



# Major, trace and rare earth element (REE) characteristics of tuffs in the Yenice-Saraycık area (Demirci, Manisa), Western Anatolia, Turkey



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## ARTICLE INFO

### Article history:

Received 3 February 2016

Revised 31 May 2016

Accepted 29 June 2016

Available online 01 July 2016

### Keywords:

Tuff

Alteration

Zeolite

REE

Turkey

## ABSTRACT

Geochemical investigation was carried out on tuffs intercalated with Neogene volcano-sedimentary rocks in the Yenice-Saraycık area (Demirci, Manisa), Turkey. The tuffs are classified as peraluminous and they show calc-alkaline character. They represent mainly rhyolitic to rhyodacitic composition.

These silicic vitric tuffs are mostly either altered to zeolites (clinoptilolite–heulandite type) or clays. Their chondrite-normalized REE distribution patterns are remarkably similar. These patterns display light REE (LREE) enrichment with nearly flat heavy REE (HREE) and the strong negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.12\text{--}0.51$ ). The existence of negative Eu anomaly is an indicator of feldspar fractionation. In primitive mantle-normalized diagram, all tuffs show nearly parallel patterns characterized by sharp negative anomalies of Nb, P and Ti along with positive anomalies of K and Pb. These findings demonstrate that they originated from a strongly evolved magma which was probably contaminated by crustal material. The negative Ti, Nb and P anomalies also show a subduction-related origin.

On the other hand, the alteration of tuffs to zeolites has a prominent effect on their major, trace and REE abundances. Zeolitic tuffs are clearly enriched in Ca, Mg, P and LOI and depleted in Na, K and Mn when compared to unaltered tuff. They have also relatively lower U content but higher Ba, Sr, Cs, Pb, Zn, Ni, As and Sb. Furthermore, a little mobility of HREEs relative to LREEs is seen in most of the zeolitic samples. The loss of alkaline ( $\text{Na}^+$  and  $\text{K}^+$ ) and gain of alkaline-earth elements ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) show that zeolitic alteration may have occurred under alkaline conditions. The source for the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  gains is presumably groundwater circulating through the carbonate rocks of study area. The remarkable loss of U is probably related to the mobility of U during the alteration of vitric tuffs under the prevailing alkaline conditions. The significant increase of Ba, Sr, Cs, Pb, Zn, Ni, As and Sb in the zeolitic tuffs is most likely due to the ability of both zeolites and clays adsorb these elements.

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## 1. Introduction

An extensional tectonic regime prevailed in the Neogene and formed a series of NE–SW trending volcano-sedimentary basins in Western Anatolia, Turkey (Ersoy et al., 2011; Bozkurt, 2003).

Since it became known that zeolites are the most common alteration minerals in tuffs of volcano sedimentary environments, most of the Neogene volcano-sedimentary basins in Western Anatolia (Turkey) have been studied and the important zeolite occurrences reported associated with tuffs deposited in these environments (Kacmaz and Kokturk, 2004; Gundogdu et al., 1996; Sirkecioglu et al., 1990; Esenli, 1992; Albayrak and Ozguner, 2013; Coban, 2014).

Demirci is one of the Neogene volcano-sedimentary basins in Western Anatolia. To date, some areas in Demirci and its vicinity (such as Gordes, Selendi and Usak–Gure basins) have been studied mainly for their stratigraphic, structural and geochemical features (Ersoy et al., 2011; Karaoglu et al., 2010). On the other hand, the tuffs located in

the southwestern part of the Demirci (Yenice-Saraycık) area have not been investigated on the basis of their mineralogical and geochemical characteristics, although they are possible source for zeolite occurrence. This study also shows the presence of zeolites within tuffs in the studied area.

The purpose of this study is to determine geochemical characteristics of tuffs around Yenice-Saraycık (Demirci) area and to evaluate the effect of zeolitic alteration on the major, trace and rare earth element chemistry of the tuffs. Additionally, the origin of tuffs was interpreted here.

## 2. Geological setting

Demirci is a district of Manisa province. The study area is located in the southwestern part of the Demirci area (Fig. 1).

Paleozoic metamorphic rocks are the basement rocks of the investigated area. They are composed mainly of gneisses and schists. The re-crystallized limestones overlying the metamorphic rocks belong to the Mesozoic. The Neogene volcano-sedimentary sequence overlies the above-mentioned rocks unconformably, and consists of (from bottom

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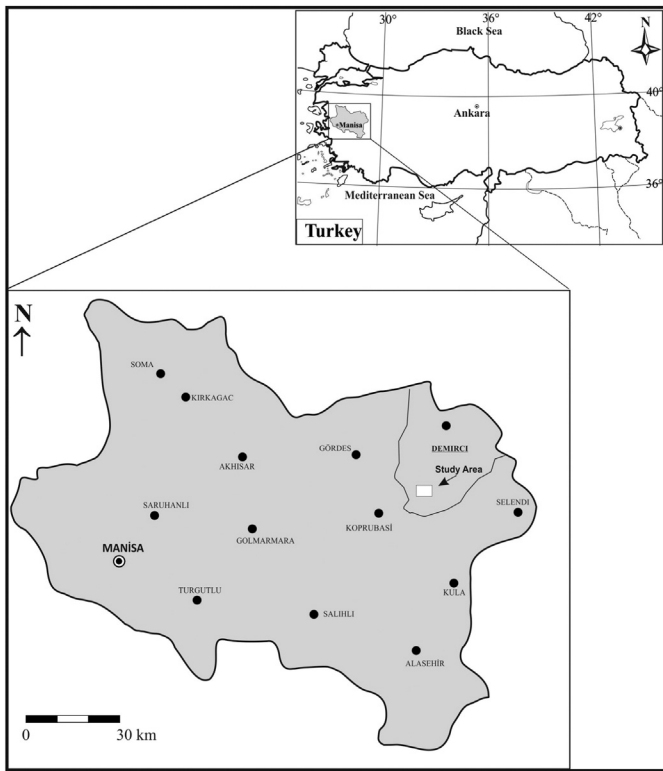


Fig. 1. Location map of the study area.

to the top) fluvial and lacustrine unit including volcanic tuff interlayer. Fluvial unit are composed of alternations of conglomerate, sandstone, siltstone, mudstone and clayey limestone with tuff layer. These units are conformably overlain by the lacustrine unit, which consists of mainly limestone, marl, siltstone, shale and claystone alternation with tuff layer. The contact between lacustrine and fluvial unit is gradual. Quaternary alluvium covers all units as the youngest in the study area (Ayan, 1973; MTA, 1976).

The Neogene volcano-sediments, fluvio-lacustrine, are commonly seen in the Demirci area. The present investigation focused on tuffs intercalated with these sediments around the Yenice-Saraycık area, southwest of Demirci (Fig. 2).

### 3. Methods

The samples were taken from outcrops of the Yenice-Saraycık tuff in the Demirci area. A portion of each sample was crushed and pulverized. All samples were prepared using an automatic agate mortar at the laboratories of Dokuz Eylül University. After, the pulverized sample were packed in suitable bags and sent to the ACME analytical laboratory, in Vancouver, Canada (an international accredited lab.) for chemical analysis. Bulk chemical analysis of samples were carried out by inductively coupled plasma-emission spectrometry (ICP-ES) for major elements and by inductively coupled plasma-mass spectrometry (ICP-MS) for trace elements, including REE. A lithium borate fusion and nitric acid digestion of a 0.2 g sample was used. In addition, several trace elements (like Pb, Cu, Zn, Ni, As, Sb) were detected by (ICP-MS) after leaching a 0.5 g sample in hot (95 °C) aqua regia. Loss on ignition (LOI) was calculated by weight difference after ignition at 1000 °C. Geochemical data are presented in Table 1.

The mineralogy of the bulk samples was determined by powder X-ray diffraction (XRD) analysis with Rigaku Miniflex II equipment with CuK $\alpha$  radiation source, operating at 30 kV and 15 mA. Pulverized powders were scanned from 2 to 65° 2 $\theta$  at a scanning speed of 2°/min. The clay mineralogy was identified from air-dried samples.

## 4. Result and discussion

### 4.1. Mineralogy

The XRD studies show that the tuffs are mostly altered, particularly to either zeolites or clays. Clinoptilolite–heulandite type zeolites and variable amounts of smectite group minerals are mainly alteration minerals in the altered tuffs. Feldspar (albite, anortite and sanidine), quartz, opal-ct and micas are the other common constituents (Fig. 3). In addition to the phenocrysts, some XRD patterns of samples contain a broad background, which is interpreted to be a glassy matrix (Opal A). Calcite was detected by XRD in one sample (YS4). Besides, one sample (YS3), contains kaolinite with significant amounts of cristobalite and tridymite. Since no authigenic phases were determined by XRD in sample YS6 (Table 1), its bulk chemistry probably reflects the original bulk composition of the tuffs.

### 4.2. Geochemistry

#### 4.2.1. Classification of tuffs

Geochemical diagrams are good indicators for the classification of rocks. So, classification of tuffs was made using some major and trace element contents. Table 1 lists the major, trace and rare earth element compositions of tuffs from the studied area. Recalculated major elements on a volatile-free basis have been used for these diagrams.

Based on the wt.% Al<sub>2</sub>O<sub>3</sub>–CaO–(Na<sub>2</sub>O + K<sub>2</sub>O) plot of Shand (1927), the tuffs are peraluminous (Fig. 4). They also show a calc alkaline trend on the AFM diagram (Fig. 5).

According to the SiO<sub>2</sub> versus K<sub>2</sub>O diagram (Peccherillo and Taylor, 1976), the tuffs mainly show a high calc-alkaline composition, with only a few samples plotting in the calc-alkaline field most likely due to removal of K during zeolitic alteration (Fig. 6). It can also be seen from Table 1.

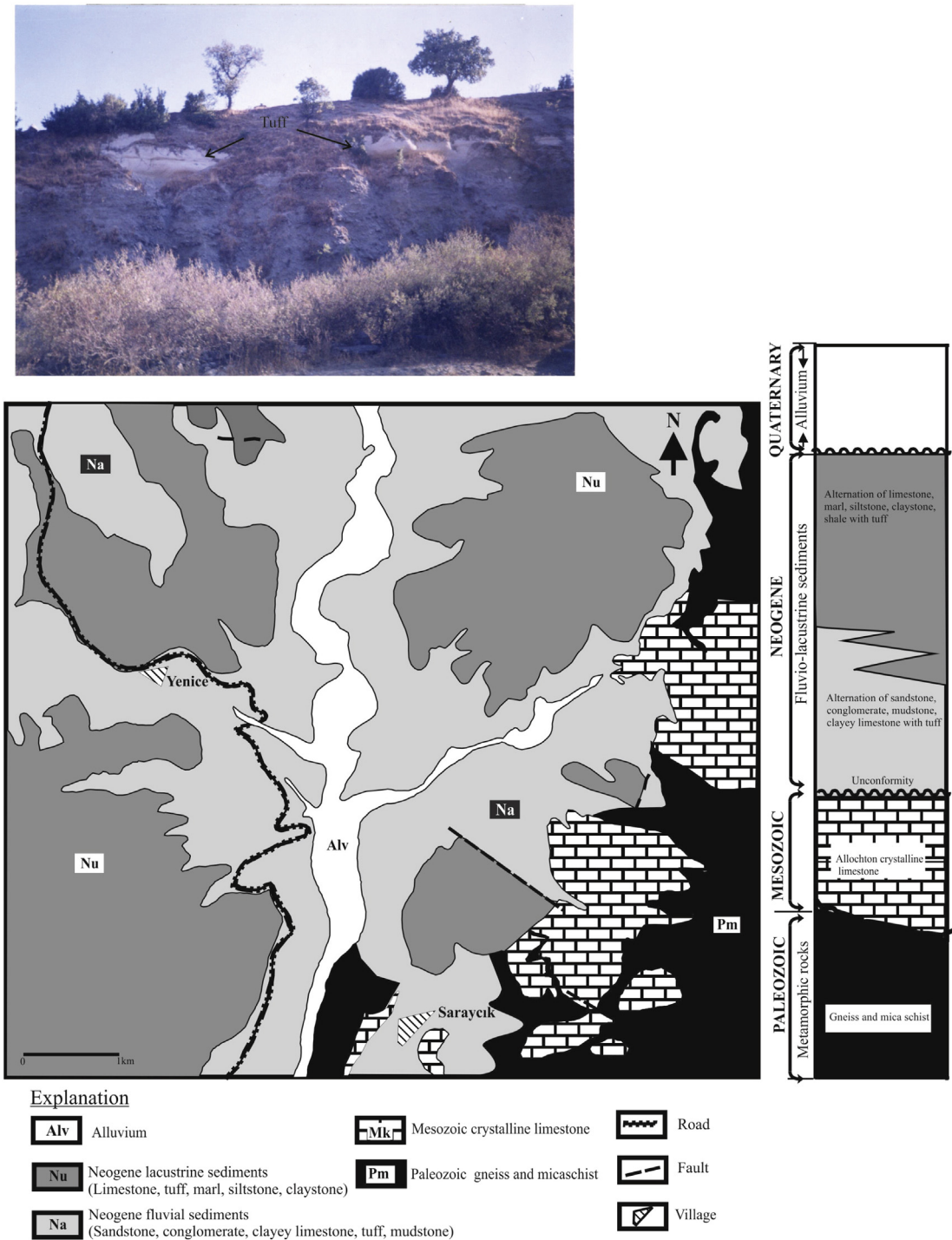
The tuff samples are mainly classified as a rhyodacite–rhyolite, using the Zr/TiO<sub>2</sub> versus Nb/Y diagram in Fig. 7 (Winchester and Floyd, 1977). Although the tuffs are interpreted as rhyodacite–rhyolite, some are shifted towards the field of trachyandesite presumably due to the mobilization of Y during the alteration of glass to zeolites and bentonites (Christidis, 1998). It is also obvious from Table 1 that the zeolitic samples have a lower Y content than zeolite-free samples. Likewise, high SiO<sub>2</sub> values in the tuffs are an indication of their rhyodacitic and rhyolitic character.

#### 4.2.2. Provenance of tuffs

REEs are useful tracers for petrogenetic processes and they are commonly used for characterization of rocks (Rollinson, 1993). So, the REE concentrations of the tuffs were normalized to the chondrite values (Boynton, 1984) and their relative REE abundances were compared. As seen in Fig. 8, REE patterns of the tuffs are fairly similar to each other. They are characterized by LREE enrichment (LaN/SmN = 2.62–5.97) and relatively flat HREE (GdN/YbN = 0.93–1.93). They also show strong negative Eu anomalies (Eu/Eu\* = 0.12–0.51).

According to Rollinson (1993), Eu anomalies are chiefly controlled by feldspar; particularly in felsic magmas and the removal of feldspar from a felsic melt by crystal fractionation give rise to a negative Eu anomaly. The negative Eu anomalies in the REE patterns of tuffs (Fig. 8) point to fractionation of feldspar. The LREE-enriched and relatively flat HREE patterns with the strong negative Eu anomalies also indicate the felsic nature of the tuffs. It is also typical for evolved magmas as noted by Calarge et al. (2006). Similar chondrite-normalized REE patterns have been reported for felsic volcanic rocks by Moghazi (2003) and Ersoy et al. (2008).

In addition, all tuffs were plotted on the primitive mantle-normalized diagram of Sun and McDonough (1989). This diagram (Fig. 9) shown that all samples have very similar patterns and the high-field



**Fig. 2.** Simplified geological map of the study area also showing generalized stratigraphic column and a field photograph of tuffs. Modified from MTA (1976).

strength (HFS) elements like Nb, P and Ti have negative anomalies while Th, U, K and Pb have positive anomalies. Distinctive negative anomalies in P and Ti are related to the fractionation of apatite and Ti-bearing minerals (like ilmenite, magnetite, and rutile) as suggested by Keshavarzi et al. (2014) and Rollinson (1993). The negative Eu anomalies together with Sr and Ba in zeolite-free tuffs reflect feldspar fractionation (both K-feldspar and plagioclase) during the magma crystallization (Speer and Hoff, 1997). Likewise, the presence of K-feldspar and plagioclase determined by XRD data in this study supports this suggestion. These data indicate that the parental magma originated from the mantle.

On the other hand, these felsic tuffs have distinct positive Pb and negative Nb anomalies similar to continental crust as proposed by (Weaver and Tarney, 1985). Their low Nb and high Pb values are characteristic of all types of island arc volcanics (Hofmann, 1988). Also, they have lower Nb/Ta ratios (see Table 1) than mantle source (typically ~17.5; Sun and McDonough, 1989). Besides, the observed negative Nb, P and Ti anomalies along with positive Th, U, K and Pb anomalies (Fig. 9) are an indication of magma contaminated by crustal material (Ernst, 2014). All of the above data suggest that they were produced from lithospheric mantle that was contaminated by crustal material. This result is compatible with previous studies made on the Neogene

**Table 1**  
Chemical composition of zeolitic and zeolite-free tuffs around Yenice-Saraycık (Demirci-Manisa) area.

Sample	Zeolitic tuffs					Zeolite-free tuffs		
	YS1	YS2	YS3	YS4	YS5	*YS6	YS7	YS8
Trace and REE (ppm)								
Ba	5425	3104	1948	420	663	140.3	110	228
Rb	209.9	110.5	42.0	69.7	78.7	140.2	224.4	294
Cs	12.5	150.8	18.5	78.7	131.8	10.8	10.6	10.8
Pb	20.3	11.8	11.1	22	110.5	4.8	2.7	9.6
U	5.2	1.3	4.2	1.3	4.5	18	14.1	17.5
Sr	522.0	1163.7	747.3	872.1	1668.7	37.6	23.6	61.8
Zr	84.3	121.0	65.8	42.7	113.8	82	84.6	91.8
Nb	14.3	9.3	15.1	7.2	21.6	18.6	16.1	20.1
Hf	3.5	4.1	3.2	2.2	4.8	4.1	4.0	4.1
Ta	1.6	0.8	2	1.1	1.9	2	1.7	2.2
Th	27.8	19.2	24.5	14.9	33.2	34.8	36.8	39.1
Cu	14.50	11.00	5.10	2.40	2.20	3.8	4.2	3.4
Zn	9	10	8	11	26	4	4	9
Ni	2.1	282.90	76.00	4.40	11.80	1.8	1.6	2.1
As	10.40	136.20	44.00	6.80	43.10	1.3	0.6	1.7
Sb	0.2	2.7	0.7	0.3	1.7	0.1	0.05	0.05
La	23.7	27.7	16.8	13.6	28.6	22.7	20.7	24.6
Ce	50.1	47.5	30.8	25.2	62.0	42.8	43.1	47.5
Pr	5.24	5.35	3.10	2.83	7.08	5.82	5.35	6.11
Nd	20.1	19.1	10.5	9.6	25.0	20.5	22.1	22.2
Sm	4.59	3.41	1.77	2.60	6.39	5.4	4.9	5.9
Eu	0.21	0.49	0.11	0.15	0.38	0.32	0.19	0.27
Gd	4.19	2.56	1.62	2.53	6.29	4.92	4.47	4.38
Tb	0.66	0.35	0.23	0.41	1.12	0.99	0.81	0.88
Dy	4.02	2.00	1.45	2.40	6.32	6.04	5.16	5.19
Ho	0.81	0.41	0.30	0.49	1.18	1.34	1.02	1.04
Er	2.57	1.16	1.05	1.30	3.53	4.03	3.01	3.25
Tm	0.43	0.18	0.18	0.22	0.54	0.68	0.47	0.54
Yb	2.56	1.07	1.06	1.43	3.50	4.28	3.33	3.54
Lu	0.37	0.15	0.16	0.19	0.50	0.64	0.5	0.55
Y	24.6	8.5	9.2	13.8	30.5	42.2	32.5	35.1
Nb/Ta	8.9	11.6	7.6	6.5	11.4	9.3	9.5	9.1
LaN/SmN	3.25	5.11	5.97	3.29	2.82	2.64	2.66	2.62
GdN/YbN	1.32	1.93	1.23	1.43	1.45	0.93	1.08	0.99
Eu/Eu*	0.15	0.51	0.20	0.18	0.18	0.19	0.12	0.16
Major oxides (wt.%)								
SiO <sub>2</sub>	67.98	61.09	67.85	39.68	64.30	70.94	70.85	68.75
Al <sub>2</sub> O <sub>3</sub>	13.10	12.82	14.29	7.61	12.46	12.81	12.48	13.35
Fe <sub>2</sub> O <sub>3</sub>	1.35	3.49	1.25	0.54	1.00	1.18	1.19	1.6
K <sub>2</sub> O	3.68	2.65	2.15	1.28	1.70	4.1	4.94	4.58
Na <sub>2</sub> O	1.57	0.39	0.36	0.75	0.26	2.99	2.16	1.95
MgO	0.51	2.69	0.58	1.28	1.12	0.16	0.17	0.38
CaO	1.52	2.52	1.70	23.54	3.99	0.72	0.79	0.9
TiO <sub>2</sub>	0.08	0.33	0.09	0.07	0.13	0.09	0.08	0.09
MnO	0.04	0.03	0.005	0.01	0.02	0.04	0.04	0.04
P <sub>2</sub> O <sub>5</sub>	0.02	0.04	0.02	0.04	0.04	0.01	0.005	0.01
LOI	9.5	13.2	11.3	25.0	14.6	7.0	7.2	8.4

Note: Marked sample (\*) is unaltered sample. Total iron as Fe<sub>2</sub>O<sub>3</sub>.

volcanic rocks in Western Anatolia, Turkey (Koralay et al., 2009; Karaoglu et al., 2010; Ersoy et al., 2008, 2012; Albayrak and Ozguner, 2013).

#### 4.2.3. Chemical changes associated with zeolitic alteration

Many deposits of volcanic ash may have undergone various types of alteration and this alteration can cause changes on its original chemical composition. Therefore, the mobility of elements during zeolitic alteration in tuffs has been studied by several authors (Münch et al., 1996; McHenry, 2009; Kirov et al., 2011). In order to assess the behaviour of major, trace and rare earth elements associated with alteration of the tuffs to zeolites, the tuff samples in the study area were normalized to the unaltered sample (Figs. 10, 11 and 12).

**4.2.3.1. Major elements.** As seen in the Fig. 10, Al and Si generally remain unchanged in the zeolitic samples. Ca, Mg and P show enrichment whereas Na, K and Mn indicate significant mobility in the zeolitic samples. Fe and Ti are somewhat variable. Zeolitic tuffs have also greater

loss on ignition (LOI) values. Likewise, their higher LOI values are an indication of zeolites and clays absorb high amount of water in their structures.

The most obvious chemical change occurring in the zeolitic tuffs is the gains of alkaline earth elements (Ca and Mg) and the losses of alkalis (Na and K). This means that the alkalinity of the environment is high during alteration of tuffs to zeolites and hence the alkaline cations (K<sup>+</sup> and Na<sup>+</sup>) were replaced by alkaline-earth cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) in these tuffs. This could be explained by Mg<sup>2+</sup> and Ca<sup>2+</sup>-bearing groundwater which circulated through the tuffs of studied area. This suggestion is consistent with the study of Gemici and Tarcan (2001), who showed Ca<sup>2+</sup> and Mg<sup>2+</sup> are dominant ions in the cold groundwater (Ca, Mg, HCO<sub>3</sub> type) discharged from spring in the Saraycık area. Similar Ca and Mg enrichments and Na and K depletions have been reported for the zeolitic altered tuffs at Yucca Mountain, Nevada (Broxton et al., 1987). On the other hand, there is no significant change in the major oxides and LOI values of the zeolite-free samples in comparison to unaltered tuff (black circles in Fig. 10).

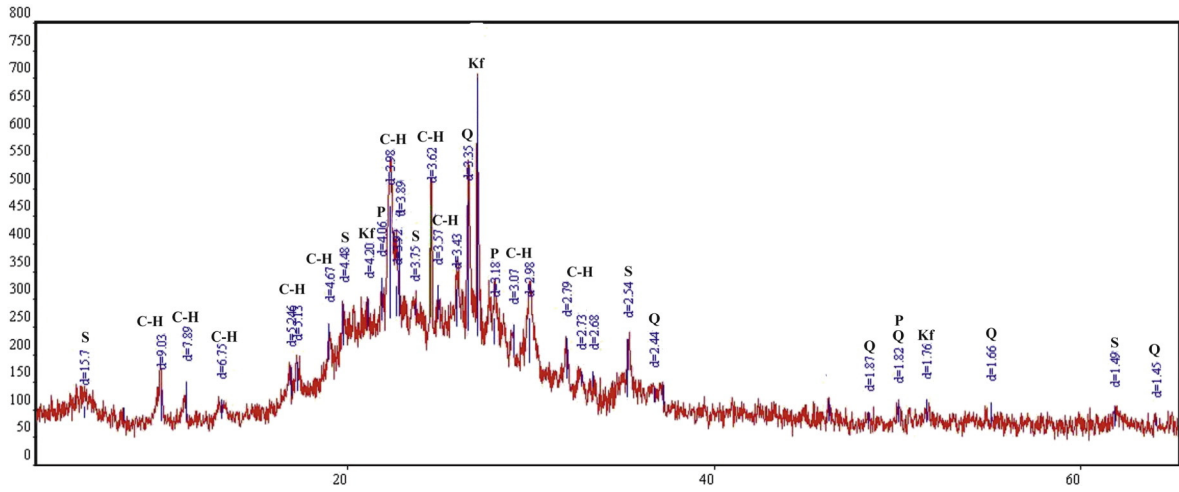


Fig. 3. A representative XRD pattern of tuff samples C-H = clinoptilolite–heulandite, S = smectite, Q = quartz, P = plagioclase, Kf = K-feldspar. Opal A can also be seen by a broad band ranging from 15 to 30° 2θ.

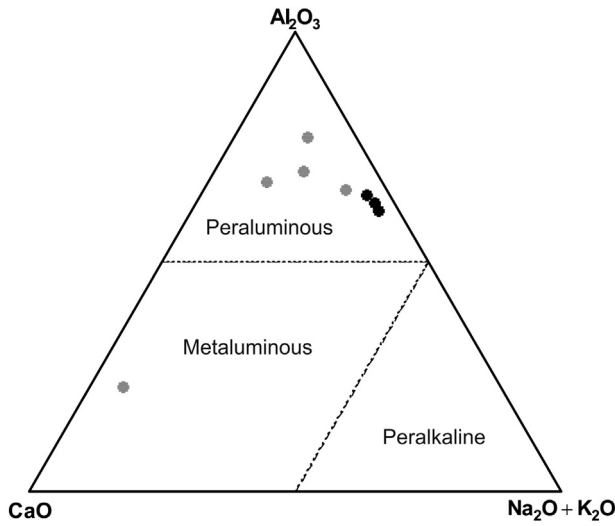


Fig. 4. The wt.% CaO–Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O + K<sub>2</sub>O ternary diagram after Shand (1927) black circles: zeolite-free tuffs, gray circles: zeolitic tuffs.

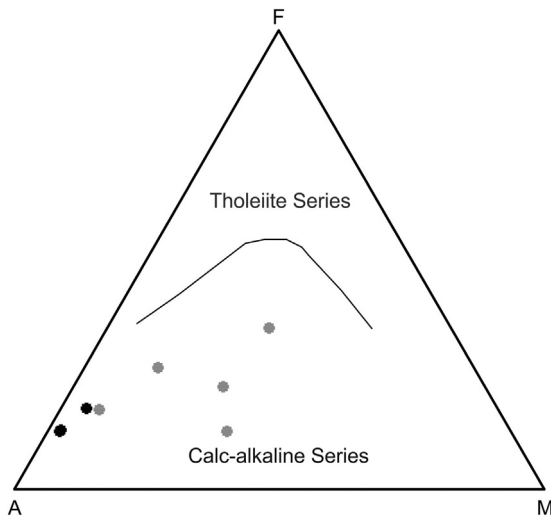


Fig. 5. AFM diagram showing compositions of tuffs in the Yenice-Saraycık (Demirci) area (Irvine and Baragar, 1971). Symbols the same as above.

4.2.3.2. Trace elements. Zeolitic alteration has led to marked changes in the trace elements abundances of tuffs. By comparison to unaltered sample, zeolitic tuffs show apparent U depletion and also Ba, Cs, Sr, Pb, Zn, Ni, As and Sb enrichment (Fig. 11). Cu does not show a clear behaviour in these samples. Other elements like Y, Rb and Th are slightly removed whereas Nb, Zr, Hf and Ta relatively remain immobile. However, the zeolite-free samples (black circles in Fig. 11) have fairly similar trace element abundances with the unaltered sample. This is probably concerned with lack of zeolite minerals in these samples.

It is known that natural zeolites (heulandite-group) can adsorb Sr, Cs and Ba due to their high cation-exchange properties (Bish, 1988). Besides, during weathering, Ba is not very mobile because is also strongly adsorbed by clays (Kabata Pendias, 2011). Therefore, the significant enrichment of Ba, Cs and Sr in the zeolitic tuffs can be attributed to adsorption of them by either zeolites or clays. This suggestion is supported by Karakaya et al. (2015) who noted extremely high Sr and Ba contents in some of the heulandite/clinoptilolite-rich tuffs in the south of Ankara (Central Anatolia, Turkey). Similarly, Albayrak and Ozguner (2013) reported high Sr concentration in Foca (Izmir) zeolitic tuffs of Western

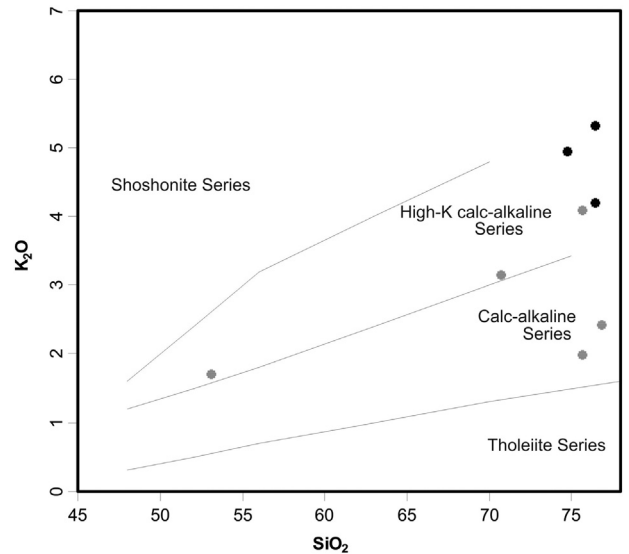


Fig. 6. Classification of the tuff samples in the SiO<sub>2</sub> versus K<sub>2</sub>O diagram of Peccerillo and Taylor (1976). Symbols the same as above.

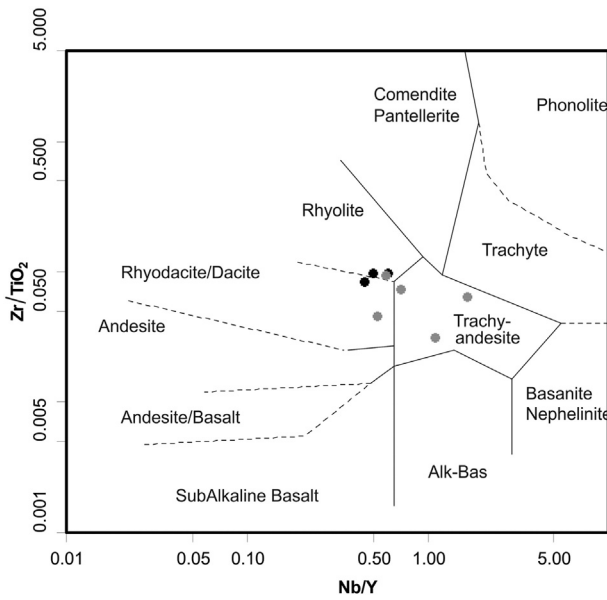


Fig. 7. The nomenclatures of tuffs in the  $Zr/TiO_2-Nb/Y$  diagrams (Winchester and Floyd, 1977). Symbols the same as above.

Anatolia, Turkey. These zeolitic tuffs also contain higher Pb, Zn, Ni, As and Sb than unaltered tuff likely due to for the same reason. On the other hand, the loss of U in the zeolitic altered tuffs may arise from leaching of uranium from siliceous vitric tuffs by alkaline groundwaters of this area. This consideration is supported by a study demonstrating the removal of U by rhyolitic volcanic glass-water interaction (Zielinski, 1981).

4.2.3.3. Rare earth elements. The unaltered sample normalized REE patterns of the tuffs show nearly similar trends for both the zeolitic and zeolite-free samples. However, relatively small shift was observed in the patterns of zeolitic samples. As indicated in Fig. 12, they are slightly depleted in HREE but to somewhat different degrees.

Mobility of HREE in the zeolitic samples can be attributed the alteration of silicic vitric tuffs to zeolites (clinoptilolite–heulandite), causing removal of the HREE in fresh glass as reported by Cridistis (1998). Small differences in HREE patterns can be associated with either difference in

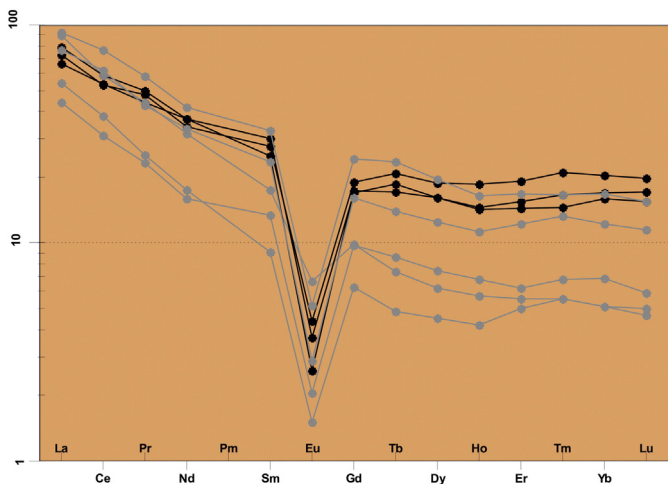


Fig. 8. Chondrite-normalized REE patterns of the tuffs (Boynton, 1984). Black circles: zeolite-free tuffs, gray circles: zeolitic tuffs.

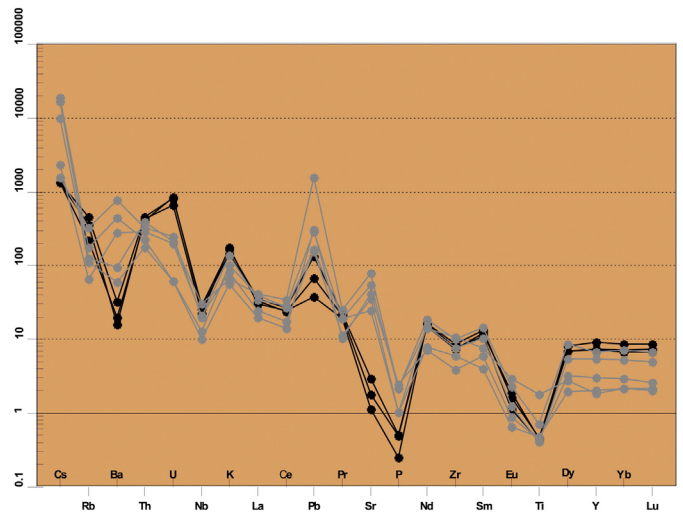


Fig. 9. Primitive mantle-normalized diagram for tuff samples from Yenice-Saraycık area. Black circles: zeolite-free tuffs, gray circles: zeolitic tuffs. Values taken from Sun and McDonough (1989).

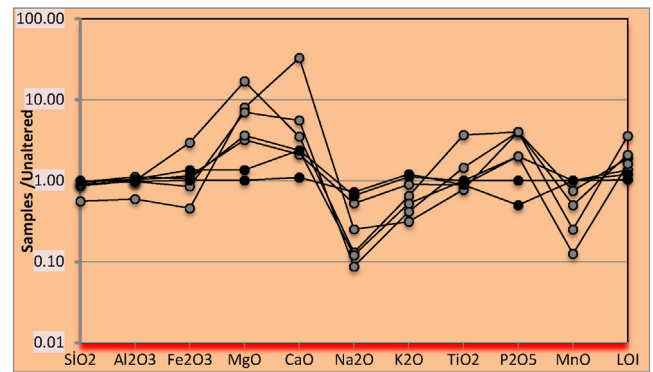


Fig. 10. Major element concentrations including LOI in the tuff samples normalized to unaltered tuff. The data are taken from Table 1. Sample YS6 corresponds to the unaltered tuff. Gray circles: zeolitic samples, black circles: zeolite-free samples.

zeolitic alteration intensity or in authigenic minerals. Also, as compared to HREE, little depletion of LREE is most likely due to present alkaline conditions of the studied area provided the greater stability of LREE relative to the HREE as suggested by Winchester and Floyd (1977) and Summa and Verosub (1992) (Fig. 12). The formation of clinoptilolite–

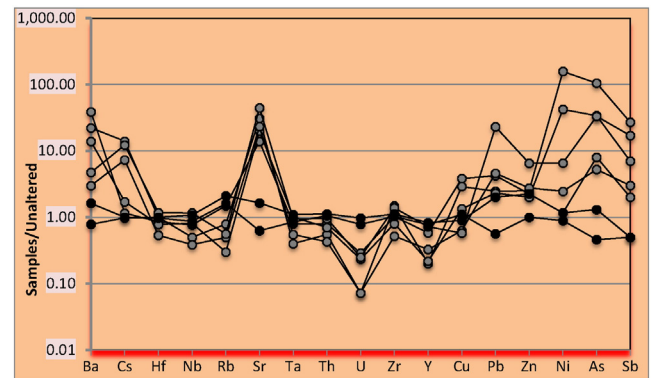


Fig. 11. Relative changes for selected trace elements in the tuff samples compared to the unaltered tuff. The data are taken from Table 1. Gray circles: zeolitic samples, black circles: zeolite-free samples.

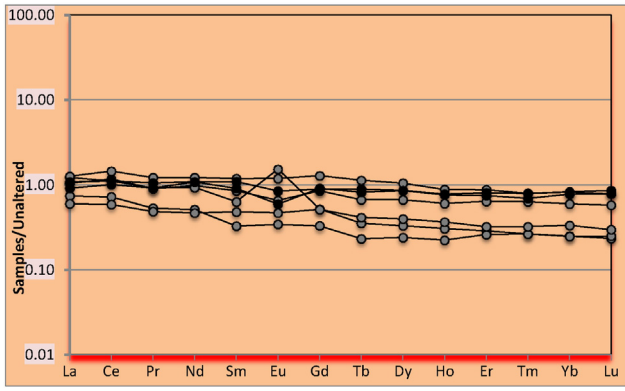


Fig. 12. Unaltered-sample normalized REE patterns of the tuffs. Gray circles: zeolitic samples, black circles: zeolite-free samples.

heulandite type zeolites favored by moderately alkaline pH of 7–9 (Mariner and Surdam, 1970) supports this idea. Likewise, a study by Muchangos (2006) shows that there is preferential enrichment in LREE while impoverishment in HREE during the alteration of rhyolitic rocks to bentonite in the Lebombo volcanics. Similarly, the enrichment of LREE relative to HREE has been reported to occur in bentonitic tuffs of Bigadic (Balıkesir) area, Western Anatolia, Turkey (Coban, 2014).

## 5. Conclusion

The intercalated tuffs in the Neogene volcano-sedimentary rocks of the Yenice-Saraycık (Demirci-Manisa) area show peraluminous and calc-alkaline character. They appear to have rhyolite or rhyodacites composition.

These silicic vitric tuffs were mostly altered either to zeolites (clinoptilolite–heulandite type) or clays. The chondrite-normalized REE patterns of the tuffs are nearly identical. These patterns are characterized by LREE enrichment, relatively flat HREE distribution and strong negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.12\text{--}0.51$ ). This negative Eu anomaly show fractional crystallization of feldspar. They indicate prominently negative P, Nb and Ti and positive Pb and K anomalies in primitive mantle-normalized diagram. Based on all these data; we can suggest that their parental magma is mantle-derived but contaminated by crustal material. The negative P, Nb and Ti anomalies also point out to a subduction-related volcanism.

However, zeolitic alteration has a significant effect on the major, trace and REE element abundances of the tuffs. The zeolitic tuffs show higher Mg, Ca, P and LOI, but lower K, Na and Mn values than unaltered tuff. In addition, depletion of U and enrichment of Ba, Sr, Cs, Pb, Zn, Ni, As and Sb in the zeolitic samples are distinctly observed. Although, a little impoverishment in HREEs compared to LREEs occurred during alteration of tuffs to zeolites, there is no big change in the REE abundances of zeolitic tuffs. Relative to the unaltered tuff, the increase in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and decrease in  $\text{Na}^+$  and  $\text{K}^+$  in the zeolitic tuffs implies that zeolitic alteration took place under alkaline conditions. The enrichment of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in zeolitic tuffs also indicates that groundwater passed through carbonate rocks of the study area and facilitated this. The loss of U in the zeolitic tuffs can be explained by removal of U by groundwater present alkaline conditions in the study area. A considerable enrichment in Ba, Sr, Cs, Pb, Zn, Ni, As and Sb is most likely related to the presence of both zeolites and clays in the altered samples.

## Acknowledgments

I thank to the reviewers for their constructive comments on this paper. Thanks are also due to Dokuz Eylul University for providing technical assistance during this investigation.

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