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## Rare earth element contents, geochemistry of soil samples between Burdur and Isparta region and assessment of their origin

Ebru TAT<sup>a\*</sup> and Mustafa Gürhan YALÇIN<sup>b</sup>

<sup>a</sup>Kahramanmaraş Provincial Directorate of Disaster and Emergency, Kahramanmaraş

<sup>b</sup>Akdeniz University, Faculty of Engineering, Department of Geological Engineering, Antalya

Research Article

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### ABSTRACT

This study was carried out in 5 locations between Burdur and Isparta in the inner southern part of Isparta Bend. The study aims to determine the rare earth element (REE) concentrations in the soil samples collected from the field and to interpret the origin of the high concentrations detected. In this context, a total of 104 samples were collected from Canaklı Village (19 samples), Cobanisa Village (34 samples), Kuyubasi Village (17 samples), Kuzca Village (17 samples), and Yılanlı Village (17 samples) in the study field. The average  $\Sigma$ REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) concentration values of the samples by their locations were determined to be Çobanisa (821.88 ppm) > Yılanlı (723.39 ppm) > Kuzca (692.54 ppm) > Çanaklı (583.46 ppm) > Kuyubaşı (484.04 ppm). The average light rare earth element (LREEs) concentration (such as La 229 ppm, Ce 378 ppm) of the samples collected from all locations is higher than the average rare earth element concentration in the Earth's crust. According to the Chondrite-normalized Rare Earth Elements diagram, the distributions of the rare earth elements in these 5 locations were determined to be very similar and the high concentrations were considered to occur under similar conditions or originated from similar sources. In this context, based on the idea that Gölcük Volcanism may be the source of high concentrations, the rare earth element concentrations of Gölcük Volcanism in the northwest of the zone were compared to those taken from the study area and the values were found to be consistent with each other.

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## 1. Introduction

Actually, the rare earth elements are not as scarce as they are expressed. They have been named in this way because they were defined between 18<sup>th</sup> and 19<sup>th</sup> centuries and they were rare compared to other earth elements such as calcium oxide and magnesium oxide (US Geological Survey, 2002). Rare earth elements (RREs) with atomic numbers between 57 (Lanthanum) and 71 (Lutetium) in the Periodic Table show similar physical and chemical properties. This

similarity is particularly related to their +3 atomic charge and electron configuration (Verplanck et al., 1999). Rare earth elements are commonly classified as Light Rare Earth Elements (LREE) and Heavy Rare Earth Elements (HREE) according to their atomic weights (Sen et al., 2012). The light rare earth elements (LREEs) have relatively enriched the Earth's crust (Alfaro et al., 2018).

The great interest in rare earth elements in geochemical studies is due to the chemical properties

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\* Corresponding author: Ebru TAT, [ebrupaksu@gmail.com](mailto:ebrupaksu@gmail.com)

of these elements. Because the rare earth elements have been enriched in certain areas due to their chemical properties (Budakoğlu et al., 2015). Therefore, these elements, which can provide precise analyses at very low concentrations of single or a few elements, can also provide hints about the origin of the rock (Henderson, 1984).

Usually, the rare earth elements are associated primarily with alkali rock complexes, carbonatites, and placers, and secondarily pegmatites and various metamorphic rocks. Therefore, these geological rock groups are usually taken into account when researching rare earth elements. However, limited scientific studies have been carried out on volcanic lands (Price and Taylor, 1973; Joron et al., 1991; Fulignati et al., 1999; Moller et al., 2003; Roy et al., 2010; Sen et al., 2012; Kaçmaz, 2016; Rahimi et al., 2016; Bragin et al., 2017; Inguaggiato et al., 2017; Carvalho et al., 2019). In the literature of various disciplines, there are scientific studies related to the study area and Taurus region (Blumenthal, 1963; Dumont, 1976; Gutnic, 1977; Poisson, 1977; Koçyiğit, 1981; 1983; Poisson et al., 1984; Şenel et al., 1992; Karaman, 1994; Görmüş and Özkul, 1995; Yağmurlu et al., 1997; Savaşın and Oyman, 1999; Francalanci et al., 2000; Piper et al., 2002; Poisson et al., 2003; Elitok and Görmüş, 2011; Platevoet et al., 2014; Budakoğlu et al., 2015). Only a scientific study conducted by Simandl (2014) on the “market of rare earth elements” provides information about the rare earth elements in Çanaklı Village. A table in this study reveals that the rare earth elements concentration in Çanaklı Village ranges between 100-1000 tons and 10-100 wt%, however, there is no more detail in this study.

Considering their usage as raw materials (in electronic devices, green energy, medical technology, telecommunication and defense industry, production of high-technology products, etc.), the studies on rare earth elements are of great importance. In this context, the study aims to examine REE contents and enrichment conditions in samples collected from 5 locations determined between Burdur and Isparta, which have not been scientifically studied before. Furthermore, interpretations of the origins of these REEs have been also provided. The results of the analysis of the samples collected from these five locations were compared to each other, as well as, the data of Gölcük Volcanism, which has been

considered to be the source of high concentrations and the relationship between them evaluated statistically.

## 2. Typical Geological Features

Extensive geological studies have been carried out in the study area located between the provinces of Isparta and Burdur (Blumenthal, 1963; Dumont, 1976; Gutnic, 1977; Koçyiğit, 1981, 1983; Poisson et al., 1984; Karaman, 1994). The area between Burdur Fault on the west and Aksu Thrust on the east in the northern part of the Gulf of Antalya was defined as Isparta Bend by Blumenthal (1963). The origin of this bend was a controversial issue for a long time. But later, it has been suggested that it represents a part separated by the break of the northeastern part of Gondwana at the beginning of the Permian-Triassic period, and it is a part of the Gondwana Supercraton (Piper et al., 2002; Poisson, 2003).

The study area and its vicinity have been evaluated in four main units in general. The oldest of these major four units that represent the study area is the unit consisting of limestones, neritic limestones, basalt, tuff, tuffite, gabbro, diabase, harzburgite blocks containing carbonate formation of Permian age and radiolarite and chert deposited in the Triassic-Cretaceous period (Şenel, 1997; Cox et al., 2013). The largest spread area in the region belongs to the Beydagları Carbonate Platform from Mesozoic age. The youngest unit in the region is the unit with molasses character belonging to Aksu formation (Poisson, 1977) from Tortonian age (Dumont, 1976; Şenel et al., 1992, 1996). The alluviums in most of the quaternary deposits are represented by unconsolidated tuffs (Cox et al., 2013) (Figure 1). It has been determined that the sample materials are not tuff, but are partly alluvium or ground cover derived from tuffs. In general, it can be stated that the samples are alluviums containing tuff fragments.

One of the important factors affecting the geomorphology and geochemical structure of the region is Gölcük Volcanism. This wide area, which covers Isparta and its vicinity, was under the influence of compression tectonics until the Upper Miocene period and the pulling tectonics in the later periods (Karaman, 1994). In this context, Gölcük Volcanism, which was affected by the post-Miocene stress regime, is volcanism related to tectonism (Elitok and

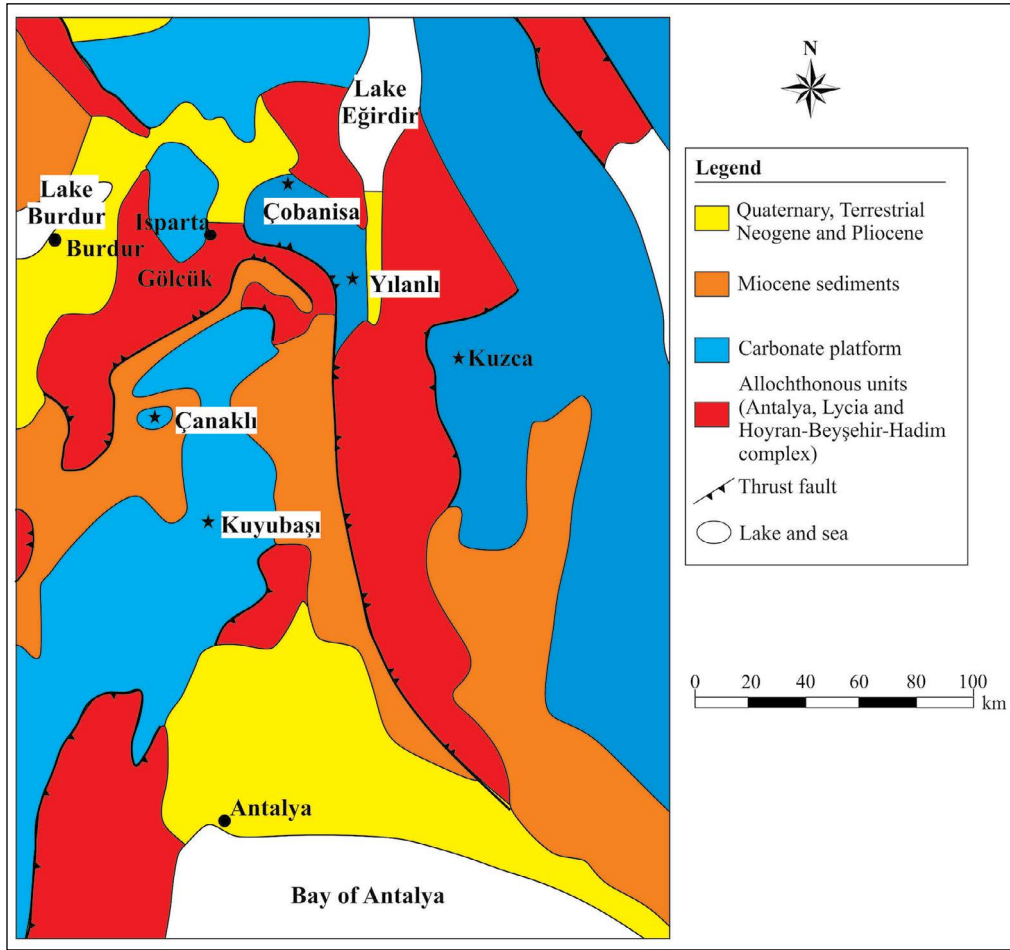


Figure 1- Geological map of the study area (see Cox et al., 2013).

Görmüş, 2011). The products of Gölçük Volcanism from Pliocene age (Savaşçın and Oyman, 1998) are in traki-andesitic composition (Görmüş and Özkul, 1995; Yağmurlu et al., 1997; Nemec and Kazancı, 1999; Francalanci et al., 2000) and they are observed in Isparta province and its vicinity.

### 3. Material and Method

The study area covers 5 locations within the boundaries of the Isparta and Burdur provinces. These locations Çanaklı, Çobanisa, Kuyubaşı, Kuzca, and Yılanlı. A total of 104 samples (i.e. 17 samples from Kuyubaşı, 17 samples from Kuzca, 17 samples from Yılanlı, 19 samples from Çanaklı, and 34 samples from Çobanisa) were collected from these locations. The samples were taken from a depth of approximately 10-15 cm, similar to each other. The samples were screened using a 0.125 mm sieve, thus,

the coarse grain contents were removed. The samples collected from the field were brought to Mine Deposits and Geochemistry Laboratory at Akdeniz University Faculty of Engineering and prepared for the chemical analysis. The samples were divided into groups of 17 samples and kept in an oven at 105°C for 24 hours.

The samples were weighed before and after the drying process and as a result, the loss on ignition (LOI) value was calculated for each sample. The samples were taken from the oven and ground; the mortar was washed with distilled water before sample grinding each sample against artificial contamination. The samples taken from the grinder were filtered through a 0.063-micron filter and filled in packages of about 25 g; then, the samples were sent to be analyzed in ACME Analytical Laboratories. Inductive Conjugate Plasma - Mass Spectrometry (ICP-MS) method was used in the geochemical analysis of the ground and packaged samples.

## 4. Findings

### 4.1. Geochemical Analysis

In this study, the geochemical structure of the rare earth elements of the samples collected from five locations in the Burdur and Isparta zone were examined. The samples were taken from the upper horizon. The average rare earth element contents of the samples are shown in table 1. The concentration values of the locations are close to each other. The following average total rare earth element concentration values were determined in the order: Çobanisa (822.82 ppm) > Yılanlı (736.45 ppm) > Kuzca (692.14 ppm) > Çanaklı (584.21 ppm) > Kuyubaşı (483.82 ppm). The location with the highest  $\Sigma$ LREE concentration is Çobanisa whereas the location with the lowest value is Kuyubaşı. Kuzca and Yılanlı locations have been relatively enriched by HREEs.

The average concentration values in the study area are quite higher than the rare earth element concentration values in the earth's crust. The rare earth element enrichments can be observed in these locations in the study area. The rare earth element concentration of the products of Gölcük Volcanism

(GV), which is the possible source of this enrichment in the vicinity (Platevoet et al., 2014), and the same element concentrations in the region between Burdur and Isparta are quite close to each other.

REE values of the samples from earth crust, Burdur – Isparta zone, and Gölcük Volcanism were normalized according to the chondrite values determined by Anders and Grevesse (1989) (Figure 2). The samples collected from Burdur and Isparta show almost the same trend as the samples from Gölcük Volcanism. However, samples collected from Burdur and Isparta were determined to be enriched in terms of heavy rare earth elements (HREE) compared to samples from Gölcük Volcanism. On the other hand, it can be suggested that the samples from Burdur-Isparta and Gölcük Volcanism were determined to be enriched in terms of light rare earth elements (LREE) compared to the earth crust.

Figure 3 shows the bar charts in which the REE contents of the samples collected from Burdur and Isparta are compared to the samples from the earth's crust and Gölcük Volcanism. The REE concentration values of the samples from the Burdur-Isparta zone are higher than the concentration values of the

Table 1- Average rare earth element concentrations (ppm) of samples taken from the study area, and the samples from earth crust, and Gölcük Volcanism (GV).

	Çanaklı	Çobanisa	Kuyubaşı	Kuzca	Yılanlı	Ortalama	Earth Crust (USGS 2014)	Gölcük Volcanism (GV) (Platevoet et al., 2014)
La	161	229	123	176	181	174	39	192.78
Ce	270	378	210	312	340	302	66.5	341.82
Pr	25.8	38.1	23.3	33.2	33.6	30.8	9.2	33.9
Nd	86.4	128	82.2	115	117	105.72	41.5	117.67
Sm	12.4	17.6	12.9	17.4	17.2	15.5	7.05	16.45
Eu	3.05	4.24	3.01	4.02	4.04	3.672	2	4.25
Gd	9.07	11.4	10	12.5	11.9	10.974	6.2	9.16
Tb	1.17	1.3	1.38	1.6	1.5	1.39	1.2	1.09
Dy	6.27	6.62	7.56	8.79	7.81	7.41	5.2	4.98
Ho	1.18	1.13	1.4	1.54	1.41	1.332	1.3	0.75
Er	3.46	3.24	4.01	4.42	4	3.826	3.5	2.09
Tm	0.51	0.48	0.6	0.66	0.6	0.57	0.52	0.29
Yb	3.38	3.22	3.86	4.35	3.89	3.74	3.2	1.95
Lu	0.52	0.49	0.6	0.66	0.6	0.574	0.8	0.3
$\Sigma$ HNYE	558.65	794.94	454.41	657.62	704.74	631.69	165.25	706.87
$\Sigma$ ANYE	25.56	27.88	29.41	34.52	31.71	29.82	21.92	20.61
$\Sigma$ NYE	584.21	822.82	483.82	692.14	736.45	661.51	187.17	727.48

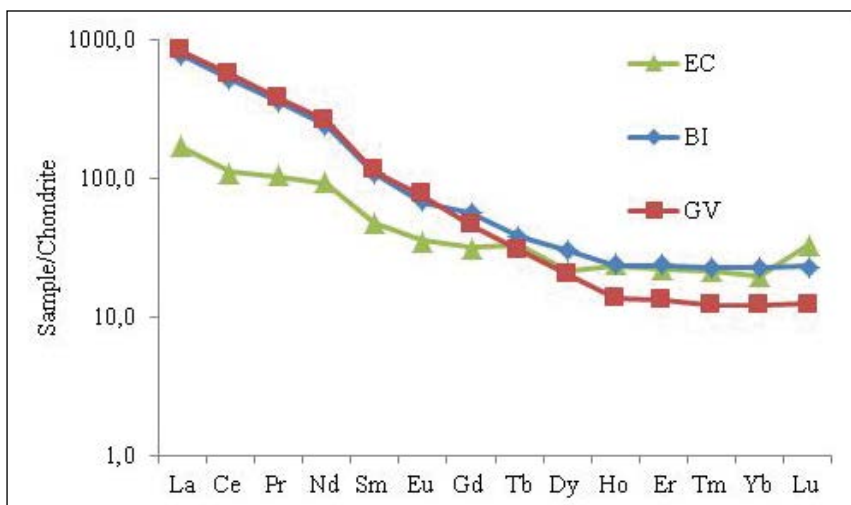


Figure 2- Chondrite-normalized REE diagram (Anders and Grevesse 1989) of the samples from Earth's Crust (EC), Burdur-Isparta (BI), and Gölcük Volcanism (GV).

samples from the earth's crust in terms of all elements except for Lu and Ho. The concentration values of La, Ce, Pr, Nd, Sm, Eu are significantly higher than the concentration values of the samples from the earth's crust and other examples. It can be suggested that these samples had an enrichment in terms of the light rare earth elements. Also, these graphics are consistent with the diagram comparing chondrite-normalized values.

Figure 4 shows the chondrite-normalized REE diagram of the locations between Burdur and Isparta zone where the samples were collected from. The REE distributions of the locations in the zone are quite similar. It can be suggested that these soils developed on the same bedrock underwent similar conditions. The concentration values of light rare earth elements (LREE) are higher than those of heavy rare earth elements (HREE) at all locations.

The trace element values of the samples from Çanaklı, Çobanisa, Kuyubaşı, Kuzca and Yılanlı were normalized according to the chondrite values determined by McDonough and Sun (1995) (Figure 5). The rare earth elements tend to be LREE > HREE. It is a typical trend for the soil samples (Aide and Aide, 2012). In this chondrite-normalized diagram, it was observed that the light rare earth elements were remarkably enriched in the samples from all of the locations. Also, this diagram shows a sharp positive anomalies of Rb, Nb, Sr, Zr, and Y elements in all samples likewise.

## 5. Discussion

There are unconsolidated tuffs in the zone between Burdur and Isparta (Cox et al., 2013). The covered units in the studied five locations are alluviums on the carbonated rocks. However, these alluviums are not the result of the decomposition of the carbonate rocks. They are considered to form by the tuffs, their fragments, and decomposition or weathering of them carried from another place. In general terms, they can be defined as alluvium placers containing tuff fragments. In the study area, it was observed that the study locations which are far from each other are quite similar in terms of the properties of basement rocks, geographical structure, and their location in the basin. The similarity of these properties indicates that the conditions enriching the REEs, which were placed secondarily, reflect the similar environmental conditions.

However, it has been observed that there is a regional difference in the distribution of REE concentration values. When the concentration values of these elements are compared, it can be seen that the northern part of the study area contains higher values of concentrations, whereas, the southern parts contain lower values. This indicates that the source causing REE enrichment is in the northern parts of the study area. The fact that the element contents of the samples from the study area show a decreasing trend from north to south suggests that the source of this enrichment is the Gölcük Volcanism, which is located in the northwest of the study area.

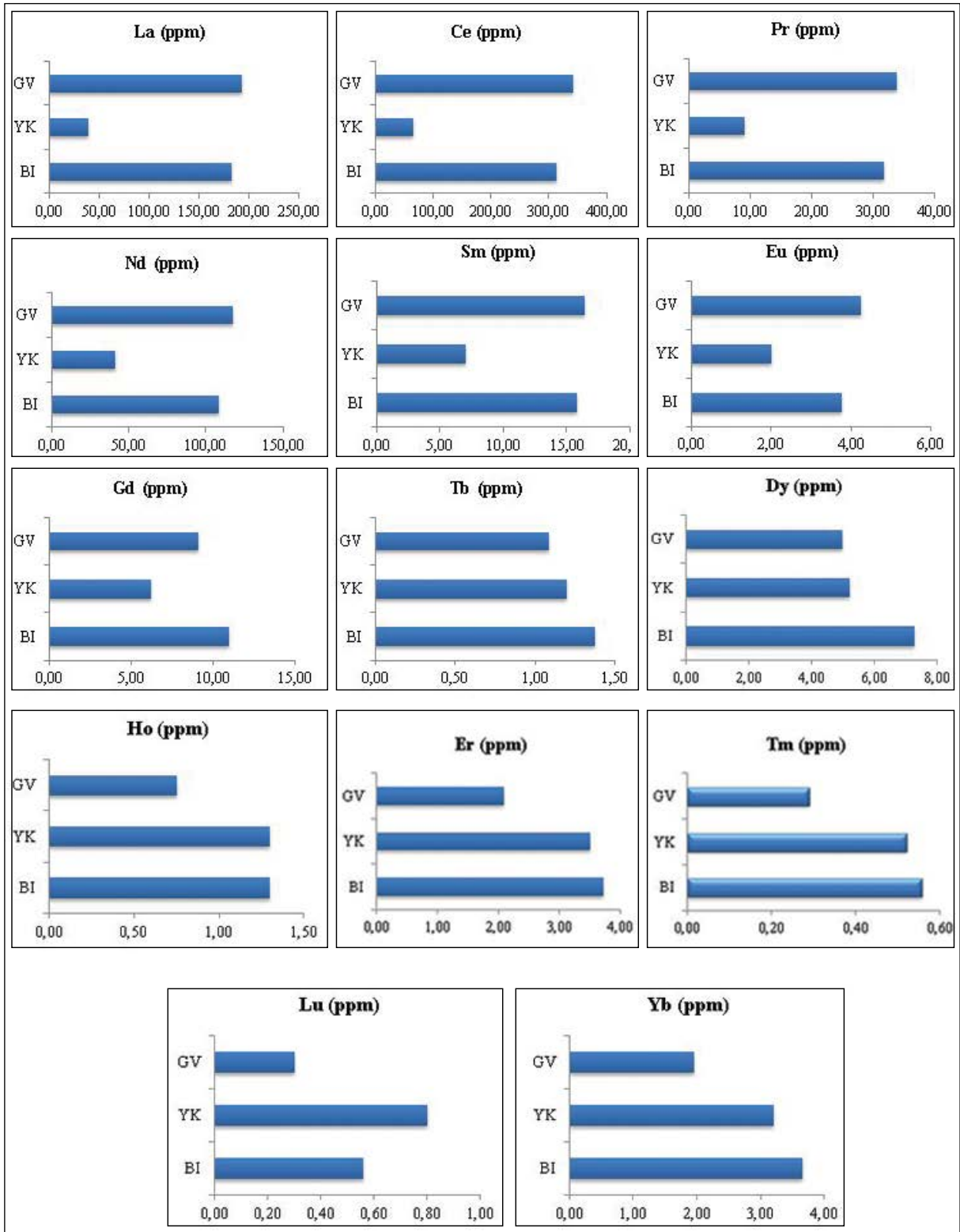


Figure 3- Rare earth element concentration values of the samples from Earth's Crust (EC), Burdur-Isparta (BI), and Gölcük Volcanism (GV).

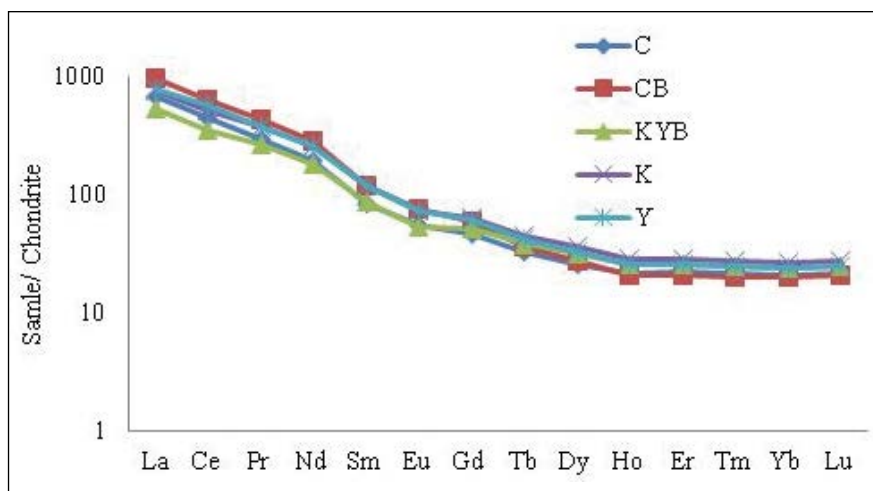


Figure 4- Chondrite-normalized Rear Earth Element Diagram of the samples from Çanaklı (C), Çobanisa (CB), Kuyubaşı (KYB), Kuzca (K) and Yılanlı (Y).

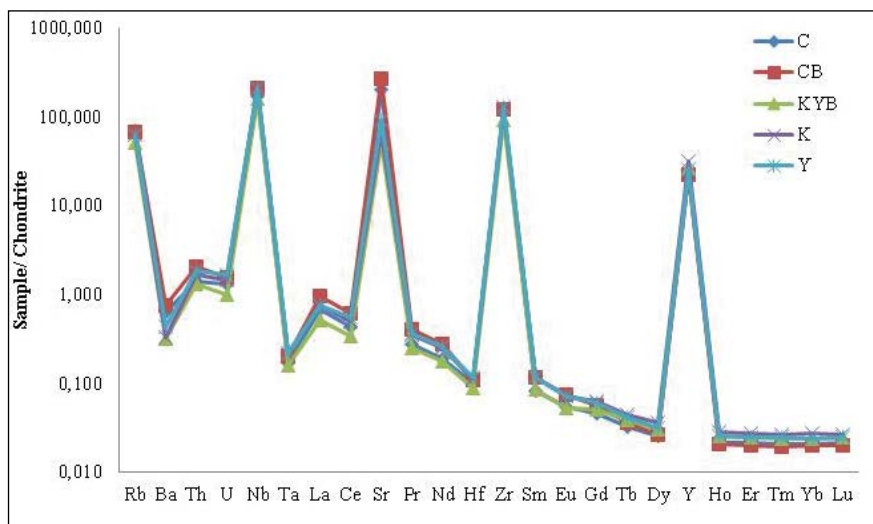


Figure 5- Chondrite-normalized trace and REE diagram (McDonough and Sun, 1995) of the samples from Çanaklı (C), Çobanisa (CB), Kuyubaşı (KYB), Kuzca (K) and Yılanlı (Y).

It has been stated that the origin of rare earth elements in placers in the Çanaklı (Burdur) location is the Pliocene Gölcük alkaline volcanism which is located approximately 8 km west of this area (<http://www.eurare.eu/countries/turkey.html>).

## 6. Conclusion

The REE contents of Kuyubaşı and Çanaklı locations in the boundary of Burdur province and Çobanisa, Kuzca, and Yılanlı locations in the boundary of Isparta province have gained importance

for the first time with this study. Considering the concentration values of REEs, it is understood that Çanaklı, Çobanisa, Kuyubaşı, Kuzca, and Yılanlı locations have anomaly values. Among these 5 locations, for which element contents and anomaly conditions were determined, the highest concentration value was observed in the samples collected from Çobanisa. However, the samples collected from Kuyubaşı location showed the lowest concentration values. In these samples, the light rare earth elements (LREE) showed higher concentration values than the heavy rare earth elements (HREE), which is a typical



characteristic. This is a typical characteristic of the soil samples.

In the chondrite-normalized trace element diagram, Rb, Nb, Sr, Zr, and Y elements show sharp positive anomalies. The positive correlation of the same elements in all samples from the study area shows similar anomalies. The positive correlation of the samples collected from the carbonated rocks and the similar anomalies presented by the discordant elements may have occurred as a result of their reaction with hydroxide minerals such as Fe and Mn and after the weathering of the minerals. The thermodynamic conditions related to the solubility of these elements weathered from the minerals may have revealed the anomaly and positive correlation of the elements.

It has been determined that the REE values of the samples collected from the study area and Gölcük Volcanism are consistent with each other. The tuff fragments and some of the weathered materials observed in the alluviums where the samples were collected are thought to be the products of the Gölcük Volcanism. Therefore, it can be suggested that the origin of REE observed in the study area is not of the primary bed type but they occurred secondarily in alluvial placers.

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