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Geochemical features and petrogenesis of Gökçeada volcanism, Çanakkale, NW Turkey

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Research Article

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ABSTRACT

Gökçeada Island, which is situated west of Biga Peninsula, has widespread magmatism with variable ages. Lower-Middle Eocene Dağiçitepe volcanics are the oldest volcanic unit in the island and consist of lavas, tuff-tuffites. They are influenced by alteration and almost all minerals, except quartz, are transformed into other minerals. Lower Oligocene Gökçeada andesitic lava/domes exhibiting hypocrystalline porphyric texture, are the products of NE-SW trending domes/cryptodomes. The phenocrysts assemblages consist of plagioclase, hornblende, clinopyroxene ± biotite and quartz. Middle Miocene Eşelek volcanics, which occur as lavas and pyroclastic rocks, exhibit hypocrystalline porphyric and intersertal textures. They are composed of plagioclase, hornblende and clinopyroxene crystals. Rhyolitic Dağiçitepe volcanics and andesitic Gökçeada lava/domes have calc-alkaline, andesitic Eşelek volcanics have tholeiitic character. They have geochemical features similar to subduction-related magmas. Lower-Middle Eocene Dağiçitepe volcanics are the products of syn-collisional magmas that have undergone processes of crustal contamination due to thickened crust. Whereas, Lower Oligocene Gökçeada andesitic lava/domes are the products of post-collisional magmas and were derived from metasomatized lithospheric mantle. Middle Miocene Eşelek volcanics were also derived from lithospheric mantle but, the mantle source generating Eşelek volcanics were relatively depleted over time. Geochemical data demonstrate the decreasing role of subduction signature and crustal contamination during the genesis and evolution of Gökçeada volcanics from Lower-Middle Eocene to Middle Miocene.

1. Introduction

Northward subduction and the following closure of the northern branch of Neo-Tethys ocean beneath the Sakarya continent, a continental collision between the Anatolide-Tauride blocks and the Sakarya continent occurred (Şengör and Yılmaz, 1981; Okay and Tüysüz, 1999). This continent-continent collision, which caused the formation of the Izmir-Ankara-Erzincan suture zone, occurred in the early Paleocene in the west (Okay and Tüysüz, 1999). Following the collision between the Sakarya continent and the Anatolide-Tauride blocks in the Late Cretaceous in northwestern Anatolia, a widespread magmatism from Eocene to Pliocene has developed, and the Tertiary magmatism has occurred in the region as a result of this collision (Şengör and Yılmaz, 1981; Yılmaz, 1989; Harris et al., 1994; Genç and Altunkaynak, 2007; Altunkaynak and Genç, 2008; Karacık et al., 2008; Yılmaz Şahin et al., 2010; Altunkaynak et al., 2012*a, b*; Altunkaynak

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and Dilek, 2013; Gülmez et al., 2013; Aysal, 2015). The Gökçeada volcanism, which is the subject of this study, is the product of magmatic activity that took place during Tertiary. Tertiary magmatism, which is exposed in Gökçeada, began in the Lower Eocene and its activity has continued until Middle Miocene in various phases.

In this study, the petrographical and geochemical features of Lower-Middle Eocene Dağiçitepe, Lower Oligocene Gökçeada lava/domes and the Middle Miocene Eşelek volcanic rocks are presented and the magmatic processes in the genesis and evolution of Gökçeada volcanic rocks are introduced with trace element ratio diagrams and petrogenetic models. Gökçeada has been investigated by various researchers in terms of geological and stratigraphic features (Akartuna, 1950; Akartuna and Atan, 1978; Temel and Çiftçi, 2002; Kesgin and Varol, 2003; Ilgar et al. 2008; Sarı et al., 2015). As a widespread volcanism was occurred on the island, recent studies have mainly focused on the geochronological, geochemical and petrological characteristics of these magmatic rocks (Elmas et al., 2017; Aysal et al., 2018).

2. Regional Geology

Gökçeada, which is the largest island of Turkey, is located at 20 km west of the Biga Peninsula. Metamorphic, magmatic and sedimentary rocks ranging from Mesozoic to Quaternary formed on the island (Figure 1). However, the geology is dominated by magmatic rocks, occupying large areas. Late Ediacaran/Early Paleozoic Çamlıca metamorphic rocks (Okay et al., 1990; Tunç et al., 2002) are the oldest rocks of the island and consist of sericitic-schist, chloritic-schist, slate and marble. Lower Eocene Karaağaç formation that is composed of submarine fan deposits unconformably overlies the Çamlıca metamorphics. The altered rhyolitic volcanic rocks outcropping in the NW of Gökçeada were first named by Sarı et al. (2015) as the "Dağiçitepe

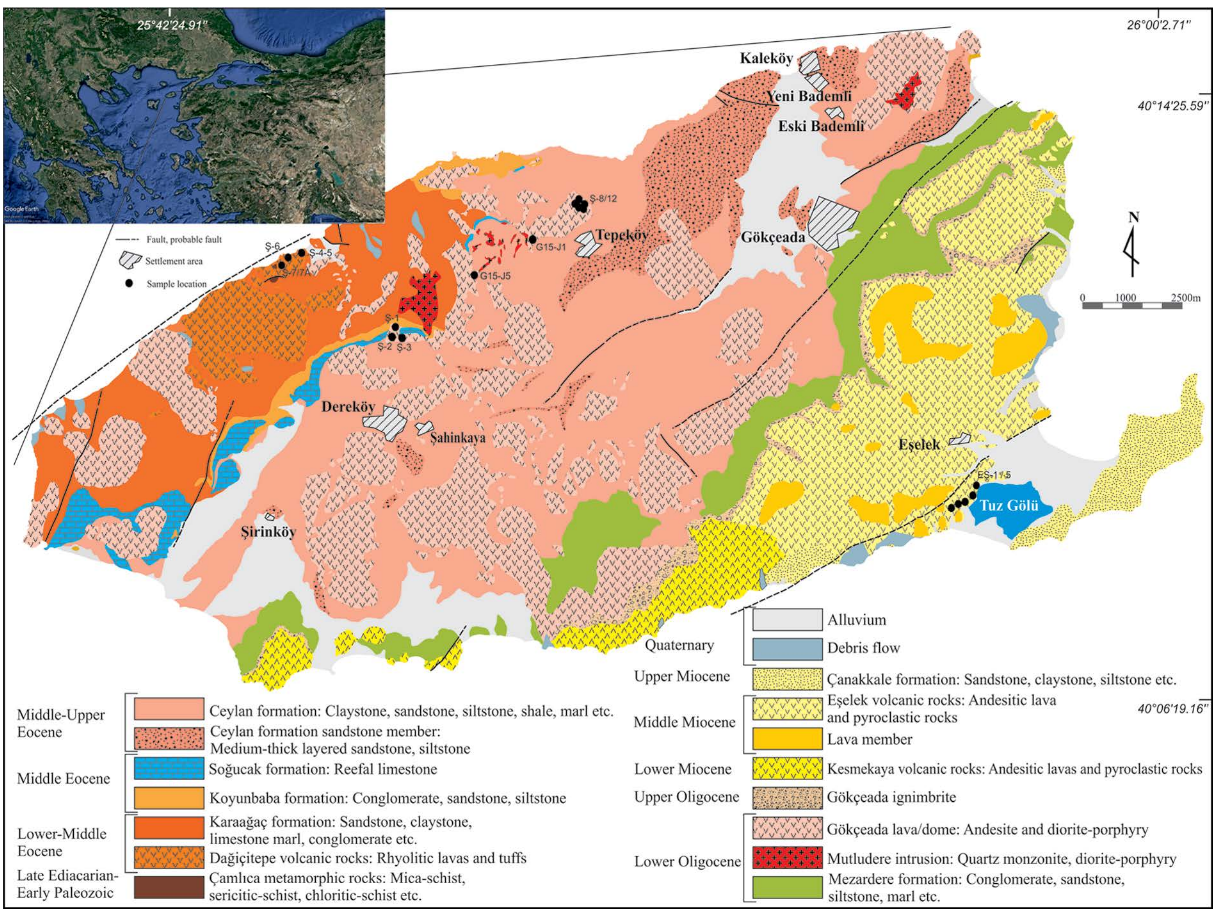

Figure 1- Geological map of Gökçeada (from Sarı et al., 2015).

volcanite member". The unit consisting of rhyolitic lava and tuff-tuffites is the oldest volcanic unit of the island**.** Elmas et al. (2017) defined these rhyolites and granitic plutons exposing in NW of the island as Marmaros Magmatic Assemblage and obtained an age of 26.2 ± 1.5 Ma from a rhyolite sample by the U-Pb LA-ICP-MS method. In the first stage of volcanic activity, the tuffs and then the lavas were erupted. The lavas of Dağiçitepe volcanic rocks were emplaced onto the Karaağaç formation by cutting Çamlıca metamorphic rocks. It is thought that they are Lower-Middle Eocene in age as the tuffs forming the unit are intercalated with the Karaağaç formation and lavas cut these deposits. Middle Eocene Koyunbaba formation, which is composed of shallow marine sandstones, unconformably overlies the Karaağaç formation and conformably underlies the reefal limestones. Middle-Upper Eocene Ceylan formation, which is formed by claystone-sandstone-shale alternation and deposited due to turbiditic currents in deep marine environment, conformably overlies the Soğucak formation. The unit is conformably overlain by the Mezardere formation. Lower Oligocene Mezardere formation (Ilgar et al., 2008) consists of the alternation of conglomerate with lesser amount of sandstone, siltstone and marl and it conformably overlies the Ceylan formation. Mezardere formation cut by the Gökçeada domes, is covered by the Gökçeada ignimbirite, and is cut and covered by the Eşelek volcanic rocks, too. The Mutludere intrusion, which is intruded into the sediments of the Karaağaç and Ceylan formations, has quartz-monzonite, diorite-porphyry composition (Sarı et al., 2015). As the Mutludere intrusion cut through the Upper Eocene sediments, it can be considered that the intrusion have been settled in the region after Eocene (Sarı et al., 2015). Andesite and diorite porphyry volcanic rocks occupying large areas on the island was named as the "Gökçeada domes" by Sarı et al. (2015). In this study, the domes will be called as the "Gökçeada andesitic lava/domes". Gökçeada andesitic lava/domes were emplaced into the Eocene sedimentary units in NE-SW trending dome-cryptodome and small lava flows in places. Gökçeada andesitic lava/domes were settled in Oligocene and their ages were detected as 28.6 ± 0.8 My by Sarı et al. (2015), and as 30.4 My and 34.3 My by Ercan et al. (1995) with radiometric age determinations using K/Ar method. These ages indicate that the magmatic activity occurred in the Lower Oligocene. However, Aysal et al. (2018) found that the U-Pb LA-ICP-MS zircon ages of the Gökçeada volcanic rocks were 25.66 ± 0.43 My and 26.0 ± 0.26 My. Pumice flows observed in east and south of Gökçeada were first named by Sarı et al. (2015) as the "Gökçeada ignimbrite". Gökçeada ignimbrite, which unconformably overlies the Ceylan and Mezardere formations, is unconformably overlain by Kesmekaya and Eşelek volcanic rocks. As the Gökçeada ignimbrite flows over the Lower Oligocene Mezardere formation and underlies the Middle Miocene Eşelek volcanic rocks, it is considered that the volcanic activity forming the ignimbrite occurred in the Upper Oligocene (Sarı et al., 2015). Lower Miocene Kesmekaya volcanic rocks composed of lava and block-and-ash flows are located on the Gökçeada ignimbrite. The andesitic lavas and pyroclastic rocks, which spread over large areas to the east of Gökçeada, were first mapped by Sarı et al. (2015) and named as the "Eşelek volcanic rocks". The pyroclastic deposits of the Eşelek volcanic rocks consist of lahar and block-and-ash flow deposits. Eşelek volcanic rocks overlies the Mezardere formation, Gökçeada ignimbrite and Kesmekaya volcanic rocks and unconformably underlies the Upper Miocene Çanakkale formation. Therefore, it is considered that the unit was formed in Middle Miocene. The Upper Miocene Çanakkale formation (Şentürk and Karaköse, 1987; Atabey et al., 2004) consists of less consolidated conglomerate, sandstone, siltstone and marl intercalations. The Quaternary deposits consist of debris flow and loose, unconsolidated conglomerate, sandstone, siltstone and mudstones unconformably overlie all formerly units.

3. Petrographical Features

Almost all of the samples from rhyolitic lavas of the Dağiçitepe volcanic rocks have been subjected to hydrothermal activity. All minerals, except quartz, were altered and transformed into other minerals. Only the external crystal forms of the original mineral are remained due to alteration (Figure 2a). Hornblende and biotite were completely opacified. While the great majority of the plagioclases were altered to sericite minerals, some of them were altered to pyrophyllite minerals (Figure 2a). The amount of glass in the groundmass is quite low. This is probably due to the subsequent development of secondary mineral formations. In addition to the silicification and carbonatization, the spherulites having a radiating structure that resulted from the intergrowth of quartz and feldspars due to silicification and devitrification, are observed (Figure 2a).

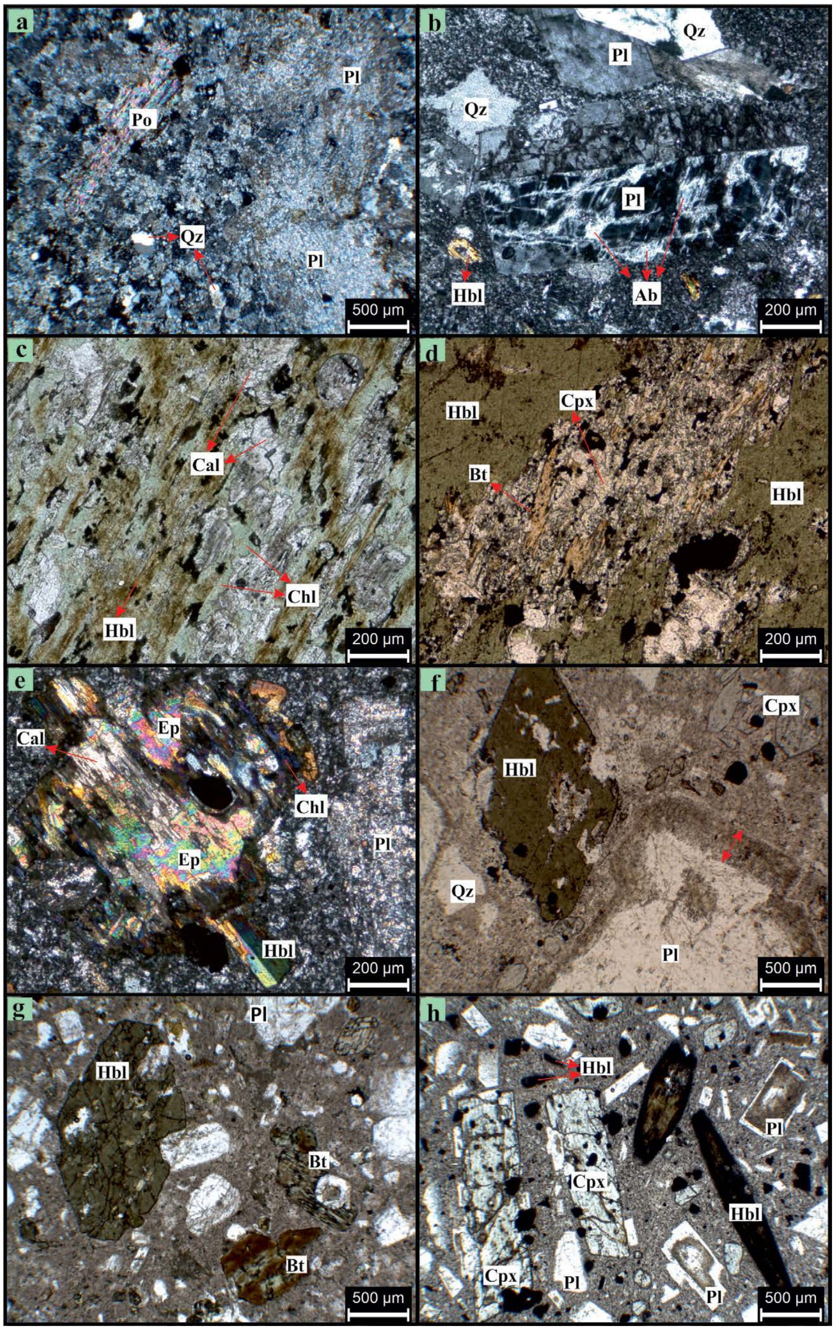

Figure 2- Photomicrographs of the Gökçeada volcanic rocks (Qz: quartz, Pl: plagioclase, Ab: albite, Hbl: hornblende, Cpx: clinopyroxene, Bt: biotite, Chl: chlorite, Ep: epidote, Cal: calcite and Po: pyrophyllite), a) quartz, sericitized plagioclase and secondary muscovite minerals in the devitrified groundmass, cross-polarized, Dağiçitepe volcanic rock Ş-5 sample, b) quartz, hornblende and albitized plagioclase phenocrysts in the silicified groundmass, cross-polarized, Gökçeada andesitic lava/domes Ş-9 sample, c) hydrothermally altered hornblende mineral, plane-polarized, Gökçeada andesitic lava/domes, d) relict clinopyroxene-based hornblende crystal and biotite minerals aligning in one direction, plane-polarized, Gökçeada andesitic lava/domes Ş-10 sample, e) pseudomorph epidote, calcite and chlorite aggregates, formed by hydrothermal alteration of sericitized plagioclase and clinopyroxene in silicified groundmass, cross-polarized, Gökçeada andesitic lava/domes Ş-1 sample, f) plagioclase with dusty zone, clear and euhedral clinopyroxene, resorbed quartz and hornblende minerals, plane-polarized, Gökçeada andesitic lava/domes Ş-10 sample, g) clear hornblende, plagioclase and partially chloritized biotite minerals, plane-polarized, Gökçeada andesitic lava/domes G15-J1, h) clear clinopyroxene, zoned plagioclase with glass inclusion, and partially or fully opacitized hornblende minerals, plane-polarized, Eşelek volcanic rock EŞ-2 sample.

Gökçeada andesitic lava/domes are andesitic volcanic products emplaced as NE-SW trending dome-cryptodome. Gökçeada andesitic lava/domes have hypocrystalline-porphyritic texture and their phenocrysts content vary between 40-75%. In general, the hydrothermal alteration is common and secondary minerals were formed. The groundmass significantly remained under the influence of silicification and carbonatization. For this reason, quartz minerals formed in the fractures and calcite are observed. There are three types of mineral assemblages in Gökçeada andesitic lava/domes; (1) plagioclase, hornblende, clinopyroxene ± quartz (crystal amount; 40-55%); (2) plagioclase, hornblende, clinopyroxene, biotite, quartz (crystal amount; 50-65%) and (3) plagioclase, hornblende, biotite ± quartz (crystal amount; 60-75%).

Plagioclase usually exhibits zoning and it was altered by sericitization, carbonatization and albitizations (Figure 2b). In plagioclase where alteration is less common, honeycomb textures and dusty zones are remarkable. Some plagioclase crystals are clustered as aggregate to form glomeroporphyric texture. The clear plagioclases exhibiting no alteration, zoning and inclusion, are rare.

Hornblende, particularly in the second and third assemblages, often occurs as clear crystals but it was also partially opacified along margins and cleavage planes. Whereas, almost all of the hornblendes in the first assemblage were either opacitized or carbonated (Figure 2c). Some hornblendes reaching up to 7 mm in grain size in the second assemblage contain relict pyroxene and biotite crystals occurred along the cleavage planes (Figure 2d).

Clinopyroxene, in the first assemblage, was subjected to intense alteration. Although it maintains its external crystal form, almost all of them are formed from secondary epidote, chlorite and calcite aggregates (Figure 2e). Except these samples, they commonly occur as clear crystals (Figure 2f).

Biotite, is usually seen as clear crystals, some have partially or completely altered to chlorite (Figure 2g).

Quartz occurs as anhedral aggregates, and present in the groundmass in large quantities. Some quartz have resorbed and rounded corners, some occur as subhedral crystals in the fractures.

Groundmass is mainly composed of anhedral quartz and plagioclase microlites and hornblende, clinopyroxene and opaque microcrystals as well. The amount of glass is low and the carbonatization, silicification and argillization are observed. Zircon and apatite are accessory minerals.

Eşelek volcanic rocks, represented by lava and pyroclastics in the east of Gökçeada, were first mapped and named by Sarı et al. (2015). The phenocryst amount of the andesitic lava samples from the Eşelek volcanic rocks is about 70%. All of them show hypocrystalline-porphyritic and intersertal texture. It consists of plagioclase, hornblende and clinopyroxene minerals.

Plagioclase; zoning, honeycomb textures and dusty zones, reflecting unstable conditions, are seen in the plagioclase crystals (Figure 2h).

Hornblende; the great majority of the hornblende crystals are completely opacitized, just the core of the coarse grains appear clear (Figure 2h).

Clinopyroxene; occur as clear pale green crystals.

The groundmass consists of microcrysts of clinopyroxene, hornblende, opaque minerals and plagioclase microlites. The glass amount is lower than crystals.

4. Analytical Techniques

Major-oxide, trace and rare earth element analyses were performed in the Department of Mineral Analysis and Technology of the General Directorate of Mineral Research and Exploration (MTA), Ankara, Turkey. The major-oxide analyses were determined on pressed pellets weighing approximately 3 gr sample, which are obtained by mixing cellulose as a binder (0.9 gr) and pressing under 40 kN pressure using the Thermo ARL brand XRF apparatus. Major element analyses were determined in the form of oxide % (SiO_2, Al_2O_3, Fe_2O_3 = total iron, MgO, CaO, Na_2O, K_2O, MnO, TiO_2, P_2O_5). The amount of loss on ignition (LOI) was determined as weight % of the sample calcified for 4 hours in an oven at 1050 ± 10 °C from the dried sample at 105 ± 5 °C for at least 4 hours.

Trace and rare earth element analyses were performed on the THERMO ICAP Q brand ICP-MS device. 0,25 g of the sample were dissolved with HCl, HNO_3, $HClO_4$ and HF acids and the dissolved sample was analysed by completing it to 50 ml. The Certified Reference Material JG-1a was used for the quality control of analyses. The measured values of the certified standard reference material during the analysis are given in table 1.

5. Geochemical Features

Major-oxide, trace and rare earth element analyses of the Lower-Middle Eocene Dağiçitepe, Lower Oligocene Gökçeada lava/domes and Middle-Miocene Eşelek volcanic rocks are given in table 1. The major-oxide results have been normalized to 100% on an anhydrous basis and then these data are plotted on the Zr/TiO_2 vs SiO_2 diagram of Winchester and Floyd (1977) (Figure 3) in order to classify the rocks. According to this diagram, Dağiçitepe volcanic rocks fall into the rhyolitic, Gökçeada andesitic lava/domes and Eşelek volcanic rocks fall into the andesitic fields, and they generally exhibit sub-alkaline character. Based on the AFM diagram with calc-alkaline-tholeiitic dividing line (Irvine and Baragar, 1971), the Dağiçitepe volcanic rocks and Gökçeada andesitic lava/domes fall into calc-alkaline, Eşelek volcanic rocks fall into the tholeiitic fields (Figure 3).

Major-oxide and trace element variation diagrams against SiO_2 (Harker diagrams) are given in figure 4. Increasing SiO_2 in Gökçeada andesitic lava/domes is correlated with i) decreasing Fe_2O_3, MgO, CaO, Sr and V and ii) slight increasing K_2O, Na_2O and Ba. These observed variations in Fe_2O_3, MgO, CaO and Sr elements are related to the fractionation of olivine, pyroxene, Ca-plagioclase and Fe-Ti minerals. K_2O, Na_2O and Ba elements also show a tendency to increase against SiO_2. The variations between SiO_2 and major-oxides, trace elements suggest that fractional crystallization processes are effective in the evolution of Gökçeada andesitic lava/domes. Increasing SiO_2 in the Dağiçitepe volcanic rocks is slightly correlated with; i) decreasing Fe_2O_3, CaO and Sr and ii) increasing Ba. However, it is observed that the Eşelek volcanic rocks show a narrow variation against SiO_2.

Primitive mantle normalized trace element abundances patterns for the selected samples from Gökçeada are presented in figure 5. Gökçeada volcanic rocks are enriched in large ion lithophile elements (LILE: Cs, Rb, Ba, K, Th, U) relative to the primitive mantle. In general, all volcanic rocks exhibit similar trace element distribution patterns. As seen in diagrams, all samples have remarkable negative Nb, Ta and Ti, and positive Th, U, Pb and K anomalies. However, the Dağiçitepe volcanic rocks are distinguished from Gökçeada andesitic lava/domes and Eşelek volcanic rocks with their low Sr, P and Ti anomalies. This is due to fractionated nature and acidic character of the Dağiçitepe volcanic rocks, since Sr and P elements are taken up by Ca-plagioclase and apatite minerals during fractional crystallization. Therefore, the negative Sr and P anomalies in the Dağiçitepe volcanic rocks can be explained by Ca-plagioclase and apatite fractionation. Trace element patterns of Eşelek volcanic rocks show similar trends to those of Gökçeada andesitic lava/domes. The Eşelek volcanic rocks show different variations in Zr and Hf elements with respect to the Dağiçitepe volcanic rocks and Gökçeada andesitic lava/domes. Negative anomalies observed in Nb, Ta and Ti, and the positive anomalies in Th, U and Pb elements are typical geochemical characteristics of subduction-related magmas. In addition, contamination by crustal rocks during magma ascent to surface causes such anomalies (Gill, 1981; Thompson et al., 1983; Fitton et al., 1988).

Chondrite normalized rare earth element (REE) distribution diagrams (McDonough and Sun, 1995) of Gökçeada volcanic rocks are given in figure 6.

REE distribution patterns of the Gökçeada volcanic rocks show similar trends. The chondrite normalized (La/Yb)n ratios (McDonough and Sun, 1995) of the Dağiçitepe volcanic rocks, Gökçeda andesitic lava/domes and Eşelek volcanic rocks vary between 11,50-14,59, 13,82-18,17 and 8,23-8,68, respectively. This ratio points out the fractionated nature of the Dağiçitepe volcanic rocks and Gökçeada andesitic lava/domes, however, the fractionation is not effective in the Eşelek volcanic rocks as they have a lower (La/Yb)n ratio than others. Besides, slight depletion in heavy rare earth elements (HREE) in Dağiçitepe volcanic rocks relative to other volcanics in the study area and the presence of negative Eu anomalies are due to fractionated nature of these rhyolitic rocks.

Table 1- Major-oxide, trace and rare earth element analysis of Gökçeada volcanic rocks. (LOI: Loss On Ignition; wt.%: weight %)

	Dağiçitepe volcanic rocks (Lower-Middle Eocene)					Gökçeada andesitic lava/domes (Lower Oligocene)										Eşelek volcanic rocks (Middle Miocene)					JG-1a (Standard Reference Material)
Sample No	**Ş-4**	**Ş-5**	**Ş-6**	**Ş-7**	**Ş-7A**	**Ş-1**	**Ş-2**	**Ş-3**	**Ş-8**	**Ş-9**	**Ş-10**	**Ş-11**	**Ş-12**	**G15-J1**	**G15-J5**	**EŞ-1**	**EŞ-2**	**EŞ-3**	**EŞ-4**	**EŞ-5**	
SiO_2 (Wt. %)	70,1	70	70,3	73,5	72,3	59,5	56,1	57,8	62,6	62,4	62,5	61,1	62,4	60,3	60,9	58,2	58	58,5	58,2	58,2	
Al_2O_3	16,3	16,7	15,8	17	16,2	16,8	16,1	16,4	17,1	17,1	17	18	17,1	16,8	16,6	17,4	17,2	17,1	17,2	17,2	
CaO	2,7	2,6	1,9	0,1	0,1	4,5	7,1	5,2	3,6	4,8	5,1	2,6	4,8	4,4	4,6	5,8	6,9	7,1	7	7,1	
Fe_2O_3	1	1	1,4	1,1	1,2	5,6	5,6	5,8	4,8	4,6	4,7	4,6	4,7	5,6	4,7	7,3	7,3	6,9	7	6,9	
MgO	0,3	0,2	0,2	0,2	0,2	2,3	2,6	3	1,4	1,4	1,3	1,3	1,4	2,1	2,3	1,3	1,3	1,3	1,3	1,3	
MnO	0,1	0,1	0,1	<0.1	<0.1	0,2	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,2	0,1	0,1	0,1	0,1	0,1	0,1	
K_2O	4	4,3	4,2	3,4	4,4	3,8	3,3	3,6	3,9	3,5	3,7	5,5	3,5	3,3	3,4	2,9	2,9	2,9	3	2,9	
Na2O	0,2	0,2	2,8	0,3	2,9	3,5	2,5	3	4,8	4,1	3,9	5,1	4,2	3,1	3,6	3,1	3,3	3,3	3,3	3,3	
P_2O_5	<0.1	<0.1	<0.1	<0.1	<0.1	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,2	0,4	0,4	0,4	0,5	0,4	
TiO_2	0,2	0,2	0,2	0,2	0,2	0,6	0,6	0,6	0,5	0,5	0,5	0,5	0,5	0,6	0,5	1,1	1,1	1,1	1,1	1,1	
A.K.	4,8	4,5	2,8	3,7	2,05	2,7	5,5	3,35	0,6	0,75	0,5	0,7	0,65	2,6	2,75	2,05	1,05	0,85	1,05	0,95	
Total	99,7	99,8	99,7	99,5	99,55	99,8	99,8	99,15	99,7	99,55	99,6	99,8	99,65	99,3	99,65	99,65	99,55	99,55	99,75	99,45	
Sc (ppm)	1,26	1,19	1,19	1,17	1,41	11,04	11,14	11,45	9,40	8,41	8,74	8,76	8,12	9,44	11,06	15,02	14,81	14,92	15,02	14,09	7
V	30,94	27,97	31,94	27,40	27,06	181,60	185,10	190,80	184,50	186,00	177,70	181,70	167,00	204,40	196,90	248,20	256,50	246,10	247,70	238,90	20,56
Cr	69,57	44,37	102,30	62,10	61,34	44,90	39,41	49,17	57,39	196,50	55,24	34,54	79,65	99,38	100,30	33,78	31,23	37,66	34,30	23,72	15,42
Rb	163,4	159,2	149,3	118,8	166,1	132,8	127,5	155,8	162,5	140,2	138,7	231	131,9	149	139,9	108	105,3	104,4	100,4	96,3	142,33
Sr	65,76	104,8	182	65,54	128,4	835,6	647,6	749,1	685,7	903	877	631,8	845,4	1072	1059	812,9	822,3	854,1	831	804,4	154,21
Y	11,59	11,85	11,77	10,03	12,19	13,88	13,78	15,49	13,97	13,52	13,92	14,05	13,97	15,68	16,53	24,89	26,68	30,46	27,32	27,92	35,27
Zr	35,23	43,5	40,87	46,49	62,71	69,66	62,69	72,6	77,83	66,8	68,58	84,6	65,48	86,66	58,96	230,5	237,9	240,4	234,5	224,6	91,84
Nb	9,59	9,77	9,12	9,01	10,72	4,86	4,21	4,07	4,89	4,81	4,89	4,92	4,58	5,30	5,58	7,08	6,90	7,06	6,85	6,90	9,37
Cs	4,26	4,06	3,84	3,43	3,39	5,88	7,03	15,50	2,56	3,15	3,21	1,89	3,15	3,87	12,90	2,90	4,11	2,62	1,97	1,90	11,21
Ba	1083	1160	1135	1092	1409	1252	1096	1214	1252	1297	1325	1333	1531	1518	1775	1372	1193	1171	1162	1222	403,82
La	26,97	23,56	22,82	22,86	24,50	25,31	25,69	28,37	30,80	31,47	35,20	38,14	30,72	40,66	37,38	30,87	33,24	39,99	34,32	34,73	19,84
Ce	58,27	50,94	49,15	46,39	51,88	53,56	54,97	56,37	62,60	63,89	64,43	68,70	62,32	74,88	72,08	65,87	65,44	76,70	68,00	68,38	39,95
Pr	5,43	4,79	4,67	4,59	5,01	5,14	5,26	5,70	6,00	6,06	6,12	6,60	5,98	7,29	7,08	7,20	7,02	8,36	7,33	7,24	5,48
Nd	21,27	18,95	18,57	18,26	19,44	22,28	22,79	24,75	25,19	25,43	25,54	27,31	25,05	30,75	30,08	32,95	31,90	37,96	33,22	32,95	18,74
Sm	3,67	3,36	3,27	3,27	3,33	4,17	4,21	4,57	4,55	4,50	4,57	4,73	4,45	5,45	5,40	6,65	6,45	7,57	6,67	6,64	4,21
Eu	0,81	0,75	0,77	0,76	0,77	1,15	1,14	1,21	1,19	1,24	1,24	1,28	1,25	1,48	1,49	1,81	1,75	1,88	1,77	1,75	0,64
Gd	3,33	3,03	3,03	3,00	3,03	4,05	4,11	4,37	4,20	4,27	4,32	4,41	4,21	5,11	5,09	6,60	6,47	7,61	6,56	6,70	3,84
Tb	0,37	0,34	0,35	0,33	0,34	0,45	0,45	0,48	0,47	0,46	0,48	0,48	0,46	0,55	0,57	0,82	0,82	0,96	0,83	0,86	0,68
Dy	1,94	1,94	1,88	1,71	1,88	2,43	2,47	2,59	2,52	2,43	2,53	2,56	2,45	2,93	3,11	4,74	4,86	5,66	4,96	5,09	3,98
Ho	0,37	0,37	0,36	0,31	0,37	0,46	0,46	0,48	0,46	0,45	0,47	0,48	0,46	0,55	0,58	0,90	0,94	1,10	0,96	0,99	0,67
Er	1,21	1,26	1,19	1,01	1,25	1,38	1,43	1,47	1,45	1,40	1,48	1,51	1,45	1,70	1,83	2,78	2,98	3,42	3,05	3,16	2,11
Tm	0,17	0,19	0,17	0,15	0,19	0,18	0,19	0,20	0,19	0,19	0,20	0,21	0,20	0,23	0,25	0,37	0,40	0,47	0,41	0,43	0,24
Yb	1,27	1,39	1,28	1,07	1,42	1,22	1,27	1,34	1,34	1,30	1,37	1,43	1,34	1,60	1,72	2,51	2,75	3,14	2,81	2,87	3,51
Lu	0,20	0,21	0,20	0,17	0,22	0,19	0,19	0,20	0,20	0,20	0,21	0,22	0,20	0,24	0,26	0,37	0,41	0,47	0,42	0,43	0,38
Hf	1,22	1,46	1,39	1,49	2,00	1,73	1,59	1,85	2,02	1,79	1,88	2,24	1,82	2,42	1,79	5,02	5,04	5,21	5,04	4,86	2,78
Ta	0,75	0,75	0,70	0,68	0,76	0,51	0,48	0,46	0,45	0,45	0,46	0,47	0,44	0,50	0,49	0,61	0,60	0,63	0,59	0,60	2,41
Pb	17,11	17,52	19,38	14,27	18,34	16,17	9,93	15,14	20,84	26,69	18,49	20,99	17,16	23,48	24,05	19,71	17,55	20,71	14,96	14,65	19,57
Th	15,16	14,16	13,41	13,80	14,54	11,83	12,18	12,02	17,10	19,79	17,96	22,03	17,67	23,96	15,15	14,25	14,16	14,78	14,14	13,84	15,24
U	3,27	3,74	4,63	2,64	3,67	3,27	3,55	3,75	5,41	4,64	5,60	6,81	4,45	7,25	4,74	3,66	4,58	5,04	4,85	4,73	4,21

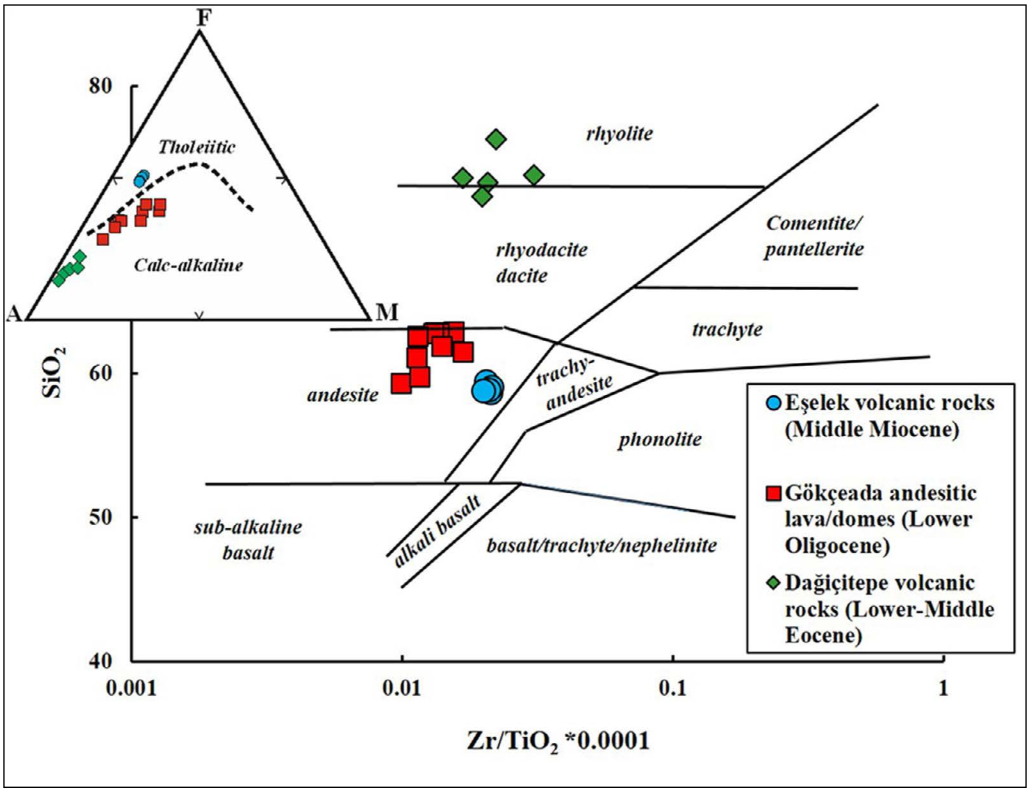

Figure 3- Zr/TiO_2 vs SiO_2 diagram of the Gökçeada volcanic rocks (Winchester and Floyd, 1977). The inset figure is the representation of sub-alkaline samples in the AFM diagram (Irvine and Baragar, 1971).

6. Discussion

6.1. Source Characteristics

Trace and rare earth element geochemistry demonstrate that subduction and/or crustal contamination processes (low Nb, Ta and Ti; high Th, U and Pb contents) are effective in the genesis and evolution of the Gökçeada volcanism. Therefore, trace element ratio and tectonic discrimination diagrams are drawn in order to clarify the tectonic setting and source characteristics of the Gökçeada volcanism. Elmas et al. (2017)'s data of Gökçeada volcanic rocks are also plotted onto diagrams. Ba/La vs Nb/La diagram is used to distinguish within-plate volcanism from orogenic volcanisms, because high Ba/Nb (>28) and Ba/Ta (>450) ratios are the characteristics of subduction-related magmas (Gill, 1981; Fitton et al., 1988) and high Nb/La (>1,5) ratio is the typical characteristic of within-plate volcanism subjected no and/or negligible crustal contamination (Haase et al., 2000). Gökçeada volcanic rocks have very high Ba/Nb (112-334) and Ba/Ta (1452-3608) ratios. As can be seen from Figure 7a, the Gökçeada volcanic rocks are located in the region represented by orogenic andesites. While the vertical trend observed in the Rb/Y vs Nb/Y diagram (Figure 7b) indicates the crustal contamination and/or subduction zone enrichment, within-plate enrichment results from a positive relationship between Rb and Nb (Edwards et al., 1991). Gökçeada volcanic rocks show a vertical trend in the direction of subduction enrichment and fall close to the field represented by Andean volcanic rocks. Also in Th/Ta vs Yb diagram, it is seen that the samples are concentrated in the field represented by arc magmatism (Figure 7c).

In (Nb/Zr)n vs Zr diagram (Figure 7d), while Dağiçitepe volcanic rocks are plotted in the collisional zone, Gökçeada andesitic lava/domes and Eşelek volcanic rocks are plotted in the subduction related zone. Additionally, all samples are plotted within the field of volcanic arc and syn-collisional granite field in Nb vs Y tectonic discrimination diagram of Pearce et al. (1984) suggested for granitic rocks (inset diagram in figure 7d). However, as the tectonic setting of granitic rocks falling at the intersection of within-plate granites (WPG), volcanic-arc granites (VAG), and syn-collisional granites (syn-COLG) is still controversial, this intersection field is regarded

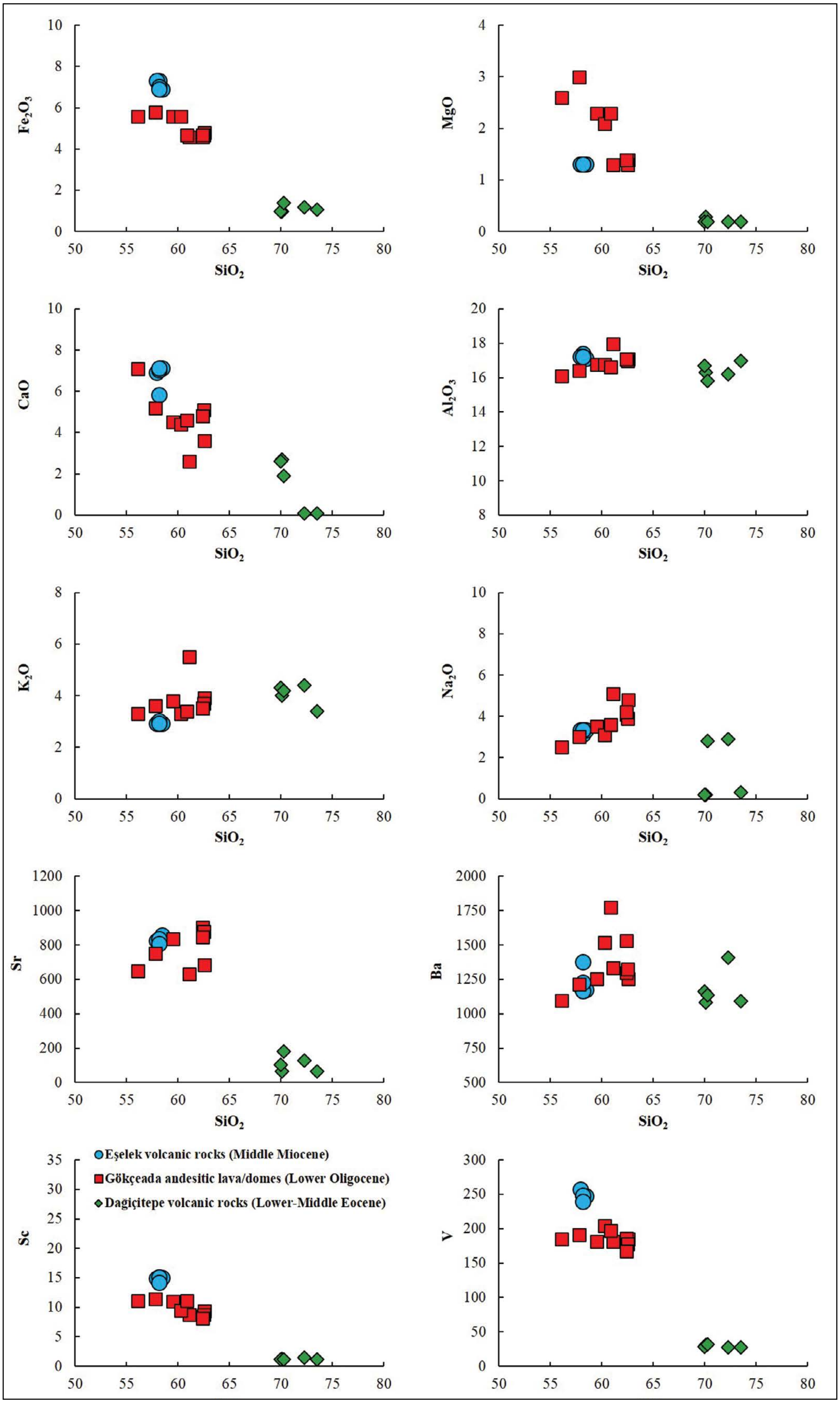

Figure 4- The major-oxide and trace element vs SiO_2 variation diagrams of the Gökçeada volcanic rocks.

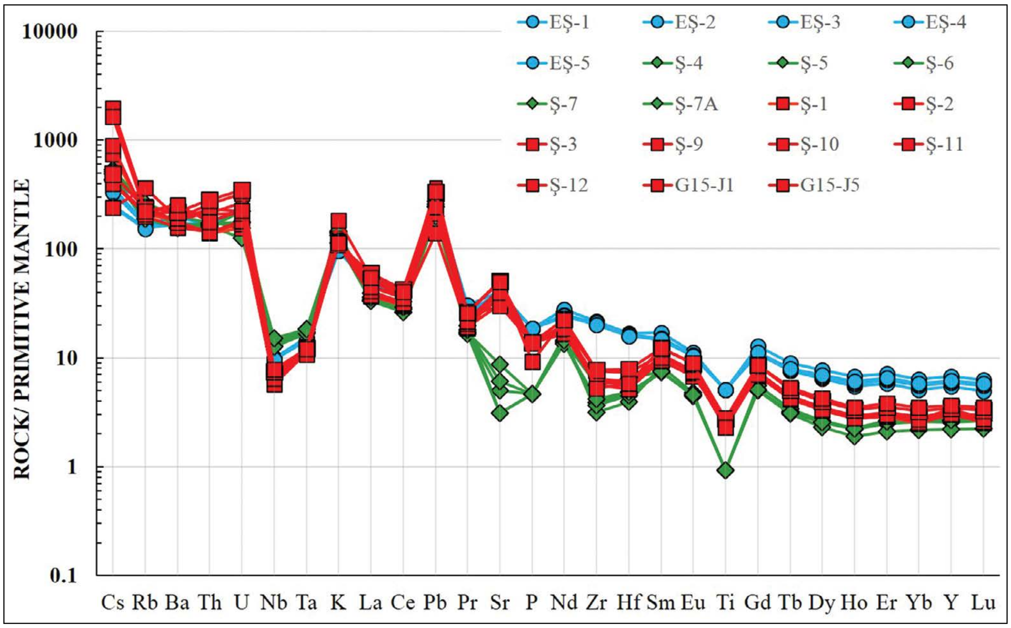

Figure 5- Primitive mantle-normalized (Sun and McDonough, 1989) trace element distribution patterns of Gökçeada volcanic rocks.

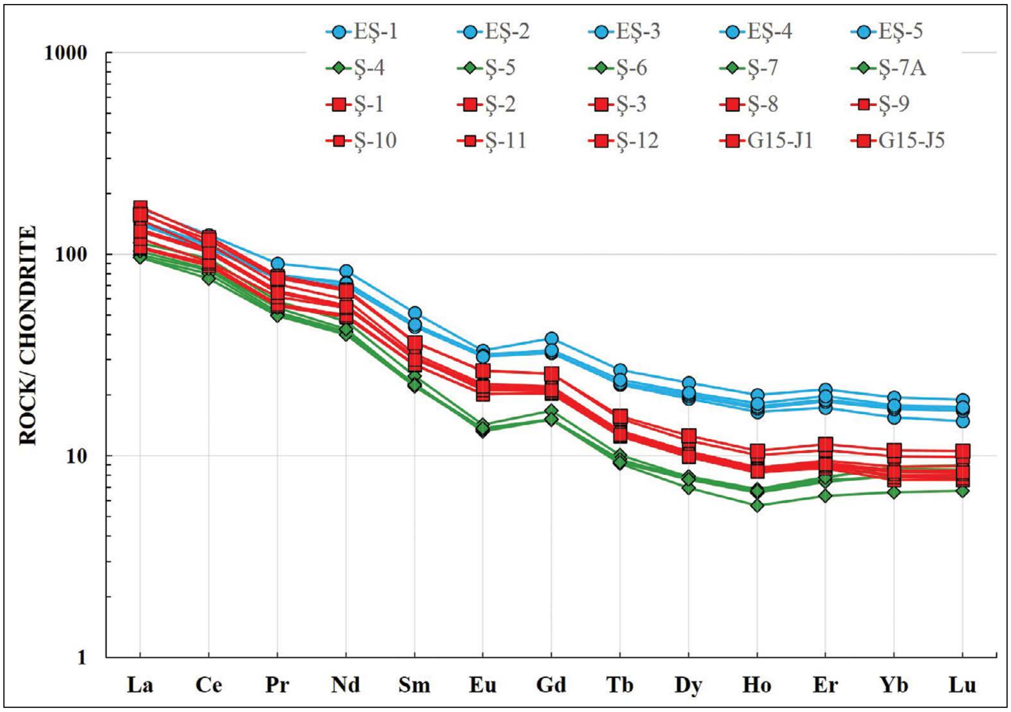

Figure 6- Chondrite normalized rare earth element distribution diagram of the Gökçeada volcanic rocks (McDonough and Sun, 1995).

as post-collisional granite (post-COLG) field (Pearce, 1996). According to this diagram, Dağiçitepe volcanic rocks and Gökçeada andesitic lava/domes slightly shifted from the field of post-collisional granite to volcanic arc granite (VAG) and syn-collisional granite (syn-COLG) field, Eşelek volcanic rocks are located in the post-collisional granite field (Figure 7d). According to the trends in figure 7d, it can be suggested that Dağiçitepe volcanic rocks are the products of collisional magmas, Gökçeada andesitic lava/domes and Eşelek volcanic rocks are the products of post-collisional magmas.

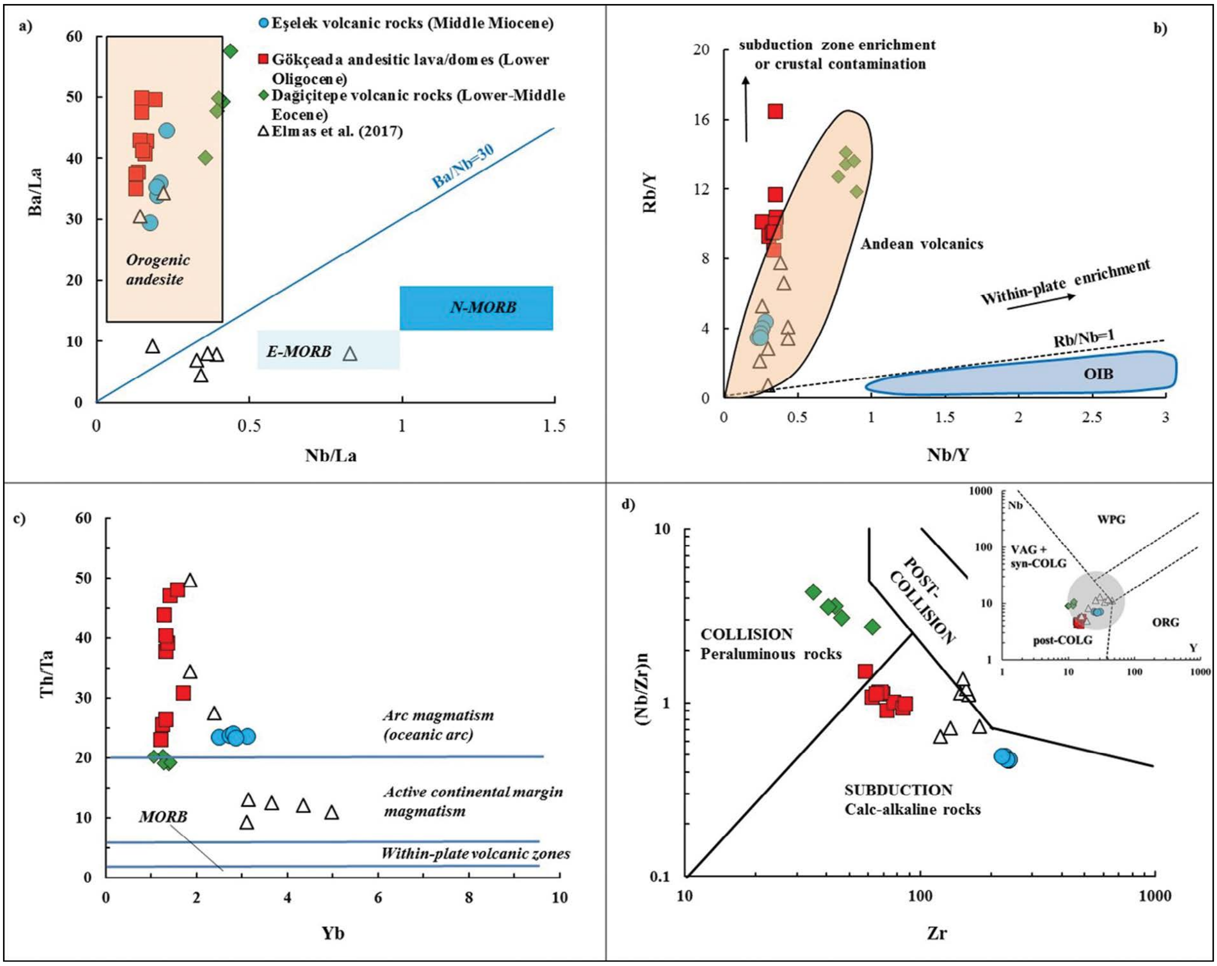

Figure 7- a) Ba/La vs Nb/La; b) Rb/Y vs Nb/Y (Edwards et al., 1991); c) Th/Ta vs Yb (from Zak et al., 2011 and Qian et al., 2013); d) (Nb/Zr) n vs Zr (Thiéblemont and Tegyev, 1994) diagrams of the Gökçeada volcanic rocks (inset figure from Pearce et al., 1984 and Pearce, 1996). Abbreviations: E-MORB: Enriched-Mid Ocean Ridge Basalt; N-MORB: Normal Mid Ocean Ridge Basalt; OIB: Ocean Island Basalts; post-COLG: Post-Collisional Granites; syn-COLG: syn-Collisional Granites; VAG: Volcanic Arc Granites; WPG: Within-plate Granites; ORG: Ocean Ridge Granites. The data of the Andean volcanic rocks are from Hickey et al. (1986; 1989) and Bryant et al. (2006).

6.2. Crustal Contamination

In order to determine the role of crustal contamination and fractional crystallization process in the evolution of Gökçeada volcanism, the AFC (assimilation - fractional crystallization) model of De Paolo (1981) has been applied in a Th/Y vs Nb/Y diagram. In the modeling, MORB (Mid Ocean Ridge Basalt) (Hofmann, 1988) and upper crust (UC) (McLennan, 2001) have been used as the initial starting composition and concomitant end-members, respectively. The ratios of the rate of assimilation to the rate of crystallization (-r values) are -0,1 and 0,7 (Figure 8). Gökçeada andesitic lava/domes and Eşelek volcanic rocks are shifted from the AFC trajectories in the direction of high Th/Y with almost constant Nb/Y ratios. This could be possibly due to the source characteristics rather than the involvement of crustal material to magmas during their ascent to the surface. However, the Dağiçitepe volcanic rocks are located close to the r=0,7, indicating the involvement of crustal material during their rise. Additionally, it can be concluded that the magmas generating Gökçeada volcanism retain the geochemical features of the subduction-related magmas, since almost all samples are located within the field of Andean volcanic rocks.

Low Ce/Pb ratio is one of the most characteristic features of the crustal contamination and/or sediment contamination to the mantle material, because the Pb content in crustal materials is remarkably higher than the mantle. Hofmann et al. (1986) have shown that OIB and MORB (Ocean Island Basalt & Mid Ocean Ridge Basalt) mantle have a high and relatively constant Ce/Pb ratio (~25). On the other hand, the upper crust and GLOSS (Global Subducting Sediment) have low Ce/Pb values (~3,8 and ~2,9) (Taylor and McLennan, 1985; Plank and Langmuir, 1998; McLennan, 2001). The AFC modeling in the Th/Y and Nb/Y diagram indicates that high Th and low Nb contents in the Gökçeada volcanic rocks can be related to the source characteristics rather than the crustal contamination, since higher Th contents already indicate the involvement of subducted sediment (Plank, 2005; Labanieh et al., 2012). Therefore, in order to assess the reasons of high Th and Pb contents in the Gökçeada volcanic rocks and to reveal the role of sediment involvement in the genesis of volcanic rocks, binary mixing model of Langmuir et al. (1978) has been performed and a mixing curve has been calculated in a Ce/Pb vs Pb diagram between 'MORB' and 'sediment', with an average Pb content (0,7) and Ce/Pb ratio (25,7) for MORB (Normand and Garcia, 1999) and Pb content (27) and Ce/Pb ratio (2,2) for the gravity core sediment sample (N17/30) from Kermadec-Hikurangi volcanic arc system (Gamble et al., 1996) (Figure 9a). The Gökçeada volcanic rocks generally lie on the mixing curve in the direction of 'sediment' end-member. Accordingly, it can be concluded that the contribution of sediment having arc signatures plays an important role.

Figure 9b displays the Rb/Ba vs Rb/Sr diagram with binary mixing curve between '*basalt-derived melt'* and '*pelite-derived melt'* (Slyverster, 1998). It is clear from this figure that the Eşelek volcanic rocks and Gökçeada andesitic lava/domes are distributed close to the '*basalt-derived melt*' end-member, indicating derivation from a mantle source rather than crustal melting, because 'basalt-derived melt' and 'pelite-derived melt' end-members in the diagram represent mantle and crustal source, respectively (Sylvester, 1998; Li et al., 2015; Chen et al., 2017). Whereas, Dağiçitepe volcanic rocks shift to higher Rb/Sr ratios with no corresponding change in Rb/Ba. This could be because the fractionated and contaminated nature of the Dağiçitepe samples. This case is also supported by the variations observed in the Th/Y-Nb/Y diagram for Dağiçitepe volcanic rocks (Figure 8).

Consequently, the geochemical evaluations reveal that the Gökçeada volcanism have geochemical

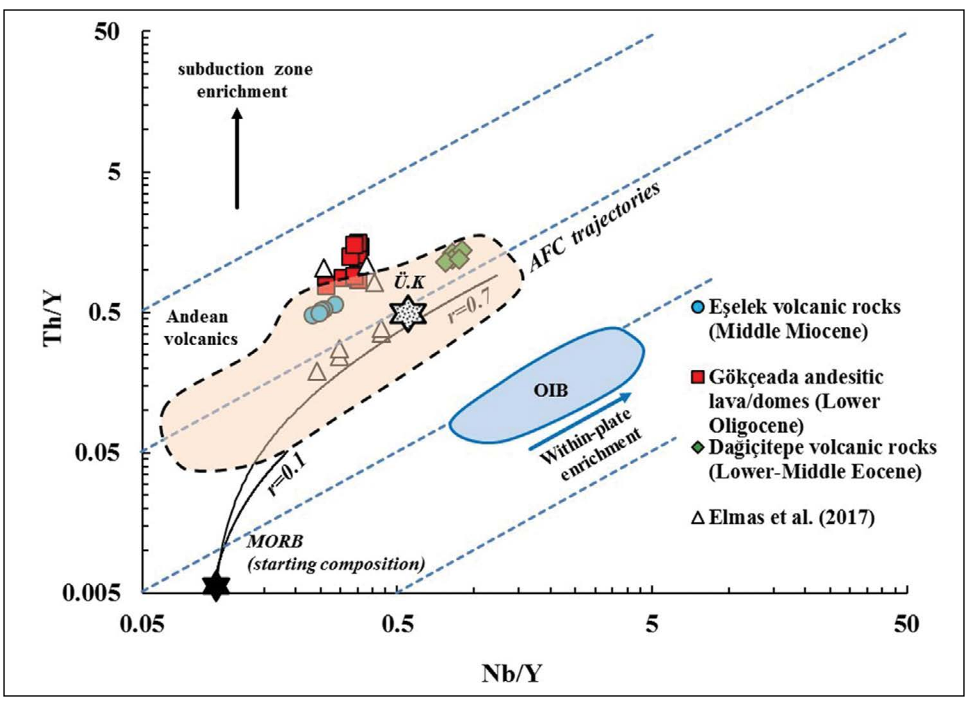

Figure 8- AFC modeling for the Th/Y vs Nb/Y diagram between Mid Ocean Ridge Basalts (MORB, Hofmann, 1988) and the upper crustal end-members. (Andean volcanic rocks are from Hickey et al. (1986; 1989) and Bryant et al., 2006). The r (the ratio of the rate of assimilation to the rate of crystallization) is shown as trajectories on the diagram.

variations similar to that of subduction-related magmatism and subduction processes in their genesis have played a major role (Figure 7). Further, the Dağiçitepe volcanic rocks are the products associated with collision-related magmas, and they have subjected to the crustal contamination during their ascent through the thickened crust. Gökçeada andesitic lava/domes and Eşelek volcanic rocks are the products of post-collisional magmas retaining subduction signatures.

6.3. Petrological Modeling

In order to determine the source mineralogy and melting depth of the Gökçeada volcanism, the non-modal batch-melting model of Shaw (1970) has been realized. In the model, the enriched lithospheric mantle component from McDonough (1990) has been chosen as the initial component (C0). Garnet bearing amphibole-peridotite for the source composition and has been used, and the non-modal batch melting

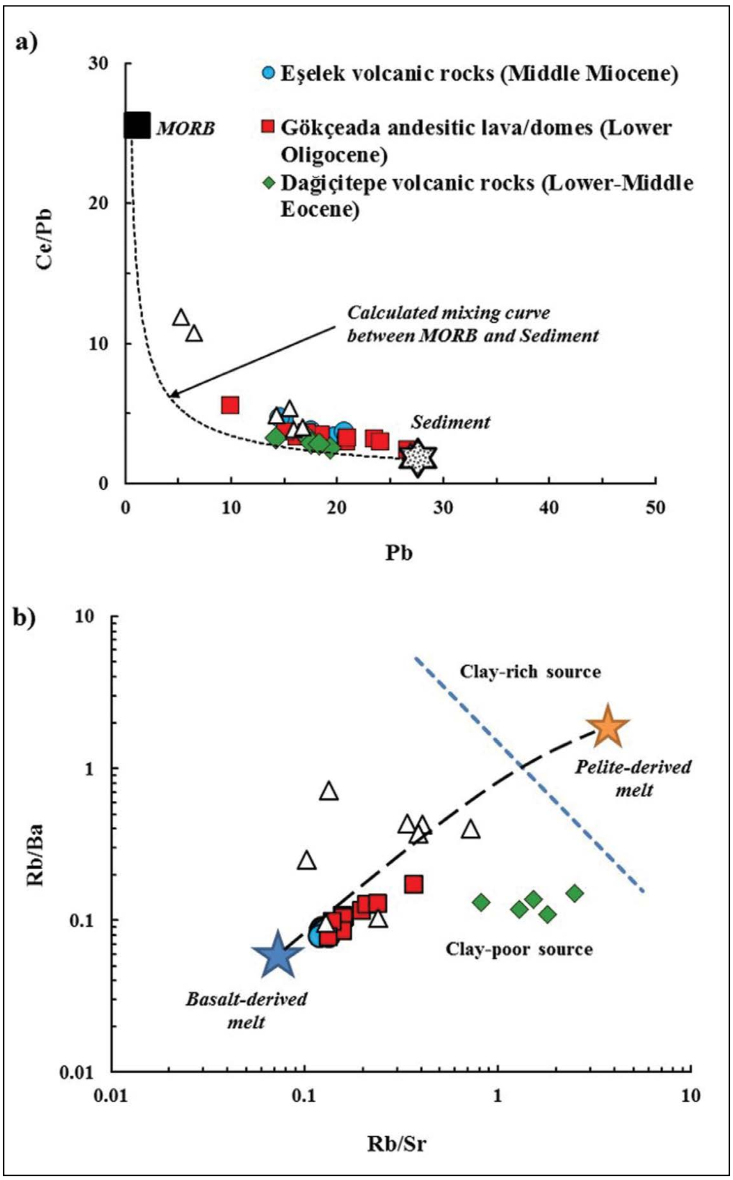

Figure 9- a) Ce/Pb vs Pb binary mixing diagram (Langmuir et al., 1978) (MORB and sediment values are from Normand and Garcia (1999) and Gamble et al. (1996), respectively); b) Rb/Ba vs Rb/Sr diagram of the Gökçeada volcanic rocks. (The mixing curve between the basalt-derived melt and pelite-derived melt from Sylvester (1998).

calculations have been performed. The mineral/melt partition coefficient (Kd) values for basaltic melts of the REEs are from Rollinson (1993), McKenzie and O'Nions (1991) and Adam and Green (2006; 2010). The modal mineralogy (X) and melting mode (Pi) values of the garnet-bearing amphibole peridotite melting facies and La, Sm and Yb concentrations of the enriched lithospheric mantle component are from McDonough (1990) and Ersoy et al. (2012). The data used in the modeling calculations are given in table 2. It can be concluded from the figure 10 that the Gökçeada andesitic lava/domes were derived from a garnet bearing amphibole-peridotite via variable degrees of partial melting, since they are clearly plotted on the melting curve drawn for the 3%, 5% and 7% garnet-bearing amphibole peridotite (Figure 10). The Eşelek volcanic rocks, on the other hand, represent a relatively depleted source with low La/Yb, Sm/Yb and (Tb/Yb)n ratios. The petrogenetic modeling diagrams show that metasomatic processes play a dominant role in the Lower Oligocene Gökçeada andesitic lava/domes. However, the mantle source generating the Middle Miocene Eşelek volcanic rocks became more depleted over time.

Table 2- Data used in the non-modal batch melting calculations. Abbreviations: Opx: orthopyroxene; Cpx: Clinopyroxene.

	Amphibole bearing garnet peridotite			
	Source Mode (X)			Melting Mode (Pi)
	7%	5%	3%	
Olivine	0,54	0,54	0,54	0,05
Opx	0,21	0,21	0,21	0,05
Cpx	0,12	0,14	0,15	0,3
Garnet	0,07	0,05	0,03	0,2
Amphibole	0,06	0,06	0,06	0,4
	Initial concentration (C0)	**Bulk Partition Coefficient (D0)**		**Melting Mode (P)**
La	2,6	0,0082		0,0292
Sm	0,47	0,0659		0,2284
Tb	0,07	0,127		0,5116
Yb	0,26	0,2282		1,1489

6.4. Geodynamic Effects

Late Cretaceous-Early Eocene tectonic evolution of the Western Anatolia is represented by the ophiolite emplacement, high pressure/low temperature metamorphism, subduction, arc magmatism and continent-continent collision (Okay et al., 2001). The consumption of the oceanic lithosphere of the northern branch of Neotethys by northward subduction beneath the Sakarya continent caused the continent-continent collision between the Sakarya continent and the Anatolide-Tauride platform. It is suggested that consumption of the northern branch of Neotethys and subsequent collision, which caused the formation of İzmir-Ankara Suture Zone occurred in the Paleocene-early Eocene (Harris et al., 1994; Okay and Tüysüz, 1999; Altunkaynak et al., 2012*b*). Tertiary magmatic activity in NW Anatolia is also the products of this collision (Şengör and Yılmaz, 1981; Yılmaz, 1989; Harris et al., 1994; Yılmaz et al., 1995). Additionally, the stratigraphic data (Akdeniz, 1980; Akyürek and Soysal, 1983; Yılmaz et al., 1997) also reveals that the collision was earlier than the Middle Eocene and the Eocene magmatism corresponded to the post-collisional magmatism (Harris et al., 1994; Genç and Yılmaz, 1997; Köprübaşı and Aldanmaz, 2004; Altunkaynak and Dilek, 2006; Altunkaynak, 2007; Altunkaynak et al., 2012*b*). Gökçeada has a widespread magmatism with variable ages and compositions. The genesis and evolution of the Lower-Middle Eocene Dağiçitepe volcanic rocks, Lower Oligocene Gökçeada andesitic lava/domes and Middle Miocene Eşelek volcanic rocks are related to the Late Cretaceous-Early Eocene tectonic evolution. The overall geochemical variations reveal that the geodynamic evolution of the region has been effective in the genesis and evolution of the volcanism. Accordingly;

(i) (Nb/Zr)n vs Zr tectonic discrimination diagram (Figure 7d) reveals that the Dağiçitepe volcanic rocks were generated in a collision related setting, and Th/Y vs Nb/Y and Rb/Ba vs Rb/Sr diagrams in which the assimilation and fractional crystallization processes are modeled reveal the effects of crustal contamination in their evolution. Accordingly, the Lower-Middle Eocene Dağiçitepe volcanic rocks carry the geochemical signatures of collisional magmas as it corresponds to the latest stages of the collision (e.g., crustal contamination).

(ii) Gökçeada andesitic lava/domes and Eşelek volcanic rocks are clearly fall into the subduction-related field (Figure 7d). Moreover, since both volcanisms are located close to the "*basalt-derived melt*" end-member, representing the mantle source in the Rb/Ba vs Rb/Sr diagram, the effects of crustal

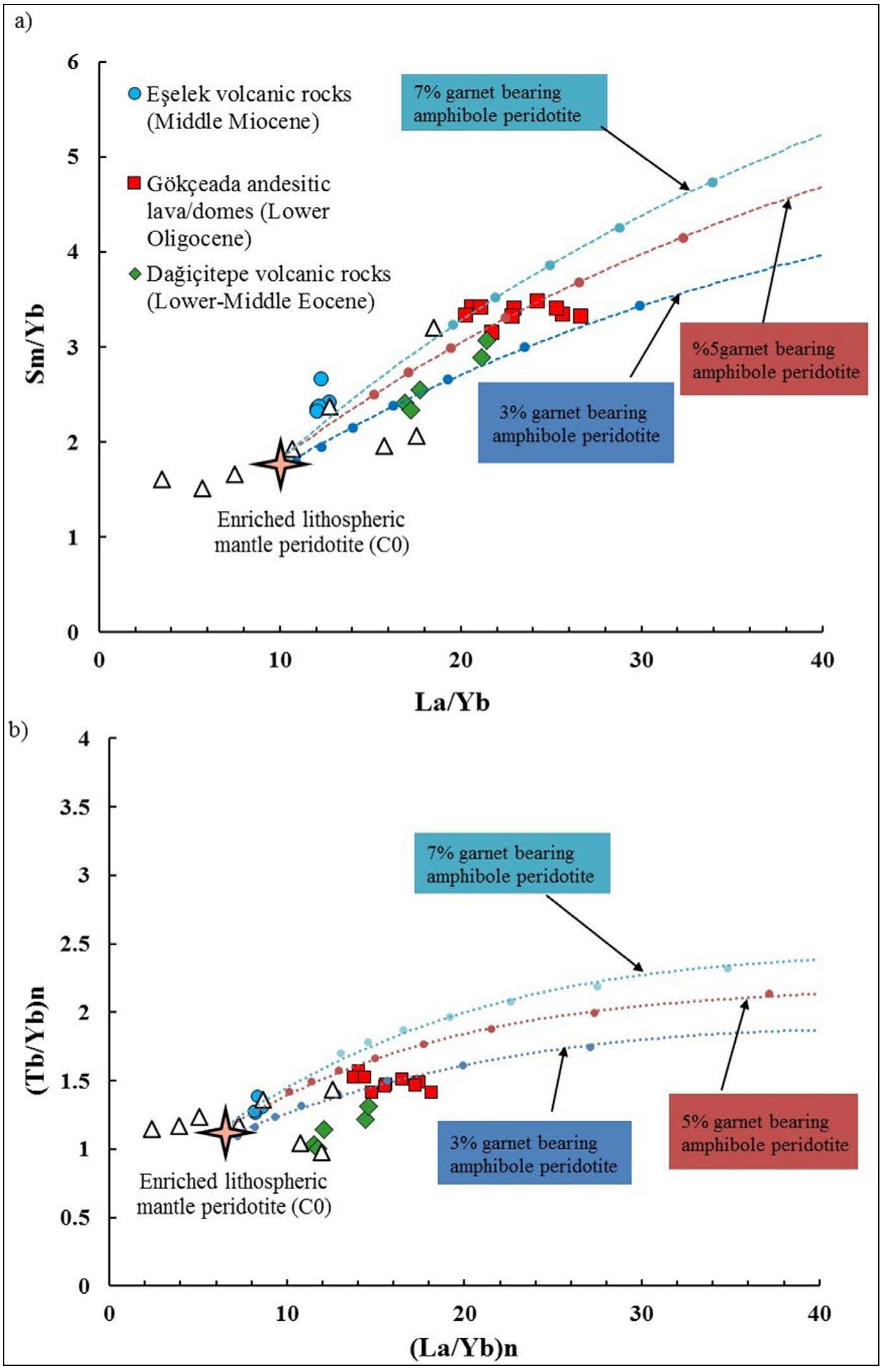

Figure 10- a) Sm/Yb vs La/Yb and b) (Tb/Yb)n vs (La/Yb)n diagrams of the Gökçeada volcanic rocks (Chondrite normalization values are from Thompson, 1982). The non-modal batch melting curves of garnet bearing amphibole peridotite were calculated using the equation of Shaw (1970). The data used in the modeling calculation are given in table 2.

contamination can be negligible. The petrogenetic modeling diagrams (Figure 10) also pointed out that both volcanisms were derived from a metasomatized lithospheric mantle source. Considering that the Eocene magmatism in NW Anatolia corresponds to the post-collisional magmatism, it can be concluded that the Gökçeada andesitic lava/domes and Eşelek volcanic rocks were generated in a post-collisional setting. However, the Eşelek volcanic rocks were derived from a relatively depleted source which became depleted over time.

7. Conclusion

In Gökçeada Island, there is a widespread magmatism with variable ages and compositions. Lower-Middle Eocene Dağiçitepe volcanic rocks, Lower Oligocene Gökçeada andesitic lava/domes and Middle Miocene Eşelek volcanic rocks on the island have calc-alkaline and tholeiitic compositions, respectively. In the rocks, which have geochemical characteristics of subduction magmas, the Lower-Middle Eocene Dağiçitepe volcanic rocks are the products of magmas in a collisional setting, hence they have experienced crustal contamination process is effective in the evolution of volcanic rocks. On the other hand, the Lower Oligocene Gökçeada andesitic lava/domes were derived from a metasomatized lithospheric mantle source in a post-collisional setting. The Middle Miocene Eşelek volcanic rocks were also derived from a lithospheric mantle, but the mantle source generating these volcanic rocks became relatively depleted over time. The geochemical data reveals that the effects of crustal contamination and subduction signatures in the evolution of the Gökçeada volcanism have decreased over time from Lower-Middle Eocene to Middle Miocene.

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