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

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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 ($Eu/Eu^* = 0.12$–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 (Na^+ and K^+) and gain of alkaline-earth elements (Ca^{2+} and Mg^{2+}) show that zeolitic alteration may have occurred under alkaline conditions. The source for the Ca^{2+} and 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.

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 recrystallized 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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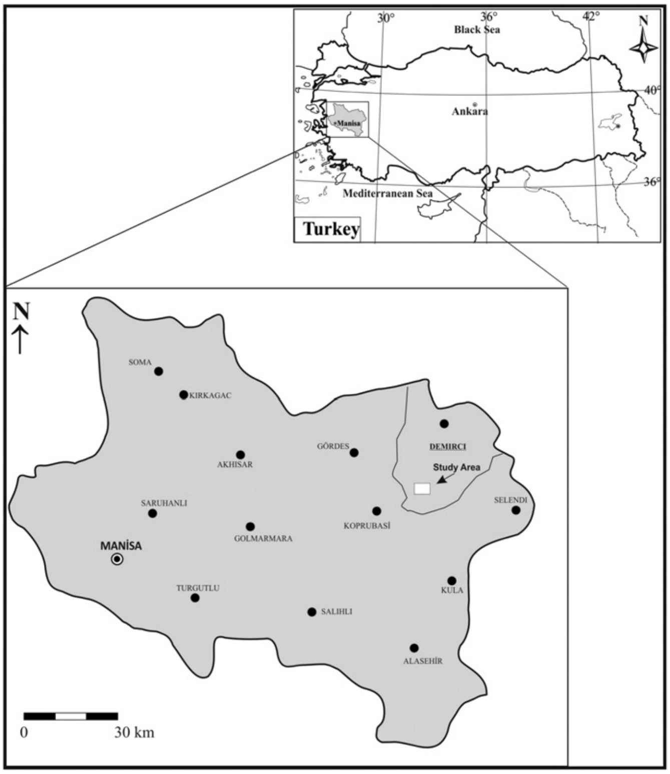

Fig. 1. Location map of the study area.

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 Eylul University. After, the pulverized sample were packed in suitable bags and sent to the at 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 CuKα radiation source, operating at 30 kV and 15 mA. Pulverized powders were scanned from 2 to 65° 2θ 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_2O_3–CaO–(Na_2O + K_2O) 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_2 versus K_2O diagram (Peccerillo 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_2 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_2 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