Subduction-related Late Cretaceous high-K volcanism in the Central Pontides orogenic belt: constraints on geodynamic implications

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Mineral chemistry, major and trace elements, $^{40}$Ar/$^{39}$Ar age and Sr–Nd–Pb isotopic data are presented for the Late Cretaceous Hamsilos volcanic rocks in the Central Pontides, Turkey. The Hamsilos volcanic rocks mainly consist of basalt, andesite and associated pyroclastics (volcanic breccia, vitroic tuff and crystal tuff). They display shoshonitic and high-K calc-alkaline affinities. The shoshonitic rocks contain plagioclase, clinopyroxene, alkali feldspar, phlogopite, analcime, sanidine, olivine, apatite and titanomagnetite, whereas the high-K calc-alkaline rocks contain plagioclase, clinopyroxene, orthopyroxene, magnetite/titanomagnetite in microgranular porphyritic, hyalo-microlitic porphyritic and glomeroporphyritic matrix. Mineral chemistry data reveal that the pressure condition of the clinopyroxene crystallisation for the shoshonitic rocks are between 1.4 and 6.3 kbar corresponds to 6–18-km depth and the high-K calc-alkaline rocks are between 5 and 12 km. $^{40}$Ar/$^{39}$Ar age data changing between 72 ± 5 Ma and 79.0 ± 3 Ma (Campanian) were determined for the Late Cretaceous Hamsilos volcanic rocks, contemporaneous with the subduction of the Neo-Tethyan Ocean beneath the Pontides. The studied volcanic rocks were enriched in the large-ion lithophile and light rare earth element contents, with pronounced depletion in the contents of high-field-strength elements. Chondrite-normalised rare earth element patterns ($\text{La}^\ast/\text{Lu}^\ast = 6–17$) show low to medium enrichment, indicating similar sources of the rock suite. Initial $\text{Sr}^{87/86}$Sr values vary between .70615 and .70796, whereas initial $\text{Nd}^{143/144}$Nd values change between .51228 and .51249. Initial $\text{Pb}^{206/204}$Pb values vary between 18.001 and 18.349, $\text{Pb}^{207/204}$Pb values between 15.611 and 15.629 and $\text{Pb}^{208/204}$Pb values between 37.839 and 38.427. The main solidification processes involved in the evolution of the volcanic rocks consist of fractional crystallisation, with minor amounts of crustal contamination ± magma mixing. According to geochemical evidence, the shoshonitic melts in the Hamsilos volcanic rocks were possibly derived from the low degree of partial melting of a subcontinental lithospheric mantle (SCLM), while the high-K calc-alkaline melts were derived from relatively high degree of partial melting of SCLM that was enriched by fluids and/or sediments from a subduction of oceanic crust.

Keywords: $^{40}$Ar/$^{39}$Ar ages; Sr–Nd–Pb isotopes; Hamsilos; subduction; Turkey

1. Introduction

The Pontides orogenic belt, a prominent part of the Alpine–Himalayan Orogen, is a typical place to understand the nature of subduction-related magmatism. Previous studies provided certain geochronological and geochemical constraints on the origin and evolution of Late Cretaceous magmatism. The geochemical nature of the great majority of Late Cretaceous magmatism is of calc-alkaline (Aydin, 2014; Erkan & Gedik, 1983; Karsli et al., 2010; Kaygusuz & Aydınçakır, 2009, 2011; Tokel, 1983). However, rare volcanic and plutonic bodies, such as those in this study, attained high-K to shoshonitic composition (Altherr et al., 2008; Asan, Kurt, Francis, & Morgan, 2014; Bektas & Gedik, 1988; Eyüboğlu, 2010; Genç et al., 2014; Gülmez & Genc, 2015; Karsli et al., 2012; Varol, 2013). According to a widely accepted tectonic model (Aydınçakır, 2014; Dokuz et al., 2013; Karsli, Uysal, Dilek, Aydin, & Kandemir, 2013; Okay & Şahintürk, 1997; Okay & Tüysüz, 1999; Şengör & Yilmaz, 1981; Ustaomer & Robertson, 2010), the Late Cretaceous magmatism is associated with the northward subduction of the northern branch of the Neo-Tethys Ocean beneath the southern margin of the Eurasian Plate during the late Cretaceous to Paleocene (Figure 1(a)).

The subduction polarity and geotectonic evolution of the eastern Pontides are controversial during the Cretaceous. Several researchers suggested that the eastern Pontides was a magmatic arc that occurred as a result of northward subduction of the Neo-Tethys along the southern border of the Sakarya Zone (Altherr et al., 2008; Karsli et al., 2010; Okay & Şahintürk, 1997; Şengör, Özener, Genç, & Zor, 2003; Ustaomer & Robertson, 2010). Conversely, Dewey, Pitman, Ryan, and Bonn (1973), Bektas, Şen, Atici, and Körprübaş (1999), Eyüboğlu, Chung, Santosh, Dudas, and Akaryali (2011), and Eyüboğlu, Santosh, Dudas, Chung, and Akaryali (2011) proposed a southward subduction that continued uninterrupted from the Paleozoic period until the end of the Eocene period.

The petrogenesis and tectonic setting of high-K to shoshonitic volcanic rocks from the Eastern Pontides remain controversial (Altherr et al., 2008; Asan et al., 2014; Bektas & Gedik, 1988; Eyüboğlu, 2010; Genç et al., 2014; Gülmez & Genc, 2015). Genç et al. (2014)
offered that ultrapotassic rocks were possibly derived from the low degree partial melting of veined subcontinental lithospheric mantle (SCLM) that occurred as a result of northward subduction of the Neotethys. Altherr et al. (2008) proposed that ultrapotassic rocks and their orogenic nature indicate that during the last stages of the closure of the northern branch of Neotethys. Conversely, Eyüboğlu (2010) suggested that these rocks were derived from enriched mantle sources that are related to southward subduction of the Neotethys.

Such high-K composition of rocks can be produced from crust and mantle rocks through various petrogenetic processes, such as (i) partial melting of basaltic rocks at the lower crust (Sisson, Ratajeski, Hankins, & Glazner, 2005), (ii) fractional crystallisation and crustal contamination (assimilation-fractional crystallisation [AFC]) of mantle-derived basaltic magmas (Chen, Hegner, & Todt, 2000) and (iii) mixing of mantle and crustal magmas (Griffin et al., 2002) in various tectonic settings, such as volcanic island arc, active continental margin and post-collision (Barbarin, 2005).

However, there has been much less work on the classification and geochemistry of the Upper Cretaceous high-K volcanic rocks exposed in the central and southern part of the Pontides. Bektas and Gedik (1988) first recognised leucite-bearing volcanic rocks (Everekhanları Formation, Bayburt) in southern part of the eastern Pontides. Eyüboğlu (2010) suggested that trachyan-desites- and analcime-bearing volcanics were derived from similar enriched mantle sources, and that they

![Figure 1. (a) Regional tectonic setting of Turkey with main tectonic units in relation to the Afro-Arabian and Eurasian plates (modified from Okay & Tüysüz, 1999). (b) Simplified geological map of the Sinop area showing the Late Cretaceous Hamsilos volcanic rocks with sample locations (modified after Baş, 1986; Gedik & Korkmaz, 1984).](image-url)
formed in the same geotectonic setting of a back-arc basin environment of the eastern Pontides magmatic arc during the Late Cretaceous. Similar shoshonitic and ultrapotassic volcanism are reported from Gümüşhacıköy near Amasya and Ankara (Çapan, 1984; Eyüboğlu, 2010; Varol, 2013). Apart from these locations, there are also Hamsilos volcanics containing analcime-bearing rocks around Sinop to the north (e.g. Baş, 1986). Asan et al. (2014) stated that Hamsilos volcanics display high-K calc-alkaline, shoshonitic and ultra-K affinities. Otherwise, the shoshonitic and ultra-K were derived from metasomatic veins related to melting of recycled subducted sediments, but the high-K calc-alkaline rocks formed by the tectonic opening of the Black Sea basin in the Early Cretaceous Period (Tüysüz, 1999) and were formed by the tectonic mixing of the Cimmerian and Eurasian continental remnants with PaleoTethys Ocean remnants (Yılmaz, Tüysüz, Yiğitbaş, Genç, & Şengör, 1997). The Istanbul Zone is dominated by passive margin type Ordovician–Carboniferous-sedimentary successions, which were unconformably covered by Triassic and younger units (Görür, et al. 1997). On the contrary, the Sakarya Zone was formed by Permo–Triassic subduction–accretion complexes and unconformably covered by Triassic and younger sediments (Genç & Yılmaz, 1995; Goncuoğlu, Turhan, & Tekin, 2003; Okay & Tüysüz, 1999; Tekeli, 1981).

Hamsilos volcanic, main topic of this study, cover a large area in the Sinop Peninsula (the shoshonitic rocks), and İnceburun Peninsula (high-K calc-alkaline rocks) (Asan et al., 2014; Aydınçakır & Şen, 2011; Baş, 1986). There is no physical contact and systematic change between high-K calc-alkaline and shoshonitic rocks. These volcanics mainly consist of basaltic lava flows, basalt dikes, brecciated volcanioclastics, agglomerates and tuffs (Figure 2). Basalt dikes and lavas are dominant in İnceburun Peninsula (Figure 2(a) and (b)). Fresh surfaces are characteristically dark and grey coloured basalt lavas (Figure 2(a) and (b)). Agglomerates, brecciated volcanioclastics and tuffs prevail on the Sinop Peninsula (Figure 2(c) and (d)). Tuffs are minor constituents of the sequence. Breccias are characterised by reddish and grey colour with fragments 5–35 cm in diameter and varying angular to rounded shape (Figure 2(c)). Euhedral to subhedral pyroxene and mica minerals are easily seen in basaltic lavas (Figure 2(d)). Cavities in the basaltic lavas have been generally filled by secondary calcite and zeolites. Hamsilos volcanites are covered by Sinop Formation, which is formed from the sandstone, claystone and marl alternation of the Miocene period. The Sarkum Formation and the alluvium are the younger sedimentary successions of the region.

3. Analytical methods

3.1 Whole-rock geochemical analyses

Based on the petrographical studies, 20 of the freshest and most representative rock samples from the volcanics were selected for major and trace element analyses (Table 5). To prepare the rock powders, .5–1 kg of the fresh samples was crushed in a steel jaw crusher, and then the samples were powdered in an agate mill to

2. Regional geology and geological setting

The northern part of Turkey comprises three main tectonic zones, namely Istranca, İstanbul and Sakarya, which are collectively known as Pontides (Figure 1(a); Şengör & Yilmaz, 1981; Okay & Tüysüz, 1999). The Pontides belt, which extends between the Lesser Caucasus in the east and the Balkans in the west, is divided into three regions because of the different tectonic units they include: ‘western Pontides’, ‘Central Pontides’ and ‘eastern Pontides’. The Sakarya Zone, which extends from the Biga Peninsula to eastern Pontides and peripheral pyroclastic deposits are also encountered during the Eocene and younger units lie in the north; it also contains Black Sea marginal basin deposits (Cretaceous–Eocene volcano-sedimentary sequences) bordered by the Black Sea in the farther north (Okay et al., 2006; Tüysüz, 1990; Ustaömer & Robertson, 1993; Yılmaz & Şengör, 1985; Figure 1(b)). These zones started to exist alongside each other together with the tectonic opening of the Black Sea basin in the Early Cretaceous Period (Tüysüz, 1999) and were formed by the tectonic mixing of the Cimmerian and Eurasian continental remnants with PaleoTethys Ocean remnants (Yılmaz, Tüysüz, Yiğitbaş, Genç, & Şengör, 1997). The Istanbul Zone is dominated by passive margin type Ordovician–Carboniferous-sedimentary successions, which were unconformably covered by Triassic and younger units (Görür, et al. 1997). On the contrary, the Sakarya Zone was formed by Permo–Triassic subduction–accretion complexes and unconformably covered by Triassic and younger sediments (Genç & Yılmaz, 1995; Goncuoğlu, Turhan, & Tekin, 2003; Okay & Tüysüz, 1999; Tekeli, 1981).

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obtain grain sizes of <200 mesh. The major and trace element compositions were measured by ICP-AES at the commercial ACME Analytical Laboratories Ltd, in Vancouver, Canada after .2 g samples of rock powder were fused with 1.5 g LiBO₂ and then dissolved via four-acid digestion steps. The loss on ignition (LOI) was determined by the weight difference after ignition at 1000 °C. The total iron concentration was expressed as Fe₂O₃. The detection limits are in the range of \(0.001 \text{–} 0.1\) wt% for major element oxides, \(0.1 \text{–} 10\) ppm for trace elements and \(0.01 \text{–} 1.5\) ppm for rare earth element (REE). Calibration and verification standards together with reagent blanks were added to the sample sequence. STD SO 18 was certified in-house against 38 certified reference material including CANMET SY-4 and USGS AGV-1, G-2, GSP-2 and W-2 as known external standards. The analytical accuracy is better than 4%.

### 3.2 Microchemical analyses

Electron microprobe analyses on polished thin sections were carried out at the New Mexico Institute of Mining and Technology, Socorro, NM, USA, using a Cameca SX-100 electron microprobe with three wavelength-dispersive spectrometers. Samples were examined using backscattered electron imagery, and selected minerals were quantitatively analysed. Elements analysed included F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Sr and Ba. An accelerating voltage of 15 kV and probe current of 20 nA were used, except for analyses using general glass labels (i.e. chlorite), which utilised a 10 nA probe current. Peak count numbers of 20 s were used for all elements, except for F (40 s; amphibole), F (60 s; glass), Cl (40 s), S (30 s), Sr (60 s) and Ba (60 s). Background count numbers were one-half the peak count times. A point beam of 1 µm was used to analyse amphibole, pyroxene, epidote, Fe–Ti oxide and zircon. A slightly defocused (10 µm) beam was used to analyse feldspar, mica and chlorite to avoid losses caused by sodium volatilisation (Nielsen & Sigurdsson, 1981). Analytical results are presented in Supplementary Table 1.

### 3.3 Radiogenic isotope analyses

Isotopic analyses of Sr, Nd and Pb were performed at the Department of Geological Sciences, New Mexico...
State University. All isotopic measurements were made by TIMS, on a VG Sector 30 mass spectrometer. All samples analysed were loaded onto rhenium filaments on either Cathodion beads (single filament only) or on the side filament of a triple filament assembly. Reproducibility of the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{143}\text{Sm}/^{144}\text{Nd}$ ratios is within .3%, and the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are within ±0.00025 and ±0.0003, respectively. An analysis of the NBS 987 standard yielded values of .710226 (11), .710213 (13), .710219 (10) and .710260 (11). Pb samples were analysed using the middle filament position of a Cathodion bead assembly. Samples were loaded using 5% HNO₃ in a matrix 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 analysed using the same procedures. The mean of standard runs was $^{206}\text{Pb}/^{204}\text{Pb} = 16.844$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.739$ and $^{208}\text{Pb}/^{204}\text{Pb} = 36.199$. Deviations of the standards are within ±.2%. The detailed analytical procedures for Sr, Nd and Pb isotopic measurements are provided by Ramos (1992).

3.4 $^{40}\text{Ar}^{39}\text{Ar}$ analyses

$^{40}\text{Ar}^{39}\text{Ar}$ incremental heating experiments were carried out in New Mexico Geochronology Research Laboratory at the New Mexico Tech University, USA. Whole rock reacted with dilute HCl followed by DI water rinse in an ultrasound. Fragments picked were free of phenocrysts. Hornblende separated by standard magmatic, heavy liquid and picking techniques. Samples were loaded onto rhenium filaments on either Cathodion beads (single filament only) or on the side filament of a triple filament assembly. Reproducibility of the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{143}\text{Sm}/^{144}\text{Nd}$ ratios is within .3%, and the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are within ±0.00025 and ±0.0003, respectively. An analysis of the NBS 987 standard yielded values of .710226 (11), .710213 (13), .710219 (10) and .710260 (11). Pb samples were analysed using the middle filament position of a Cathodion bead assembly. Samples were loaded using 5% HNO₃ in a matrix 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 analysed using the same procedures. The mean of standard runs was $^{206}\text{Pb}/^{204}\text{Pb} = 16.844$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.739$ and $^{208}\text{Pb}/^{204}\text{Pb} = 36.199$. Deviations of the standards are within ±.2%. The detailed analytical procedures for Sr, Nd and Pb isotopic measurements are provided by Ramos (1992).

4. Results

4.1 Petrography

The modal mineralogy and common textural features of Late Cretaceous Hamilos volcanic rocks are summarised in Table 1. The high-K calc-alkaline rocks are observed on the western side of the Inceburun Peninsula; whereas, the shoshonitic rocks crop out around the Sinop Peninsula (Figure 1). In the light of volcanic stratigraphy, the high-K calc-alkaline rocks are represented by basaltic lavas and dikes. The shoshonitic rocks are represented by volcanioclastic (breccias and tuffs) and lavas (pillow lavas and basaltic lavas). Basaltic lavas are dark grey and are generally observed as lava flows in limited areas. Around the Sinop Peninsula, brecciated volcanioclastics are interbedded with shoshonitic basalts form the basement. Basaltic lavas also contain visible pyroxene and brown mica crystals.

Petrographically, the high-K calc-alkaline volcanic rocks are composed of clinopyroxene, orthopyroxene, plagioclase and opaque minerals and display hyalomicroitic porphyritic and glomeroporphyritic textures (Figure 3(a)–(f)). They include olivine and apatite as accessory phases. Plagioclase phenocrysts are generally euhedral and show normal zoning, albite twinning, sieved texture and overgrowth rim (Figure 3(b)–(d) and (f)). Some of these plagioclases contain clinopyroxene inclusions (Figure 3(f)). Euhedral or subhedral clinopyroxene phenocrysts show twinning, as well as resorbed rims and embayments (Figure 3(a), (d), and (e)). They also contain opaque mineral inclusions.

The shoshonitic volcanic rocks display microlitic porphyritic, glomeroporphyritic, microgranular and vesicular textures (Figure 3(a)–(f)), and comprise clinopyroxene + plagioclase + phlogopite + analcite + sanidine ± oliv ine ± Fe-Ti oxide ± apatite. Clinopyroxene phenocrysts, including inclusions of opaque minerals and apatite, are euhedral and characterised by oscillatory zoning (Figure 4(a), (b) and (f)). Plagioclase phenocrysts are generally euhedral and show albite twinning. Some of the microlites are sanidine (Figures 4(c) and 3(d)). Phlogopites are observed as euhedral to anhedral crystals with inclusions of Fe-Ti oxide and rarely have resorbed rims and embayments (Figure 4(d) and (e)). Alkalines are mostly observed in groundmass. However, rare alkaline (possibly derived from leucite) phenocrysts are rounded and six-sided (Figure 4(a) and (b)). Olivines are generally euhedral and iddingsitized along rims and cracks (Figure 4(a)). Apatites are abundant as subhedral crystals (Figure 4(f)). Zeolite, calcite and chlorite are common secondary minerals.

4.2 Mineral chemistry

4.2.1 Clinopyroxene

The mineral compositions of the Hamilos volcanic rocks are listed in Supplementary Table 1. The clinopyroxenes observing as normally and reversely zoned
crystals from the shoshonitic volcanic rocks are classified (Morimoto, 1988) as augite and diopside with Wo42–49En37–49Fs4–17 and Mg number (Mg#) ranging from .69 to .92 (Figure 5(a), supplementary Table 1). Clinopyroxene is augite (Wo41–44En42–46Fs11–17) in composition with Mg# ranging from .71 to .81 and orthopyroxenes are clinoenstatite (Wo3–5En65–67Fs42–31) in compositions with Mg# varying from .67 to .70 from the high-K calc-alkaline volcanic rocks (Figure 5(a)).

The normally zoned clinopyroxenes are characterised by core composition with Mg-number varying from .71 to .92 in the shoshonitic, and .72–.81 in the high-K calc-alkaline rocks. The rim compositions range from .69 to .75 in the shoshonitic and .71 in the high-K calc-alkaline rocks, respectively. The reversely zoned clinopyroxenes have Mg-number in the core .71 for the shoshonitic and .71 for the high-K calc-alkaline rocks, and in the rim .73 for the shoshonitic and .81 for the high-K calc-alkaline rocks. Orthopyroxenes do not show zoning in the high-K calc-alkaline volcanic rocks.

### 4.2.2 Feldspar

Plagioclase phenocrysts in Hamsilos shoshonitic volcanic rocks comprise broad compositions ranging from andesine to bytownite (An48–84). K-feldspar phenocrysts are sanidine (Or40–98).

Microlites in groundmass appear as labradorite to bytownite (An40–84) and sanidine (Or48–98) (Figure 5(b)). While the core compositions of normally zoned plagioclases are An76–81 for the shoshonitic rocks and An76–81 for the high-K calc-alkaline rocks, the rim compositions of these rocks are An56–67 and An65–76 respectively. Plagioclases from the high-K calc-alkaline volcanic rocks are characterised by labradorite and bytownite (An65–86) (Figure 5(b)).

### 4.2.3 Brown mica

The Mg# of brown micas varies from .61 to .66 for the shoshonitic volcanic rocks. Brown micas are classified as the phlogopite (Speer, 1984) (Figure 5(c)).

### 4.2.4 Analcime

Euhedral to subhedral analcimes in the Hamsilos shoshonitic volcanic rocks present high contents of Na2O (10–13 wt%) and low contents of K2O (0–1 wt%).

### 4.2.5 Fe–Ti oxide

Fe–Ti oxides generally possess similar compositions in the Hamsilos shoshonitic volcanic rocks present high contents of Na2O (10–13 wt%) and low contents of K2O (0–1 wt%).

### 4.3 Intensive parameters

#### 4.3.1 Clinopyroxene thermobarometry

The temperature, pressure and crystallisation depth of volcanic rocks can be estimated on the basis of clinopyroxene composition (Nimis, 1995; Nimis & Taylor, 2000; Nimis & Ulmer, 1998) and clinopyroxene-liquid equilibria (Putirka, 2008; Putirka, Johnson, Kinzler, & Longhi, 1996; Putirka, Mikaelian, & Ryerson, 2003). Putirka (2008) re-evaluated many quantitative temperature and pressure estimates on clinopyroxene composition and obtained an equilibrium constant using Fe–Mg...
exchange and \( K_D(\text{Fe}–\text{Mg})^{\text{cpx-liquid}} = 0.28 \pm 0.08 \). The clinopyroxene thermobarometry-yielded temperature ranges from 1133 to 1187 °C for clinopyroxenes from the shoshonitic volcanic rocks and from 1004 to 1174 °C for the high-K calc-alkaline volcanic rocks. The estimated crystallisation pressures of clinopyroxenes range from 1.4 to 6.3 kbar for the shoshonitic volcanic rocks and from 1.5 to 3.6 kbar for the high-K calc-alkaline volcanic rocks. The microphotographs of the Hamsilos high-K calc-alkaline volcanic rocks (a) twinned clinopyroxene phenocryst with embayed in glomeroporphyritic texture, (b) sieve texture and overgrowth rim in plagioclase and anhedral olivine, (c) normal zoning, sieve texture and oscillatory zoned plagioclase phenocryst, (d) and (e) albite twinning, sieved texture and opaque mineral inclusions in zoned clinopyroxene, (f) opaque inclusions in resorbed rim plagioclase, clinopyroxene in microgranular porphyritic texture (cpx: clinopyroxene, pl: plagioclase, ol: olivine, op: Fe–Ti oxide, crossed polarized light).
volcanic rocks. These pressures obtained using clinopyroxene barometer correspond to crystallisation depths of 6–18 and 5–12 km, respectively (Table 2).

4.3.2 Biotite thermobarometry and oxygen fugacity

The empirical equation proposed by Uchida, Endo, and Makino (2007) was used to estimate the crystallisation
pressures for the studied volcanics. The equation was calibrated using the Al\textsuperscript{III} (total aluminum) content in biotite on the basis of 11 oxygens. The calculated mean pressure is 1.41–1.71 kbar (mean = 1.54 ± .10 kbar) for the shoshonitic volcanic rocks (Table 3). The mean crystallisation temperature was calculated using the formula of Luhr, Carmichael, and Varekamp (1984) as range from 724.68 to 993.46 °C (mean = 804.18 ± 90.20 °C), for the shoshonitic volcanic rocks (Table 3). The proposed quantitative estimation of oxygen fugacity by Wones and Eugster (1965) was tested using the biotite temperature (Luhr et al., 1984) and pressure (Uchida et al., 2007) values obtained for the studied rocks. The calculated mean oxygen fugacity condition is between 16.02 and 9.44 (mean = 13.89 ± 2.19) for the shoshonitic volcanic rocks (Table 3).

4.4 \textsuperscript{40}Ar/\textsuperscript{39}Ar dating

The results of Ar–Ar dating are given in Table 4. Age spectras for three biotite separates and a whole-rock sample are shown in Figure 6. Three Hamsilos shoshonitic samples (S-1, S-3, and S-5) yielded \textsuperscript{40}Ar/\textsuperscript{39}Ar plateau ages of 79.0 ± 3, 77.3 ± 4 and 78.2 ± .7 Ma, respectively. A high-K calc-alkaline sample (I-6) yielded a \textsuperscript{40}Ar/\textsuperscript{39}Ar age of 72.3 ± .5 Ma (Figure 6 and Table 4), which corresponds to the Late Cretaceous period (Campanian). Asan et al. (2014) reported that two Hamsilos shoshonitic samples yielded \textsuperscript{40}Ar/\textsuperscript{39}Ar age of 82.08 ± 1.13 and 81.37 ± Ma and a high-K calc-alkaline sample yielded a \textsuperscript{40}Ar/\textsuperscript{39}Ar age of 82.18 ± .41 Ma.

4.5 Whole-rock geochemistry

4.5.1. Effects of the alteration and analcimization

The analytic results showed that the LOI values of the Hamsilos volcanic rock samples vary in the range of 2.8–6.7 wt% for the shoshonitic rocks, and 4.4–1.0 wt% for the high-K calc-alkaline rocks (Table 5). The shoshonitic rocks which have high LOI values are likely related to alterations (chemical or weathering) or analcimization.
of the leucite. Therefore, several geochemical parameters have been used to test the effects of alteration and weathering processes; the Weathering Index of Parker (WIP; Parker, 1970), Chemical Index of Alteration (CIA; Nesbitt & Young, 1982) parameters have been calculated, and rocks having WIP values (70–100) close to 100, with CIA values (33–46) lower than 50 (Table 5), are considered to have been unaffected by weathering and/or alteration processes (Ersoy & Helvacı, 2016; Kasapoğlu et al., 2016). MFW plot of Ohta and Arai (2007) was also used to fresh magmatic rocks follow a ‘magmatic trend’, and all of the Hamsilos volcanic rocks lie along this trend (Figure 7(a)). In case of the data for the Hamsilos volcanic rocks (Asan et al., 2014), only three samples fall off the trend and it has been excluded from following sections.

According to this result, the relatively high LOI value ranges from 2.8 to 6.7 wt% for the shoshonitic rocks is mainly due to the presence of analcime phenocrysts (analcimization). Although the replacement of leucite by analcime is common on potassic rocks in older ages, the origin of these analcimes is matter of debate (Asan et al., 2014; Eyüboğlu, 2010; Varol, 2013; Yücel, Temizel, Abdıoğlu, Arslan, & Yağcıoğlu, 2014) There are two ideas in order to explain whether or not the analcimes primary or secondary: (1) the analcimes in these rocks are primary, but the presence of analcimes as primary occurrences is very limited (e.g. Luhr & Kyser, 1989; Pearce, 1993), (2) transformation of analcimes from pre-existing mineral phases as leucite, nepheline (e.g. Gupta & Fye, 1975; Karlsson & Clayton, 1991; Putnis, Putnis, & Giampaolo, 1994; Moradian, 2008). Moreover, the higher Fe content of analcime (Fe > .025) can be accepted as a distinguishing evidence for primary origin by Luhr and Kyser (1989). The analcimes in shoshonites of Hamsilos volcanic rocks are possibly derived from leucite with a low Fe content of analcimes. The fresh character of host rocks and the absence of hydrous minerals such as amphibole and phlogopite according to Karlsson and Clayton (1991) are supporting the idea of secondary origin of analcimes in shoshonites. Additionally, the primary crystallisation of analcime required the crystallisation other Na-bearing phases as Na-pyroxenes instead of augite and diopside present in shoshonites of Hamsilos volcanic rocks.

### 4.5.2. Major and trace elements

Representative results of geochemical compositions for Hamsilos volcanic rocks are presented in Table 5. SiO2 content varies from 46.64 to 51.51 wt% for shoshonitic rocks and from 53.79 to 54.55 wt% for high-K calc-alkaline rocks. Mg# values range between 48 and 62 (Table 5). Both lava types have contents of Al2O3 (14.77–18.51 wt%), K2O (1.36–5.38 wt%), Na2O (2.50–3.62 wt%), Fe2O3 (7.30–8.66 wt%) and low TiO2 (<1.0 wt%). The relatively high LOI values of the shoshonitic samples (2.8–6.7 wt%) are related to their glassy texture and secondary minerals (zeolite and calcite infillings) as well as the presence of analcime minerals (analcimization) and minor primary hydrous phases, such as phlogopite. Besides, the shoshonitic rocks contain normative nepheline and olivine revealing silica undersaturated compositions (Table 5). The normative nepheline is consistent with modal analcime contents of the shoshonitic rocks.

In the SiO2 vs. Na2O + K2O diagram (TAS) of (Le Bas, Le Maitre, Streckeisen, & Zanettin, 1986), high-K calc-alkaline volcanic rocks fall into the basaltic andesite field, whereas shoshonitic volcanic samples fall into the

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**Table 2.** Termobarometry and temperature calculations from the clinopyroxene chemistry of the Hamsilos volcanic rocks.

| Hamsilos volcanic rocks | K/D(Fe-Mg)\text{max} = .28±.08 | Eqn 32b (kbar) | Eqn 32d (°C) |
|-------------------------|-------------------------------|----------------|---------------|
| Shoshonitic rocks (n = 21) | Core                          | 4.4 ± 1.2      | 1168 ± 18.5   |
| Mean                     | 6.3                           | 1187.2         |                |
| Max                      | 1.4                           | 1133.4         |                |
| High-K calc-alkaline (n = 3) | Eqn 32a (kbar)               | 2.5±1.1        | 113.6 ± 95    |
| Mean                     | 3.6                           | 1004.3         |                |
| Min                      | 1.5                           | 1174.3         |                |

**Table 3.** Biotite temperature, pressure and oxygen fugacity calculations for the studied volcanics.

| Hamsilos volcanic rocks | Shoshonitic rocks | Uchida et al. (2007) | Wones and Eugster (1965) |
|-------------------------|------------------|----------------------|---------------------------|
| (n = 7)                 | °C               | kbar                 | (fo2)                     |
| Mean                    | 804.18 ± 90.20   | 1.54 ± .10           | −13.89 ± 2.19             |
| Max                     | 993.46           | 1.71                 | −9.44                     |
| Min                     | 724.68           | 1.41                 | −16.02                    |
Table 4. $^{39}$Ar/$^{40}$Ar age spectra of four volcanic rock samples (A, B, C: shoshonite, D: high-K basaltic andesite) from the Hamsilos volcanic rock.

| ID     | Power (Watts) | $^{40}$Ar/$^{39}$Ar | $^{37}$Ar/$^{39}$Ar | $^{36}$Ar/$^{39}$Ar ($\times 10^{-3}$) | $^{39}$ArK ($\times 10^{-15}$ mol) | K/Ca | $^{40}$Ar* (%) | $^{39}$Ar (%) | Yaş (Ma) ±1 sigma (Ma) |
|--------|---------------|----------------------|---------------------|----------------------------------------|---------------------------------|------|----------------|----------------|-------------------|
| S-1, biotite, 3.94 mg | 1 | 78.08 | 2.055 | 138.9 | 368 | .25 | 47.6 | 21.7 | .56 |
| | 1.8 | 72.92 | 1.033 | 136.8 | 2.49 | 44.7 | 37 | 78.99 | .62 |
| | 2.3 | 35.95 | 9.976 | 9.924 | 1.81 | .52 | 92.1 | 47.7 | .71 |
| | 2.5 | 36.59 | 1.639 | 14.27 | 1.49 | .31 | 88.8 | 56.5 | .86 |
| | 3 | 36.06 | 3.928 | 13.51 | 1.81 | .13 | 89.8 | 67.2 | .77 |
| | 3.5 | 40.94 | 3.262 | 35.14 | 1.65 | .16 | 75.3 | 70.5 | .74 |
| | 4 | 35.4 | 4.848 | 6.491 | 1.03 | .11 | 95.7 | 72.4 | .83 |
| | 4.5 | 38 | 12.68 | 21.56 | .047 | .04 | 85.9 | 75.1 | .79 |
| | 5 | 36.51 | 8.527 | 14.14 | .025 | .06 | 90.4 | 76.6 | .80 |
| | 6 | 36.79 | 27.81 | 28.56 | .044 | .018 | 83.1 | 79.1 | .76 |
| | 8 | 43.37 | 74.59 | 63 | .139 | .007 | 70.9 | 87.3 | .94 |
| | 21 | 45.36 | 313.3 | 148.9 | .215 | .002 | 58.6 | 100 | .82 |
| Integrated age ± 1 s | | | | | | | | | .81 |
| | n = 12 | 1.697 | .009 | | | K$_{2}$O = .12% | 81.7 | .3 |
| | | | | | | | | | .33 |
| | Steps B–K n = 10 | MSWD = .99 | 1.114 | 65.6 | 79.04 | .3 |

| S-2, biotite, 4.92 mg | 1 | 228.9 | .3728 | 631.6 | .519 | 1.4 | 18.5 | 8.1 | 102.09 |
| | 1.8 | 65.12 | .3623 | 113.4 | .602 | 1.4 | 48.6 | 17.5 | .63 |
| | 2.3 | 42.66 | .4535 | 37.19 | .719 | 1.1 | 74.3 | 28.7 | .77 |
| | 2.5 | 45.76 | .9432 | 49.25 | .643 | 1.5 | 68.4 | 38.7 | .70 |
| | 3 | 38.35 | 2.011 | 21.65 | 1.055 | 2.5 | 83.7 | 55.1 | .78 |
| E | 3.5 | 40.22 | 2.982 | 28.35 | 1.523 | .17 | 79.8 | 78.8 | .12 |
| | 4 | 48.47 | 7.658 | 60.73 | 1.289 | .067 | 64.2 | 98.9 | .15 |
| H | 4.5 | 36.77 | 8.994 | 25.59 | .074 | .057 | 81.4 | 100 | .73 |
| Integrated age ± 1 s | | | | | | | | | 1.6 |
| | n = 8 | 6.42 | .18 | | | K$_{2}$O = .37% | 79.11 | .11 |
| | | | | | | | | | .37 |
| | Steps B–H n = 7 | MSWD = 28.24 | 5.905 | 91.9 | 77.29 | .37 |

| S-3, biotite, 4.3 mg | 1 | 112.3 | 1.576 | 296.1 | .164 | .32 | 22.2 | 28.6 | 60.99 |
| | 1.8 | 116 | 2.642 | 281.8 | .127 | 1.9 | 28.3 | 45.6 | 79.8 |
| | 2.3 | 38.59 | 6139 | 23.65 | .074 | .83 | 82 | 54.2 | 77 |
| | 2.5 | 41.74 | 9792 | 26.41 | .043 | .52 | 81.5 | 58.6 | 82.7 |
| | 3 | 37.38 | 1.536 | 13.61 | .062 | .33 | 89.6 | 64.7 | 81.4 |
| | 3.5 | 36.96 | 2.149 | 16.73 | .051 | .24 | 87.1 | 69.3 | 78.4 |
| | 4 | 37.95 | 3.376 | 22.78 | .046 | .15 | 83 | 73.1 | 76.8 |
| | 4.5 | 37 | 3.583 | 12.33 | .044 | .14 | 91 | 76.6 | 82.2 |
| | 5 | 34.4 | 4.291 | 9.214 | .067 | .12 | 93.1 | 81.6 | 78.1 |
| | 6 | 44.65 | 13.11 | 49.15 | .098 | .039 | 69.8 | 88.3 | 76.6 |
| | 8 | 37.07 | 90.98 | 52.03 | .087 | .006 | 78.3 | 93.5 | 75.4 |
| | 21 | 42.39 | 481.3 | 196.8 | .119 | .001 | 54.2 | 100 | .83 |
| Integrated age ± 1 s | | | | | | | | | 1.4 |
| | n = 12 | 983 | .006 | | | K$_{2}$O = .06% | 76.1 | .5 |
| | | | | | | | | | .72 |
| | Steps B–K n = 10 | MSWD = 1.53 | 7 | 55 ± .58 | 71.2 | 78.18 | .72 |

(Continued)
| ID | Power (Watts) | $^{40}$Ar/$^{39}$Ar | $^{37}$Ar/$^{39}$Ar | $^{36}$Ar/$^{39}$Ar ($\times 10^{-10}$) | $^{39}$ArK ($\times 10^{-15}$ mol) | K/Ca | $^{40}$Ar* (%) | $^{39}$Ar (%) | Yaş (Ma) | ±1 sigma (Ma) |
|----|---------------|------------------|------------------|-----------------|-----------------|------|--------------|--------------|-----------|-------------|
| A  | 1             | 2998.1           | 23.29            | 10051.5         | .175            | .022 | 1            | 4.6          | 73.9      | 7.8         |
| B  | 2             | 321.6            | 35.29            | 990.1           | .27             | .014 | 9.9          | 11.6         | 79.6      | 1.3         |
| C  | 3             | 240.2            | 33.3             | 712.8           | .345            | .015 | 13.4         | 20.7         | 80.6      | .95         |
| D  | 4             | 151.8            | 30.84            | 419.8           | .395            | .017 | 19.9         | 31           | 75.5      | .69         |
| E  | 5             | 122.5            | 29.77            | 320.9           | .377            | .017 | 24.5         | 40.9         | 74.93     | .64         |
| F  | 6             | 98.86            | 29.07            | 242.3           | .414            | .018 | 29.9         | 51.7         | 73.82     | .54         |
| G  | 7             | 59.6             | 27.64            | 114.1           | .306            | .018 | 47.2         | 59.7         | 70.12     | .52         |
| H  | 8             | 52.31            | 24.21            | 89.41           | .298            | .021 | 53.2         | 67.5         | 69.26     | .49         |
| I  | 9             | 40.56            | 18.07            | 55.45           | .233            | .028 | 63.2         | 73.6         | 63.59     | .54         |
| J  | 10            | 30.77            | 14.2             | 33.84           | .175            | .036 | 71.2         | 78.2         | 54.37     | .65         |
| K  | 12            | 32.37            | 13.62            | 38.5            | .168            | .037 | 68.2         | 82.6         | 54.76     | .62         |
| L  | 21            | 40.95            | 19.12            | 41.78           | .665            | .027 | 73.6         | 100          | 72.3      | .5          |

Integrated age ± 1 s: $n = 12$, 3.82, .02 K2O = .24%, 71.24, .4
Plateau age ± 1 s: No plateau
trachy-basalt, basaltic trachy andesite and phonotephrite fi-
elds (Figure 7(b)). In the chemical classification dia-
gram of Hastie, Kerr, Pearce, and Mitchell (2007), the
high-K calc-alkaline samples fall into the calc-alkaline
field, while those from the shoshonitic samples are plot-
ted on the high-K and shoshonitic fields (Figure 7(c)). In
a K₂O vs. Na₂O diagram, high-K calc-alkaline rocks fall
into the calc-alkaline field, but shoshonitic samples are
plotted in the shoshonitic field (Figure 7(d)).

The SiO₂ vs. major and trace element variation dia-
grams of Hamsilos volcanic rocks generally exhibit neg-
ative or positive correlation with various scattering
(Figure 8). An increase in the SiO₂ content of Hamsilos
volcanites displays decrease in CaO, MgO, TiO₂, Ni and
Sr content and an increase in Al₂O₃, Fe₂O₃(t), P₂O₅, Zr,
Rb and Ba content. Although K₂O and Na₂O show show-
ter, they display increasing trend with SiO₂ (Figure 8).
Decreasing CaO with increasing SiO₂ shows clinopyrox-
ene and plagioclase fractionation. The scatter of K₂O
and Na₂O for the samples could be related to analcimiza-
tion of the leucite within these rocks. P₂O₅ content
shows opposite behaviour in the high-K calc-alkaline and
shoshonitic volcanic rocks. These variations can be
explained by the fractionation of common mineral
phases, such as plagioclase + clinopyroxene ± biotite
± Fe–Ti oxide ± olivine ± Fe–Ti oxide in high-K
calc-alkaline rocks.

Hamsilos volcanic rocks are enriched in large-ion
lithophile (LILE) elements and light rare earth elements
(LREEs) relative to high-field-strength elements (HFSEs)
(Figure 9(a)–(d)). The primitive mantle normalised multi-
element variation diagrams of the studied samples show
enrichment in LILE (e.g. Rb, Th, and K) relative to
HFSE and also negative Nb, Ta and Ti anomalies
(Figure 9(a) and (b)). These characteristics are typical of
subduction-related magma (Elliott, Plank, Zindler, White,
& Bourdon, 1997; Gill, 1981; Hofmann, 1997; Pearce
et al., 1990; Tatsumi, Hamilton, & Nesbitt, 1986).

However, compared to those derived from depleted mantle,
slight enrichment in LILE and decrease in negative Nb,
Ta and Ti anomalies can be ascribed to the some contri-
bution of melts from asthenosphere to the mantle wedge.
Although the trace element variations in shoshonitic and
high-K calc-alkaline samples are similar to each other,
there is a systematic increase in the trace element con-
centrations from the high-K calc-alkaline lavas to the
shoshonitic lavas (Figure 9(a) and (b)). The trace ele-
ment compositions of the Hamsilos volcanic rocks are
generally similar to the Ultra-K and shoshonitic rocks in
Asan et al. (2014) and the Ultra-K and shoshonitic rocks
from the eastern Pontides (Altherr et al., 2008; Asan
et al., 2014; Eyüboğlu, 2010; Gülmez & Genc, 2015).

Chondrite-normalised (Boynton, 1984) REE patterns
(Figure 9(c) and (d)) for the shoshonitic and high-K
calc-alkaline samples display enrichment in LREEs rela-
tive to HREE. The field of REE abundances of samples
from the Hamsilos volcanics is also shown for compari-
sion that the previous study by Asan et al. (2014) has
slightly higher abundances of LREE and HREE. The
shoshonitic and high-K calc-alkaline samples show moder-
ately fractionated condritenormalised REE patterns
subparallel to each other with (La/Lu)ₙ of 7.47–16.7 and
5.75–6.70, respectively. REE distributions also have charac-
teristic concave patterns in shoshonitic and high-K

![Figure 6. 40Ar/39Ar age spectra of four volcanic rock samples
(A, B, C: shoshonite, D: high-K basaltic andesite) from the
Hamsilos volcanic rock. MSWD: mean square of the weighted
deviates.](image)
Table 5. Whole-rock major element oxide (wt%), CIPW norms, trace and rare earth elements (ppm) and weathering alterattion indexes (CIA and WIP) of the Hamsilos volcanic rocks.

| Sample no. | Shoshonitic Hig-K calc-alkaline |
|------------|---------------------------------|
| SiO₂       | 49.2                            |
| TiO₂       | 0.87                            |
| AI₂O₃      | 15.3                            |
| FeO        | 7.84                            |
| MnO        | 0.14                            |
| MgO        | 4.59                            |
| CaO        | 9.46                            |
| Na₂O       | 0.71                            |
| K₂O        | 8.74                            |
| Nb         | 8.50                            |
| Rb         | 8.20                            |
| Sr         | 371                             |
| Nb         | 0.87                            |
| Zn         | 50.0                            |
| Total      | 99.7                            |

| Sample no. | HiK calc-alkaline |
|------------|-------------------|
| SiO₂       | 50.4              |
| TiO₂       | 0.80              |
| AI₂O₃      | 16.7              |
| FeO        | 7.49              |
| MnO        | 0.13              |
| MgO        | 4.65              |
| CaO        | 7.99              |
| Na₂O       | 2.96              |
| K₂O        | 4.25              |
| Nb         | 50.0              |
| Rb         | 8.64              |
| Sr         | 38                |
| Ne         | 371               |
| Total      | 99.8              |

| Shoshonitic Hig-K calc-alkaline | HiK calc-alkaline |
|---------------------------------|-------------------|
| Sample no.                      |                   |
| SiO₂                            | 49.2              |
| TiO₂                            | 0.87              |
| AI₂O₃                           | 15.3              |
| FeO                             | 7.84              |
| MnO                             | 0.14              |
| MgO                             | 4.59              |
| CaO                             | 9.46              |
| Na₂O                            | 0.71              |
| K₂O                             | 8.74              |
| Nb                               | 8.50              |
| Rb                              | 8.20              |
| Sr                               | 371               |
| Nb                               | 0.87              |
| Zn                               | 50.0              |
| Total                           | 99.7              |

| HiK calc-alkaline | Sample no. |
|-------------------|------------|
| SiO₂              | 50.4       |
| TiO₂              | 0.80       |
| AI₂O₃             | 16.7       |
| FeO               | 7.49       |
| MnO               | 0.13       |
| MgO               | 4.65       |
| CaO               | 7.99       |
| Na₂O              | 2.96       |
| K₂O               | 4.25       |
| Nb                | 50.0       |
| Rb                | 8.64       |
| Sr                | 38         |
| Ne                | 371        |
| Total             | 99.8       |

| Shoshonitic Hig-K calc-alkaline | HiK calc-alkaline |
|---------------------------------|-------------------|
| Sample no.                      |                   |
| SiO₂                            | 49.2              |
| TiO₂                            | 0.87              |
| AI₂O₃                           | 15.3              |
| FeO                             | 7.84              |
| MnO                             | 0.14              |
| MgO                             | 4.59              |
| CaO                             | 9.46              |
| Na₂O                            | 0.71              |
| K₂O                             | 8.74              |
| Nb                               | 8.50              |
| Rb                              | 8.20              |
| Sr                               | 371               |
| Nb                               | 0.87              |
| Zn                               | 50.0              |
| Total                           | 99.7              |

| HiK calc-alkaline | Sample no. |
|-------------------|------------|
| SiO₂              | 50.4       |
| TiO₂              | 0.80       |
| AI₂O₃             | 16.7       |
| FeO               | 7.49       |
| MnO               | 0.13       |
| MgO               | 4.65       |
| CaO               | 7.99       |
| Na₂O              | 2.96       |
| K₂O               | 4.25       |
| Nb                | 50.0       |
| Rb                | 8.64       |
| Sr                | 38         |
| Ne                | 371        |
| Total             | 99.8       |

| Shoshonitic Hig-K calc-alkaline | HiK calc-alkaline |
|---------------------------------|-------------------|
| Sample no.                      |                   |
| SiO₂                            | 49.2              |
| TiO₂                            | 0.87              |
| AI₂O₃                           | 15.3              |
| FeO                             | 7.84              |
| MnO                             | 0.14              |
| MgO                             | 4.59              |
| CaO                             | 9.46              |
| Na₂O                            | 0.71              |
| K₂O                             | 8.74              |
| Nb                               | 8.50              |
| Rb                              | 8.20              |
| Sr                               | 371               |
| Nb                               | 0.87              |
| Zn                               | 50.0              |
| Total                           | 99.7              |

| HiK calc-alkaline | Sample no. |
|-------------------|------------|
| SiO₂              | 50.4       |
| TiO₂              | 0.80       |
| AI₂O₃             | 16.7       |
| FeO               | 7.49       |
| MnO               | 0.13       |
| MgO               | 4.65       |
| CaO               | 7.99       |
| Na₂O              | 2.96       |
| K₂O               | 4.25       |
| Nb                | 50.0       |
| Rb                | 8.64       |
| Sr                | 38         |
| Ne                | 371        |
| Total             | 99.8       |
| Element | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   | (La/Yb)_N | (La/Lu)N | (Yb)N | Eu/Eu* | CIA  | WIP  | Mg#  |
|--------|------|------|------|------|------|------|------|------|------|-----------|-----------|--------|--------|-------|------|------|
|        | 1.70 | 6.06 | .87  | 4.62 | .83  | 2.42 | .34  | 2.11 | .31  | 11.18     | 10.10     | 11.73  | .80   | 37.10 | 91.90| 54   |
|        | 1.65 | 5.66 | .83  | 4.01 | 9     | 2.14 | .31  | 1.92 | .31  | 15.73     | 15.01     | 15.01  | .77   | 41.86 | 92.32| 55   |
|        | 1.84 | 6.33 | .74  | 4.6   | .77  | 2.64 | .38  | 2.36 | .37  | 16.28     | 16.00     | 16.00  | .77   | 42.47 | 97.49| 48   |
|        | 1.34 | 4.68 | .9   | 4.72  | .84  | 2.28 | .34  | 2.02 | .37  | 12.28     | 12.75     | 12.75  | .76   | 34.60 | 94.49| 61   |
|        | 1.8  | 6.24 | .87  | 4.42  | .84  | 2.23 | .33  | 2.11 | .29  | 12.00     | 14.79     | 14.79  | .75   | 39.52 | 97.52| 54   |
|        | 1.79 | 5.94 | .96  | 5.16  | .94  | 2.62 | .33  | 2.1  | .32  | 14.79     | 16.30     | 16.30  | .74   | 42.69 | 95.24| 56   |
|        | 1.97 | 4.94 | .76  | 4.07  | .73  | 2.29 | .39  | 1.8  | .37  | 16.30     | 16.56     | 16.56  | .73   | 42.11 | 95.99| 62   |
|        | 1.43 | 5.86 | .81  | 4.4  | .71  | 2.13 | .33  | 1.8  | .37  | 12.25     | 13.06     | 13.06  | .72   | 38.35 | 99.35| 54   |
|        | 1.64 | 5.83 | .74  | 5.03  | .83  | 2.06 | .29  | 1.8  | .38  | 15.80     | 14.90     | 14.90  | .72   | 41.11 | 95.91| 62   |
|        | 1.63 | 6.18 | .66  | 2.78  | .83  | 2.25 | .28  | 1.8  | .29  | 15.31     | 14.90     | 14.90  | .72   | 39.31 | 95.91| 62   |
|        | 1.34 | 4.64 | .47  | 2.85  | .97  | 1.75 | .29  | 1.8  | .29  | 6.00      | 6.00      | 6.00   | .72   | 29.95 | 96.94| 62   |
|        | .83  | 2.84 | .48  | 2.75  | .75  | 1.79 | .29  | 1.8  | .29  | 6.35      | 6.70      | 6.70   | .72   | 45.42 | 96.96| 62   |
|        | .87  | 4.64 | .45  | 2.63  | .57  | 1.56 | .27  | 1.8  | .29  | 6.70      | 6.97      | 6.97   | .72   | 45.59 | 95.96| 62   |
|        | .76  | 2.84 | .45  | 2.76  | .53  | 1.56 | .27  | 1.8  | .29  | 6.35      | 6.97      | 6.97   | .72   | 46.05 | 96.96| 62   |
|        | .78  | 3.63 | .44  | 2.76  | .51  | 1.56 | .27  | 1.8  | .29  | 6.70      | 6.97      | 6.97   | .72   | 46.06 | 96.96| 62   |
|        | .75  | 4.67 | .45  | 2.76  | .51  | 1.56 | .27  | 1.8  | .29  | 6.35      | 6.97      | 6.97   | .72   | 46.15 | 96.96| 62   |
|        | .8  | 2.84 | .45  | 2.76  | .51  | 1.56 | .27  | 1.8  | .29  | 6.70      | 6.97      | 6.97   | .72   | 46.02 | 96.96| 62   |
|        | .81  | 2.84 | .45  | 2.76  | .51  | 1.56 | .27  | 1.8  | .29  | 6.35      | 6.97      | 6.97   | .72   | 45.96 | 95.96| 62   |
| Notes: Fe₂O₃tot = total iron as Fe₂O₃, LOI = loss on ignition, Eu/Eu* = (Euₙ)/(1/2(Smₙ / Gdₙ)) and Mg# (Mg-number) = 100 × MgO/(MgO + .9Fe₂O₃tot). WIP: Weathering Index of Parker = 100 × [(2Na₂O/.35) + (MgO/.9) + (2K₂O/25) + (CaO/7)]; 1970; CIA: Chemical Index of Alteration = 100 × molar [(Al₂O₃)/(Al₂O₃ + CaO + Na₂O + K₂O)] (Nesbitt & Young, 1982).
calc-alkaline samples that tend to flatten towards LREE and HREE, come up with the significant effect of clinopyroxene fractionation (Thirlwall et al., 1994) on the evaluation of the studied rocks (Figure 9(c) and (d)). The shoshonitic and high-K calc-alkaline samples display no or slight negative Eu anomalies (mean EuN/Eu* = 0.76–0.82 and 0.81–0.91, respectively) suggesting insignificant plagioclase fractionation or oxygen fugacity (Figure 9(c) and (d)).

4.5.3. Sr–Nd–Pb isotopes

Initial Nd–Sr–Pb isotope ratios and epsilon neodymium values (εNd) of shoshonitic volcanic rocks were calculated using the ages of 78 and 72 Ma, respectively (Tables 6 and 7). ⁸⁷Sr/⁶⁶Sr₀ (0.70615–0.70796) and ¹⁴⁳Nd/¹⁴⁴Nd₀ (0.51228–0.51249) isotopic ratios (Table 6), are plotting in the enriched mantle quadrant of a Sr–Nd correlation diagram, and indicating a pronounced negative correlation between Sr and Nd isotopic composition (Figure 10(a)). The high-K calc-alkaline volcanic rocks show ificação de la edad de 72 Ma. Los valores de εNd (72 Ma) son −0.0 a −2.0. La edad model de Nd (⁷⁷⁴Nd/⁷⁷⁵Nd) varía desde 1.08 a 1.19 Ga. Las composiciones isotópicas Sr–Nd de los volcanes shoshoníticos y de alta-K calc-alkalina se encuentran cerca del campo de las rocas potássicas centrales-orientales Pontides (Altherr et al., 2008; Asan et al., 2014; Eyüboğlu, 2010) (Figure 10(a)).

La razón isotópica de Pb de los volcanes calc-alkalina son similares a las de los shoshoníticos [(²⁰⁶Pb/²⁰⁴Pb) = 18.74–18.80, (²⁰⁷Pb/²⁰⁴Pb) = 15.65, and (²⁰⁸Pb/²⁰⁴Pb) = 38.84 to 38.88]. La línea de referencia hemisférica del norte se utilizó para...
Figure 8. Harker variation diagrams for the studied volcanic rocks (symbols are the same as in Figure 7(a)).
in the plots because $^{208}\text{Pb}$ data are more radiogenic than $^{206}\text{Pb}$ data. Also plotted for comparison are EM1 (enriched mantle with intermediate $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$ and low $^{206}\text{Pb}/^{204}\text{Pb}$) and EM2 (enriched mantle with high $^{87}\text{Sr}/^{86}\text{Sr}$, intermediate $^{143}\text{Nd}/^{144}\text{Nd}$, and high $^{206}\text{Pb}/^{204}\text{Pb}$; Zindler & Hart, 1986). All of the samples are highly homogeneous in lead isotopic compositions (Figure 10(b) and (c)) and are plotted between EM1 and EM2 (albeit closer to EM2).

5. Discussion

5.1. Petrogenesis of Hamsilos volcanic rocks

The basic factors that determine the major element, trace element and isotope contents of Hamsilos volcanites include the chemical compositions of the magma source and the petrogenetic processes exposed during magma formation. Geochemical characteristics show that the magma that forms the Hamsilos volcanites was differentiated from a mantle-derived enriched magma. Fractionation and assimilation processes following partial melting seem to have effective role in the formation of final geochemical composition of the studied volcanic rocks. In this section, the importance and function of magmatic processes in the petrogenesis of the analysed volcanics are discussed and interpreted.

5.1.1. Partial melting

Significant components of arc magmas are derived from mantle wedge (Hochstaedter, Kepezhinskas, Defant, Drummond, & Koloskov, 1996), metasomatized by fluids (from altered oceanic crust or subducted sediments) (Greene, Debari, Kelemen, Blusztajn, & Clift, 2006). The Hamsilos volcanic rocks possess MgO ($\text{Mg}^\# = 48$–61) value of 4–6%, Ni value of 5–20 ppm and Cr value of 14–199 ppm. These values indicate that Hamsilos volcanic rocks substantially differ from basaltic rocks that have primitive composition (Mg number $> 70$, Ni $> 200$ ppm, Cr $> 400$ ppm; Green, Schmidt, & Hibberson, 2004). Low $\text{Zr}/\text{Y}$ and high $\text{Zr}/\text{Nb}$ ratios (Menzies & Kyle, 1990) generally attributed to a high-level partial melting in subduction-related volcanic arcs. The Hamsilos volcanic rocks have low $\text{Zr}/\text{Y}$ (5–9) and
Table 6. Whole-rock Sr and Nd isotopic composition for the Hamsilos volcanic rocks.

| Sample | Rb (ppm) | Sr (ppm) | $^{87}\text{Rb} / ^{86}\text{Sr}$ | $^{87}\text{Sr} / ^{86}\text{Sr}$ | $I_{\text{Sr}}$ | Sm (ppm) | Nd (ppm) | $^{147}\text{Sm} / ^{144}\text{Nd}$ | $^{143}\text{Nd} / ^{144}\text{Nd}$ | $\epsilon_{\text{Nd}(0)}$ | $\epsilon_{\text{Nd}}$ | $T_{\text{DM}}$ (Ga) |
|--------|----------|----------|-----------------|-----------------|--------------|---------|---------|-----------------|-----------------|--------------|-------------|----------------|
| Shoshonitic (78 Ma) | | | | | | | | | | | | | |
| S-1    | 38.0     | 371.0    | .30             | .70784          | 13           | .70751  | 6.76    | .1173           | .51236          | .512300      | $-5.4$     | $-4.6$      | 1.19        |
| S-3    | 140.6    | 393.0    | 1.03            | .70911          | 10           | .70796  | 7.84    | .1030           | .51233          | .512280      | $-6.0$     | $-5.0$      | 1.08        |
| S-5    | 86.5     | 559.8    | .45             | .70836          | 11           | .70787  | 5.10    | .1239           | .51242          | .512360      | $-4.2$     | $-3.5$      | 1.17        |
| High-K calc-alkaline (72 Ma) | | | | | | | | | | | | | |
| I-6    | 49.6     | 339.3    | .42             | .70662          | 11           | .70618  | 2.91    | .1370           | .51256          | .512490      | $-1.0$     | $-1.0$      | 1.10        |

Notes: $\epsilon_{\text{Nd}} = ((^{143}\text{Nd} / ^{144}\text{Nd})_{\text{s}} / ^{143}\text{Nd} / ^{144}\text{Nd})_{\text{CHUR}} - 1) \times 10,000$, $(^{143}\text{Nd} / ^{144}\text{Nd})_{\text{CHUR}} = 0.51308$ (Jacobsen & Wasserburg, 1980). Nd single-stage model ages ($T_{\text{DM}}$) are calculated with a depleted-mantle reservoir and present-day values of $^{143}\text{Nd} / ^{144}\text{Nd} = 0.513$ and $^{147}\text{Sm} / ^{144}\text{Sm} = 2.19$ (Liew & Hofmann, 1988).
medium-level Zr/Nb (14–27) ratios (Figure 11(a)), indicating that the parental magma of the analysed volcanics was originated from a mantle source by low partial melting. Degree of partial melting rate in volcanic arc settings generally depends on the thickness of the subducted crust and varies from 2 to 25% (Plank & Langmuir, 1998).

In magmatic systems, La/Sm ratio is a significant parameter that is controlled by partial melting as well. Meanwhile, low La/Sm ratio points a high degree of partial melting and the presence of remnant spinel, whereas high La/Sm ratio indicates a low degree of partial melting and a garnet remnant balance. Therefore, relatively low La/Sm and partially depleted HREE contents of the studied rocks may have resulted from relatively high-level partial melting of the source, namely a mantle rock that contains spinel. The REE models developed using fractional and batch partial melting equations of Shaw (1970) suggest that Hamsilos volcanics originated from a mantle material with the spinel–peridotite composition through 1–3% partial melting (Figure 11(b)).

The shoshonitic volcanic rocks are characterised by the enrichment of large ion lithophile elements and LREEs compared with the high-K calc-alkaline volcanic rocks, and these differences in source characterisation indicate a low degree of partial melting for the shoshonitic volcanic rocks. The shoshonitic melts in the Hamsilos volcanic rocks can be derived from a low degree of partial melting of an enriched SCLM, while the high-K calc-alkaline melts can be derived from relatively high degree of partial melting of an enriched SCLM source (Figure 9(c) and (d)).

5.1.2. Fractional crystallisation and assimilation vs. magma mixing

Hamsilos volcanic rocks possess low MgO, Ni and Co contents. Major and trace element variation diagrams show that fractionation from a more basic magma has been playing affective role in the development of volcanites (Figures 8 and 9). The eventual decrease in the TiO$_2$ and Fe$_2$O$_3$ contents as opposed to the increase in the SiO$_2$ content of Hamsilos volcanic rocks indicates the fractionation of Fe–Ti oxides; meanwhile, the negative relations in SiO$_2$ vs. CaO, Fe$_2$O$_3$ and MgO reveal the fractionation of plagioclase (An > 50) and clinopyroxene phases from the parental magma. The presence of a relatively negative anomaly in Eu values of the rocks in the chondrite-normalised REE distributions of the analysed volcanic rocks indicates that plagioclase fractionation is influential in rock development (Figure 9(c) and (d)).

There is not a clear fractional crystallisation trend in Figure 12(a) and (b) for high-K calc alkaline rocks. All the high-K calc-alkaline rocks are clustered within the narrow range but in Figure 12(a) and (b), negative variations between Zr vs. Co and Ni indicate the function of crystal fractionation in the development of the shoshonitic rocks in the Hamsilos volcanic rocks. The decreasing CaO/Al$_2$O$_3$ ratio against increasing Fe$_2$O$_3$/MgO ratio of Hamsilos volcanites imply that clinopyroxene fractionation from the parental magma exerts a certain influence (Figure 12(c)). Moreover, increasing Al$_2$O$_3$ against decreasing CaO/Na$_2$O exhibits that clinopyroxene fractionation affects the evolution of volcanic rocks (Figure 12(d)).

The relation between the source metasomatism by fluids from subduction zone and/or crustal assimilation and fractionation can be explained in the diagram where trace element ratios such as Nb/Y vs. Rb/Y are used (Figure 13). Considering this diagram, whereas the high-K calc-alkaline samples indicate subduction zone enrichment trends, the shoshonitic rocks samples show specific subduction zone enrichment or crust contamination trends. This plot also indicates that when the Hamsilos volcanics are generally similar trends of the samples of the previous study by Asan et al. (2014). $(^{143}\text{Nd}/^{144}\text{Nd})$, vs. SiO$_2$ (wt%) and Zr/Y vs. Zr (ppm) plots reveal the influence of assimilation, rather than fractional crystallisation on the evolution of shoshonitic rocks but not say anything high-K calc-alkaline rocks (Figure 14(a) and (b)). Another important argument is that some of the variation diagrams, such as the element vs. element ratio (Figure 14(c) and (d); Langmuir, Vocke, Hanson, & Hart, 1978), display a linear trend of the studied volcanic rocks, all of which confirm the derivation assimilation and/or magma mixing.

The texture and composition of minerals are related to the different types of disequilibrium that occur during volcanic evolution. The magma mixing processes can be determined by following as (1) petrographic or textural criteria, which contain the disequilibrium of textures such as sieved plagioclases (Dungan & Rhodes, 1978), the reaction rim and resorption in clinopyroxenes, the presence of unsieved and sieved plagioclases in the same sample (Stimac & Pearce, 1992), and the rounded and embayed crystals (Stimac & Pearce,
(2) compositional criteria, which include the determination of normally and reversely zoned crystals and presence of these crystals in the same sample (Halsort & Rose, 1991; Luhr & Carmichael, 1980). The broad compositional variation, sieved texture and complex zoning of plagioclase are commonly observed in subduction-related basaltic and andesitic rocks, which may refer the presence of highly dynamic magmatic systems (Tepley, Davidson, Tilling, & Arth, 2000). The Hamsilos volcanic rocks include the sieved textured, rounded and embayed plagioclases (Figure 3(b) and (f)). Sieve texture in plagioclases occurs because of magma mixing processes (Tsuchiyama, 1985) or forms because of decompression while rises to a shallower depth (Nelson & Montana, 1992).

The clinopyroxenes in the Hamsilos volcanic rocks (high-K calc-alkaline and shoshonitic rocks) show different types of disequilibrium textures, as zoning, resorbed, rounded crystals and embayed and breakdown clinopyroxenes megaclast (Figures 3 and 4). Clinopyroxenes are represented by rounded and embayed crystals similar to sieved plagioclase crystals that are generally caused by magma mixing (Hibbard, 1981; Simonetti Shore, Bell, 1996; Streck, 2008) or decompressional melting (Nelson & Montana, 1992). Normally zoned clinopyroxenes in the Hamsilos volcanic rocks represent more Mg-rich composition in the core compared to the rim coupled with higher Cr and lower Ti and Al contents (Figure 15(a) and (b)). Reverse zoning exhibits the opposite case. In addition, the normally and reversely zoned clinopyroxenes are present both in the shoshonitic and high-K calc-alkaline rocks, suggesting the presence of mixing processes.

5.1.3. Source characteristics

Hamsilos volcanics exhibit the characteristics of typical subduction zone volcanic rocks with depletion of HFSEs (e.g. Nb, Zr, and Ta), enrichment (Figure 9(a) and (b)) of LILEs (e.g. Sr, K, Rb and Ba) and high ratio of Ba/La. These characteristics are present in previously analysed trace element variation diagrams (Baier, Audétat, & Keppler, 2008; Pearce, 1983). Subduction-related continental arc magmas are characterised by LILE enrichment against HFSE, LREE against HREE and negative Nb, Ta, Zr, Hf and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983). Ocean island basalts (OIB) differ from subduction zone continental arc volcanites in terms of the presence of positive Nb, Ta and Ti anomalies (Hawkesworth, Turner, McDermott, Peate, & Van Calsteren, 1997; Pearce, 1983).
to metasomatism) by fluids emerging from the subducted slab and/or sediments (Münker, Wörner, Yogodzinski, & Churikova, 2004). In chondrite-normalised REE diagrams, the HREE values of Hamsilos volcanites exhibit an almost-horizontal trend. This horizontal trend of HREE values suggests that the parental magma that forms Hamsilos volcanic rocks may originate from a spinel lherzolitic (<50 km depth) mantle source, rather than a lherzolitic mantle source that contains garnet (Figure 10(c) and (d)).

Low Sr/Th ratio and moderately radiogenic $^{87}\text{Sr} / ^{86}\text{Sr}$ values (.70662–.70911) (Figure 16(a)) indicate that the mantle source was contaminated by fluids or melts derived from subducted sediments. On the basis of $^{87}\text{Sr} / ^{86}\text{Sr}$ vs. Sr/Th relationships in a number of arcs, Hawkesworth et al. (1997) noted that high Sr/Th ratios are developed in rocks with low $^{87}\text{Sr} / ^{86}\text{Sr}$ (~.704). The rationale for using this plot is that as a result of the preferential mobilisation of the LILE into hydrous fluids, high Sr/Th ratios will be a signature of the fluid phase. The Sr isotope ratios might be expected to be variable, depending on whether the fluids have interacted mainly with altered basaltic crust (≥.7047; Bickle & Teagle, 1992; Staudigel, Davies, Hart, Marchant, & Smith, 1995) or subducted sediment (> .709). Thus, these researchers asserted that low $^{87}\text{Sr} / ^{86}\text{Sr}$ value supports the addition of fluid component, whereas the high $^{87}\text{Sr} / ^{86}\text{Sr}$ values point out the contribution of sediment component. The $^{87}\text{Sr} / ^{86}\text{Sr}$ vs. Sr/Th diagrams of rocks in depleted and enriched arcs present a hyperbolic trend (Figure 16(a)). The Hamsilos volcanic rocks together with their low Sr/Th (< .55) ratios and high $^{87}\text{Sr} / ^{86}\text{Sr}$ (> .709) values resemble those rocks formed in enriched arcs (Macdonald, Hawkesworth, & Heath, 2000).

The role of fluid and melt components in subduction zones can be evaluated using a combination of geochemical parameters. Ba is selectively enriched in fluids because of its higher mobility relative to La, while Th displays preferential enrichment in sediment-derived melts (Kirchenbaur, Munker, Schuth, Garbe-Schönberg, & Marchev, 2012).

The Ba/La vs. Th/Yb diagram (Pearce, 1983) in Figure 16(c) has been used for the discrimination of the mantle sources and the determination of possible additional components such a subduction and/or crustal contamination of the mantle (Figure 16(c)). All the Hamsilos volcanic rocks have high Th/Yb ratios relative to the mantle array. According to this diagram, while the high-K calc-alkaline rock patterns present subduction enrichment, the shoshonitic rock patterns show the addition of a subducted component to the mantle and

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**Figure 11.** (a) Zr/Y vs. Zr/Nb plot (Menzies & Kyle, 1990) as a measure of amount of partial melting involved in the genesis of the Hamsilos volcanites. The fields of N-, T-, P-type MORBs are taken from Le Roex (1987), (b) La/Sm vs. Sm/Yb diagram showing the melting curves of the samples from the Hamsilos volcanic rocks. Fractional and batch melting equations of Shaw (1970) were used to construct the melting model. Modal mineralogy for the spinel- and garnet-peridotites are taken from Wilson (1989), and ol.66 + opx.24 + cpx.08 + sp.02 and ol.63 + opx.30 + cpx.02 + gt.05, respectively (ol: olivine, opx: orthopyroxene, cpx: clinopyroxene, sp: spinel, gt: garnet). Trace element composition of the spinel-peridotite (C0 values) is from McDonough (1990), while that of garnet peridotite is from Frey (1980). Ks between the basaltic melts and minerals given in the inset are compiled from Irving and Frey (1978), Fujimaki, Tatsumoto, and Aoki (1984), McKenzie and O’Nions (1991) and Rollinson (1993) (symbols are the same as in Figure 7(a)).
contamination from the crust (upper crust). Moreover, the similar interpretations are also supported by data obtained from the study helded by Asan et al. (2014). The combined data show that the calc-alkaline and shoshonitic rocks were derived from same mantle source with different degrees of partial melting.

In Figure 16(d), Bradshaw and Smith (1994) and Smith, Sánchez, Walker, and Wang (1999) implied that because HFSE (such as Nb and Ta) are depleted in the lithospheric mantle relative to the LREE, high Nb/La ratios (>1) indicate an OIB-like asthenospheric mantle source for basaltic magmas, and lower ratios (<0.5) indicate a lithospheric mantle source. Similar to arc volcanites, Hamsilos volcanic rocks possess higher La/Nb (3–5) and Ba/Nb (34–124) ratios than MORB, OIB and continental volcanites (Sun & McDonough, 1989). Considering that HFSEs (e.g. Nb and Ta) are depleted in the lithospheric mantle relative to LREEs, the Nb/La (20–30) and La/Yb (9–25) ratios of Hamsilos volcanic rocks suggest a lithospheric mantle source (Figure 16(d)). Average Nb/Ta ratios of 11–12 and ~17 indicate the presence of crust-derived magma and mantle-derived magma, respectively (Green, 1995). The Nb/Ta ratios of Hamsilos volcanic rocks vary between 14 and 19. These values support the derivation of the parental magma of the volcanites from the mantle. In addition, the Zr/Sm ratios of the volcanic rocks range between 20 and 29. Meanwhile, the Zr/Sm values are lower than those in chondrites (~25); in N-MORB, E-MORB and OIB (~28); in the lower crust (24); in the middle crust (32) and in the upper crust (41). This enriched mantle is metasomatised by subduction components and resembles the source of island arc rocks (Wilson, 1989). This result proves that Hamsilos volcanites are derived from a metasomatized-enriched lithospheric mantle at spinel stability field.

The production of high-K and calc-alkaline associations can be supported by two different theory; (i) the calc-alkaline and high-K magmas were derived from a different lithospheric mantle source at variable levels and enriched by metasomatic events in different degree, (ii) the magmas in these different affinities can be generated from same magma source at same level effected by metasomatic events resulted in heterogeneous source composition (Conticelli, Avanzinelli, Marchionni, Tommasini, & Melluso, 2011). Foley (1992) suggest that coeval occurrence of potassic and calc-alkaline magmas can be evolved from progressive melting of veined upper
mantle source. The production of two mafic end members by a two-stage partial melting processes was suggested by Maria and Luhr (2008) that the high-K magmas are generated mostly from net-veined metasomatic agents, while the magmas in calc-alkaline affinity can be evolved from surrounding lithospheric mantle.

The previous study performed by Asan et al. (2014) in same area suggests that the shoshonitic and ultra-K rocks were derived from metasomatic veins related to melting of recycled subducted sediment, but high-K calc-alkaline rocks from lithospheric source metasomatized by fluids from subduction zone. The enriched LILE, LREE values and more radiogenic $^{87}$Sr/$^{86}$Sr ratios observed in shoshonitic volcanic rocks in this study can be interpreted that the melts can be derive from a low degree partial melting of an enriched SCLM in heterogeneous composition, while the high-K calc-alkaline melts can be derive from relatively high degree partial melting of the same enriched lithospheric mantle source.

5.2. Geodynamic implications and magma chamber processes
The Pontides orogenic belt has been considered to be an example of well-preserved continental magmatic arcs
This tectonic unit comprises a mountain chain, which is 200 km in wide and extending along the southern Black Sea coast for 500 km. This unit occurs within the Alpine metallogenic system. Through the late Cretaceous period, the Sakarya Zone experienced intensive magmatic activity associated with subduction (Aydin, 2014; Eyüboğlu, 2010; Genç et al., 2014 et al., 2010; Karsli et al., 2012; Kaygusuz & Aydınçakır, 2009, 2011; Varol, 2013). However, the subduction polarity and geotectonic evolution of the eastern Pontides are
controversial for the Cretaceous period. Several researchers suggested that the eastern Pontides was a magmatic arc that occurred as a result of northward subduction of the Neotethys along the southern border of the Sakarya Zone (Altherr et al., 2008; Karsli et al., 2010; Okay & Şahintürk, 1997; Şengör & Yılmaz, 1981; Şengör et al., 2003; Ustaomer & Robertson, 2010; Yılmaz et al., 1997). Conversely, Dewey et al. (1973), Bektaş et al. (1999), Eyübolğlu, Chung, et al. (2011), and Eyübolğlu, Santosh, et al. (2011) proposed a southward subduction that continued uninterruptedly from the Paleozoic period until the end of the Eocene period. In the light of our finding and results, we can propose that the Hamsilos lavas were possibly generated in a subduction zone at around 78 Ma in the Sakarya Zone.

The Hamsilos volcanic rocks exhibit the characteristics of subduction zone volcanic rocks with depletion of HFSEs (e.g. Nb, Zr, and Ta), enrichment (Figure 9(a) and (b)) of LILEs (e.g. Sr, K, Rb, and Ba) and high ratio of Ba/La. These characteristics are shown in the trace element variation diagrams (Figure 9(a) and (b)). The Hamsilos volcanics have geochemical characteristics typical for those of subduction-related arc magmas, characterised by LILE enrichment relative to HFSE and LREE.
enrichment relative to HREE, and negative Nb, Ta, Zr, Hf and Ti anomalies (Hawkesworth et al., 1997; Pearce, 1983). However, OIB-like features such as high-K nature, LILE enrichment and weak negative Ta, Nb and Ti anomalies indicate some melt addition from undepleted mantle source. In addition, samples of Hamsilos volcanic rocks present Sr–Nd isotopic characteristics that are markedly similar to shoshonitic trachyandesites (80 Ma), which were interpreted as mantle-derived rocks by Eyüboğlu (2010) and Gülmez and Genc (2015) that formed at an extensional environment of subduction setting (Figure 10(a)).

On the basis of the above discussion, a simplified cartoon can be used to illustrate relationships between the petrogenesis and tectonic environment of Hamsilos volcanics. I recommend that the Hamsilos volcanics formed in an extensional environment above subduction zone. During the middle Campanian (~78 Ma), fore arc/inter-arc region of the Sakarya Zone was underwent an extensional regime, as evidenced by the high-K nature of basic volcanic rocks (Altherr et al., 2008; Asan et al., 2014; Aydın, 2014; Eyüboğlu, 2010; Gülmez & Genc, 2015).

According to geochemical evidence, the parent magma of the Hamsilos volcanic rocks has been interpreted as generated in a sub-continental lithospheric mantle source that enriched by fluids and/or sediments from a subduction of oceanic crust. The enriched magmas composing the shoshonitic and high-K calc-alkaline volcanic rocks have polybaric evolutional mechanism during the magma transportation at crustal levels. The fracturing of the crust because of extension in back-arc setting can provide appropriate pathway for rising magma. These magmas are stalled at different crustal levels and can be explained by different petrological processes such as FC, AFC and magma mixing to modify the observed disequilibrium of the textural, petrographic and mineral chemical features of the Hamsilos volcanic rocks.

The clinopyroxene thermobarometric calculation combined with the petrographic and mineral chemistry data reveal that the two different magma storage levels were specified for shoshonitic volcanic rocks (Figure 17(a)). The clinopyroxene barometer were yielded pressures between 1.8 and 6.2 kbar, thus indicating early crystallisation processes at deep to mid-crustal level.
(~18 km). The crystallisation of olivine and clinopyroxene with high Mg number was present at this level and they were accompanied by the crystallisation of high-Ca plagioclases. The presence of clinopyroxenes having Mg- and Cr-rich mantle composition (Figure 15(a) and (b)) than their core and rim can be accepted as evidence for replenishment of this magma chambers by relatively mafic and hot magma. Moreover, the assimilation of host lower crust may takes place at this level. The mentioned magmas were rised and ponded at shallow crustal level. These magma chambers were characterised by the presence of phlogopite and relatively low-Ca plagioclase, clinopyroxenes. The data obtained from biotite thermobarometer indicate that the magma reservoir take place around 5 km in depth. The occurrence of disequilibrium textures as zoned, resorbed and embayed clinopyroxenes and sieved, embayed and rounded plagioclases (Figure 4(a)–(e)) was arise from petrological processes as magma mixing, as well as decompression. The presence of normally and reversely zone clinopyroxene in same sample can support the idea of the mixing processes. The magmas rises again and ponded pre-eruptive shallow level magma chambers. The crystallisation of low-Ca plagioclases and analcimes (replacement of leucite) happened at this level. All of the textural and thermobarometric parameters can be interpreted as open-system behaviours during crystallization as indicated by Yücel, Arslan, et al. (2014).

The crystallisation history of high-K calc-alkaline volcanic rocks has similarities with the shoshonitic volcanic rocks (Figure 17(b)). The only-clinopyroxene thermobarometer yielded the crystallisation pressure are between 1.5 and 3.6 kbar corresponding ~5–12 km crystallisation depth. The crystallisation of clinopyroxene, plagioclases and olivine started at mid crustal magma chambers approximately 12 km in depth. The magmas raise and stalled at higher level magma chamber. At this level, the magma chamber is replenished by orthopyroxene bearing relatively more primitive magmas and the mixing processes took place. The mixing of fractionated and primitive magmas leads to the occurrence of reversely zoned clinopyroxenes and plagioclases. The magma rises again and ponded at shallow level crustal magma chamber and underwent the processes of FC and mixing. These magma chambers are characterised by crystallisation of fractionated phases as sieved-textured plagioclases with low anorthite content, sanidine and clinopyroxene microlites with relatively low Mg number.

6. Conclusions

This study provides new constraints for the geodynamic evolution of the Central Pontides. The results are as follows:

1. Late Cretaceous Hamsilos volcanic rocks consist of basaltic andesite, trachy-basalt, basaltic trachy andesite and phono-tephrite that display porphyric, microlitic porphyric, hyalo-microlitic porphyric, vesicular and glomeroporphyric textures. The rocks include clinopyroxene, plagioclase, biotite, analcime and magnetite/Ti-magnetite.

2. On the basis of clinopyroxene thermobarometric calculations, magmas of the shoshonitic rocks crystallised at temperature ranging from 1133 to 1187 °C and at pressure ranging from 1.4 to 6.3 kbar. Whereas, the high-K calc-alkaline rocks were characterised at temperature ranging from 1004 to 1174 °C and at pressure ranging from 1.5 to 3.6 kbar.

3. The results of clinopyroxene thermobarometry calculations reveal that the ascending magma ponded at 6–18-km depths from shallow crustal magma chambers for the shoshonitic rocks at 5–12-km depths from mid-crustal levels for the high-K calc-alkaline rocks.

4. The 40Ar/39Ar dating of the exhibits ages between 72.3 ± 5 and 79.0 ± 3 Ma (Campsian). The volcanic rocks indicate high-K calc-alkaline and shoshonitic affinities. All samples from the studied volcanic series exhibit similar geochemical features, which are characterised by LILE and LREE enrichment and HFSE depletion with no or slightly negative Eu anomalies, suggesting the subduction-related magmas. Fractional crystallisation with minor contamination by upper crustal materials occurred during the evolution of the volcanic rocks.

5. Late Cretaceous Hamsilos volcanic rocks present a narrow isotopic range (78 Ma), and the εNd (78 Ma) values of high-K calc-alkaline and shoshonitic rocks define and array with 70615 to 70796 and −1.0 to −5.0, respectively. The lead isotopic ratios of high-K calc-alkaline rocks (208Pb/204Pb) = 18.75, (207Pb/204Pb) = 15.64 and (206Pb/204Pb) = 38.79) are similar to those of shoshonitic rocks (208Pb/204Pb) = 18.74–18.80, (207Pb/204Pb) = 15.65 and (206Pb/204Pb) = 38.84–38.88).

6. In addition, Sr–Nd isotopic and geochemical data reveal that upper crustal assimilation appears plausible in the generation of Hamsilos volcanic rocks. With these geochemical characteristics, an arc setting can be deduced during the generation of Hamsilos volcanic rocks. As a consequence, it can be concluded that the shoshonitic and high-K calc-alkaline rocks were derived from different degree partial melting of an enriched SCLM material metasomatized by fluids and/or sediments from subduction zone.

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No potential conflict of interest was reported by the author.

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**Supplemental data**

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