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Geochemical characteristics of the Eocene Karataş volcanics (Northeast Sivas, Turkey) in the İzmir-Ankara-Erzincan Suture Zone

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ABSTRACT

Karataş volcanics, is the product of Eocene volcanics crop out in the form of two belts along the northern and southern boundaries of the İzmir-Ankara-Erzincan Suture Zone. According to geochemical data, these volcanics have alkaline basic-intermediate character and consist of basaltic trachyandesite, trachyandesite and trachyte. This volcanic activity has been controlled by fractional crystallization and crustal contamination from basaltic trachyandesite to trachyte. Orientation of the samples towards amphibole area on the Rb/Sr - Ba/Rb ratio diagrams, dispersion of the Zr/Ba ratios (0.08 - 0.33) in the lithospheric mantle range, increase in the Ba/Rb ratio, decreases in the MgO, Ni and Cr contents point out that this volcanism originated from enriched lithospheric mantle rather than asthenospheric mantle. Geochemical data show that this enriched lithospheric mantle material is upper continental crustal material, main part of enrichment resulted by the subduction related fluids and also the contribution of the sedimentary materials. This situation may be explained that; the melts, derived from N-MORB or OIB bearing material ascended into the continental crust in a pre-collisional period and were reactivated by extensional tectonic and/or delamination processes during the post-collisional period, possibly caused the partial melting within the upper continental crust and produced the Karataş volcanics.

1. Introduction

İzmir-Ankara-Erzincan Suture Zone (IAESZ) which is one of the most important tectonic units of Turkey, separates the Sakarya continent from the Kırşehir block in the northern part of central Anatolia. Products of Eocene volcanism cover large areas along the northern and southern border of this suture zone. (Figure 1). These volcanics have been studied by a number of researchers (Yılmaz and Tüysüz, 1984; Büyükönal, 1985; Tüysüz and Dellaloğlu,1992; Yılmaz et al., 1994, 1997; Alpaslan and Terzioğlu, 1998; Alpaslan, 2000; Koçbulut et al., 2001; Keskin et al., 2008; Akçay et al., 2008; Dalkılıç et al., 2008; Atakay Gündoğdu, 2009; Görür vd., 2010; Tiryaki and Ekici, 2012; Akçay and Beyazpirinç, 2017; Göçmengil et al., 2018). And, various models have been proposed for the origin of these volcanics which outcrops from west of Sivas to Çankırı and Çorum; development in the compressional regime (Bozkurt and Koçyiğit, 1995; Tüysüz et al., 1995; Görür and Tüysüz, 1997; Görür et al., 1998; Kaymakçı et al., 2003; Okay and Satır, 2006), slab break off oceanic lithosphere in the North plunging subduction environment (Keskin et al., 2008), development in the post-collisional regime (Genç and Yılmaz, 1997; Keskin et al., 2004;

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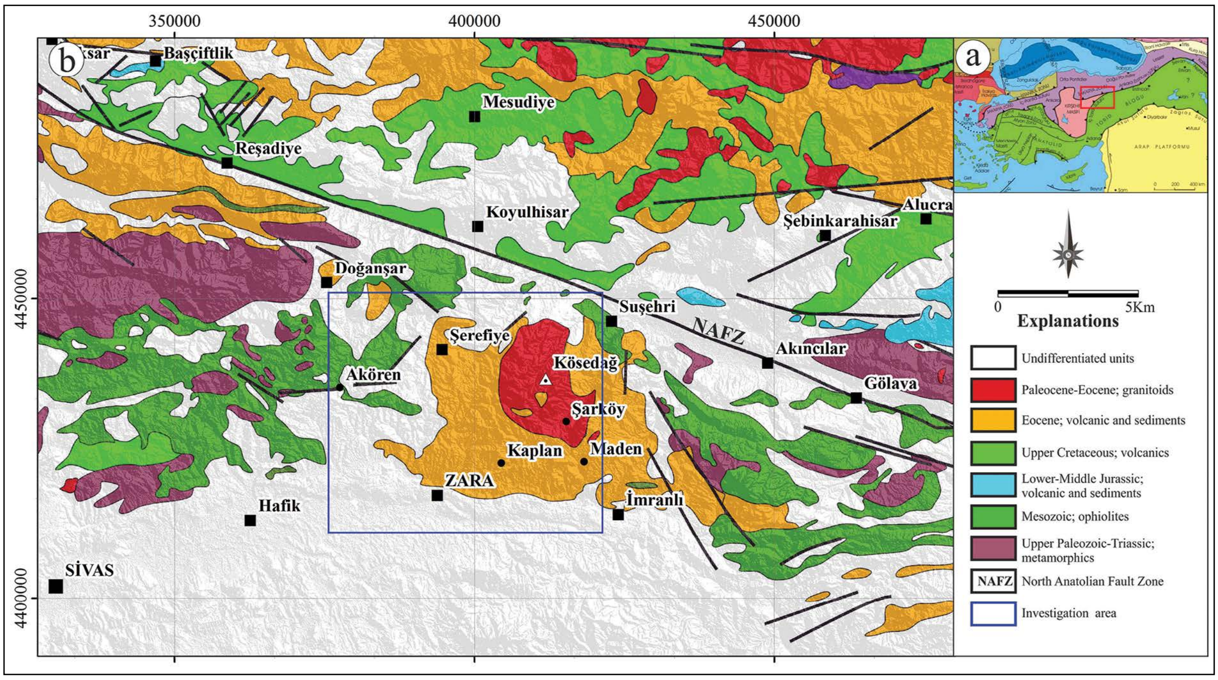

Figure 1- a) Tectonic map showing main sutures and continental blocks (Okay and Tüysüz, 1999) and b) regional geological map (Revised from MTA, 2002).

Altunkaynak and Dilek, 2006; Altunkaynak, 2007), crustal thickening (Topuz, 2005), crustal delamination and lithospheric subduction (Temizel et al., 2016; Yücel et al., 2017; Göçmengil et al., 2018).

Karataş volcanics are located in the area between Zara, İmranlı and Suşehri towns at the east of Sivas, on the IAESZ. In this study, petrographic and geochemical characteristics of Karataş volcanics have been investigated to be able to determine their source and formation environment, comparing the obtained results with those of rocks from different sources and volcanic rocks occurred in different tectonic environments, and give help to understanding geodynamic evolution of the region during Eocene.

2. Geology of the Study Area

Paleozoic metamorphic rocks (Tokat massif in the north and Akdağmadeni metamorphics in the south) and tectonically overlaying ophiolitic rocks with Upper Cretaceous emplacement age (Refahiye ophiolite melange) form the basement of the study area. Eocene Akıncılar Formation consists of alternations of sandstones and volcanic materials-siltstone interlayers discordantly overlie these units (Yılmaz et al., 1985). Eocene Karataş volcanics (Yılmaz et al., 1985) cut and overlie this formation and the basement rocks. Lutetian Kösedağ syenite (Kalkancı, 1974; Yılmaz et al., 1985; Başıbüyük, 2006; Boztuğ, 2008; Eyüboğlu et al., 2017) intruded all these units. In places younger volcanics and sedimentary units discordantly overlay Karataş volcanics and Kösedağ syenite (Figure 2-3).

Karataş volcanics with basaltic-andesitic lavas and pyroclastics (agglomerates and tuffs) cover large areas in and around the study area. Andesitic rocks in general have greenish-black, altered parts have yellowish-brown colour. Depending upon cooling and regional tectonics they are heavily fractured. Quartz and calcite filled gas cavities (vesicular texture) are seen macroscopically in various parts of the study area. Rocks with basaltic composition are greyish-black in generally, altered parts have yellowish colours, massive structure are dominated and flow structures are developed in some places. The base levels of the pyroclastic rocks consist of light green colored, hard and compact agglomerates, while the upper and middle levels are loose and easily disintegrable tuffs.

3. Age of the Volcanism

Karataş volcanics cut the Akıncılar formation which contains Eocene fossil at the outcrops in the Aluçlubel area at the north of Zara (Yılmaz et al.,

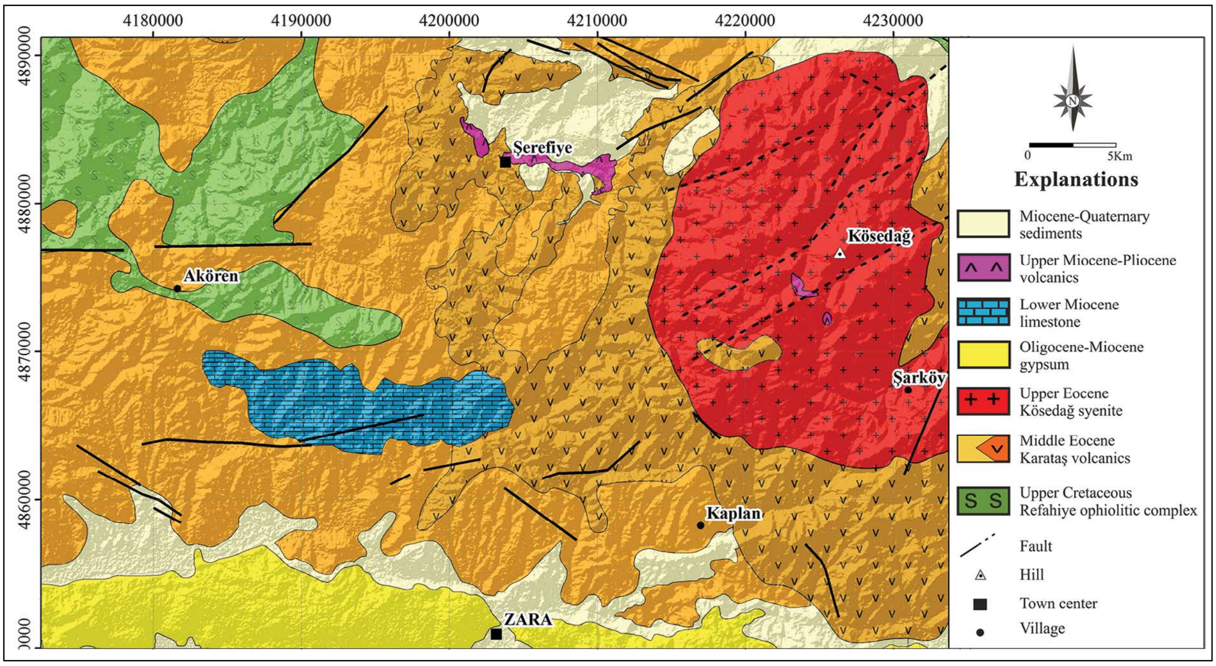

Figure 2- Geological map of the study area (Revised from Kalkancı, 1974; Yılmaz et al., 1985; MTA, 2002; Başıbüyük, 2006; Özdemir, 2016; Canbaz et al., 2018).

1985). These units have been intruded by Kösedağ syenite. Kalkancı (1974) estimated the age of syenite as Upper Eocene with Rb-Sr method; Boztuğ et al. (1994) estimated the age as Ypresian with Zircon $^{207}Pb/^{206}Pb$ method; Başıbüyük (2006) estimated Lutetian age with K-Ar method on alunites and Eyüboğlu et al. (2017) estimated same age with zircon U-Pb method. All these data indicate that the age of volcanism was younger than Lutetian and not older than Lower Eocene. In this study, the age of Karataş volcanics has been considered to be Middle Eocene.

4. Analytichal Methods

Representative rock samples were collected during the field study for petrographic and geochemical investigations. In addition, representative core samples were taken from the drillings carried out by MTA (General Directorate of Mineral Research and Exploration). Thin sections of these samples have been studied (with the criteria's described by Moorhouse, 1969; Erkan, 1972, 1994; MacKenzie and Guilford, 1980; Yardley et al., 1990) using polarizing microscope. Following thin section studies, representative 24 unaltered samples were selected for geochemical analyses. These samples were crushed and powdered in the laboratory to prepare for the analyses. Major element analyses of the samples were carried out in the ACME laboratory in Canada by using ICP-ES (inductively coupled plasma emission spectrometer) and ICP-MS (inductively coupled plasma mass spectrometer) spectrometers. ICP-ES spectrometer was used for major and trace element analyses. 0.2 gr powdered samples were mixed with 1.5 gr $LiBO_2$, then heated to 1050 °C to have the dissolved mixture. The mixtures were dissolved in a 100 ml %5 HNO_3 liquid, then were evaporated and then were analysed with ICP-ES spectrometer. The samples prepared for the above mentioned analyses were also used for the Rare Earth Element analyses by using ICP-MS spectrometer. For the major oxides, lower determination limit was 0.01%, for the trace elements it varied between 0.01-1.0 ppm. During the analyses in the ACME analytical laboratory GS311-1, GS910-4, SO-19, DS-11, OREAS45EA and SY-4(D) standards were used and analyses of 8 samples were repeated. For the evaluation of the diagrams, GCDkit 3.0 program was used.

5. Results

5.1. Mineralogy and Petrography

Mineralogical and petrographical studies show that Karataş volcanics have basaltic, andesitic and trachytic mineralogical compositions. Rocks with

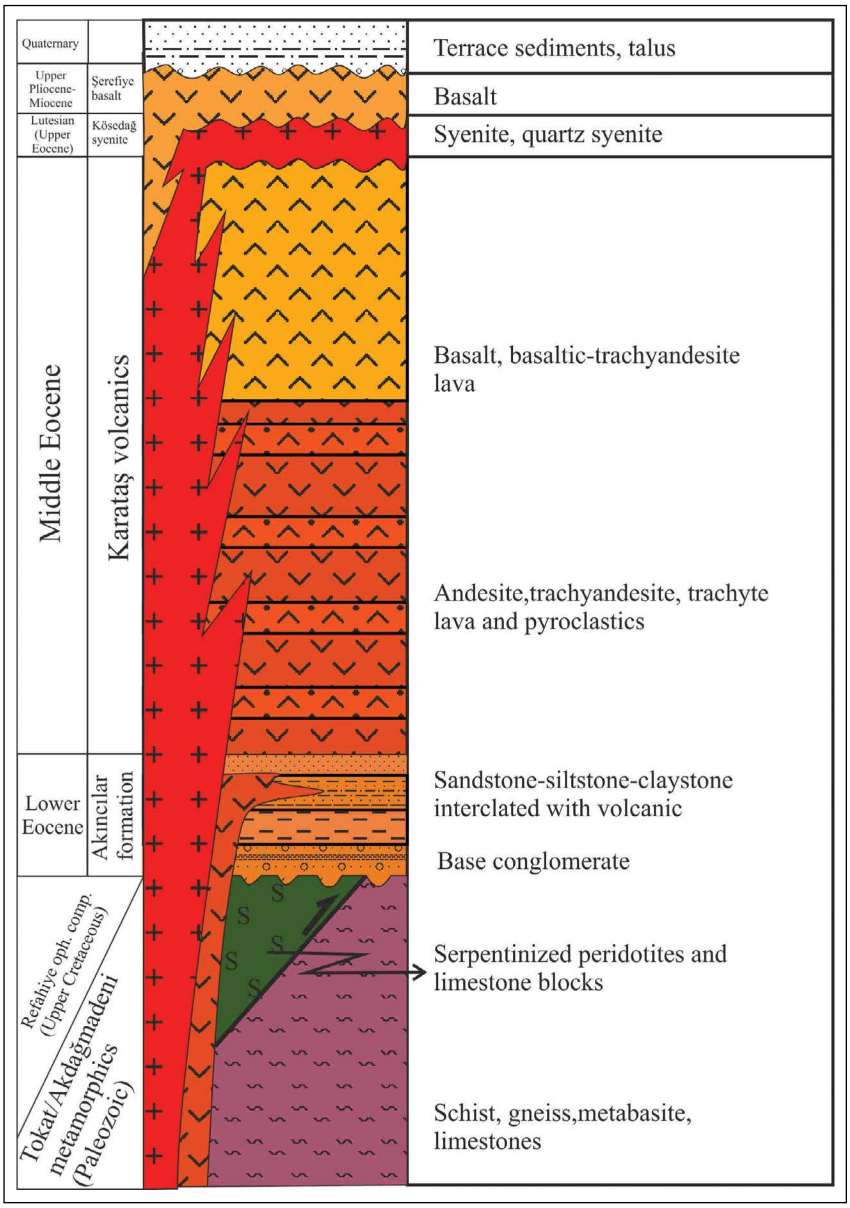

Figure 3- Stratigraphic section of the study area.

basaltic composition have generally hypocristalline porphyritic texture, and contain olivine, plagioclase, pyroxene (augite) phenocrysts. Plagioclase microlites and volcanic glass are also found in the matrix (Figure 4a-b).

Andesitic rocks consist of larger plagioclase phenocrystals (1-3 cm) and finer grained mafic minerals such as augites and hornblends comparing with the basaltic rocks levels, (Figure 4c-d). Trachytic rocks show holocrystalline and hypocrystaline porphyritic textures and contain plagioclase and sanidine phenocrysts (Figure 4e-f). Besides plagioclase and sanidine microlites, pyroxene and amphibole microlites are also present in the matrix of the trachytes.

Some sieve textures developed around some large plagioclase phenocrysts and the presence of small plagioclase crystals with different extinction angle within some thin sections of basaltic and andesitic rocks of Karataş volcanics (Figure 4g-h) were accepted as prints of magma-solid interaction and mixtures of magmatic melts with different compositions (e.g. Hibbard, 1991; Boztuğ et al., 1994).

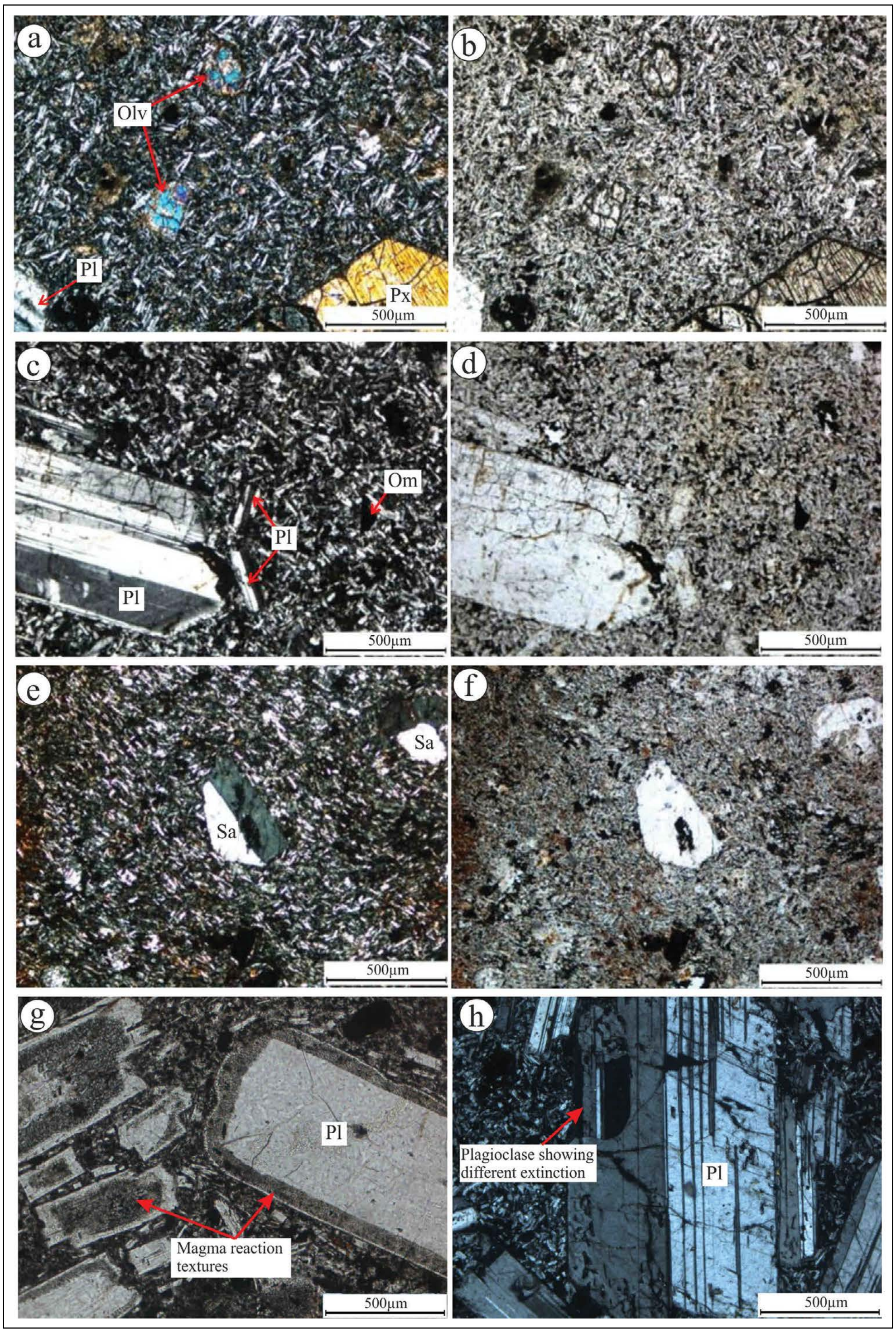

Figure 4- Microscopic characters of samples collected from various levels of Karataş volcanics. a-b) In basaltic samples olivine and pyroxene phenocrysts matrix made of plagioclase microliths (sample no: OK-108, cross/plane polarised light, c-d); plagioclase phenocrysts and microlites (sample no: OK-35, cross/plane polarised light), e-f) in a trachyte sample sanidine phenocrysts and matrix made of sanidine and plagioclase microlites (sample no: Ok-7, cross/plane polarised light), g) view of magma reaction textures on plagioclase phenocrysts, h) view of plagioclases with different extinctions in plagioclase phenocrysts (sample no: Ok-7, cross/plane polarised light). (Pl= Plagioclase, Px=Pyroxene, Olv=Olivine, Sa=Sanidine, Om=Opaque Mineral).

5.2. Geochemistry

Major, trace and rare earth elements contents of Karataş volcanics are given in tables 1, 2, 3. The samples fall in the basaltic trachyandesites, trachyandesite and trachyte fields of the TAS diagram (LeMaitre et al., 1989) (Figure 5). Most of the samples, excluding 5 of them, of the rock groups fall above the alkaline-sub alkaline (tholeiitic) separating line and have strong alkaline character.

We have tried to compare and discuss the geochemical characteristics of Karataş volcanics with the results of the earlier works carried out on the Eocene volcanics by Akçay and Beyazpirinç (2017) and Göçmengil et al. (2018) in the west of the study area, between Yozgat and Sivas provinces.

5.2.1. Major Elements Geochemistry

SiO_2 contents of Karataş volcanics show variation in the range of 50.30-61.80% (basaltic trachyandesites 51.20-54.60%; trachyandesites 54.00-58.10%; trachyte 61.80%).

Some selected major oxides versus SiO_2 diagrams; while CaO, Fe_2O_3, MgO and TiO_2 contents show negative trend from basaltic andesites to trachytes, Na_2O, K_2O, Al_2O_3 and P_2O_5 contents show positive trends (Figure 6). Those indicate that negative trend showing major oxides were used by the olivine, pyroxene, calcic plagioclases and titanomagnetites crystallized in earlier stage of crystallization and separated from the melt, and these earlier crystallized minerals did not use much Na and K, so the melt became enriched with Na and K showing positive correlation

Table 1- Major elements results of Karataş volcanics (weight %).

Rock types	Sample No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	P_2O_5	Loss of ignition	Total
Basaltic trachyandesite	Ok-109	52.40	15.90	7.96	7.47	5.17	3.18	3.28	0.15	0.80	0.39	3.27	99.48
	Ok-114	51.20	17.20	8.57	7.82	4.26	3.20	2.72	0.10	0.97	0.38	3.06	99.70
	Ok-120	53.70	19.30	6.73	6.97	2.71	3.55	2.84	0.10	0.77	0.47	2.56	100.41
	Ok-124	52.60	17.60	8.79	9.06	4.62	3.32	2.08	0.15	0.82	0.29	1.08	99.93
	Ok-193	52.80	17.70	8.90	7.59	3.45	3.51	3.02	0.17	0.89	0.41	1.49	99.98
	Ok-205A	54.60	18.90	6.06	7.82	2.83	3.40	2.96	0.11	0.78	0.47	2.05	100.16
	Ok-206A	52.50	17.30	9.50	7.43	4.97	3.17	2.40	0.16	0.84	0.30	1.59	99.76
	Ok-210	54.30	19.00	7.59	6.21	2.66	3.78	2.99	0.23	0.77	0.47	1.76	100.53
	Ok-215B	52.30	17.80	9.18	6.47	4.79	4.36	2.29	0.12	0.85	0.31	2.06	100.28
	Ok-247	51.80	18.10	8.87	7.97	4.39	3.30	2.06	0.15	0.80	0.25	2.59	100.30
	Ok-248	53.00	16.90	8.55	6.10	4.31	4.13	2.99	0.10	0.84	0.33	3.05	99.91
	Ok-255C	54.60	19.00	6.96	7.70	3.06	3.80	3.09	0.11	0.81	0.46	0.32	99.33
Trachyandesite	Ok-35	54.00	19.30	5.34	6.82	1.59	4.02	3.81	0.13	0.72	0.45	3.15	99.55
	Ok-57	58.10	18.60	6.96	2.96	0.64	4.01	5.60	0.26	0.80	0.45	1.17	99.47
	Ok-58	57.30	20.60	5.79	4.49	0.19	4.29	4.26	0.13	0.78	0.50	1.14	99.74
	Ok-84	54.50	18.70	9.95	6.01	1.16	3.91	3.72	0.07	0.73	0.46	0.53	98.61
	Ok-99	55.50	17.70	5.59	5.05	2.09	3.92	4.54	0.09	0.76	0.45	2.92	99.86
	Ok-131A	54.20	19.50	6.46	7.38	1.54	3.95	3.71	0.12	0.71	0.45	1.84	99.68
	Ok-141	55.50	19.40	8.05	5.64	1.10	4.01	3.85	0.08	0.73	0.46	0.86	99.80
	Ok-222	54.60	19.90	6.72	6.43	2.46	4.03	3.62	0.06	0.75	0.49	0.74	100.08
	Ok-223	54.70	18.90	6.64	5.79	3.08	3.68	3.34	0.20	0.71	0.46	2.58	99.73
	Ok-244	54.70	19.50	5.78	5.62	1.34	4.07	4.67	0.08	0.67	0.47	2.83	100.42
	Ok-253	56.60	20.40	6.08	4.57	1.17	4.39	4.81	0.05	0.77	0.50	1.08	99.67
Trachyte	Ok-7	61.80	16.60	6.31	1.38	0.20	4.13	7.04	0.28	0.72	0.29	0.92	100.34

Table 2- Trace elements results of Karataş volcanics (ppm, *=ppb).

Rock type	Sample No	Ba	Co	Cs	Ga	Hf	Nb	Rb	Sr	Th	U	V	Zr	Cu	Pb	Zn	Mo	Ni	As	Sb	Hg	Au*
Basaltic trachyandesite	Ok-109	510	26.1	1.4	12.3	4.3	10.3	83.2	529.2	10.4	3.4	203	172.7	129.0	3.3	92	2.2	58.8	35.6	0.1	0.05	1.2
	Ok-114	558	24.3	0.7	14.2	3.6	8.5	55.3	591.8	6.5	2.4	256	133.2	205.4	9.0	85	1.7	16.3	5.7	0.1	0.03	2.7
	Ok-120	766	15.5	0.5	15.5	3.9	10.0	54.3	742.2	8.7	3.2	158	154.3	238.9	5.3	73	1.9	11.1	3.5	0.2	0.04	1.9
	Ok-124	516	23.8	0.6	14.0	2.8	5.5	46.8	645.7	5.0	1.7	255	98.8	66.3	2.7	52	1.7	15.4	1.4	0.2	0.04	<0.5
	Ok-193	608	21.4	0.6	15.7	3.7	9.2	74.0	708.8	7.7	3.2	236	143.5	140.0	8.6	50	4.7	10.6	8.7	0.4	0.02	7.4
	Ok-205A	765	18.1	0.3	15.7	3.7	9.9	53.9	775.6	8.8	3.3	167	156.4	22.7	3.3	58	1.7	12.5	14.2	0.3	0.02	2.9
	Ok-206A	1377	27.1	0.8	14.8	2.7	5.8	45.6	635.8	5.4	2.2	260	105.7	122.9	1.6	20	1.5	12.5	5.5	1.2	0.02	1.2
	Ok-210	691	36.6	0.9	16.0	3.8	9.6	76.5	752.2	9.2	3.2	171	157.5	19.3	2.8	38	2.2	17.0	4.3	<0.1	0.01	0.8
	Ok-215B	627	27.9	4.4	15.1	2.8	6.7	49.7	565.7	6.4	2.5	251	110.7	177.1	5.3	39	1.9	12.0	33.9	1.2	0.02	2.2
	Ok-247	526	26.4	0.8	14.4	2.4	4.8	42.0	627.4	4.5	1.9	277	87.7	228.0	4.4	30	1.7	10.7	5.6	0.1	0.02	1.4
	Ok-248	609	24.3	2.1	15.7	3.3	7.2	66.9	556.5	6.7	2.3	235	127.7	235.8	2.1	19	1.6	14.2	18.2	0.3	0.01	1.5
	Ok-255C	715	18.2	0.8	17.6	3.5	9.9	81.5	767.6	8.3	3.0	194	146.4	262.9	2.0	54	2.3	9.7	6.3	0.6	0.03	2.6
Trachyandesite	Ok-35	705	12.8	0.9	15.3	4.0	10.3	99.3	762.3	9.3	3.7	169	162.9	11.1	4.1	34	2.2	8.9	4.0	0.3	0.01	3.9
	Ok-57	826	13.2	1.5	14.9	5.8	14.9	138.3	390.7	13.8	5.3	137	234.1	11.3	5.0	67	1.8	8.7	7.6	1.1	0.06	0.7
	Ok-58	911	9.1	1.2	15.9	4.3	10.2	113.3	648.5	9.4	3.6	177	171.0	123.8	5.6	69	1.8	7.4	15.2	0.3	0.01	1.6
	Ok-84	666	9.2	0.6	14.4	3.9	9.8	96.7	733.7	9.3	3.3	172	160.1	52.5	7.6	59	3.6	5.5	29.1	0.9	0.04	2.6
	Ok-99	704	12.2	1.2	13.9	5.6	13.2	127.0	523.2	13.1	5.2	146	217.4	19.2	5.2	150	3.1	6.4	9.0	1.8	0.04	2.8
	Ok-131A	692	10.1	0.8	15.9	3.9	9.6	97.5	784.5	9.1	3.7	160	158.3	25.5	4.8	56	3.8	7.5	8.6	0.3	0.02	5.8
	Ok-141	793	10.0	1.2	15.1	4.0	9.9	102.7	743.9	9.3	3.7	173	162.3	14.0	9.6	55	2.2	6.7	18.0	0.2	0.03	5.8
	Ok-222	734	15.1	1.7	15.9	3.6	8.3	91.3	859.3	7.6	3.0	218	140.2	43.2	7.2	104	2.3	14.6	7.1	0.2	<0.01	2.0
	Ok-223	1013	16.1	1.7	15.4	3.4	8.2	82.4	774.9	7.5	4.0	242	134.9	733.8	4.2	38	1.9	9.9	6.0	0.3	0.04	1.1
	Ok-244	600	12.0	2.0	15.4	4.1	11.1	112.9	673.5	9.0	2.7	104	174.3	55.8	2.9	64	1.3	4.8	6.4	0.8	0.03	<0.5
	Ok-253	780	8.5	3.2	18.7	4.7	12.7	131.0	742.9	10.3	3.3	173	197.8	224.0	4.3	44	1.8	3.8	6.1	0.1	0.03	5.2
Trachyte	Ok-7	977	12.5	2.6	17.3	7.9	21.4	203.3	156.0	20.0	7.7	109	331.9	62.5	11.4	74	4.9	4.5	11.8	0.1	0.01	3.6

Table 3- Rare Earth Elements results of Karataş volcanics (ppm).

Rock type	Sample No	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Basaltic trachyandesite	Ok-109	25.0	47.4	5.57	22.5	4.71	1.18	4.48	0.66	3.76	0.84	2.54	0.37	2.46	0.37
	Ok-114	23.0	45.1	5.19	21.4	4.69	1.22	4.28	0.63	3.69	0.76	2.36	0.32	2.24	0.34
	Ok-120	27.3	52.8	5.83	23.3	4.47	1.27	4.24	0.63	3.49	0.77	2.33	0.33	2.14	0.36
	Ok-124	18.1	35.0	4.08	17.6	3.57	1.07	3.72	0.58	3.38	0.72	2.08	0.30	1.81	0.31
	Ok-193	24.6	48.9	5.56	21.5	4.69	1.31	4.72	0.69	3.91	0.84	2.45	0.35	2.42	0.37
	Ok-205A	27.2	52.9	5.96	24.2	4.58	1.29	4.50	0.68	3.87	0.79	2.33	0.32	2.19	0.34
	Ok-206A	19.9	36.2	4.47	18.7	4.21	1.18	4.20	0.61	3.58	0.74	2.17	0.31	2.06	0.31
	Ok-210	28.1	53.3	6.08	25.4	4.94	1.30	4.59	0.67	3.77	0.71	2.41	0.33	2.21	0.35
	Ok-215B	21.1	39.3	4.62	19.4	4.00	1.14	3.90	0.59	3.48	0.73	2.11	0.29	1.96	0.28
	Ok-247	16.4	31.4	3.62	15.0	3.22	1.03	3.41	0.51	2.95	0.62	1.80	0.24	1.74	0.28
	Ok-248	20.9	41.0	4.69	19.3	3.97	1.15	4.18	0.63	3.84	0.77	2.30	0.32	2.14	0.34
	Ok-255C	26.8	53.1	5.89	23.6	4.58	1.31	4.38	0.65	3.65	0.77	2.34	0.36	2.32	0.35
Trachyandesite	Ok-35	27.2	52.7	5.90	23.0	4.72	1.26	4.33	0.63	3.73	0.76	2.32	0.35	2.24	0.35
	Ok-57	37.6	67.9	7.76	31.0	6.10	1.47	5.60	0.82	4.89	1.07	3.01	0.46	3.01	0.46
	Ok-58	29.8	53.2	6.41	26.1	4.90	1.40	4.65	0.70	3.98	0.77	2.59	0.33	2.30	0.37
	Ok-84	26.3	50.7	5.73	21.7	4.49	1.22	4.19	0.65	3.77	0.77	2.41	0.34	2.40	0.36
	Ok-99	33.4	62.6	7.03	28.0	5.56	1.27	4.85	0.72	4.22	0.89	2.73	0.42	2.63	0.46
	Ok-131A	26.9	50.9	5.84	23.9	4.49	1.23	4.22	0.64	3.49	0.76	2.32	0.32	2.20	0.36
	Ok-141	27.3	52.8	6.03	23.5	4.79	1.30	4.30	0.65	3.81	0.79	2.27	0.34	2.26	0.35
	Ok-222	27.4	49.4	5.76	22.9	4.74	1.35	4.36	0.64	4.00	0.74	2.29	0.32	2.20	0.34
	Ok-223	25.2	47.6	5.50	22.0	4.46	1.27	4.18	0.61	3.65	0.67	2.18	0.30	1.98	0.32
	Ok-244	28.6	55.0	6.07	24.5	4.37	1.21	4.19	0.63	3.69	0.77	2.29	0.35	2.35	0.37
	Ok-253	36.0	63.6	7.28	27.8	5.22	1.40	5.00	0.74	4.40	0.94	2.82	0.41	2.64	0.44
Trachyte	Ok-7	40.9	75.6	8.18	30.6	5.97	1.17	5.45	0.84	5.05	1.09	3.40	0.52	3.53	0.56

with SiO_2 trough the later stage of crystallization and they formed the sodium plagioclases and mica minerals.

MgO contents of Karataş volcanics show wide variation range (0.19%-6.09). Basaltic trachyandesites 3.06-5.17%; trachyandesites 0.19-3.08%; trachyte 0.20%.

In the Harker correlations diagrams, trends of major oxides plotted against SiO_2, especially the negative correlation of the MgO indicate the importance of fractional crystallization process during the formation of Karataş volcanics. CaO/Al_2O_3 vs. MgO, Al_2O_3 vs. CaO and Zr/Nb vs. MgO variation diagrams prepared by various workers which indicate the fractionations of olivine, clinopyroxene, amphibole and plagioclase fractionations from basic trough intermediate composition also support the effectiveness of fractional crystallization idea for the formation of Karataş volcanics (Figure 7).

Akçay and Beyazpirinç (2017) and Göçmengil et al. (2018) also indicated that fractional crystallization processes were effective in the development of Eocene volcanics, crop out in Almus, Yıldızeli, Kiremitli and Pazarcık area, at the west of the study area.

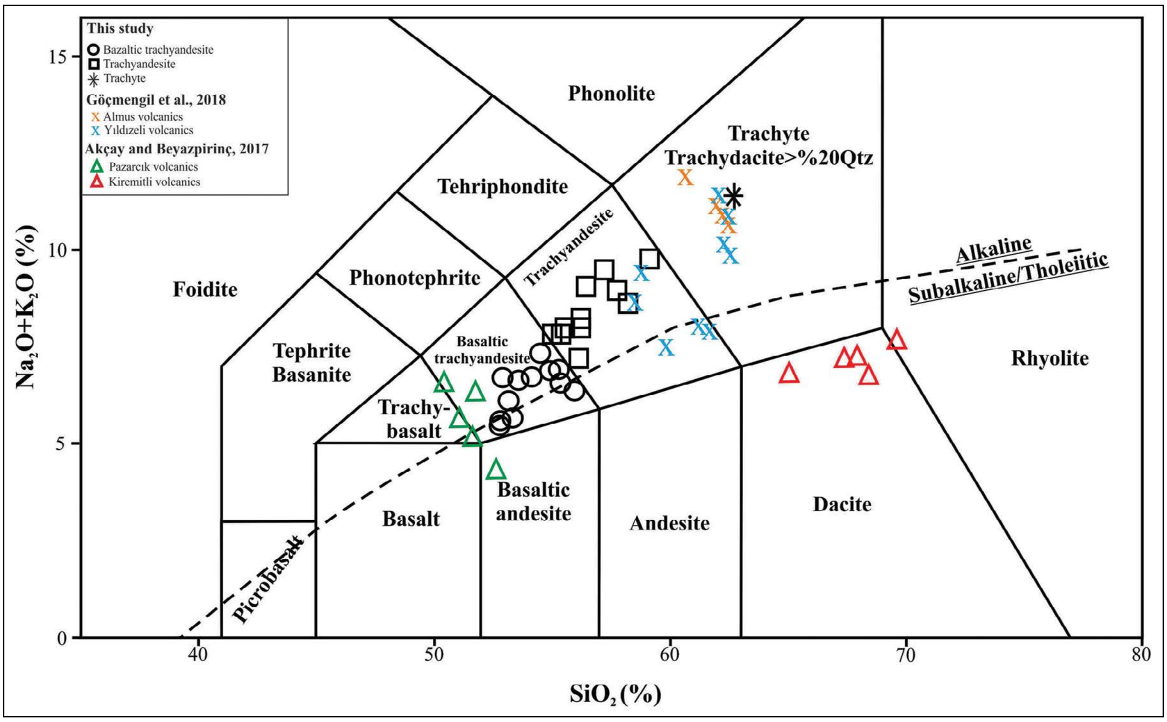

Figure 5-Total Alkali-Silica classification for Karataş volcanics (LeMaitre et al., 1989), Alkali/Sub alkali line (Irvine and Baragar, 1971).

5.2.2. Trace and Rare Earth Elements Geochemistry

Ba, Rb, Nb, Zr, Th, La and Ce values are increased but Sr values are decreased in accordance with SiO_2 values on the trace elements versus SiO_2 diagrams (Figure 8). Ba, Rb, Th, and Hf show positive correlation with SiO_2 because they are taken place within the feldspars and hornblendes which occur in later stage of crystallization. Positive correlation of Zr is related magnetite differentiation. In addition, positive correlation of Y with SiO_2 may be related with apatite crystallizations. Depletion in the Sr values may be explained as the entrance of Sr in place of Ca in the earlier formed calcic plagioclases.

Trace elements spider diagrams were prepared to make some approaches to the origin of the material and tectonic environments of Karataş volcanics occurred (Figure 9a). Samples of Karataş volcanics show enrichments in some lithophile elements with large-ion lithophile elements (LILE) like Ba, Sr, K, Rb, Cs and also high field strength elements (HFSE) like Zr, U, Th, Y, while they show decreases in Nb, Ce, Ti values. Noticeable enrichment of the elements with large ion radius and negative Nb anomalies present similarity to the magmatism developed in active continental edge or in arc environment and point out to the subduction component (Gill, 1981; Pearce, 1983; Fitton et al., 1988; Hall, 1989; Hawkesworth et al., 1997). In addition, Göçmengil et al. (2018) indicated that similar characteristics may also reflect assimilated continental crust. The lack of deep negative Eu anomalies in those samples indicates that the effect of plagioclase fractionation was not very important during the formation of these volcanics. Negative Ti anomaly is thought to be related to the early crystallization and abandonment from melt of Ti-bearing oxide minerals like Ti-magnetite (Kerrich and Wyman, 1997). On the other hand, negative Nb and Ti anomalies are quite common in the magmas associated with subduction developed in post collisional environment (Ekici, 2016).

All REEs, especially the lighter ones, show noticeable enrichments comparing to the Primitive Mantle normalized REEs dispersion diagram (Figure 9b). This distribution trend indicates the effect of differentiation of amphiboles and pyroxenes during crystallization. The presence of hydrous minerals like amphiboles in trachyandesite and trachyte samples point out the continental crust origin and/or contamination. The similarity of the dispersion patterns of the samples with upper continental crust pattern on the spider diagrams support this approach.

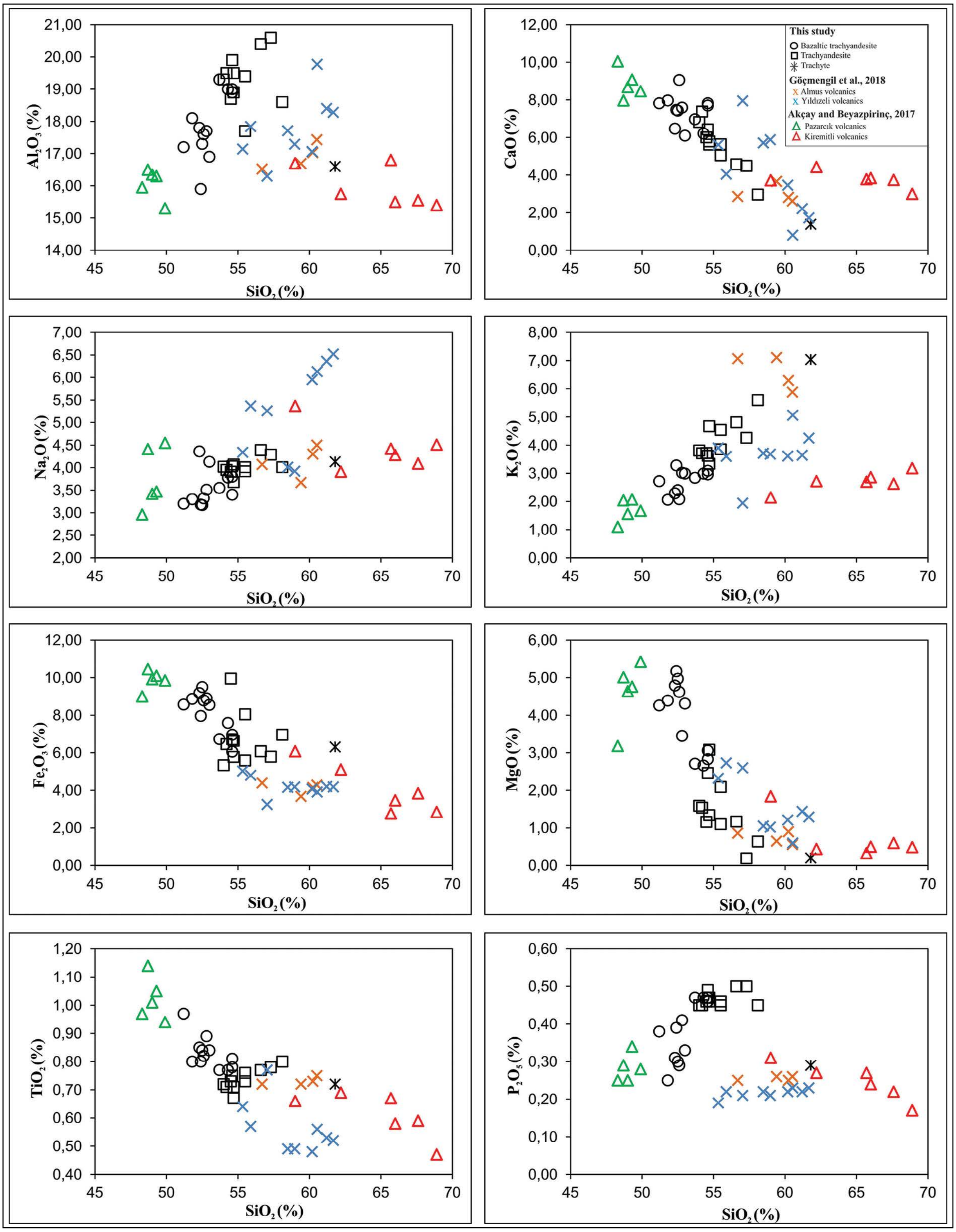

Figure 6- Variation of selected major elements vs. SiO_2 in Karataş volcanics.

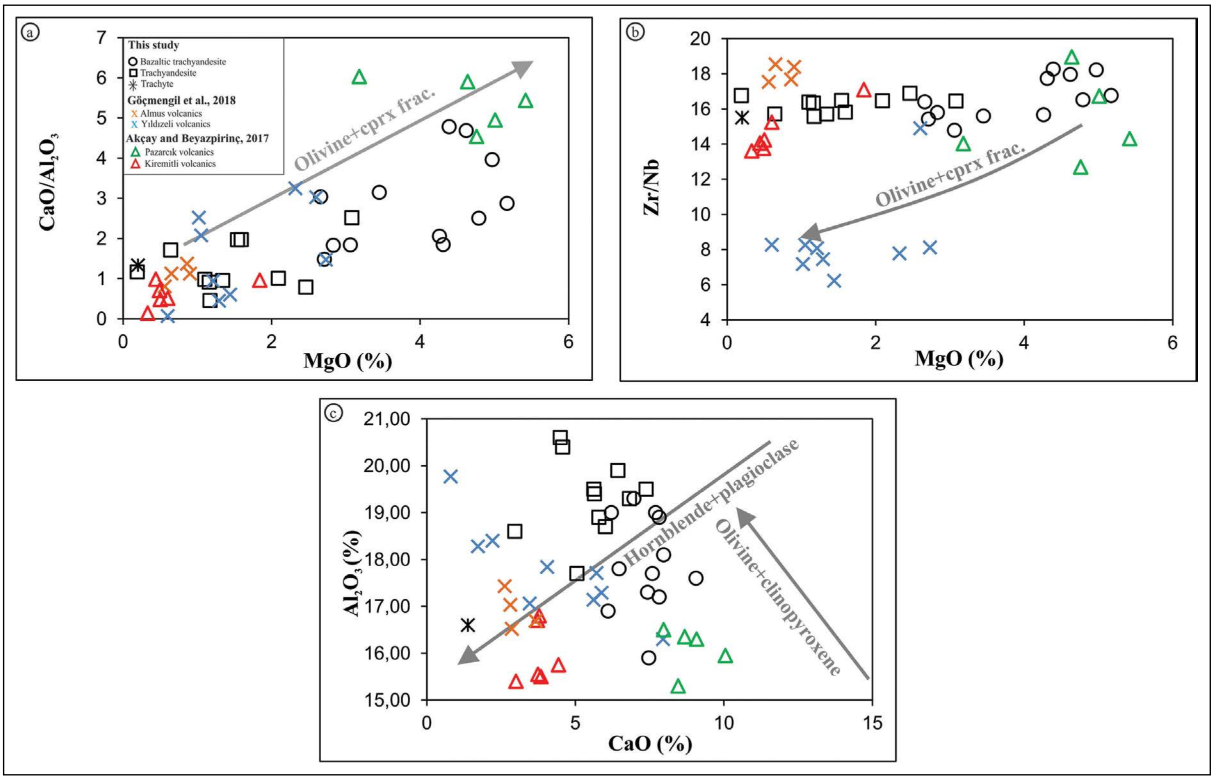

Figure 7- In Karataş volcanics, distribution of a) CaO/Al_2O_3-MgO ratio diagram, b) distribution in the Al_2O_3-CaO ratio diagram, c) distribution in the Zr/Nb-MgO ratio diagram.

Karataş, Pazarcık, Almus and Yıldızeli volcanics, which have similar SiO_2 content, show parallel pattern on the Harker and spider diagrams, Kiremitli volcanics with higher SiO_2 contents differ from the others.

6. Discussion

6.1. Crustal Contamination

Karataş volcanics Nb/U ratios vary between 2.53-3.54 in the basaltic trachyandesites and 2.05-4.11 in the trachyandesites. Nb/La ratios show variations between 0.29-0.41 and 0.30-0.40, K_2O/P_2O_5 ratios between 6.04-9.06 and 7.26-12.44 in basaltic trachyandesites and trachyandesites respectively.

Haase et al. (2000) suggest that Nb/U ratios close to MORB values (average 47.00, Hofmann et al., 1986) in the rocks which have not been subjected to sedimentary assimilation, and this value will considerably get lower with the sedimentary assimilation. On the other hand, Hoffman et al. (1986) claims that Nb/La ratios higher than 1.00 would be indicative for typical mantle derived and uncontaminated magmas. Since these ratio values in Karataş volcanics are low (Nb/U; 2.05-4.11, Nb/La; 0.29-0.41), it may be said that the source magma was subjected to crustal/sedimentary contamination (Figure 10a). Carlson and Hart (1988) say that basalts generated from mantle have K_2O/P_2O_5 ratio values ≤2 value, with the crustal assimilation or apatite fractionation, this ratio would increase. The quite high K_2O/P_2O ratio values (6.04-12.44) of Karataş volcanics indicate that the magma produced Karataş volcanics was either subjected to crustal assimilation or to apatite fractionation. The plots of these values on the SiO_2 versus K_2O/P_2O_5 diagram show that the effects of crustal contaminations increase from basaltic trachyandesites towards trachyte (Figure 10b).

Akçay and Beyazpirinç (2017), indicated that subduction zone enrichment and/or crustal contribution had important part in magmas generated Pazarcık and Kiremitli volcanics, and these more significant in Kiremitli volcanics. Göçmengil et al. (2018) indicated that Almus volcanics had negligible amounts of crustal contamination comparing with Yıldızeli volcanics.

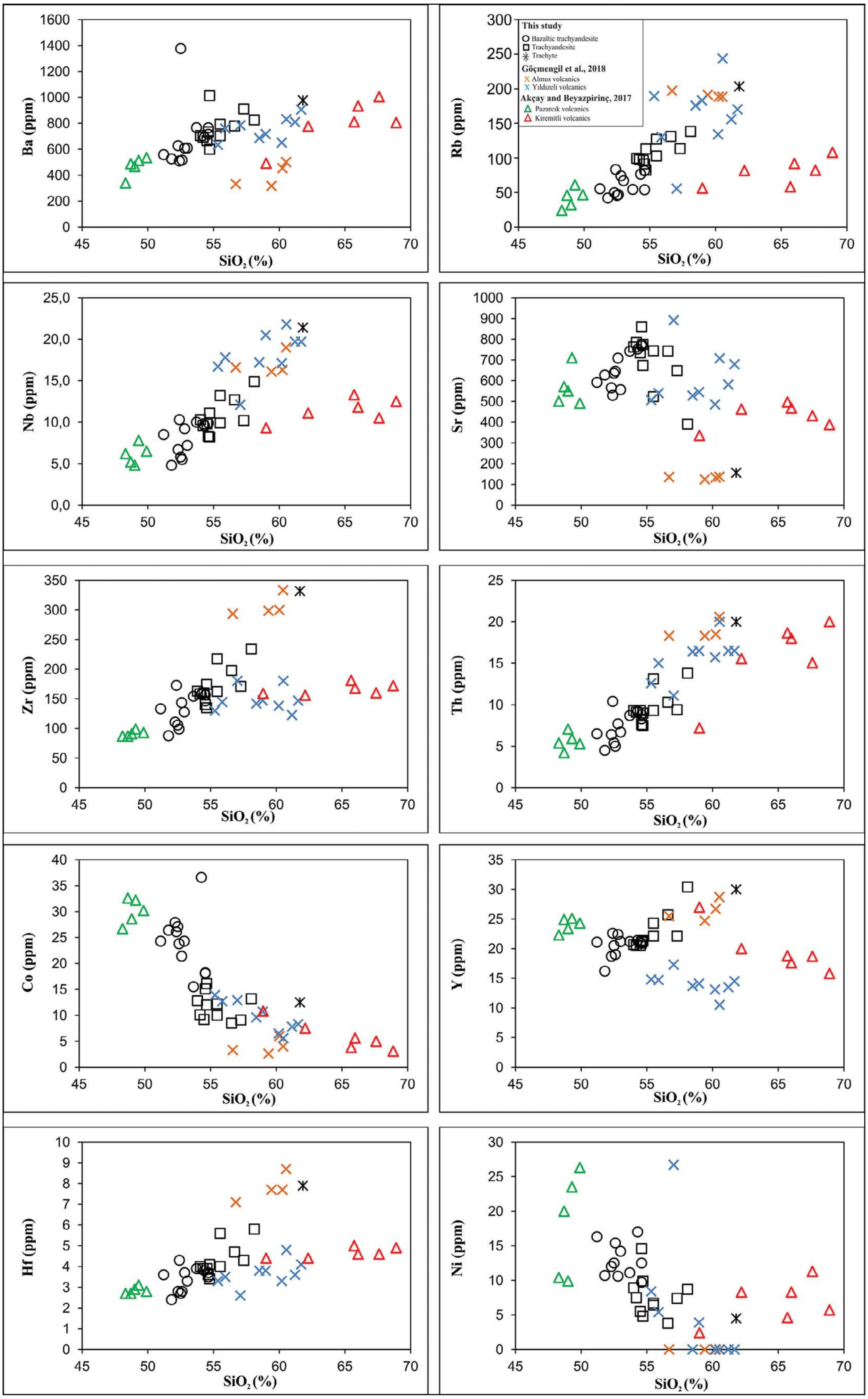

Figure 8- Variation of selected trace elements vs. SiO_2 in Karataş volcanics.

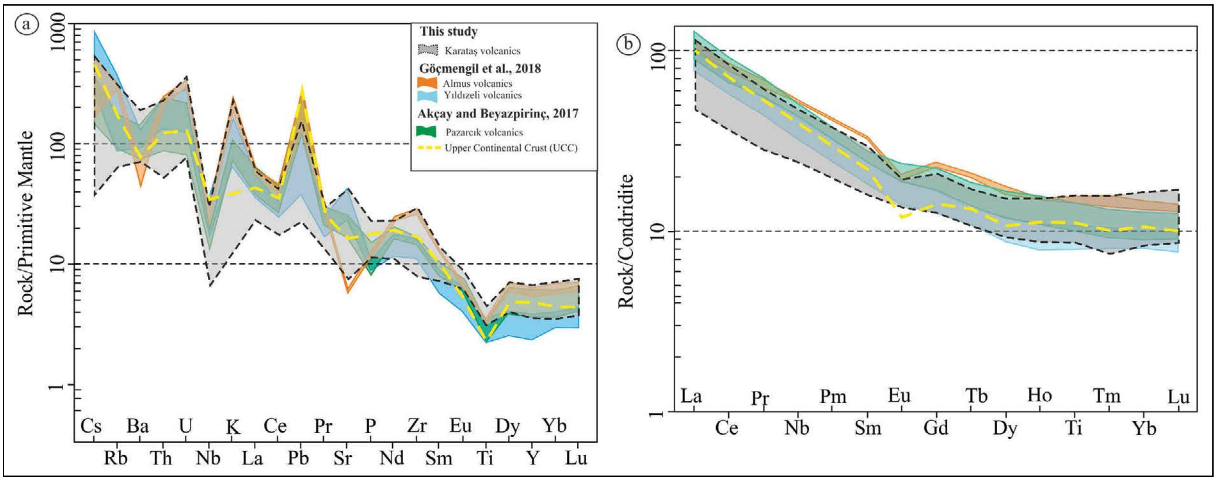

Figure 9- Multiple element variation diagram of Karataş volcanis, analyses normalized based on primary mantle Normalized based on primary mantle. a) Trace element (Primary mantle values from Sun and McDonough, 1989), b) Rare Earth Elements (REE values is normalized based on Boynton, 1984). Upper continental crust values are taken from Taylor and McLennan (1985), as Kiremitli volcanics have much higher SiO_2 contents than Karataş volcanics so they were not included in the evaluations.

6.2. Partial Melting

No mantle xenoliths were determined in Karataş volcanics and in their equivalents along IAESZ during this and previous studies. Because of the lack of isotope data, the partial melting degree was tried to be explained with only geochemical data.

In the samples of Karataş volcanics, MgO contents show following ranges; 5.17-2.66% in basaltic trachyandesites, 3.08- 0.19% in trachyandesites. The La/Yb(N) ratios are 6.76 - 9.15 and 7.86-9.78, Zr/Nb ratios are 14.78-18.27 and 15.5-16.89, in the same order. These values may suggest a low degree partial melting (normalized values have been calculated according to Sun and McDonough, 1989). In addition, Zr vs. La, La/Yb vs. Tb/Yb, La/Yb vs. La and La/Sm vs. La diagrams have been prepared. Again, to be able to evaluate partial melting degrees. it is observed that the samples fall in compatibility with each other on these diagrams (Figure 11). When this compatibility in the samples and the enrichments in the LILE/HFSE ratio diagrams evaluated together, it was concluded that even it was low degree; still some partial melting might have developed.

Karataş volcanics fall in the same fields on these diagrams with Pazarcık, Kiremitli and Yıldızeli volcanics. Alpaslan (2000) suggested that Pazarcık volcanics developed from partial melting of mantle under extensional tectonic regime, following collision. Akçay and Beyazpirinç (2017) interpreted

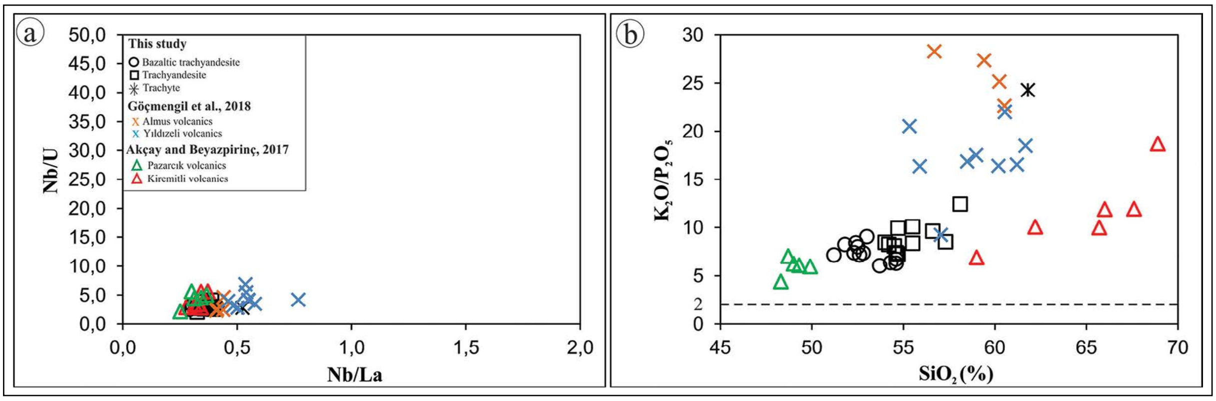

Figure 10- a) Nb/U vs. Nb/La, b) SiO_2 vs. K_2O/P_2O_5 diagrams for Karataş volcanics ($K_2O/P_2O_5 \leq 2$, from Carlson and Hart 1988).

that Pazarcık and Kiremitli volcanics derived from the partial melting of the continental lithosphere basement material which was metasomatized by subduction events. Göçmengil et al. (2018) concluded that basaltic trachyandesites with basic-intermediate (neutral) compositions of Yıldızeli volcanics were developed from the partial melting of their metasomatic source area.

The plots of the data of Karataş volcanics close to Pazarcık volcanics in all geochemical diagrams suggest that Karataş volcanics were formed in a similar environment with Pazarcık volcanics; partial melting of upper mantle in the extensional tectonic regime in post collisional period suggested by Alpaslan (2000). But the composition of magma occurred Karataş volcanics was significantly changed by crustal contamination/sedimentary addition.

6.3. Origin of Magma

Karataş volcanics show mostly shift towards amphibole field and very weakly to the phlogopite field on the Rb/Sr vs. Ba/Rb diagram (Figure 12a). Kürkçüoğlu et al. (2015) suggest that high Ba/Rb ratios indicate enriched lithosphere with high amphibole contents. But the shift towards phlogopite field, even if it is weakly, suggest that the source was probably enriched from asthenospheric mantle. But the similarity of the Zr/Ba ratio values of Karataş volcanics (for basaltic trachyandesite; 0.08-0.33 and for trachyandesites; 0.13-0.30) to those of lithospheric mantle (0.12-0.34) rather than those of asthenospheric mantle suggest the lithospheric mantle source (lithospheric and asthenospheric mantle values; after Menzies et al., 1991). Low Nb/U, Nb/La and Tb/Yb ratios also suggest that the origin of this magma is not asthenospheric. Again, low MgO, as well as low Ni, Cr values and enrichments in trace and rare earth elements also suggest that the source of the magma might have been evolved and differentiated lithospheric rather than asthenospheric mantle. Göçmengil et al. (2018) also suggested similar conclusions for Almus and Yıldızeli volcanics.

The samples fall above the mantle metasomatic array on the Th/Yb vs. Ta/Yb binary diagrams developed by Pearce (1983) (Figure 12b). This may be explained that the products of Karataş volcanics occured from a source enriched either during subduction or contamination by sedimentary materials.

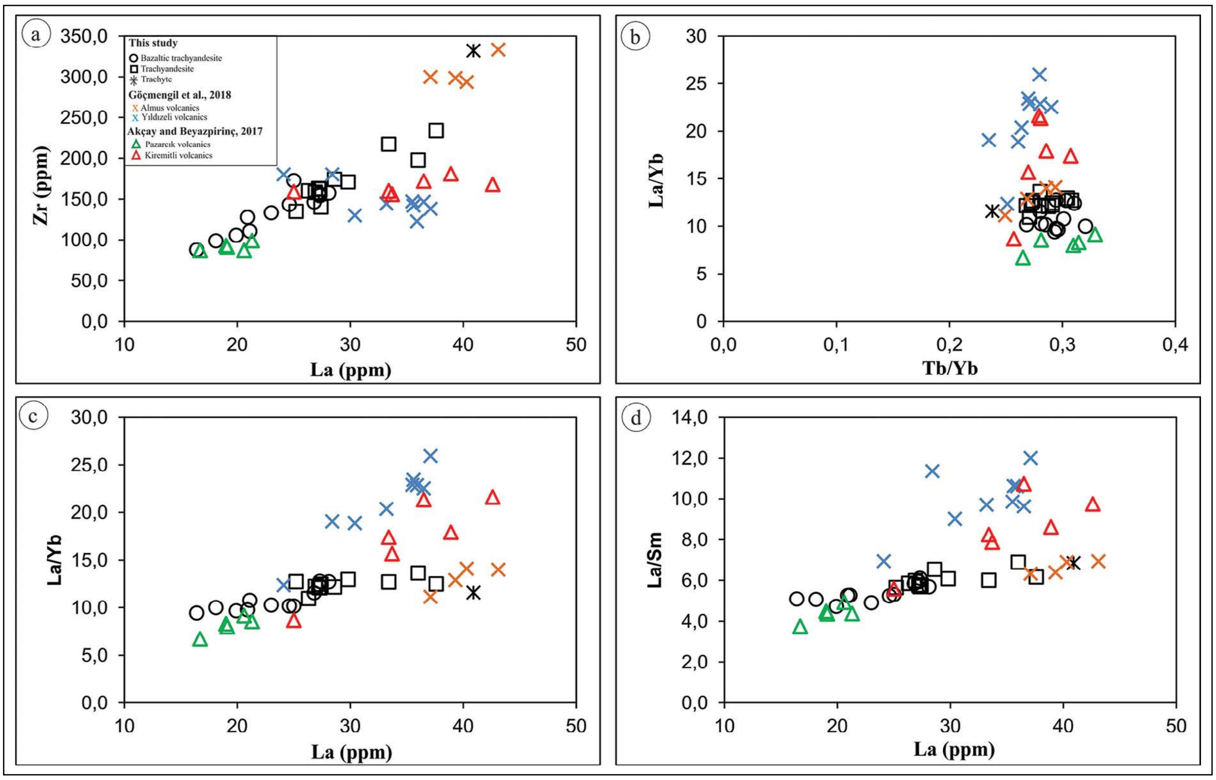

Figure 11- a) Zr vs. La, b) La/Yb vs. Tb/Yb, c) La/Yb vs. La, d) La/Sm vs. La diagrams for Karataş volcanics.

Various element ratio diagrams proposed by different researchers have been prepared to be able to determine whether this source, which forms volcanics has been enriched during subduction or by contamination with sedimentary materials. Hawkesworth et al. (1997) suggest that high Ba/Th ratio values in the arc magmatism products indicate enrichment resulted from subduction related aqueous solutions / or melt enrichment. Th and LILE contents significantly contributed to the enrichment of subduction related sediments. The results of Karataş volcanics mostly shift towards subduction related enrichment field on the Th/Yb vs. Ba/La and Ba/Th vs. Th binary diagrams indicate the significant subduction related enrichment. The weak shift toward the melt sourced from sedimentary material suggest also the possibility of presence sedimentary materials in the source area and sedimentary contamination (Figure 12c-d). It may be said that sedimentary related materials contributed to the development of Yıldızeli and Kiremitli volcanics

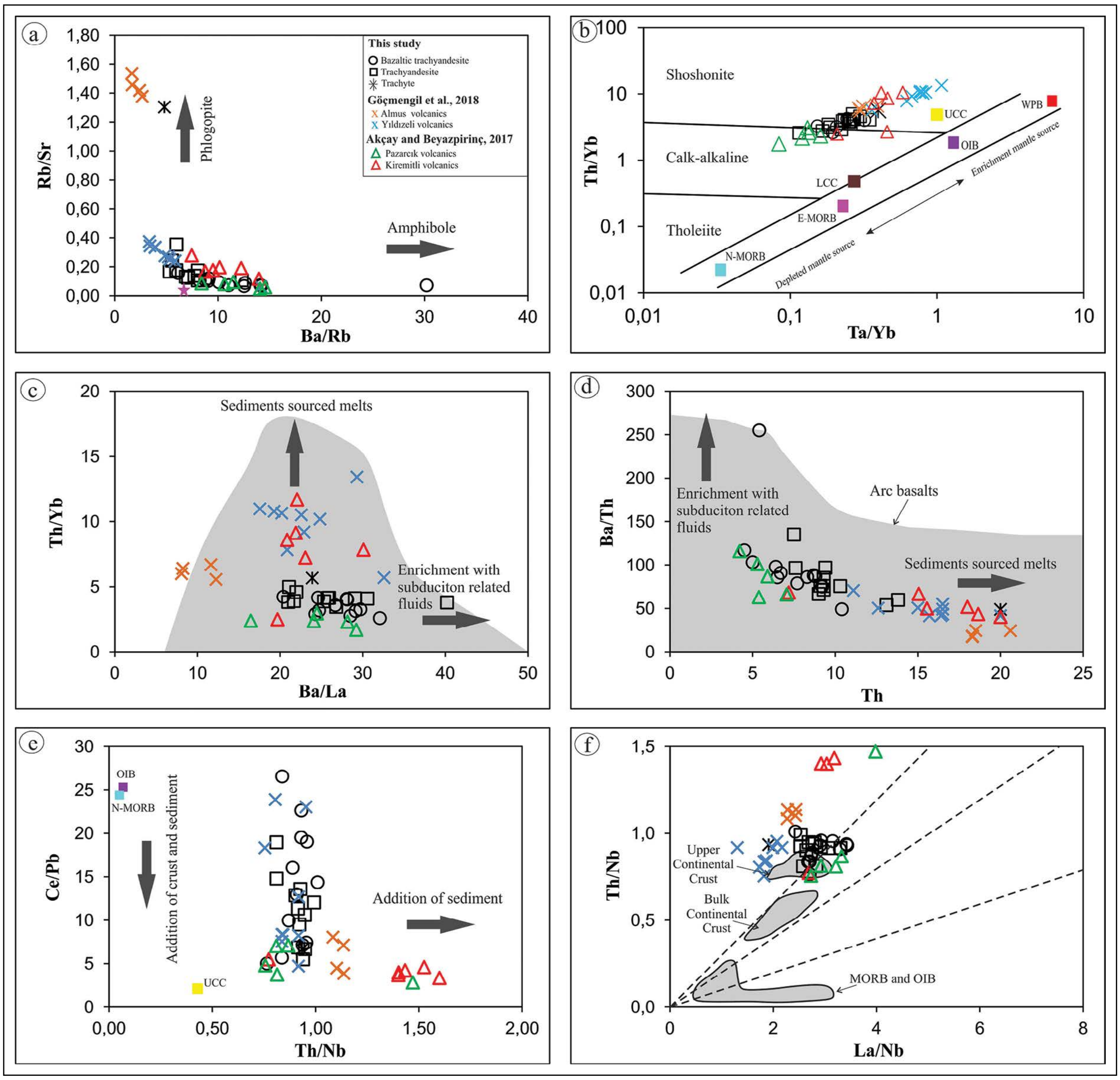

Figure 12- a) Rb/Sr vs. Ba/Rb (Ionov et al., 1997; Tommasini et al., 2011), b) Th/Yb vs. Ta/Yb (Pearce, 1983), c) Th/Yb vs. Ba/La (Kirchenbaur et al., 2012), d) Ba/Th vs. Th (Hawkesworth et al., 1997), e) Ce/Pb vs. Th/Nb (Hofmann et al., 1986), f) Th/Nb vs. La/Nb (Plank, 2005; Kürkçüoğlu et al., 2015). Upper continental crust (UCC) and Lower continental crust (LCC) values from Taylor and McLennan (1985), Ocean Island Basalt (OIB), Normalized Middle Ocean Ridge Basalt (N-MORB) and Enriched Middle Ocean Ridge Basalt (E-MORB) (values from Hofmann (1988) and Sun and McDonough (1989), Within Plate Basalt (WPB) (values from Pearce, 1982).

more than Karataş volcanics. Distribution pattern of the samples on the Ce/Pb vs. Th/Nb binary diagram show that crust and sedimentary materials were both effective in the source area (Hoffmann et al., 1986; Kürkçüoğlu et al., 2015) (Figure 12 e). Similarities of the distribution patterns to the upper continental crust on the spider diagrams, and plots of the samples in the upper continental crust field on the Th/Nb vs. La/Nb binary diagrams suggest the involvement of the crust material (Figure 12f). The basic product of Karataş volcanics fall close to normalized mid ocean ridge basalts (N-MORB) and Ocean Island Basalt (OIB) locations and acidic and intermediate products fall close to the Upper Continental Crust (UCC) area on the Ce/Pb vs. Th/Nb diagrams. These locations of the samples on this diagram suggest the presence of crust of the Tethys Ocean before the collision, the basic products of these volcanics were derived from N-MORB or OIB and acidic and intermediate products were formed by possible partial melting of the Upper Continental Crust material.

Keskin et al., (2008) studied Eocene volcanics in the Amasya and Çorum areas which have similar tectono-stratigraphic features with Karataş volcanics. They indicated that Eocene volcanics were the products of asthenospheric mantle giving rise as a result of the slab breakoff and concurrent uplift that occurred following the collision of the Sakarya continent and the Kırşehir block. But, Karataş volcanics shows data that is the enriched lithospheric mantle rather than the asthenospheric mantle, it was interpreted that the volcanics were not interacted with the asthenospheric mantle.

Göçmengil et al. (2016), interpreting the distribution of the samples on the Ce/Pb vs. Th/Nb diagram, also suggested the possibility of melt source derived from N-MORB or OIB material and enrichment continental crust and/or sedimentary material in the formation model of Almus and Yıldızeli volcanics. But, Göçmengil et al. (2018) suggested that the basic trachytic volcanism was possibly developed with trench tectonics controlled mainly by delamination and/or lithospheric removal processes at the first step, basic-intermediate (basaltic trachyandesite) rocks developed from the partial melting of metasomatic source area and trachytic lavas of latest period developed following reactivation of these basic-intermediate rocks by processes of extensional tectonic and decompression of the magma chamber.

Since the magma forming Karataş volcanics is geochemically lithospheric mantle characteristic, it is interpreted as the lithospheric removal either not developed or slightly developed during the formation of Karataş volcanics. Although Karataş volcanics were post collisional products, they show signs of subduction related enrichment. This complexity was interpreted as the lithospheric mantle material enriched in the crust during subduction developed in a pre-collisional episodes was reactivated by post collisional extensional tectonic and/or delamination processes (Topuz et al., 2011; Temizel et al., 2016; Göçmengil et al., 2018) the reactivated melt gave rise into the aggregated / accumulated material and produced Karataş volcanics causing to melt and assimilation of this material.

7. Conclusions

Karataş volcanics outcropping at the NE Sivas have alkaline character and represent last stages of Eocene volcanism. They consist of basaltic trachyandesites, trachyandesites and trachytes which are the products of basic and intermediate magma. In generally, this volcanism was controlled by fractional crystallization and the effects of crustal contamination increased from basaltic trachyandesites to trachytes.

According to geochemical data, the samples shift towards the amphibole area on the Rb/Sr vs. Ba/Rb ratio diagrams, variation of Zr/Ba ratios in the range of 0.08-0.33, high Ba/Rb ratio, low MgO, Ni, Cr contents indicate that the magma which produced these volcanics started being enriched from lithospheric rather than asthenospheric mantle. It could be suggested that enrichments were associated to subduction related fluids and probably to small amount of sedimentary materials.

In this study, when petrological and geochemical characteristics of Karataş volcanics evaluated with together, it is considered that these volcanics occurred as follows; oceanic crust situated between the Kırşehir block and the Sakarya continent subducted toward north, beneath the Sakarya continent during the pre-collision period, developed subduction related melt derived from N-MORB or OIB gave rise into the continental crust, following collision these melts were reactivated by extensional tectonics and/or delamination processes during post collisional period and Karataş volcanics were occurred.

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