Cumhuriyet Sci. J., 44(1) (2023) 120-129
DOI: https://doi.org/10.17776/csj.1229221

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Interpretation of Geochemical Data of Eocene Volcanism in Eastern Sivas Province (Central Anatolia, Türkiye)

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Research Article

History
Received: 04/01/2023
Accepted: 08/03/2023

ABSTRACT

The study area covers the eastern part of Zara district (Sivas) located in East-Central Anatolia. The units found in the region from bottom to top are characterized by the Upper Createaceous-Paleocene Refahiye Complex, the Middle-Upper Eocene Akıncılar Formation, the Karataş volcanics and Kösedağ Syenite, the Lower Miocene Onarı Formation, the Upper Miocene-Pliocene İsola volcanics, the Şerefiye volcanics, the Kadıköy Formation and the uppermost Quaternary sediments. In the frame of this study, the Karataş volcanics, which were formed as a result of the second magmatic activity of the Eocene period, are studied in detail. The Karataş volcanics are greenish black on their undisturbed clean surfaces, and some parts are brown-purple in color and have distinctive crack systems. It shows a reddish-pinkish color distribution in regions where degradation is observed intensely. The SiO2 content, which is the main criterion for determining the magma character of Karataş volcanics, is between 52.09 % and 58.45 %. MgO contents of similar importance are between 0.53 % and 2.21 %. Some of the light rare earth elements, La have 22.2-40.7 ppm, Ce 44.4-67.3 ppm, Pr 5.23-8.88 ppm, Sm 4.41-7.15 ppm, Eu 1.24-1.83 ppm; one of the heavy rare earth elements, Lu have 0.20-0.45 ppm and Yb 1.88-2.98 ppm values. The Karataş volcanics consist of basaltic-trachyandesite and trachyandesite. Evidence of liquid-crystal fractional crystallization (FC) in the phenocryst phase during the formation of the Karataş volcanics is clearly observed in the geochemical diagrams. Traces of partial melting and crustal contamination were found in geochemical studies. Following the closure of the Neo-Tethys ocean in the region, a widespread crustal thickening occurred in the region with the northward divergence of the northern branch of Neo-Tethys, and a suture zone was formed along this line. The Karataş volcanics were formed as a product of active volcanism after the collision in the region.

Keywords: Geochemistry, Geochemical data, Major-minor-rare earth element analysis, Volcanics, Petrology.

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Introduction

İzmir-Ankara-Erzincan Suture Zone (IAESZ) which is one of the most important tectonic units of Turkey. As a result of the subduction of the Neo-Tethys Ocean in the northern part of Turkey, the İzmir-Ankara-Erzincan suture zone (IAESZ) has developed. After the end of the suturation process, tension and magmatism developed simultaneously on both sides of the IAESZ and above. Products of Eocene volcanism cover large areas along the northern and southern border of this suture zone. Volcanic products are widely observed in the post-collisional basins that developed after the continental collision between the Anatolide and Pontide belt. The Middle Eocene magmatism is represented by volcano-sedimentary units, and at the same time, gabbro and diorite type plutonic rocks constitute the other element of this magmatism. The Middle Eocene volcano-sedimentary units in north-central Anatolia can be regarded as post-collisional. IAESZ and Intra Pontide suture zones with a regional unconformity. Geological records indicate that the lower levels of the Middle Eocene formations are represented by subaerial to shallow marine clastic sediments, but the middle and upper levels are made up almost entirely of subaerial volcanic units. All these findings imply that the suture zone was subjected to a sudden uplift around Lutetian, before the initiation of a widespread volcanism. Karataş volcanics (KV) products also crop out in large areas in the Zara (Eastern Sivas) region. The KV seems to be post-collisional volcanics and are very wide spread along the IAESZ.

The Middle-Upper Eocene KV, which form the basis of this study, cover the north and surrounding areas of the Zara district located in the northeastern parts of the Sivas basin in east Central Anatolia (Figure 1). While the units in the study area generally consist of magmatic and sedimentary rocks, the main subject of the study is the Middle-Upper Eocene KV. Although sedimentary rocks are not very common, there are lacustrine fluvial deposits belonging to the Upper Miocene-Pliocene Kadıköy Formation in the study area. The Refahiye complex, which consists of Upper Cretaceous-Paleocene serpentinized peridotites forming the oldest of the units not only in the study area but also in the region. The Refahiye complex is unconformably overlain by the Akıncılar Formation, which contains Eocene green-black colored serpentinized peridotite, yellow-colored dolomite interbedded gray-green-black colored sandstone siltstone alternation, black-gray thick bedded agglomerate levels. The Akıncılar Formation is overlain by the Middle-Upper Eocene KV consist of greenish-black colored porphyritic textured basaltic trachyandesite, trachyandesite, and trachyte-containing KV, which are the basic units of this study. In addition, Kösedağ syenite has a hot-hot contact relationship with Karataş volcanic [1]. The Kösedağ syenite mainly has alkaline feldspar syenite, quartz alkaline feldspar syenite, syenite and quartz syenite and locally monzonitic composition.

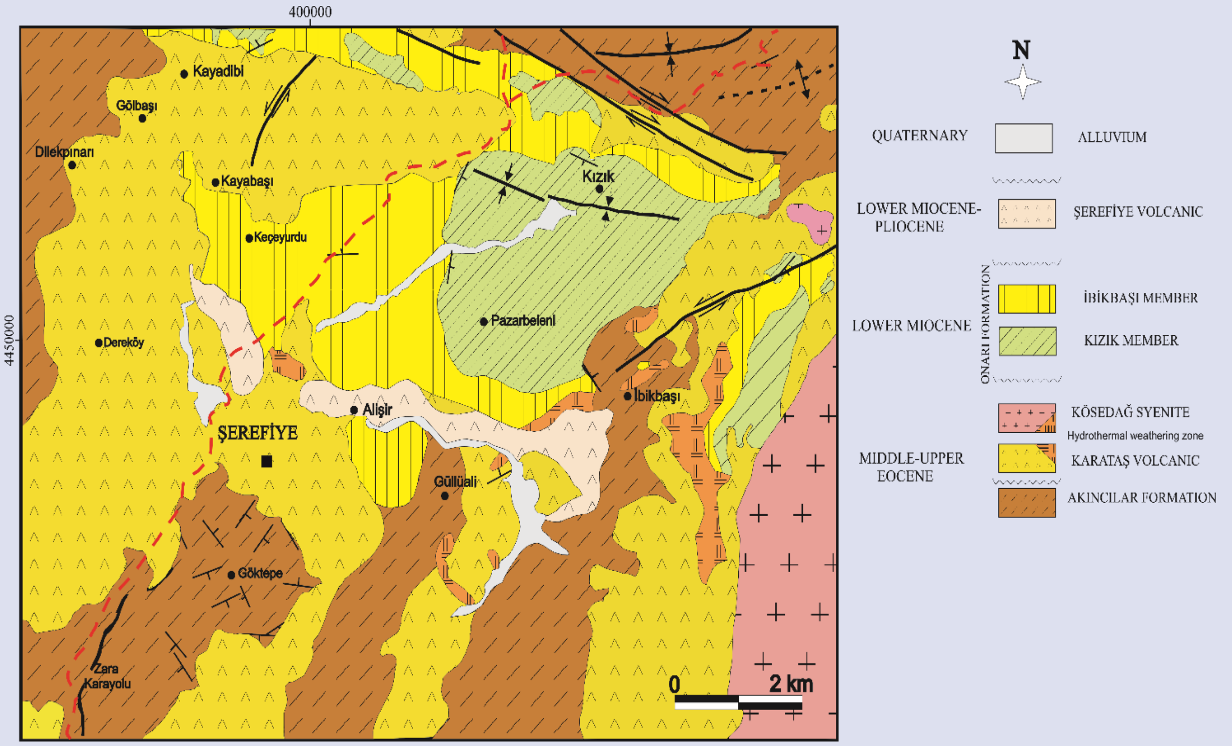

Figure 1. Geological map of the study area (modified from [1-4]).

These units are unconformably overlain by Lower Miocene red-orange colored conglomerate, yellowish medium-thin-bedded limestone and claystone-marl intercalations of white-gray colored thick-bedded gypsum, sandstone and the Onarı Formation, which contains yellowish-gray colored limestone with conglomerate intercalations, sandy and pebbly limestone layers in places. The Isola volcanics and the Upper Miocene-Pliocene Şerefiye volcanic, which are black color and contain abundant gas cavities, overlie the Onarı Formation. Kadıköy Formation, which consists of lacustrine-fluvial sediments unconformably, overlies these units. All these successions are covered by Quaternary alluvium (Figure 2).

Middle-Upper Eocene KV within the study area; It crops out around Dereköy, Keçeyurdu, Dilekpınarı, Kayabaşı, Güllüali and Pazarbelen. While the KV are generally greenish-black, in some parts brown-purple, the weathered areas are observed in the light brown-yellow-white color range. In addition, some parts contain distinctive fissure systems [1].

Materials and Methods

Petrographic thin sections of the rock samples collected from the study area were made in Sivas Cumhuriyet University Geological Engineering Department laboratories. Mineralogical-petrographic thin sections were made by McKenzie and Guilford [6], Yardley [7], Erkan [8], using a backlit Nikon Eclipse 50i POL type binocular research microscope, according to optical mineralogical criteria.

The rock samples, which were geochemically analyzed, were first brought to a particle size of less than 0.5 cm with a Fritisch brand crusher in the crushing-grinding-sieving laboratories of Sivas Cumhuriyet University, Department of Geological Engineering. Then, silicon-carbide was ground with a vibrating mill with a mortar until it reached a grain size that could pass under a 200 mesh sieve. Major, trace and rare earth element (REE) analyzes of 20 rock samples were analysed in ACME laboratories in Canada. The method of geochemical analysis is given on the website of the relevant company.

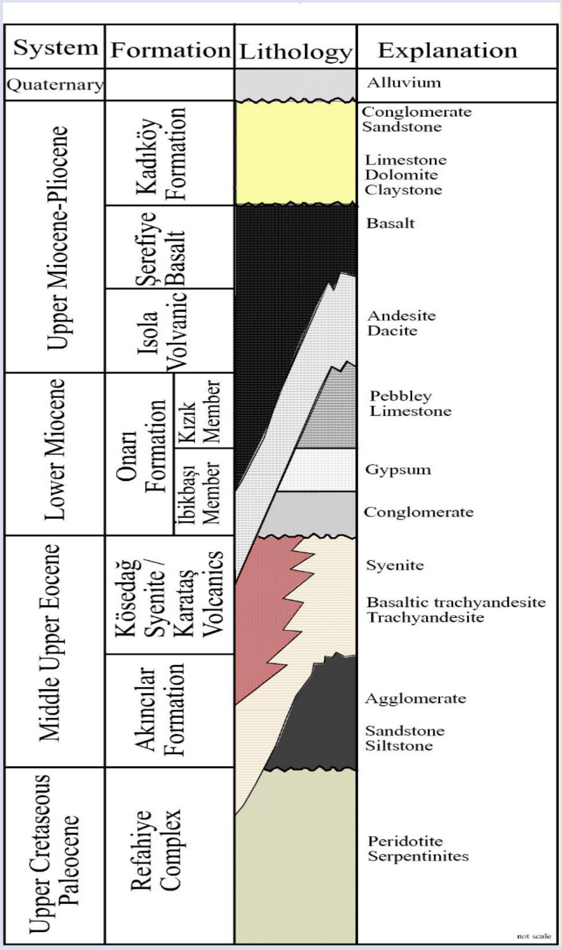

Figure 2. Generalized stratigraphic column section of the study area ([2-5].

Results and Discussion

Petrography

Thin sections of unaltered rock samples taken from the Middle-Upper Eocene KV were made and examined under a polarized light microscope[6-8]. Field and the textural observations on these rocks and the pulp of the rock have been very helpful in defining the volcanic rocks in the study area. These observations were examined under a polarized light microscope, and defining methods based on whole-rock geochemistry data [9] were used to name volcanic rocks (Figure 3). When we look at the positions of the Middle-Upper Eocene aged KV in the total alkali-silica [9] description diagram; It consists of basaltic trachyandesite and trachyandesite (Figure 3).

Plagioclase minerals in the form of microphenocryst and phenocryst have been observed intensively in the rock. Sanidine phenocrysts, augite and olivine minerals have been detected together with plagioclases. While hypocrystalline porphyric texture is commonly observed in the investigations made in KV, hypohyaline porphyric texture is also rarely observed. Plagioclase minerals are particularly common and are colorless and gray-white interference colored, low optically bumpy, subhedral/euhedral and prismatic shaped.

Polysynthetic twinning and zoned textured phenocrysts are observed.

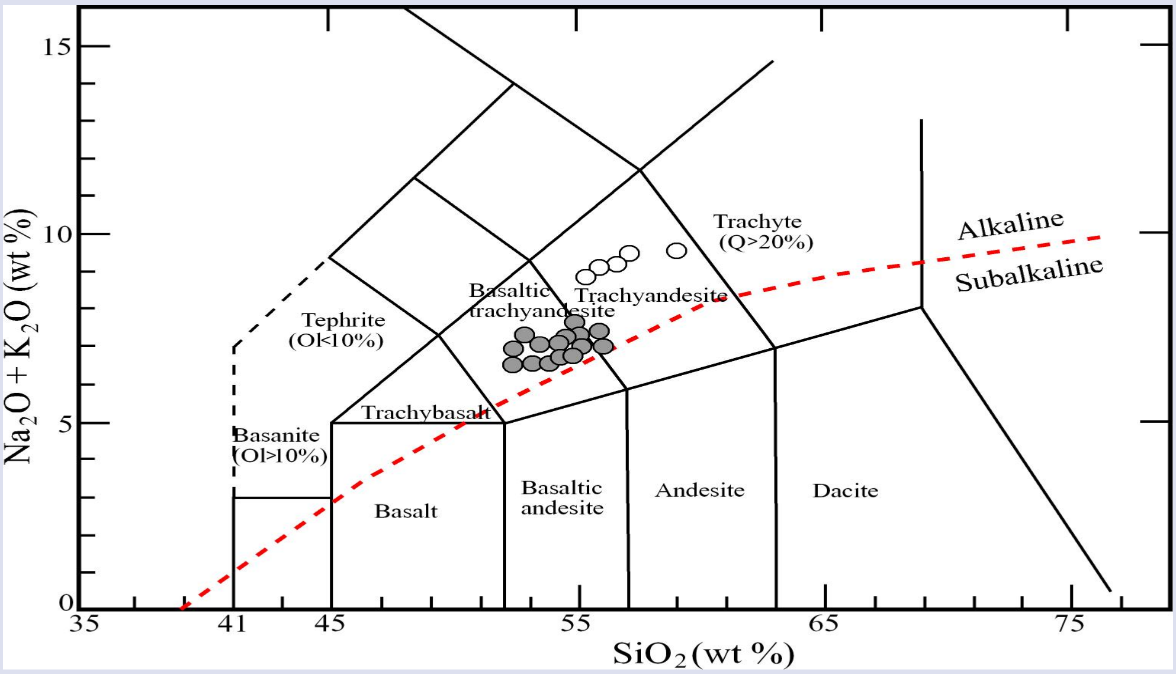

Figure 3. Total alkali-silica nomenclature diagram for Karataş volcanics (A: Alkali, SA: Subalkali, [9]).

There is interaction with magma at edges of plagioclase phenocrysts (Figure 4a,b). Plagioclase minerals are observed as phenocrysts and also microliths in thin sections. A sieve texture is rarely observed at the edges of the plagioclase phenocrysts. Sanidine mineral, which is rarely observed in the rock, is colorless in thin section and has low optical roughness. They display usually karsbald twinning, and rarely polysynthetic twinning, with euhedral crystal shapes. Rarely, sanidine phenocrysts containing plagioclase microphenocryst as inclusions were also observed (Figure 4c). Augite minerals, which are almost colorless in thin section, are generally observed as phenocrysts and microliths (Figure 4d). Augites observed as euhedral to subhedral in crystal shape and are also encountered as octagonal. The augite mineral shows vivid interference colors with its high optical roughness. Abundant carbonated augite phenocrysts are observed to be surrounded by the plagioclase. Olivine minerals in KV are generally seen as microphenocryst sizes. Olivine minerals are seen as highly optically rugged and completely iddingsitized.

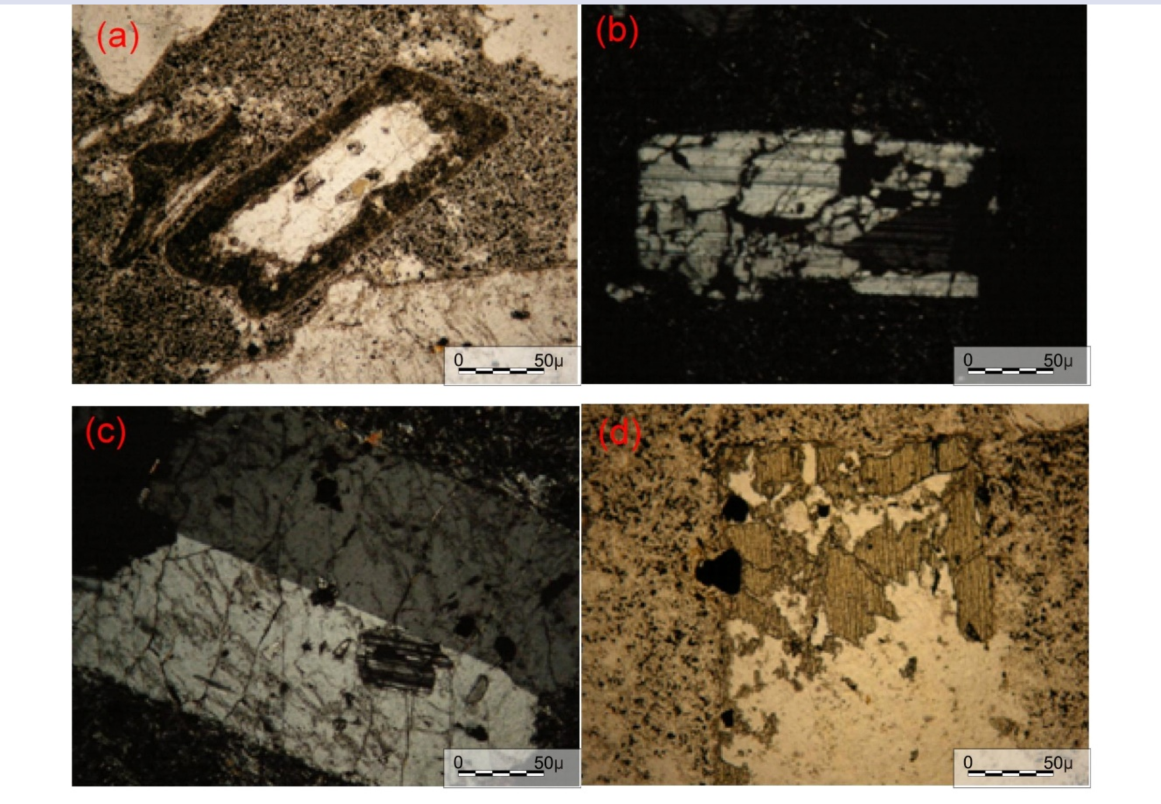

Figure 4. Thin section views of the Karataş volcanics. a-Cooling interactions with plagioclase minerals in the groundmass; b- Sieve texture in palgioclase mineral; c- Sanidine phenocryst and plagioclase microphenocryst seen as inclusions; d-Augite phenocrystal.

Geochemistry

The major, trace and rare earth element contents of the Middle-Upper Eocene KV are given in Table 1. Middle-Upper Eocene KV, which exhibit geochemically alkaline character, are composed of basaltic-trachyandesite and trachyandesite (Figure 3).

Fractional Crystallization

Evidence of liquid-crystal fractional crystallization (FC) in the phenocryst phase during the formation of the KV is clearly observed in the harker diagrams. Fractionation is quite evident in the variation diagrams of the major elements against SiO_2 (Figure 5). A distinct hyperbolic trend is exhibited in the variation diagrams of all major elements versus SiO_2. This identical hyperbolic trend indicates the presence of a fractional crystallization from trachyandesites to basaltic-trachyandesites. In this diagram, while the amount of Na_2O, K_2O, and P_2O_5 increases with the increase in SiO_2 content, whereas a clear trend of decrease is observed in Fe_2O_3, CaO, MgO, Al_2O_3, TiO_2 contents with the increase in SiO_2 content.

Similarly, selected trace elements against SiO2, also display hyperbolic trend from trachyandesites to basaltic trachyandesites (Figure 6). Trace element contents are observed to increase for Ba, Rb, Nb, Zr, Th, La and Y elements together with the increase in SiO_2 content. However, a decrease is observed in Sr element.

It is also observed that the fractionation in the KV develops in the form of olivine and clinopyrosexene fractionation from basaltic-trachyandesites to trachyandesites, and petrographic data confirm this fractionation. Traces of olivine and clinopyroxene fractionation are also evident in the Al_2O_3 versus CaO, CaO/Al_2O_3 versus MgO and Zr/Nb versus MgO diagrams (Figure 7). The fractionation in these diagrams is represented partly by olivine and partly by olivine+clinopyroxene

Table 1: Major, trace and rare earth element contents of the Karataş volcanics

Sample	K-2	K-4	K-6	K-8	K-11	K-15	K-20	K-27	K-28	K-32	K-35	K-36	K-37	K-44	K-45	K-47	K-49	K-50	K-54	K-64
SiO_2	54.68	54.55	55.14	53.57	56.09	55.09	55.45	56.61	58.45	52.56	54.20	55.45	52.79	52.68	55.42	54.36	53.92	53.07	52.09	52.26
TiO_2	0.84	0.87	0.86	0.82	0.72	0.68	0.70	0.79	0.78	0.83	0.90	0.86	0.87	0.85	0.85	0.89	0.89	0.85	0.81	0.83
Al_2O_3	19.52	19.41	18.96	18.73	19.52	19.12	19.62	18.52	18.56	18.58	19.98	19.70	18.65	18.22	19.58	20.42	19.69	19.07	18.85	18.82
Fe_2O_3	8.12	8.80	8.10	8.34	6.23	6.44	6.20	6.80	6.09	8.20	8.07	7.89	8.53	8.50	7.34	6.94	8.46	8.71	7.87	8.31
MgO	0.99	0.96	0.81	2.02	0.89	0.78	0.66	1.07	0.54	2.00	1.26	1.28	2.18	2.21	1.40	0.66	0.66	0.53	0.81	2.15
MnO	0.07	0.07	0.16	0.27	0.21	0.09	0.23	0.19	0.16	0.14	0.15	0.09	0.16	0.17	0.12	0.18	0.20	0.10	0.20	0.16
CaO	4.96	5.26	4.98	6.39	4.17	5.20	4.53	3.61	3.15	6.59	5.16	4.88	6.07	6.29	5.00	5.41	5.16	6.39	7.63	6.39
Na_2O	3.91	4.04	4.01	3.82	4.19	4.09	4.13	4.26	4.27	3.91	4.53	4.45	3.82	3.74	4.68	4.18	3.91	3.70	3.68	2.87
K_2O	3.53	3.03	2.93	2.96	4.94	4.82	4.83	5.16	5.24	3.14	2.73	2.60	3.14	3.12	2.51	3.17	3.02	3.04	3.98	3.16
P_2O_5	0.42	0.39	0.38	0.41	0.41	0.39	0.42	0.40	0.41	0.41	0.41	0.41	0.40	0.39	0.41	0.43	0.42	0.40	0.40	0.40
LOI	2.6	2.3	3.4	2.3	2.3	3.0	2.9	2.3	2.0	3.3	2.3	2.1	3.1	3.5	2.4	3.0	3.3	3.8	4.2	3.3
Total	99.64	99.68	99.73	99.63	99.67	99.70	99.67	99.71	99.65	99.66	99.69	99.71	99.71	99.67	99.71	99.64	99.63	99.66	99.52	98.65
Rb	74.4	55.7	50.5	57.6	125.8	126.5	119.6	152.7	148.0	61.2	52.1	44.5	66.4	65.7	45.2	72.5	69.0	55.0	53.9	64.4
Sr	862	784	690	802	712	777	848	661	584	730	788	759	742	736	777	830	814	808	795	789
Y	17.4	20.0	19.4	20.3	27.1	18.9	19.4	25.3	28.6	19.4	20.0	20.3	19.4	20.8	21.3	24.1	20.4	21.9	25.4	19.9
Zr	124	122	125	124	179	170	181	244	242	112	123	128	120	122	127	126	130	124	121	122
Nb	6.7	6.9	7.3	6.8	9.8	9.3	9.9	14.1	12.9	6.7	7.0	6.9	6.6	6.4	6.9	7.3	6.8	7.3	6.6	7.1
Ba	734	640	652	683	920	763	1024	687	820	679	632	600	675	653	571	749	970	671	776	693
La	24.5	23.8	25.0	22.7	40.7	29.4	31.7	36.5	36.9	22.2	25.3	24.9	23.0	22.5	26.6	26.8	24.7	26.1	25.7	23.9
Ce	50.7	47.1	51.6	46.0	67.3	56.2	59.0	66.5	66.0	44.2	51.4	49.2	44.4	47.4	50.2	48.5	48.7	46.7	48.2	47.8
Pr	6.35	5.68	5.69	5.49	8.88	6.33	6.76	7.94	7.72	5.23	5.58	5.64	5.44	5.39	5.84	6.23	5.75	5.90	5.78	5.45
Nd	24.0	22.0	24.2	22.6	38.3	25.4	27.4	30.0	31.0	21.7	23.5	23.4	21.6	22.4	23.2	25.4	22.7	24.9	22.7	21.7
Sm	5.23	4.79	4.41	5.03	7.15	4.55	5.61	5.71	5.99	4.65	4.76	4.88	4.42	4.94	5.20	5.25	5.02	4.73	4.91	4.77
Eu	1.51	1.39	1.37	1.36	1.83	1.37	1.29	1.46	1.44	1.24	1.31	1.27	1.30	1.29	1.34	1.51	1.37	1.38	1.41	1.34
Gd	4.37	4.33	4.18	4.35	6.49	4.33	4.64	5.15	5.59	4.14	4.24	4.42	4.50	4.63	4.62	5.25	4.19	4.51	4.96	4.31
Tb	0.72	0.69	0.64	0.67	0.93	0.62	0.68	0.81	0.85	0.61	0.66	0.67	0.71	0.67	0.72	0.79	0.67	0.71	0.75	0.66
Dy	3.62	3.83	3.57	3.67	4.98	3.58	3.75	4.36	4.81	3.46	3.78	3.94	3.98	3.75	4.34	4.33	3.89	3.87	4.41	3.90
Ho	0.73	0.88	0.73	0.82	1.03	0.70	0.81	0.87	1.01	0.76	0.78	0.80	0.74	0.75	0.84	0.89	0.86	0.83	0.87	0.76
Er	2.28	2.45	2.49	2.47	3.18	2.19	2.43	2.64	2.98	2.15	2.42	2.20	2.45	2.29	2.27	2.63	2.50	2.44	2.89	2.17
Tm	0.29	0.34	0.35	0.35	0.49	0.33	0.35	0.41	0.44	0.33	0.37	0.31	0.34	0.34	0.37	0.43	0.33	0.36	0.39	0.35
Yb	1.88	2.35	2.51	2.19	2.98	2.18	2.21	2.60	2.70	1.96	2.34	2.28	2.27	2.38	2.35	2.64	2.29	2.21	2.73	2.23
Lu	0.24	0.23	0.36	0.27	0.23	0.27	0.20	0.21	0.28	0.25	0.37	0.33	0.35	0.36	0.35	0.45	0.35	0.36	0.45	0.35
Th	7.5	6.7	7.0	7.2	11.9	11.3	11.2	18.4	17.1	7.0	6.4	7.3	7.0	6.7	7.6	7.1	7.5	6.9	7.3	7.3
P	1833	1702	1658	1789	1789	1702	1833	1745	1789	1789	1789	1789	1745	1702	1788	1876	1832	1745	1745	1745
K	29304	25153	24323	24572	41009	40013	40096	42835	43499	26066	22663	21584	26066	25900	20837	26315	25070	25236	24738	26232
Ti	5035	5215	5155	4915	4316	4076	4196	4735	4675	4975	5395	5155	5215	5095	5095	5335	5334	5095	4855	4975

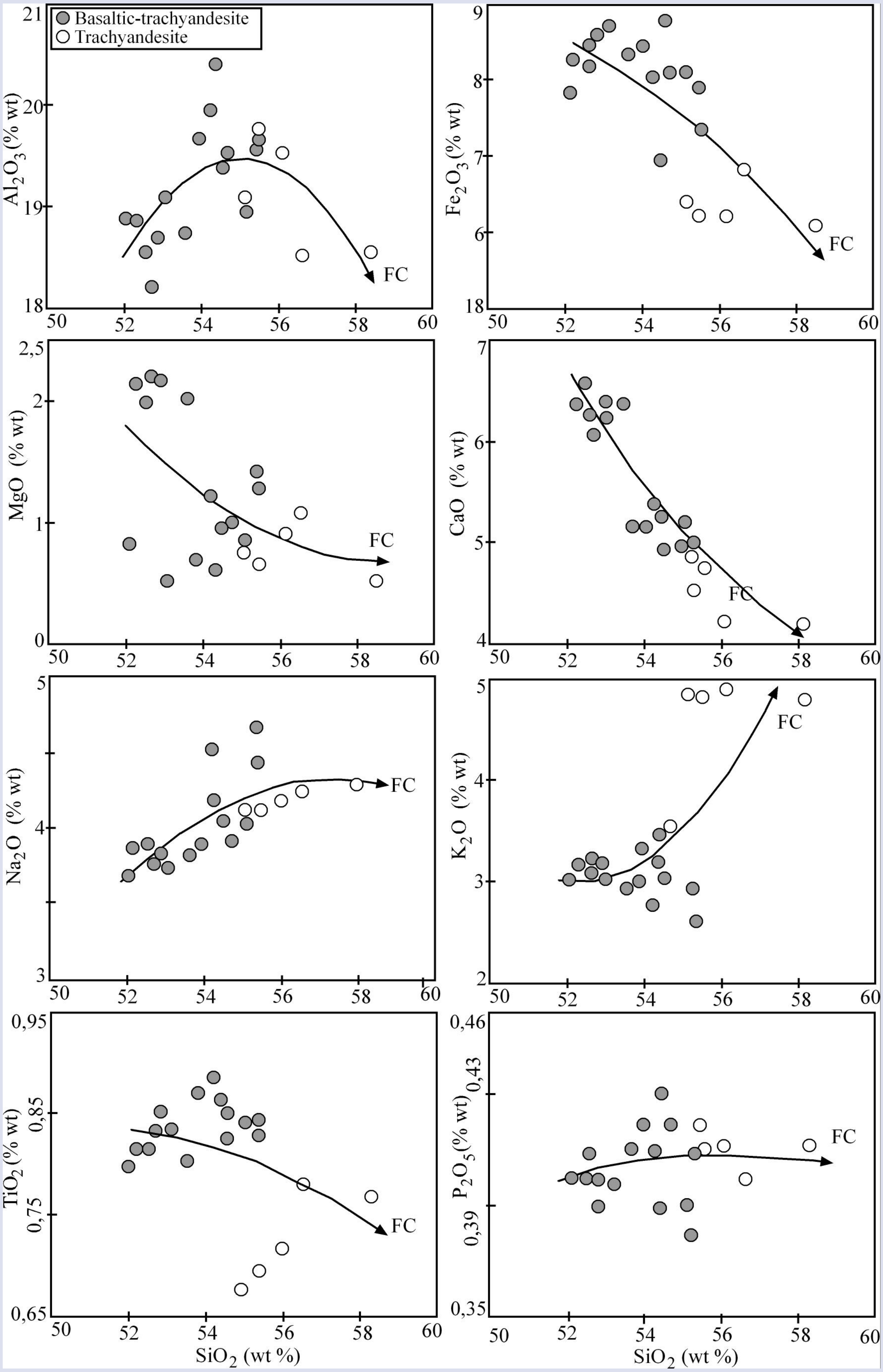

Figure 5. Variation of selected major elements versus SiO_2 for Karataş volcanics.

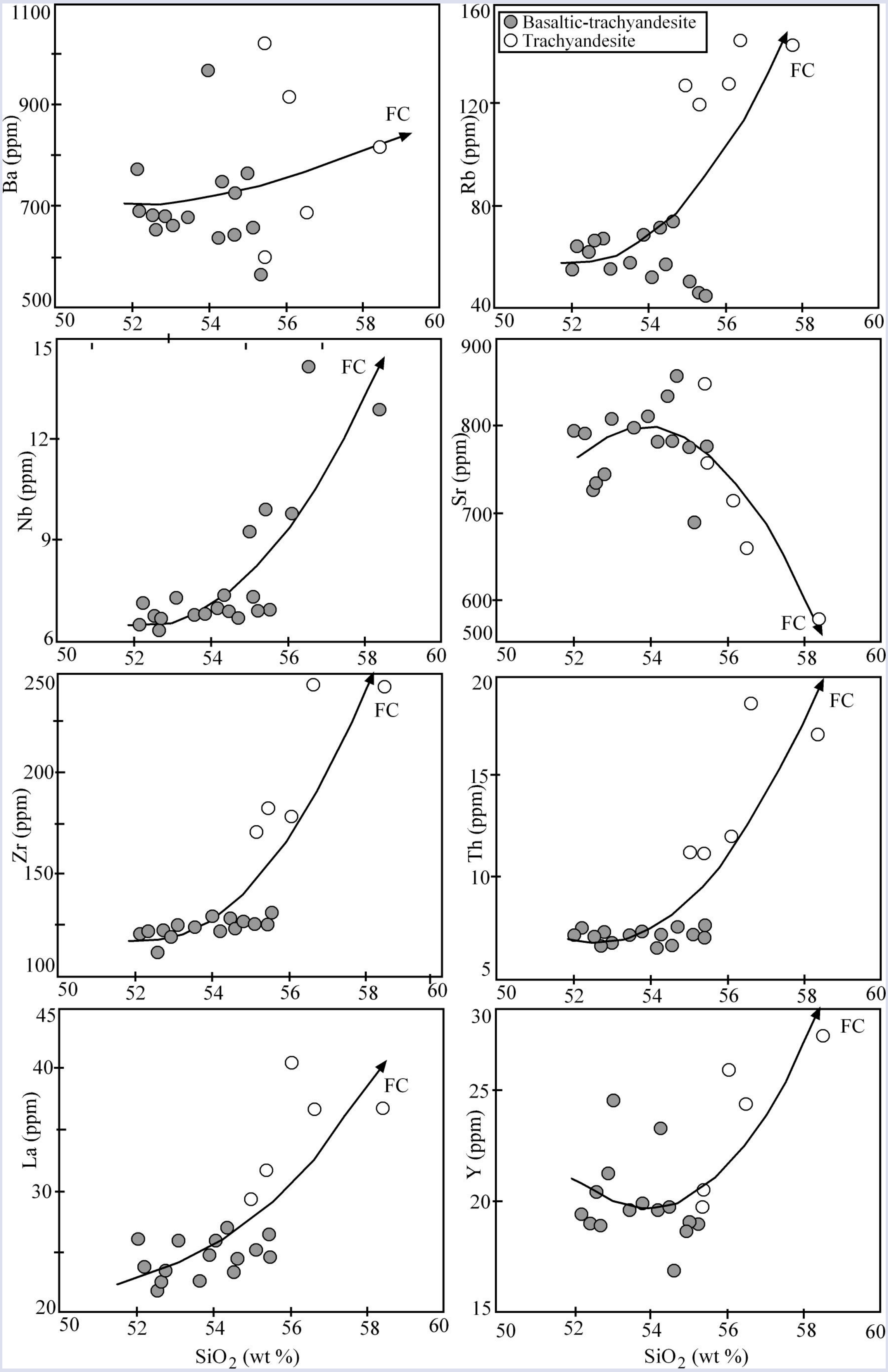

Figure 6. Variation of selected trace elements versus SiO_2 for Karataş volcanics.

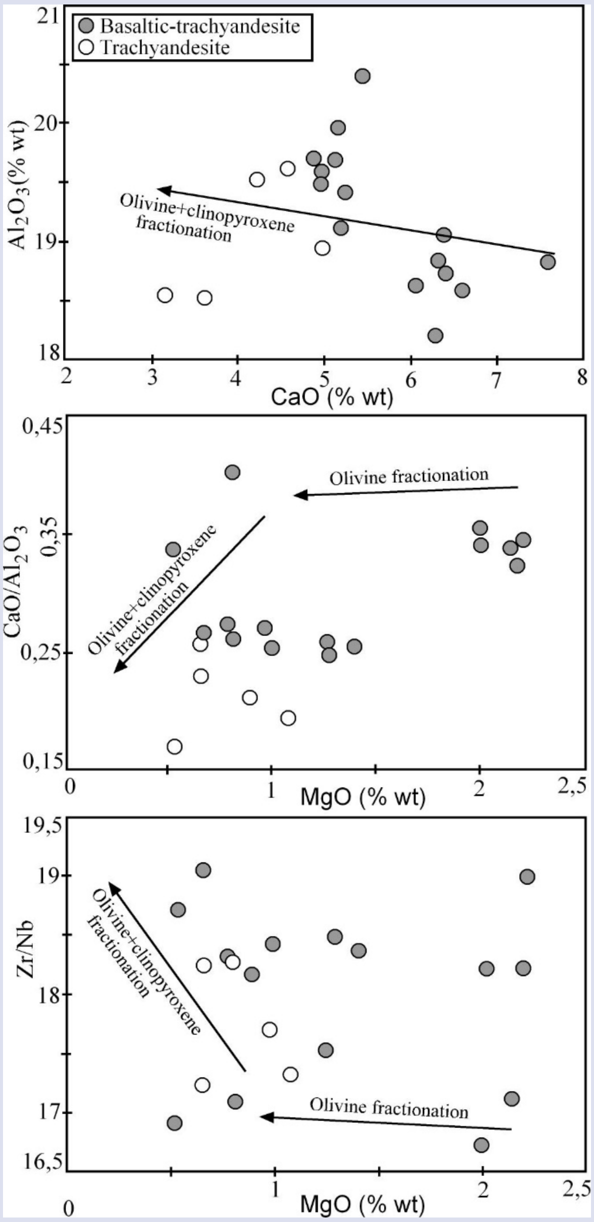

Figure 7. (a) Al2O3 versus CaO, (b) Cao/Al2O3 versus MgO, (c) Zr/Nb versus MgO for the Karataş volcanic.

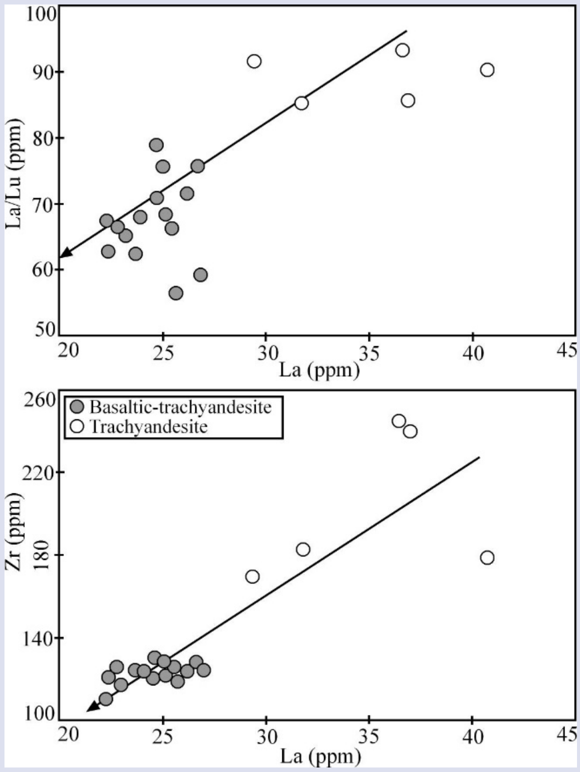

Figure 8. (a) La/Lu, Zr/La for the Karataş volcanics.

Partial Melting

Table 1 shows that the MgO contents of basaltic-trachyandesite and trachyandesite forming the KV are in the range of 0.5-2.2%. Considering that the amount of partial melting increases with the increase of MgO content, it is possible to state that the amount of partial melting of basaltic trachyandesites is higher than that of trachyandesites. In addition, when we look at the Harker diagrams of trace elements relative to each other, it is clearly seen that the amount of partial melting increases from trachyandesites to basaltic-trachanadesites in the La/Lu versus La diagram (Figure 8a). Similarly, in the variation diagram Zr versus La, it is seen that the amount of partial melting in basaltic trachyandesites is higher than in trachyandesites (Figure 8b).

Crustal Contamination

Considering the effects of crustal contamination in the KV, crustal contamination effects are observed in both basaltic trachyandesites and trachyandesites. It is also seen that there is an increase in the effects of crustal contamination from basaltic-trachyandesites to trachyandesites (Figure 9). When the trace element profiles in the spider diagram normalized to the primary mantle and chondrite are evaluated, light rare earth elements enrichment compared to heavy rare earth elements. The enrichment of these light rare earth elements in the KV compared to the heavy rare earth elements shows that the contribution of crustal origin material is higher during the crystallization in the magma (Figure 10). While large ion lithophile (LIL) elements such as Sr, Ba, Rb in the KV show enrichment pattern, Nb and Ti show a depletion pattern (Figure 10). The enrichment pattern of the LIL elements indicates that these elements participate in the partial melting during the partial melting processes; It shows that elements with high persistence such as Nb and Ti do not participate much in partial melting processes [10] [11]. In addition, the negative Nb anomaly also shows that the crustal contamination effect is important. When geochemical environments are considered, negative Nb and Ti anomalies are also characteristic of post-collisional and subduction-related volcanics.

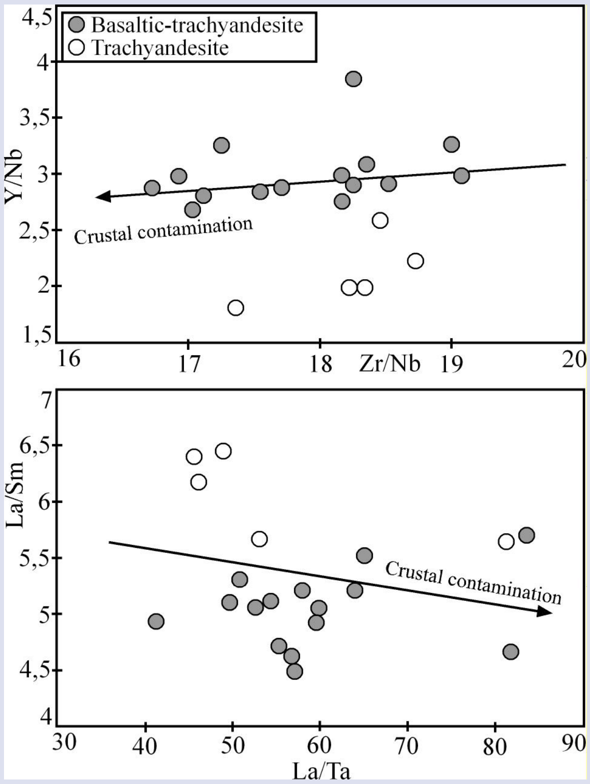

Figure 9. (a) Y/Nb versus Zr/Nb, (b) La/Sm versus La/Ta for the Karataş volcanics.

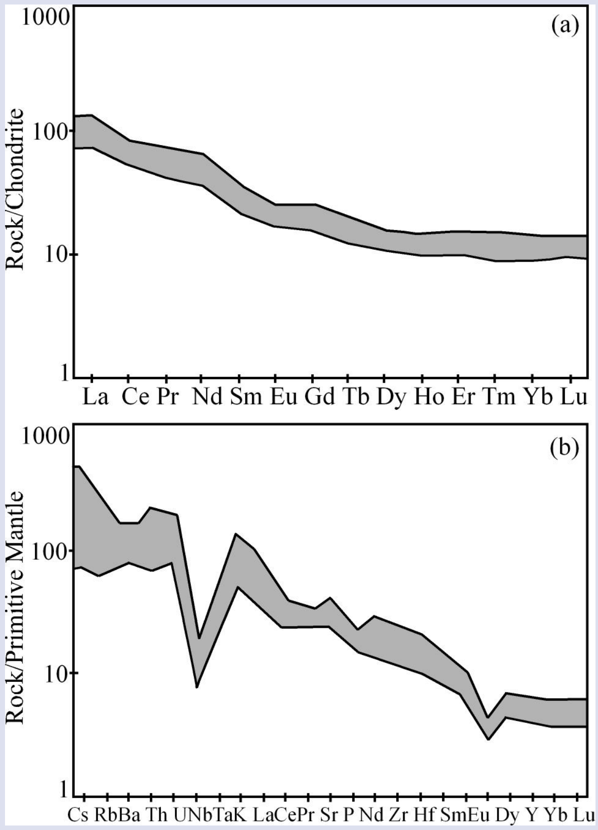

Figure 10. (a) Chondrite normalized rare earth element (REE) and (b) primitive mantle normalized multi element diagrams for the KV. Chondrite values are from [12], primitive mantle values are from [13].

Igneous rocks are formed from magma. The "primitive magma", which initially has a definite and homogeneous composition, undergoes compositional changes in the solidification process, leading to the formation of igneous rocks of different composition. These processes that cause changes in the composition of the primitive magma; It consists of processes such as fractional crystallization, partial melting, magma mixing, crustal contamination. Fractional crystallization, crustal contamination and partial melting at different rates were detected in all of the volcanic rocks observed along IAESZ.

When we look at the evolution processes of the magma forming the Eocene aged Karataş volcanism, which is formed along the İzmir-Ankara-Erzincan suture zone, consisting of basaltic-trachyandesite and trachyandesites and exhibiting alkaline character, it is seen that fractional crystallization is effective. Also, the amount of partial melting increases from basaltic trachyandesites to andesites. Crustal contamination effects are observed in both basaltic trachyandesites and trachyandesites; it is also seen that there is an increase in the effects of crustal contamination from basaltic trachyandesites to trachyandesites in KV. All these magmatic events are seen in Harker change and multi-element diagrams.

Conclusions

Middle-Upper Eocene KV, which present important outcrops in the Central-Eastern Anatolian alkaline province, are composed of basaltic-trachyandesite and trachyandesite**.** The KV, exhibiting hypocrystalline porphyritic texture, contain plagioclase minerals in the form of microliths and phenocrysts. In addition to plagioclase minerals, sanidine, augite and olivine minerals were also observed. The alkaline Karataş volcanics are geochemically display evidence of fractional crystallization (FC). Major and traces elements support the existence of a fractional crystallization from trachyandesite to basaltic-trachyandesite. It was observed that the fractionation in the Karataş volcanics is dominated by olivine and clinopyroxene. Partial melting ratio in the Karataş volcanics increased with the increase of MgO content and the partial melting ratio of basaltic-trachyandesites is higher than trachyandesites. Crustal contamination played and important role for the Karataş volcanics increasing from basaltic-trachyandesites to trachyandesites. In the Santonian-Campanian period, the oceanic crust forming the northern branch of the Neo-Tethys ocean subducted briefly beneath the Pontides (Eurasian plate). In the continuation of the subduction event, a widespread crustal thickening occurred in the region and the İzmir-Ankara-Erzincan suture zone was formed along this line [14-22]. The Middle-Upper Eocene aged Karataş volcanics are the product of an active post-collisional volcanism that occurred as a result of this collision in the region.

Conflicts of interest

There are no conflicts of interest in this work.

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