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Petrography, Geochemistry, Petrogenesis and Tectonic Situation of Volcanic Units in Zaker area (Northwest of Iran)

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Abstract

Zaker volcanic units are located in the western Alborz Zone (northeast of Zanjan). Volcanic rocks of this area are combinations of basalt, andesite and trachy andesite. In these units, pyroxene, plagioclase and rarely olivine crystals are as phenocrysts in a background of fine crystals and glass minerals. Of course, also, some small outcrops of andesite tuff units are observed. These units are metaluminous and are located in ranges from high calcium calc alkaline to shoshonitic rocks natures. The significant feature of these units is the enrichment of LREE elements relative to HREE. Furthermore, positive anomalies of LILE elements such as Cs, Ba, K and Sr along with negative anomalies of HFSE elements such as Ti, Nb and P are observed in all samples. Negative anomalies of Nb and enrichment of light rare earth elements relative to heavy rare earth elements, represent the subduction zone environments. The formation environments of these units are continental arcs and the primary magma is composed of partial melting of garnet spinel lherzolite with a very small amount of garnet during the melting process. The low ratio of (La / Yb) N (6.79-4.6) in all volcanic units indicates the absence of garnet at the origin or the partial presence of this mineral in the source of the magma. The geochemical characteristics of these units indicate that magma has originated from high horizons of the mantle (probably a lithospheric mantle) and has tolerated some crust contaminations during the ascent.

Keywords: Clinopyroxene; Calc-alkaline; Garnet spinel lherzolite; Subduction; Western Alborz Zone; Zanjan



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Introduction

Zaker area is located in 16 km of northeast of Zanjan and between 48 $^{\circ}$ 29 ' and 48 $^{\circ}$ 53' E geographical longitudes and 36° 33' to 36 $^{\circ}$ 45' latitudes (Fig. 1). This area is located in the central part of the 1/250000 map of Zanjan (Eftekharnezhad and Stocklin, 1968), and the south half of the 1/100000 map of Tarom (Hirayama et al., 1966). The study area in geological zoning of Iran is part of the Tertiary-Quaternary magmatic belt of western Alborz (Fig. 1) (Aqanbaty, 2004). This area is classified in the structural division of Iran from the point of view of Alavi (1991) and Nabavi (1976) and is a part of the Alborz-Azerbaijan zone. Generally, in the northwest of Iran, three sedimentary and tectonomagmatic basins are known: 1) Western Alborz Belt or Talesh mountain range, 2) Urmia – Dokhtar magmatic belt and 3) sedimentary basin of southern Caspian. Due to the location of the area in the western Alborz zone, from the geological view can say that the northern boundary of Alborz bounded to the ancient tethys joint that this boundary composed from the collision of the continental lithosphere of Alborz with Turan lithosphere in the Late Triassic. However, in most places, the location of the joint is covered with sheets driven from north to south.

The south end of Alborz is not so distinct. Tabriz fault (Alavi, 1991) (Anti Alborz), Garmsar fault (Berberian, 1996), Semnan fault (Nabavi, 1977) and Attari fault is considered as the southern border of Alborz. The western border of Alborz is to the small Caucasus and its eastern border is to the Parapa Maysus Mountains of Afghanistan (Alavi, 1991).

Alborz zone tolerates northern-southern shortening and various volcanic and sedimentary rocks with the late precambrian to quaternary age are observed in it (Allen et al., 2004). There are a lot of ambiguities about the history of this basin. Some scientists like Stampfli et al., (1991), believe that the separation of the Alborz block from Gondwana occurred during ordovician-silurian. From the other side, Wensink and Varekamp (1980) believe that this basin has been a part of Gondwana in the upper devonian to carboniferous. Eventually, the basin in the late triassic encountered the eurasian block (Sengor et al., 1988). During the late eocene - oligocene, along with the central belt of the western Alborz basin, there was intense magmatic activity (Berberian, 1981) and various types of volcanic and intrusive units have outcrops in the northwestern part of Iran with different ages. As regards the volcanic units of Zaker area have not been studied petrologically, the aim is to be investigated the accurate petrography, geochemical characteristics, petrogenesis and tectonic environment of these units in this study.





Fig.1. Structural position and access routes to Zaker area (northeast of Zanjan).

Geology

Volcanic units in Zaker area are often extended to the southeast and northwest. These units occupy 13 km² of area and are often seen as not so high hills. Volcanic rocks are generally formed on the margin of Zaker granitoid, and along with the granitoid, have a northwest - southeast direction. Under the influence of physical and chemical factors, the morphology of the outer units is in the form of the hill, and their color varies from black to dark green.

The oldest apparent formations in Alborz area are metamorphic rocks and non-metamorphic shales belonging to Kahar formation and Duran Granite. These rocks make up the lower part with the precambrian age. But according to the geological map of Tarom plate on 1/100000 scale (Hirayama et al., 1966), the oldest rock units of the area are sericite quartz schist and phyllite with protrozoic age and crystalline limestone of devonian. In the next step, the shale units and thick limestone (Lar Formation) with jurassic age is formed. The eocene border is determined with the red conglomerate (Fajan Formation) that this trend continues with nummulitic limestone, sandstone units and andesite, and eventually ends to the Eocene Crystal Lithic Tuff. In Zaker area, volcanic units have not been identified yet. For the first time, the author has identified volcanic units with pyroxene basalt, andesite basalt, pyroxene andesite and andesitic tuff compositions in this area. Field surveys show that the outer units are older than the intrusive masses of the area and no mineralization has been made in them.

Methodology

In the field survey, the relationships among the existing rock units in the area are identified and for microscopic studies and geological mapping with a 1/20000 scale, more than 90 samples were taken from the all rock units. 25 samples of these samples are from the volcanic rocks of the area and 7 samples with the least alteration and weathering were sent to the East Amethyst lab for XRF analysis to determine the main elements of the geochemical



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studies of the rocks. Also, in order to determine the trace and rare earth elements, all these samples were sent to the Acme lab of Canada that in this lab, the samples were prepared by using the alkaline melting method that was performed by a metaborate / tetraborate solvent and nitric acid and then were analyzed by inductively coupled plasma mass spectrometry (MS-ICP).

Petrography

Mafic lavas of Zaker area have porphyry and rarely amigodal structures in the manual sample. It is clear in field surveys that the coarse plagioclase and pyroxene crystals are in an aphanitic background. Based on the types of mafic minerals and texture properties, these rock units are divided into four groups: pyroxene basalt, andesite basalt, pyroxene andesite and andesite tuff (Fig. 2). According to the studies, the relative ages of the volcanic units are older than the intrusive units (Fig. 3A).

Pyroxene Basalt

This unit has been expanded to the northwest of the region with 2.5 km² of surface outcrop (Fig. 2). In the vicinity of the basalt unit, pyroxene andesite and porphyry pyroxene diorite units are located. In microscopic studies, the main texture of this unit is porphyric and amygodal and glomeroporphyritic textures are also observed (Fig. 3B). The phenocryst percentage of this sample varies between 30% and 35% and range of size changes is from 0.5 to 2 mm. The most important phenocrysts of the rock are clinopyroxene and plagioclase crystals. As well as, olivine coarse crystal is seen rarely. These phenocrysts are made of plagioclase, mafic minerals and glass in a microcrystalline background. Frequency of plagioclase in phenocrysts varies between 15% and 20%, and their size range varies from 0.3 to 2 mm. Analytically, plagioclase have been altered to epidote, chlorite, carbonate and a little to clay minerals (Fig. 3E). Clinopyroxene, the other coarse crystal of this unit, has abundancy between 5% and 13%, and this mineral is often from diopside and augite type, 0.2 to 1.5 mm in size. This mineral has partially decomposed into epidote, iron oxide, carbonate and a little chlorite. The pyroxene basalt unit shows weak to moderate intensity of propylitic alteration.

Andesite Basalt

A small outcrop (0.5 Km^2) of this unit is seen as small hills in the center of the area (Fig. 2). The textures of this unit in the microscopic sections are porphyry and glomeroporphyric, with a phenocrystal percentage about 20%. The main mineral of this unit is plagioclase with 17% of abundancy, representing approximately 0.3 to 3.5 mm of size. It has been decomposed into sericite, chlorite and epidote.

Other mineral in this unit includes 3% of clinopyroxene mineral (Fig. 3C), the size range of this mineral varies from 0.2 to 0.7 mm, and its average size is 0.3 mm, which is strongly



altered to chlorite (Fig. 3-5A). The alteration of this propylitic unit is poor and the background is very fine crystalline and fine plagioclase microlites are observed in the background.

Pyroxene Andesite

Among the volcanic rocks, the pyroxene andesite unit has the largest expansion in the region. Pyroxene andesite unit with approximately 12 km² of area is located in the southeast and northwest of the region (Fig. 2), and this unit is melanocratic. Coarse milky -colored plagioclase crystals appear in very fine crystalline and dark-colored background. In thin sections, the main texture of this unit is porphyry and its secondary textures are glomerophyric, seriate and poikilitic.

The percentage of phenocrysts of this unit varies from 35% to 50% at different sections, which 25% to 35% of this amount is attributed to plagioclase mineral (Fig.3D). This mineral exhibits a size range between 0.3 and 3 mm. The plagioclases have often polysynthetic twinning and occasionally zoning twinning. It has identified two minerals from the family of clinopyroxenes in this unit that are augite and diopside, which their abundance range is from 5% to 15%, and their approximate size varies from 0.2 to 2 mm, and this mineral rarely shows the blade twinning. Analytically, this mineral is converted to carbonate, iron oxide, epidote and rarely chlorite in different sections. In addition to these minerals, hornblende mineral has also been identified in this unit, with an abundance percentage about 4%. The background of this unit is fine-grained and dark-colored that composed of plagioclase and microcrystalline pyroxenes. This unit has no alteration and in a small number of samples, the weak propylitic alteration is observed.

Andesite tuff

A small outcrop of this unit is observed in the center to the southeast of the region. This unit is strongly fine grained and is rarely detected by plagioclase crystals (Fig. 3F). This unit shows a moderate propylitic alteration and it is within the mass of the veins with 0.2 to 0.5 mm of thickness that these veins are filled with epidote and carbonate.



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Fig.3A) A view of granitoid units penetration into the volcanic rocks of Zakir area. B) Amigodal texture and cavity filling with carbonate in pyroxene basalt unit. C) Microscopic image of andesite basalt unit. D) Phenocrysts of pyroxene and plagioclase in pyroxene

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andesite unit. E) Plagioclase transformation into the epidote secondary mineral in pyroxene basalt unit. D) Microscopic image of microcrystalline andesite tuff unit.

Geochemistry of the volcanic units

Based on accurate microscopic studies, 7 samples of volcanic units with the least alteration were selected for the analysis of the main oxides, rare earth elements and trace elements, and the results of their chemical analysis are presented in Table 1.

Table 1. Results of chemical analysis of the main oxides based on weight percent and minor elements and rare earth elements to ppm from Zaker area.

| Sampl | A21 | D7 | C9 | D29 | D19 | A23 | C9 |
|--------------------------------|-------|-------|--------|-------|-------|-------|-------|
| Rock | 3 | 1 | 3 | 3 | 1 | 2 | 2 |
| SiO ₂ | 59.58 | 58.42 | 60.79 | 59.69 | 61.52 | 53.01 | 54.52 |
| Al ₂ O ₃ | 17.31 | 15.6 | 17.44 | 17.28 | 14.68 | 17.15 | 17.01 |
| TFeO | 3.01 | 4.93 | 3.09 | 2.96 | 4.44 | 6.95 | 5.88 |
| MgO | 2.84 | 4.12 | 1.82 | 3.79 | 3.17 | 3.84 | 4.69 |
| CaO | 4.13 | 4.31 | 4.28 | 4.06 | 3.37 | 5.88 | 5.99 |
| Na ₂ O | 3.28 | 3.28 | 3.61 | 3.48 | 3.3 | 2.85 | 2,28 |
| K ₂ O | 3.02 | 3.32 | 2.72 | 2.63 | 4.39 | 2.46 | 3.06 |
| TiO ₂ | 0.44 | 0.70 | 0.52 | 0.38 | 0.72 | 0.57 | 0.63 |
| P_2O_5 | 0.08 | 0.16 | 0.11 | 0.19 | 0.18 | 0.17 | 0.12 |
| MnO | 0.04 | 0.34 | 0.06 | 0.05 | 0.16 | 0.24 | 0.05 |
| L.O.I | 1.59 | 3.03 | 0.48 | 2.31 | 3.33 | 2.91 | 1.38 |
| Ва | 743 | 814 | 839 | 914 | 900 | 956 | 870 |
| Cs | 1.50 | 1.4 | 1.20 | 1.60 | 2.70 | 2.30 | 2.10 |
| Hf | 4.70 | 5.19 | 4.9 | 5.10 | 5.40 | 5.50 | 5.10 |
| Nb | 10.4 | 9.1 | 10.9 | 10.6 | 11 | 11.4 | 10.6 |
| Rb | 103.1 | 112.1 | 95.4 | 90.1 | 119.1 | 121.3 | 110.2 |
| Sr | 504.8 | 422.3 | 478.10 | 468.3 | 342.8 | 395.1 | 363.1 |
| Та | 0.70 | 0.6 | 0.70 | 0.60 | 0.90 | 4.60 | 3.20 |
| Zr | 174.8 | 182.1 | 199.40 | 174.1 | 184.1 | 164.8 | 144.3 |
| Y | 21.2 | 22.9 | 22.6 | 22.1 | 22.8 | 22.4 | 23.1 |
| La | 26.10 | 27.3 | 25.50 | 24.70 | 24.50 | 24.7 | 25.7 |
| Ce | 51.60 | 52.2 | 50.60 | 49.50 | 51.80 | 51.3 | 51.8 |
| Pr | 5.93 | 5.11 | 5.49 | 5.06 | 5.55 | 5.68 | 6.2 |
| Nd | 21.10 | 20.4 | 21.50 | 22.10 | 20.90 | 20.60 | 21.30 |
| Sm | 3.98 | 3.73 | 4.30 | 4.41 | 4.30 | 4.10 | 4.89 |
| Eu | 1.16 | 1.09 | 1.10 | 1.11 | 0.96 | 0.93 | 0.98 |
| Gd | 4.02 | 4.38 | 4.00 | 4.63 | 4.37 | 4.45 | 4.01 |
| Tb | 0.62 | 0.64 | 0.63 | 0.66 | 0.62 | 0.73 | 0.65 |
| Dy | 3.56 | 3.81 | 3.95 | 3.86 | 3.98 | 3.66 | 3.84 |
| Но | 0.83 | 0.85 | 0.86 | 0.91 | 0.81 | 0.84 | 0.79 |
| Er | 2.70 | 2.52 | 2.65 | 2.63 | 2.48 | 2.41 | 2.32 |
| Tm | 0.40 | 0.42 | 0.37 | 0.39 | 0.40 | 0.41 | 0.41 |



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| Yb | 2.69 | 2.71 | 2.60 | 2.51 | 2.75 | 2.86 | 2.62 |
|----|------|------|------|------|------|------|------|
| Th | 7.1 | 10 | 10 | 8.9 | 9.1 | 11.2 | 7.3 |
| Lu | 0.39 | 0.42 | 0.40 | 0.41 | 0.41 | 0.42 | 0.41 |

The main elements

In Zaker volcanic samples, the weight percentage of SiO2 content ranges from 54.52 to 61.52%, Na2O ranges from 2.28 to 3.61% and K2O is between 2.46 and 3.32% (Table 1). As the results show, the percentages of potassium and sodium oxides in these samples are relatively high. In these samples, the Al2O3 content is less than 14.68% and for MgO varies between 1.82 and 4.69% of weight percentage. Classification of volcanic units based on the ratio of major oxides according to the SiO2 curve versus (K2O+ Na2O) (COX et al., 1979) shows that the volcanic units of the region are in trachy andesite, andesite basalt and andesite groups (Fig.4A). Due to the omission of the effect of alteration and weathering on volcanic samples and for the more precise naming of these units, SiO2 versus Zr /TiO2 diagram (Winchester& Floyd, 1977) has been used. Based on this diagram, all volcanic units of the area are divided into two groups: trachyandesite and andesite (Fig.4B).

To separate the calc-alkaline magmatic series from the toleitic, the K2O versus SiO2 graph (Peccerillo and Taylor, 1976) has been used. According to this graph, most volcanic units are in the high calcium calc alkaline range. While, the other two samples, and esite-basalt and trachy-andesite, show the shoshonite series nature (Fig.4C). Based on the Al2O3/ (Na2O +K2O) versus Al2O3/ (CaO +Na2O + K2O) molar ratio diagram (Shand, 1947), the above rock units are in the metaluminous range (Fig. 4D).



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Fig. 4 A) Naming of volcanic units by TAS method based on the percentage of the major oxides of SiO2 against the sum of K2O + Na2O (Cox et al., 1979). B) Classification of volcanic units in Zaker area according to Zr/ TiO2 against SiO2 diagram(Winchester& Floyd, 1977). C) Determination of magma series of the analyzed samples from the Zaker area based on the SiO2 versus K2O diagram (Peccerillo &Taylor, 1976). D) The A / NK versus A/ CNK diagram related to the volcanic rocks of Zaker (Shand, 1947).

Trace elements and rare earth elements

The pattern of normalized rare earth elements and trace elements relative to the original mantle (Sun & McDonough, 1989) is shown in Fig.5A. In this graph, there are clear and distinct negative anomalies of Ti, P and Nb. While, some elements such as Sr, Ba, K and Cs show the enrichment. This enrichment of the LILE elements than the HFSE elements is attributed to the contamination of magma with the continental crust and to subducting plate interference during the subduction (Sajjona et al., 1996).

Also, this enrichment of LILE can be inherited from the mantle origin, but the subduction role in this enrichment is more important. Normalized to chondrite distribution pattern of rare earth elements (Boynton, 1984), for Zaker volcanic samples is given in Fig.5B. In this graph, the enrichment of light rare earth elements (LREE) relative to heavy rare earth elements (HREE) is visible in the mafic lavas of Zaker. This pattern is characterized by a relatively descending slope.

In the normalized graph to the chondrite, negative anomaly of Eu is seen, which this negative anomaly of Eu is as a result of the separation of the plagioclagase or potassium feldspar from



the felsic magma, either by crystal differentiation or by partial melting, which feldspar remains in the slag (Tepper et al., 1993).



Fig. 5A) The frequency graph of the normalized trace and rare elements relative to the original mantle (Sun & McDonough, 1989). B) Normalized graph of rare earth elements relative to chondrite for volcanic units in Zaker area (Boynton, 1984).

Discussion

In the normalized spider diagram versus chondrite (Fig. 5B), the pattern of rare earth elements in volcanic rocks are parallel with together and have the same trend. This pattern indicates the common origin of these rocks or similarity in formation processes (Nicholson, 2009). The proportions of (La_N/Yb_N) , (La_N/Sm_N) and (Ce_N/Yb_N) in the studied rocks were between 4.6-6.79, 2.7-4.13 and 3.7-5.6. The low ratio of (La_N/Yb_N) indicates the low amount or absence of garnet in the source magma and can be said that the magma has formed from the depths below the garnet persistence depth.

In the normalized graph relative to the original mantle (Sun & McDonough, 1989), Ti-Nb and P elements are negative anomalies. The negative anomalies of Ti reflect the role of Fe-Ti oxides (Rollinson, 1993). This anomaly can be created by Ti entering in the buildings of minerals such as titanomagnetite, ilmenite and rutile in the early stages of differentiation. Also, remaining of apatite mineral in the mother magma at the chamber causes a negative anomaly of P (Rollinson, 1989). In subduction-related magmatisms, the high fugacity of O2 in the subduction zone causes the depletion of Ti (Edward et al., 1994).

Negative anomalies of Nb are due to the contamination and mixing of the magma with the crust materials, because the average composition of the continental crust has depleted from Nb strongly. In other words, the negative anomaly of Nb is an index of subduction zones and its depletion is typical of magmas derived from oceanic crusts in the subduction zones (Saunders et al., 1992; Nagudi et al., 2003). Also, partial enrichment of Sr indicates the origin



of the magma that forms these rocks from the mantle sources, because the magmas that originate from the melting of the continental crust have a negative anomaly of Sr.

Positive anomalies are observed in Rb, Sr, K elements. The cause of the positive anomaly of Rb is that this element is related to K element so that due to the replacement of Rb instead of K, the changes in these two elements are positive and incremental relative to each other. This Positive anomaly can be due to the contamination of magma with the crust materials (due to the high concentration of these elements in the continental crust) because continental crust is enrich in K and Rb elements unlike Ta and Nb. Therefore, the stopping of the generative magmas of these rocks, though short time in the lower continental crust, with the influence of the crust fluids inside the magma or the assimilation of crust by the generative magma of these rocks during the ascent, have been caused this anomaly in this rocks.

Amphibole is an important host mineral for these elements in the upper mantle and can control the anomalies of these elements in magmatism associated with subduction (Ionov and Hofmann, 1995), which is the main characteristic of arc environments (Al -Saleh and Boyle, 2001). The anomalies of these elements can also be caused by the contamination of mother magma with the continental crust (Wilson, 1989). The high anomalies of Rb, K, and Ba can be attributed to the role of continental crust or contamination with the continental crust.

Tectonic environment

In the AFM diagram of Irvine and Baragar (1971), the volcanic rocks in the area show the calc- alkaline nature (Fig. 6). Many evidences such as negative values of Nb and the enrichment of LREE elements than HREE in basalts and andesites of Zaker indicate the relationship of the area with subduction zones. In the Th, Nb /16, Zr /117 tectonic diagrams, (Wood, 1980), all volcanic units plotted in the position of volcanic arcs (calc-alkaline basalts) (Fig. 7A), which expresses the same relationship to the subduction zones. To determine the type of the arc, the Th /Ta versus Yb graph (Schandl and Gorton, 2002) have been used. In this graph, the continental arc basalts are distinguishable from the oceanic arc within-plate basalts. As shown in Fig.7, most specimens have arc environments and only trachy andesite samples are located in Within Plate environments (Fig. 7B).





Fig.6. The AFM diagram for determining the magma series of intrusive bodies (Irvine and Baragar, 1971).



Fig.7. A) (Nb /16, Th, Zr /117 triangular diagram (Wood, 1980) for determining the tectonic position of volcanic units in Zaker area; B) Determining the type of the volcanic arc in Zaker area (Schandl and Gorton, 2002).

Source

To determine the magmatic nature of the volcanic units, the (La/Yb) $_{\rm N}$ versus Yb_N diagram, (Martin, 1995) is used. The amount of (La/Yb) $_{\rm N}$ in the analyzed samples varies from 4.6 to 6.79. Also, the amount of Yb_N changes from 12.01 to 13.68. Accordingly, all specimens fall into the normal calc-alkaline magma range (Fig. 8). Zr /Nb versus La/Yb diagram from Aldanmaz et al., (2006) is plotted to determine the mineralogy of the rock source and estimate the amount of partial melting (Fig.9). In this diagram, the Shaw equation (1970) and also the fusion pattern of McKenzie and ONios (1991 and 1995) have been used. The samples of the Zaker area in this diagram are within the garnet lherzolite range and have a partial melting percentage from 5 to 3.



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Fig.8. Position determining of the generative magma of the volcanic units of Zaker area in the (La/ Yb) N versus YbN diagram (Martin 1995).



Fig.9. Zr / Nb versus La/ Yb diagram in order to calculate the amount of partial melting in the volcanic units (Aldonmaz et al., 2006).

Conclusion

In the Zaker area, the intrusive units have penetrated into the volcanic units. Based on petrographic studies and geochemical results, volcanic units are divided into three groups: trachy andesite, andesite and basalt. The most important constituent minerals of these units are two minerals: plagioclase and clinopyroxene. These units are under the influence of poor propylitic alterations. The generative magma of these units is mainly high-potassium calcalkaline to a little shoshonitic and this magma shows a metaluminous nature. Geochemical studies show that volcanic units of the Zaker area are enrich in light rare earth elements than heavy rare earth elements. The tectonic environment of these lavas is associated with subduction environments. This association is proven by the negative anomalies of Nb, the



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enrichment of LREE than HREE elements and the placement of specimens in the normal calc-alkaline arc range. Due to the low proportion of (La /Yb) $_N$ in all volcanic units, the presence of garnet in the magma origin is problimatic. Various reasons including the negative anomaly of Eu, the pattern of normalized rare elements compared to chondrite and a low proportion of (Ce /Yb) $_N$, all testify to the presence of garnet in the source. Thus, according to the results, the generative magma of the volcanic rocks of the area is probably derived from spinel garnet lherzolite with greater spinel content than garnet that between 3% and 5% of this magma has been from partial melting. This magma has been contaminated with the continental crust during the ascent.

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