enrichment and mantle metasomatism are from Pearce et al. (1990), (d) La/Yb versus Nb/La diagrams for Narman Volcanics. Dashed lines separating fields of the asthenospheric, lithospheric and mixed mantle are plotted based on data given in Smith et al. (1999), the HIMU-OIB area is reported in Weaver et al. (1987), (e) Dy/Yb_N versus La/Yb_N nonmodal batch melting curves were calculated by using partition coefficients from Rollinson (1993), McKenzie and O'Nions (1991) and Keskin (2002), (f) Th (ppm) versus Tb_N/Yb_N horizontal line separates fields expected for melting garnet– and spinel–lherzolite as determined for Basin and Range basalts (Wang et al., 2002), (symbols are as in Figure 4). Data sources for comparison of other Eocene volcanic rocks are as in Figure 7d.

Narman (Erzurum) (Keskin et al., 2008; Arslan et al., 2013; Yücel et al., 2017; Göçmengil et al., 2018, 2022; Aydınçakır et al., 2022). Considering detailed geochronological and geochemical studies, the geodynamic evolution of the Eastern Pontides was considered a paleo-arc environment by numerous authors. Though much data has been produced using modern analytical techniques in recent years, debates related to the geodynamic evolution of the region continue and a final model has still not been developed. Though debates focus on studies related more to subduction polarity, timing of collision and postcollisional events, the following geodynamic models were proposed; (1) slab breakoff model (Altunkaynak, 2007; Keskin et al., 2008; Dokuz et al., 2019), (2) delamination model in a north-dipping subduction system (Dilek et al., 2010; Arslan et al., 2013; Temizel et al., 2012, 2016; Aydınçakır and Şen, 2013; Kaygusuz et al., 2020, 2022; Aydınçakır et al., 2022), and (3) ridge subduction model in a south-dipping subduction system (Eyuboglu et al., 2011, 2016). Despite contrasting beliefs about the geodynamic evolution of the Eastern Pontides, most researchers have reached consensus that the region evolved through consecutive crustal thickening and collisional processes with an initial north-dipping subduction zone (Şengör and Yilmaz, 1981; Yilmaz et al., 1997; Okay and Sahinturk, 1997; Boztuğ et al., 2004). Though the slab breakoff model was proposed as an applicable model to explain the narrow Middle Eocene volcanism along the İzmir–Ankara–Erzincan Suture Zone (İAESZ) in the Central Pontides, the applicability of the lithospheric delamination model is accepted to explain the common Middle Eocene volcanism in the north of the Eastern Pontides. Additionally, the Eastern Pontides were affected by postcollisional extensional collapse with delamination. During the middle Eocene, widespread magmatism developed along the entire range of the İAESZ, from the western to eastern parts of Türkiye (Yilmaz et al., 1997; Keskin et al., 2008). The Eastern Pontides was associated with slab breakoff with adakitic dominant magmatism on very localized scales in the Early Eocene (57–47 My; Karsli et al., 2011; Dokuz et al., 2013). Middle Eocene volcanic units are more common compared to Early Eocene magmatic units. Additionally, a geodynamic tectonomagmatic event on lithospheric scale (delamination and/or lithospheric removal) appears to be much more reasonable than a local tectonomagmatic event (slab breakoff) due to the distribution of similar units in different sections of the Central and Eastern Pontides (Keskin et al., 2008; Arslan et al., 2013; Göçmengil et al., 2018; Aydınçakır et al., 2022). The lack of high-pressure metamorphism along the crustal blocks in the south section and surroundings of the Pontides during the Eocene means that the probability of subduction-related magmatism is not possible for the investigated units. Mixing of mantle previously metasomatized by subduction-related solutions and lower continental crust source magmas caused the Middle Eocene magmatism (Yilmaz and Boztug, 1996). The geodynamic evolution of Middle Eocene magmatism along the Eastern Pontides is best explained by the delamination model, as supported by the data obtained during this research. The formation of partial melts for Middle Eocene magmatism in the Eastern Pontides may be explained by geothermal perturbation subsequent to asthenospheric elevation linked to fragmented and asymmetrical delamination (Arslan et al., 2013, 2022; Temizel et al., 2016; Yücel et al., 2017). The E-W, NE-SW, and NW-SE strike-slip movements controlling the neotectonic evolution of the Eastern Pontides contributed to the block-fault architecture of the region and formed important extensional tectonic structures in the region (Bektaş and Çapkınoğlu, 1997; Maden et al., 2009; Öztürk and Kaya, 2019). Extensional tectonics probably assisted in reducing pressure in uppercrust magma chambers. Extension related to lithospheric delamination controlling regional strike-slip movements in the postcollisional environment caused asthenospheric upwelling. Similar extensional tectonics may trigger delamination and lithospheric uplift processes in several regions around the world (Ducea et al., 2013). Decompression and sudden disruption at uppercrustal levels probably reactivated partially melted magma and caused the development of fractional crystallization along with some crustal assimilation (AFC) processes in the region. The whole-rock geochemistry and isotopic characteristics of volcanic rocks in the Narman region show that the magma source for these rocks formed in a postcollisional extensional geodynamic environment because of partial melting of lithospheric mantle previously metasomatized by fluids with subduction composition.

6. Conclusion

(1) The Narman volcanic rocks are divided into basic dyke, basaltic lava, and basaltic volcanic breccia facies. The volcanic rocks contain plagioclase (An_{34-80}), clinopyroxene ($Wo_{38-47}En_{41-50}Fs_{5-18}$), and olivine ($Fo_{68-90}$) phenocrystals with magnetite/titanomagnetite.

(2) ^{40}Ar-^{39}Ar plateau ages range from 44.5 ± 0.1 Ma to 43.4 ± 0.1 Ma for the studied volcanic rock samples and the period of the postcollisional extensional regime in the EPOB.

(3) Positive and negative correlations observed on variation diagrams show that fractional crystallization was very effective during the evolution of the rocks. Harker diagrams show clinopyroxene + plagioclase + olivine ± magnetite fractionation played important roles in the development of the rocks.

(4) The plotting of Sr-Nd-Pb-Hf isotope values from all samples close to the mantle interval indicates the Narman volcanic rocks derived from an isotopically depleted mantle source.
(5) Considering the petrographic, geochemical and petrological features and isotopic data for volcanic rocks from the Narman region, an attempt was made to model magmatic processes during the evolution of the volcanic rocks. The modeling results indicate with high probability that the magma is derived from the partial melting of a mantle source that experienced metasomatism by subduction fluids (enriched) and later evolved through magmatic events such as fractionation ± assimilation in shallow magma chambers within the continental crust.

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Supplementary information
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