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KRİTİK MİNERALLER İÇİN GELENEKSEL OLMAYAN BİR KAYNAK; DÜŞÜK KALİTELİ BAZI TÜRK KÖMÜRLERİNİN NADİR TOPRAK + Y VE Sc İÇERİĞİ

A NON-TRADITIONAL RESOURCE FOR CRITICAL MINERALS: RARE EARTHS +Y (REY), AND Sc CONTENTS OF SOME TURKISH LOW-RANK COALS

Nazan YALÇIN ERİK (ORCID: 0000-0001-7849-8660)

Sivas Cumhuriyet Üniversitesi, Jeoloji Mühendisliği Bölümü, Sivas, Türkiye

*Sorumlu Yazar / Corresponding Author: Nazan YALÇIN ERİK, nyalcin@cumhuriyet.edu.tr

ABSTRACT

REY (Rare Earth Elements + Y) and Sc are strategic materials that are needed globally for areas requiring high technology such as the energy sector and electronics. Coals contain Rare Earth Elements along with many trace elements in their composition. In recent years, as the gap between REE's global demand and supply increases, the search for alternative sources has become increasingly important, especially for countries that depend heavily on imports of these materials. Particularly considered as waste material, coal and coal ash are considered a possible source for many elements, including REE. Turkish low-rank coals analyzed in this study have an average critical mineral abundance of 73.73 ppm (on a dry whole coal basis). Materials collected from the various Neogene coal fields in Turkey were found to contain a relatively higher amount of REY (>100 ppm) relative to the rest of the samples, which may be attributed to the volcaniclastic character of the sediment associated with the seams. In this study, it was determined that although the critical mineral contents of the investigated coals were higher than Turkish, World, USA, and China coals, they were not economic for production and could be taken into consideration by the development of production techniques.

Keywords: Rare earth elements, yttrium, Sc, Turkish lignites, critical minerals.

ÖZET

NTE (Nadir Toprak Elementleri + Y) ve Sc, enerji sektörü ve elektronik gibi yüksek teknoloji gerektiren alanlar için küresel olarak ihtiyaç duyulan stratejik malzemelerdir. Kömürler, bileşimlerinde birçok eser element ile birlikte Nadir Toprak Elementleri içerir. Son yıllarda, NTE'nin küresel talep ve arzı arasındaki uçurum arttıkça, özellikle bu malzemelerin ithalatına büyük ölçüde bağımlı olan ülkeler için alternatif kaynak arayışları giderek daha önemli hale gelmiştir. Özellikle atık madde olarak değerlendirilen kömür ve kömür külü, NTE dahil birçok element için olası bir kaynak olarak kabul edilmektedir. Bu çalışmada incelenen Türk düşük dereceli kömürleri (kuru tam kömür bazında) ortalama 73,73 ppm kritik mineral bolluğuna sahiptir. Türkiye'deki çeşitli Neojen kömür yataklarından toplanan materyallerin, diğer örneklere göre nispeten daha yüksek miktarda NTE (>100 ppm) içerdiği bulunmuştur, bu durum, kömür damarlarının ilişkili sedimanter birimlerin volkaniklastik özelliğine atfedilebilir. Bu çalışmada incelenen kömürlerin kritik mineral içerikleri Türk, Dünya, ABD ve Çin kömürlerine göre daha yüksek olmasına rağmen üretim açısından ekonomik olmadığı ve üretim tekniklerinin geliştirilmesi ile dikkate alınabileceği tespit edilmiştir.

Anahtar Kelimeler: Nadir toprak elementi, yitriyum, Sc, Türk Linyit, Kritik mineral

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INTRODUCTION

Rare earth elements (REE) are a group of seventeen elements of the periodic table, with the inclusion of fifteen lanthanides (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, together with lutetium) plus yttrium and scandium. Rare Earth Elements and Scandium have gained more importance and started to be researched due to the developing technology and the need for raw materials needed in this context. The need for these elements of technological developments has caused them to be defined as the strategic elements of the century (Alonso et al. 2012, Franus et al. 2015; Haque et al. 2014, Kumar et al. 2018). The fact that REE-containing materials are more stable, high-temperature and corrosion-resistant lightweight materials has been vital for the production of indispensable components of normal life, especially refining technology, computers, hybrid vehicles, batteries, mobile phones, flat television screens (U.S. Department of Energy, 2011; Humphries, 2013; Massari and Ruberti, 2013; Zhang and Honaker, 2018). Because of their critical role in the modern economy, both the European Commission (2014, 2017) and the US Department of Energy (2011) refer to REE as critical raw materials. The fact that their production is difficult and high in cost has also caused the development of production methods to meet the market demand. Removing these elements from the earth's crust, then turning them into metals or alloys is extremely costly, environmentally hazardous, especially dangerous for workers' health. For this reason, some countries do not prefer to produce these elements despite the existence of reserves. As such, more than eighty percent of global production is made by China alone due to the advantage of cheap and negligible craftsmanship (Haxel et al. 2002).

The rare earth elements (REE) and yttrium (hereinafter referred to as REY) are a group of 16 elements, including the lanthanides and yttrium, which exhibit similar physicochemical properties and tend to coexist in nature (McLennan, 1989; IUPAC, 2005). Scandium is chemically similar to the lanthanides and yttrium and is sometimes included in REEs (Long et al. 2012). The increasing global demand for REY (or REE and Y), especially in China, and the decrease in supply in recent years necessitated the discovery of new source areas or production methods to these materials. The increase in the variety of metal used in the industry and the high price of the end high-tech products directed the countries to investigate their underground resources more effectively and to supply the mines necessary for their domestic consumption either from their resources or through imports. For this reason, several kind of research are ongoing around the world to obtain REE not only in ores but also in coal and coal-bearing rocks (Zheng et al. 2007; Ketris and Yudovich, 2009, Całus-Moszko and Białecka, 2013, Dai et al. 2011a and 2012; Adamczyk et al. 2015). Many studies have suggested that coal ash is a potential alternative source for REY (Seredin and Dai, 2012; Franus et al. 2015; Hower et al. 2016; Hower et al. 2015; Zhang et al. 2015), and with traditional REY deposits. In comparison, some fly ash generally contains a higher critical REY fraction (Seredin and Dai, 2013; Seredin et al. 2012; Pazand, 2015; Taggart et al. 2016).

The coal industry globally generates significant amounts of mineral waste, both during mining and during its use, the bulk of which consists of components of economic importance. Therefore, recovering REY from alternative sources such as coal by-products and waste can maintain the sustainability of coal mining and ensure the reliable supply of high-tech materials. REY recovery as a by-product from coal deposits actively mined in many countries could alleviate the current raw material crisis and, from the environmental point of view, make “dirty” coals into a REY source for “clean” energy. In this context, low-rank coal/lignite is especially noteworthy.

In this study, REY properties of low-quality coal in Turkey were evaluated and conducted an investigation as to whether the production potential in future periods. The total coal reserves of Turkey reach around 19 Gt and are mostly composed of Cenozoic, low-rank coals, which display high ash yields and total sulfur contents (Tuncalı et al. 2002; MTA, 2020). In addition, environmentally sensitive elements (B, Cr, As, Ni) have been enriched in these coals (Querol et al. 1997; Karayiğit et al. 2000; Palmer et al. 2004) and therefore have potential adverse effects on the environment and human health. There are notable studies evaluating the major and trace element characteristics of Turkish Tertiary low rank coals (Altunsoy et al. 2017; Altunsoy et al. 2016; Altunsoy et al. 2015; Cicioğlu ve Karayiğit, 2015; Çelik et al. 2017; Demir & Kurşun, 2012; Eraslan et al. 2014; Eraslan & Öngün, 2017; Erkoyun et al. 2017; Gürdal, 2011; Gürdal, 2008; Hoş Çebi et al. 2009; Kalender & Karamazi, 2017; Karayiğit et al. 2019; Karayiğit et al. 2017; Karayiğit & Çelik, 2003; Karayiğit et al. 2001; Karayiğit & Gayer, 2000; Karayiğit et al. 2000; Karayiğit et al. 1999; Özçelik et al. 2016; Palmer et al. 2004; Saydam Eker et al. 2016; Tozşin, 2014; Yalçın Erik & Ay, 2020; Yalçın Erik, 2019; Yalçın Erik & Ay, 2018; Yalçın Erik, 2018).

Also, due to environmental concerns and inadequate competitiveness during mining, the REE supply of Turkey is only covered by imports In this study, some literature data and the author's recent studies of REY values in some Turkish coal basins are interpreted to explain whether coal deposits are potential new sources for REY elements. Therefore, the study is of great importance in terms of protecting the environment from the effects of the harmful components that emerge as a result of the use of coal and exposing the industrial use potential of Turkish coals.

Usage Areas, Industrial And Economic Importance Of REY

The demand for rare earth elements containing scandium and yttrium as well as lanthanides in the World has increased over the last few decades (Zhao et al. 2017; Balaram, 2019). In modern life, they have unique magnetic and chemical properties that are utilized in many areas such as crude oil extraction or refining, in the production of electronic and optical products. They are also widely used in the manufacture of the special compounds, catalysts, industrial ceramics, high-quality glass, superconductors, fiber optics, and accumulators. With the widespread use of renewable energy sources on a global scale, the need for such elements has started to grow. For example, the construction of electric vehicles and wind turbines requires high-tech generators and motors using super strong magnets (Neomagnets) made of neodymium and dysprosium. Elements such as yttrium, terbium, and europium are the most important components in laptops, mobile phones, and TV screens (Seredin et al. 2013; Balaram, 2019).

Conventionally, REY is extracted and taken it back from rare earth minerals such as monazite, xenotime, and bastnasite or ion-adsorbed clays (Taggart et al. 2016). The production of REY has been limited to a few countries due to the limited areas of reserve areas, technical difficulties, legal difficulties, and capital costs. Reserves are not homogeneously distributed throughout the world for geological reasons, and China, Brazil, Vietnam and Russia have more than 88% of the estimated global reserves (US Geological Survey, 2018). While supplying> 80% of all REEs consumed, China has long been the leading REE producing country with proven reserves of more than 30% (US Geological Survey, 2018). Increasing global REY demand with the continuous development of modern technology, together with the tight export quota imposed by China, has led to significant fluctuations in the REY global supply market, especially in the last decade. Given the global impacts of the rare earth element scarcity, a large number of private companies and national governments have started promoting alternative REY resources. World REE production is approximately 130×10^3 tons/year and the monetary value of this production is around 4×109 $/year and China is the main manufacturer country of this sector (WEC, 2007). A similar trend is also valid for REY prices. For example, the price of some critical metals hit historic records in mid-2011 (Cox and Kynicky, 2018).

REY Geochemistry

"Rare earth elements nomenclature refers to scandium and yttrium together with lanthanide group elements (lanthanides), which are chemically similar metallic elements" (IUPAC, 1968). These elements feature high melting points, high density, high thermal and electrical conductivity (Huang et al. 2018). Lanthanide elements are divided into two main groups as cerium and yttrium. The Cerium (or light) group consists of elements Ce, La, Pr, Eu, Pm, Sm, and Nd, and the Yttrium (or heavy) group consists of Ho, Lu, Dy, Gd, Y, Tm, Yb, Tb, and Er elements.

According to geochemical evaluations, REY elements can be classified as total REY, light, medium, and heavy. The light REY elements (also called cerium group; La, Pr, Nd, and Ce; LREY), medium (Sm, Gd, and Eu; MREY), and heavy (also called yttrium group Lu, Er, Ho, Tb, Yb, Dy, Sc, Tm and Y; HREY) groups (Zhang et al. 2015). In addition, as suggested by Seredin and Dai (2012), according to abundance and potential uses of use, critical (Y, Dy, Eu, Er, Nd, Tb), excessive (Lferenru, Tm, Ho, Yb, Ce), and non-critical (La, Pr, Sm Gd). Recently, the US Secretary of the Interior (2018) classified the REY + Sc group as "critical minerals".

The total content of lanthanide in the Earth's crust is 0.0015% and is the same as the copper content. Traditionally, REY is commercial product from rare earth deposits that contain REY-bearing minerals such as bastnaesite, monazite, and xenotime (Haxel et al. 2002; Jordens et al. 2013). Also, ion-adsorbed clays are another important source, especially for HREY (Jha et al. 2016). The world's rare earth reserves are estimated to be 130 million tons in total, 44 million tons of which is in China. The other major producers are Australia, the USA, Russia, Malaysia, and Vietnam (Balaram, 2019).

REY Characteristics In Coals and Abundance Of Coals

Coal is a sedimentary rock formed as a result of a heterogeneous mixture of inorganic materials (quartz, clay minerals, carbonate minerals, sulfur minerals, etc.), mainly terrestrial organic materials (Swain, 1990). Each coal layer is unique due to its formation process (deposition environment, origin material, and other Pysico-chemical factors) and has the different elemental composition (Swain, 1990). While many elements are related the mineral matter in coal, some elements are also related to organic matter. Elements with inorganic affinity are mostly concentrated in ash as a result of the combustion reaction (Dai et al. 2012). The primary sources of REEs in coal ash are clay minerals (Kokowska-Pawłowska et al. 2013). Coal contains many metallic elements that can be used as a source of industrially valuable, critical elements. In particular, it reminds us that the major environmental impacts of coal for domestic or energy purposes can be evaluated with different uses. Instead of burning low-calorie and dense ash composition coals, the evaluation of mineral compositions seems to be a more appropriate solution for the environment and industry (Kumar et al. 2018).

According to the abundance in coal, four different types of REY can be defined in terms of their origin; 1) Terrigenous type, REY transported by surface waters; 2) tuffaceous type, relates to acid and alkali volcanic ash; 3) meteoric water leaking from the surface or groundwater driven type, and 4) hydrothermal type. The first two types are formed in the peat bog stage, while the seepage type is epigenetic and the hydrothermal type can occur at any stage of coal formation (Ward, 1978; Eskenazy, 1987a,b, 1995; Finkelman, 1993; Hower et al. 1999; Arbuzov, et al. 2000; Dill, 2001; Arbuzov and Ershov, 2007; Dai et al. 2010a, 2011c; 2008).

This elemental richness (REY) in coal-bearing units did not attract attention for a long time, because conventional deposits (e.g., carbonatites, alkaline granites) were thought to have sufficient levels of these metals and there was no need to search for different resources. Although this situation started to change significantly after 2009, by this time the world economy was already faced with a crisis in REY supply (Lifton, 2009). Trace element studies in coal and coal by-products in different coal areas indicate that the average abundance of REY + Sc varies between coals (Hower et al. 1999; Arbuzov et al. 2000; Nifantov, 2003; Seredin et al. 2006b; Dai et al. 2011b). For example, the average REY content of Chinese and US coals is reported to be 136 ppm (Dai et al. 2012) and 65.5 ppm (Lin et al. 2018), respectively. At the Far East coal mines in Russia with a content of 300 to 1000 ppm, in the East Clayton Fire Clay coal bed at a content of 500–4000 ppm (Hower et al. 1999), in the Sydney Basin of Nova Scotia, Canada, it has a high content of REE content of 72-483 ppm are found in coal deposits (Birk & White, 1991) and Mazino Coal Mine, Iran, this ratio range of 16.4184 mg/g with an average of 88.9 mg/g (Pazand, 2015). A recent study suggests that combustion waste from the Appalachian coalfield may contain one of the largest sources of REE in the United States (Taggart et al. 2016). Moreover, the coals of the Democratic People's Republic of Korea contain about 77 ppm REY (Kumar et al. 2018) while Turkish coals contain about 116 ppm REY + Sc. (Karayigit et al. 2000; Özbayoğlu, 2010; Palmer et al. 2004).

According to the studies on REY + Sc distributions, the total amount of critical minerals in the world's coal is estimated to be 50 million metric tons; this equates to about 50% of the reserves detected in traditional rare earth minerals (Zhang et al. 2015; Mohr & Evans, 2009; World Energy Council, 2007). Sun et al. (2016) and Ketris and Yudovich (2009), 300 mg/kg REY content in coal constitute the minimum value for mining. Based on the calculation of average lanthanide and Y concentration, the average total REY content of world coals (Ketris & Yudovich, 2009) is estimated to be 68.5 million metric tons (Mohr & Evans, 2009; Wang et al. 2012; Zhang et al. 2015). The most interesting situation in this regard is; Rare earth concentrations in the ashes of some types of coal are a hundred times higher than those found naturally in the Earth's crust (Zhang et al. 2015).

According to experimental data on REY production from combustion wastes of some Russian Far Eastern coals in pre-crisis periods, the REO content in ash was ≥1000 ppm (0.1%), which was accepted as the threshold value for useful recovery of metals from low carbonization grade coals (Seredin & Dai, 2012). However, current REY prices are much higher than in the past and so it is believed that values below this value can be used for coals. In addition, this threshold value can be reduced to 800-900 ppm for coal seams greater than 5 m thick; here, relatively thick coal seams with REO≥1000 ppm (in ash) suitable for selective mining can be found (Seredin & Dai, 2012).

In addition, as a result of electricity generation using coal in thermal power plants all over the world, a large amount of trace element-rich coal by-products are obtained. For example, the USA produces about 81.0 million tons of ash per year, of which about 44% is used for cement making and soil enrichment. The remaining part is usually stored in open ground. When we consider the figures given for a single country (US) for countries that use coal as the primary energy source all over the world, the size of the figures will be remarkable (US Geological Survey, 2018).

Physical And Chemical Characteristics Of Turkish Lignites

As mentioned earlier, Turkey's main energy source is low-grade coal. Among these coals, bituminous coals are mostly in the Carboniferous Zonguldak Basin on the western Black Sea coast of Turkey, while lignite and to a lesser extent lower bituminous coal are Tertiary Basins in the country (Figure 1) (Tuncalı et al. 2002; Palmer et al. 2004). The maximum depth and thickness of lignite seams in Turkey shows significant differences between the different basins: the Eocene basin 605 m and 0.35-14.90 m, in the Oligocene basin 332 m and 0.05 – 5.10 m, in the Miocene basin 828 m and 0.10-57.00 m, and Pliocene basin respectively 426 m and 0.10-87.00 m (Tuncalı et al. 2002).

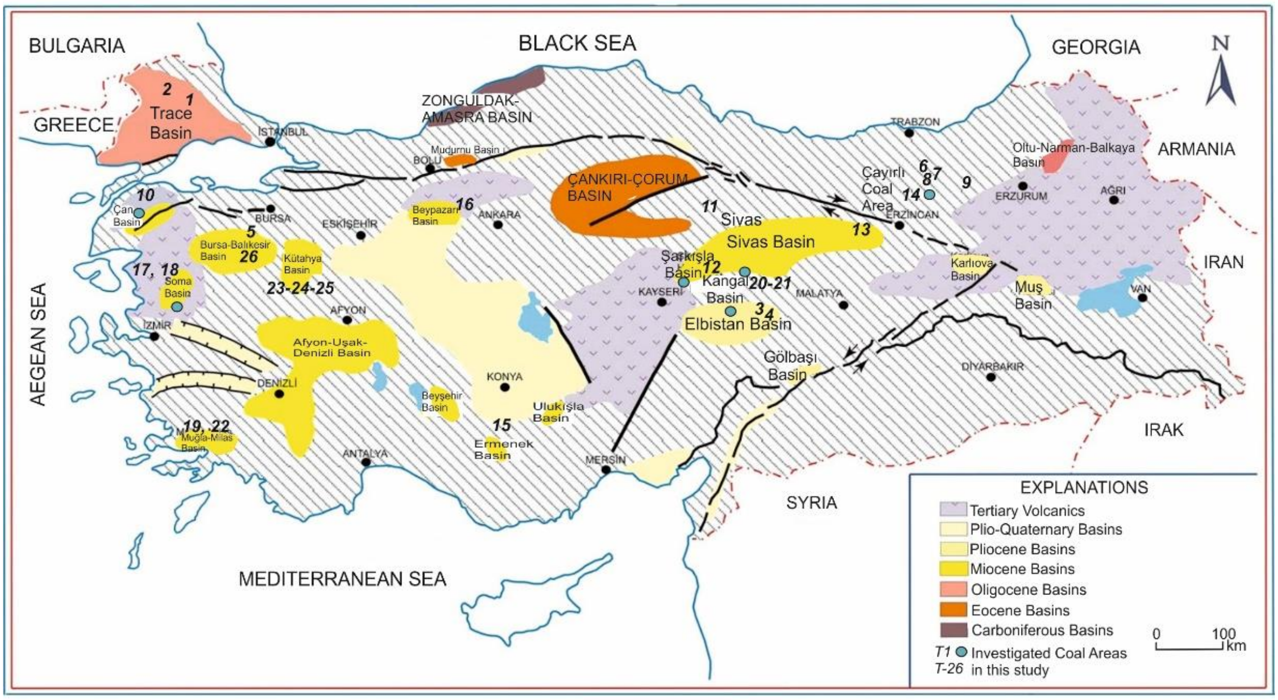

Figure 1. Location of Turkish Tertiary Coal Fields and Investigated Coal Mines

Basins containing lignite show quite different geological environment characteristics from each other (Görür and Okay, 1996; Şengüler, 2010; MTA, 2010) but the most common basins are the grabens and half-grabens, which were formed in the Aegean Region as a consequence of the westerly escape of the Anatolian continent during Neogene (e.g., Barka et al. 1994). Lignite veins are mainly formed with volcano-clastics and carbonates accumulating in lakes and streams in tectonically active basins (Tuncalı et al. 2002). Lignites formed in such environments are mostly limnic and the continuity of the veins is generally not found due to faults limiting the coal-forming environments. In addition, the deposition conditions in these basins caused the coal seams and mineral-dense layers (clay, carbonate alternation) to be abundant. These geological features both reduce the quality of Turkish lignite and make the coal uneconomical for the mine as it is very thin and fragmented (MTA, 2010).

Lignites in Turkey are mostly low calorie, high volatile matter, moisture, ash, and sulfur content (Palmer et al. 2004; Tuncalı et al. 2002). Chemical properties are quite different; for example, its calorific values vary between 1185 kcal/kg and 5574 kcal/kg (Tuncalı et al. 2002). According to Şengüler (2010), approximately 75% of Turkish lignites have caloric values below 2500 kcal/kg, 17% between 2500 and 3000 kcal/kg and only 8% above 3000 kcal/kg.

Having performed proximate and ultimate analyses they found that the moisture, ash, volatile matter, fixed carbon, and sulfur contents of Turkish lignites range between 1.2 and 57.7%, 5.2–56.1%, 18.3–43.8%, 8.9–44.1%, and 0.2–10.7%, respectively. However, according to the ultimate analysis results, elementary carbon between 14.31% and 61.39%, hydrogen range between 1.30% and 4.29%, nitrogen 0.21% and 3.31%, and oxygen at 0.0%, It ranges from 8.0 to 23.20%. The most common minerals are oxides (quartz and opal), clays (kaolinite and smectite), silicates (mica, chlorite, zeolite), carbonates (calcite, siderite, dolomite), sulfur (pyrite) and sulphates (gypsum).

MATERIALS AND METHODS

For this study, trace element data belonging to 26 coal fields made by different researchers and the research results made by the author of this study were evaluated together (Table 1 and Fig.1). In the selection of these coal sites, it was taken into consideration that coal fields to be of similar age (Tertiary), the data were the result of whole dry coal-based analyzes and that the analyzes were performed in the same laboratories.

Data for 420 samples from 26 underground and open-pit mines, drill holes, and natural outcrops located outside of mines are listed in Table 1. The content of some REY (Sc, Y, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu) was determined using Instrumental Neutron Activation Analysis (INAA). Loss on ignition (LOI) was measured gravimetrically. These tests were carried out at ACME Laboratories Ltd. (ACMELABS) in Canada.

RESULTS AND DISCUSSIONS

Rare Earth Element Characteristics Of Turkish Low-Rank Coals

In this study, Seredin and Dai (2012) REY classification was used and includes classes such as light (LREY), medium (MREY) and heavy (HREY) REY and critical, Non-critical and extreme groups (Seredin, 2010).

The results of the REE and ash yield are provided in Table 1. Based on the results of the coals examined for this study, the total REY concentration ranges from 18.69 ppm to 177.2 ppm, and for coal and coal-bearing lithologies, a total average abundance of REY + Sc was found to be 73.73 ppm (21.83 to 185.20 ppm) on dry whole coal basis (Fig.2). The ∑LREE value in the analyzed samples is between 10.11 and 113.8 ppm (avg. 48.12 ppm). The ∑LREE / ∑HREE ratios in the studied coals range from 1.19 to 11.48 (avg. 3.36) and indicate that LREEs are enriched according to HREEs (Table 2).

Table 1. Rare-Earth Element (REE) Content (whole coal basis, in ppm) Of The Investigated Coal Area Samples.

Coal Area	Referance	Area Code	Element Values (ppm)														Ash
			Sc	Y	La	Ce	Nd	Sm	Eu	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Saray (Tekirdağ)	Eraslan & Ergün (2017)	T1	5.5	9.09	7.8	15.64	7.08	1.38	0.34	0.26	1.41	0.32	0.99	0.15	0.99	0.15	28.31
Pınarhisar (Kırklareli)	Eraslan & Ergün (2017)	T2	3.94	12.64	8.58	16.18	7.34	1.57	0.39	0.3	5.39	0.77	1.18	0.17	1.14	0.18	24.36
Afşin-Elbistan Outcrop (K.Maraş)	Cicioğlu & Karayiğit (2015)	T3	1.82	4.37	6.03	11.93	5.48	1.05	0.26	0.15	0.95	0.17	0.5	0.07	0.43	0.06	31.15
Afşin-Elbistan Well (K.Maraş)	Cicioğlu & Karayiğit (2015)	T4	4.81	8.62	11.6	21.54	10.08	1.95	0.48	0.29	1.54	0.32	0.92	0.12	0.75	0.11	39.86
Orhaneli (Bursa)	Karayiğit et al. (2003)	T5	3.9	4.8	10.0	16.0	7.0	1.2	0.4	0.2	1.0	0.2	0.5	0.1	0.5	0.1	41.0
Özyurt (Gümüşhane)	Saydam Eker et al. (2016)	T6	n.d.	n.d.	7.72	14.73	7.18	1.6	0.46	0.3	1.66	0.36	1.02	0.16	0.91	0.15	n.d.
Kayadibi (Gümüşhane)	Saydam Eker et al. (2016)	T7	n.d.	n.d.	19.35	35.1	17.3	3.89	1.02	0.75	4.42	0.89	2.5	0.37	2.32	0.36	n.d.
Tarhanas (Gümüşhane)	Saydam Eker et al. (2016)	T8	n.d.	n.d.	25.9	51.48	19.55	3.61	0.86	0.56	3.32	0.66	1.88	0.3	1.9	0.3	n.d.
Manas (Bayburt)	Saydam Eker et al. (2016)	T9	n.d.	n.d.	30.85	47.3	21.88	4.43	0.93	0.71	4.27	0.88	2.59	0.39	2.62	0.42	n.d.
Çan (Çanakkale)	Gürdal (2008)	T10	n.d.	3.81	3.78	8.3	2.73	0.57	0.14	0.1	0.49	0.13	0.36	0.043	0.339	0.07	11.69
Arguvan (Malatya)	Yalçın Erik & Ay (2020)	T11	6.83	7.05	7.77	13.85	5.93	1.17	0.27	0.19	1.31	0.24	0.73	0.09	0.74	0.11	63.26
Gemerek (Sivas)	Yalçın Erik (2018)	T12	3.8	3.47	4.3	7.43	3.3	0.59	0.15	0.1	0.57	0.12	0.33	0.06	0.33	0.06	37.0
Divriği (Sivas)	Yalçın Erik (2019)	T13	13.86	7.97	7.99	14.5	6.57	1.38	0.31	0.22	1.47	0.3	0.98	0.13	0.91	0.14	28.43
Çilhoroz (Erzincan)	Yalçın Erik & Ay (2018)	T14	3.14	2.46	2.75	4.66	2.21	0.42	0.25	0.09	0.64	0.15	0.45	0.08	0.45	0.08	34.0
Ilgın (Konya)	Altunsoy et al. (2017)	T15	5.86	9.09	12.31	23.97	10.34	1.86	0.44	0.28	1.51	0.31	0.89	0.13	0.85	0.13	26.0
Çayırhan (Ankara)	Karayiğit et al. (2011)	T16	4.4	8.1	12.0	23.0	10.0	2.1	0.6	0.4	2.0	0.4	1.2	0.2	1.2	0.2	n.d.
Işıklar (Muğla)	Karayiğit et al. (2017)	T17	3.45	9.35	13.1	21.73	11.15	1.58	0.41	0.25	1.44	0.27	0.73	0.13	0.8	0.14	12.1
Deniş (Muğla)	Karayiğit et al. (2017)	T18	7.6	3.81	24	39.5	26.1	2.95	0.71	0.49	2.85	0.55	1.45	0.26	1.55	0.25	24.96
Yeniköy (Muğla)	Çelik et al. (2017)	T19	8.78	5.74	5.54	10.43	5.3	0.81	0.22	0.15	0.89	0.34	0.48	0.1	0.5	0.13	13.6

Kangal (Outcrop)	Kalender & Karamazi (2017)	T20	2.59	4.18	4.95	9.24	4.09	0.76	0.18	0.12	0.68	0.14	0.38	0.25	0.35	0.13	73.23
Kangal (well/core sample)	Kalender & Karamazi (2017)	T21	3.53	4.73	7.25	14.07	5.83	1.08	0.26	0.12	0.84	0.14	0.41	0.25	0.45	0.14	37.27
Yatağan (Muğla)	Karayiğit et al. (2000)	T22	8.0	29.0	26.0	55.0	26.0	5.4	1.1	0.9	5.2	1.1	3.2	0.5	3.0	0.5	39.0
Seyitömer	Karayiğit et al. (2000)	T23	12.0	11.0	19.0	36.0	15.0	2.8	0.8	0.4	2.2	0.4	1.2	0.2	1.3	0.2	50.0
Tunçbilek (A3) (Kütahya)	Karayiğit et al. (2002)	T24	4.4	8.1	14.0	29.0	12.0	2.2	0.5	0.3	1.5	0.3	0.8	0.1	0.8	0.1	23.0
Tunçbilek (B4-5) (Kütahya)	Karayiğit et al. (2001)	T25	6.5	13.0	39.0	7.7	32.0	5.4	1.3	0.6	3.0	0.5	1.5	0.2	1.4	0.2	53.0
İsaalan (Balıkesir)	Karayiğit et al. (2017)	T26	2.5	4.16	4.21	8.05	4.2	0.62	0.9	0.45	0.6	0.35	0.2	0.2	0.59	0.2	37.0

Also, the relationship between ash ratio and REY and HREE / LREE ratios for coal samples are shown in Figures 3a and 3b, respectively. The correlation between the REY and coal ash yield is a nonlinear relationship (Fig.3). Further, as shown in Figure 4 HREE / LREE ratio and yield visible in the ash sample are not inclined. This is because HREY has a greater affinity with organic matter in coal (Eskenazy, 1987a, 1999; Arbuzov and Ershov, 2007; Pazand, 2015; Dai et al. 2016a, 2016b) and therefore HREY is released from coal and subsequently incorporated or adsorbed into the fly ash. This result is not consistent with previous studies stating that REEs are associated with aluminosilicate groups (Lin et al. 2017a, b). In the samples, L / H ratios are greater than 1 (avg. 3.36; Table 2) and La / Yb values (avg. 6.49) indicate that the coals are enriched in light REE and the LREE-HREE is highly fractionated. Table 3 shows the correlation coefficients of REE (based on whole coal).

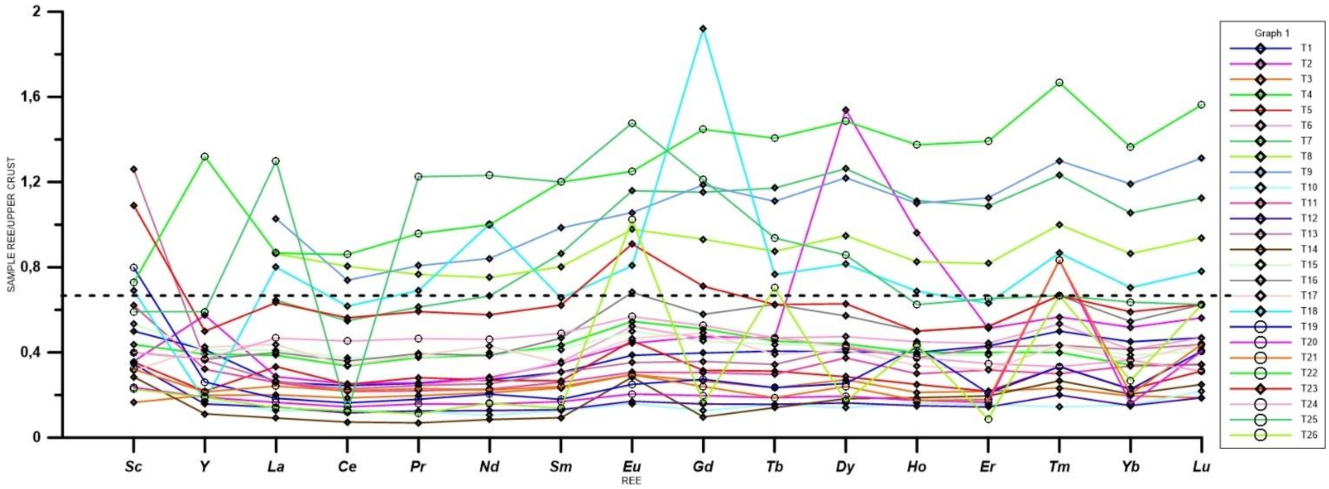

Figure 2. Upper Continental Crust Normalized Rare-Earth-Element (REE) Content of Investigated coals

The light REY elements are slightly depleted in T-8 (Tarhanas), T-9 (Manas), T-18 (Deniş), T-22 (Yatağan), and T-25 (Tunçbilek B4-5) coal samples. Heavy REY elements are slightly enriched in T-2 (Pınarhisar), T-13 (Divriği), T-22 (Yatağan), and T-25 (Tunçbilek B4-5) samples but slightly depleted in the T-6 (Özyurt) coal sample.

LREY elements are highly depleted in T-14 (Çilhoroz) coal samples, whereas MREY and HREY are moderately depleted compared with the upper continental crust (Taylor & McLennan, 1995). Eu in all samples shows slight or no anomalies. In addition, the critical element content of the investigated coal samples is 21.58 ppm (6.10ppm to 65.4 ppm) on average and the most important coalfield is Yatağan. Based on these results, the studied samples were characterized by LREY enrichment types.

Comparison Of Turkish Lignites With Other Coals And Crustal Materials

As stated in the previous sections, the average REY abundance for studied Turkish coals is 73.73 ppm; this value is slightly higher than the world, US an average rare-earth content and lower than Chinese coals (i.e. 69 ppm, 65.5 ppm, and 138 ppm, Ketris & Yudovich, 2009; Lin et al. 2018; Dai et al. 2008). According to an early study of Dai et al. (2016b), the smoothness of a normalized REY distribution pattern (to Upper Continental Crust, UCC) provides a simple but reliable way to validate the quality of REE chemical analyses of coal and other sedimentary rocks.

The normalized REY dispersion model (Upper Continental Crust, UCC) is a simple but reliable way to validate the quality of REE chemical analysis of coal and other sedimentary rocks (Dai et al.2016b). In this study, the normalized REY distribution model of average World, Chinese, US and, Turkish coals is drawn (Fig. 4).

Table 2. Various Rare Earth Element Ratios (based on whole coal) Of The Studied Coal Samples.

Coal Area Symbol	Total REE	Total LREE	Total HREE	Critical Elements	UnCritical El. Ratio	Excessive El. Ratio	L/H Ratio	REE+Sc Ratio	La/Sm Ratio	Gd/Yb Ratio	H/L Ratio	Med. REE Ratio
T1	54.42	32.33	18.86	190017	12.5	17.25	1.71	59.92	5.65	1.53	0.58	3.23
T2	63.40	33.93	25.71	27.24	13.78	18.44	1.32	67.34	5.46	1.58	0.76	3.76
T3	35.68	24.84	8.52	11.71	9.49	12.66	2.92	37.50	5.74	2.35	0.34	2.32
T4	67.74	45.89	17.48	21.93	18.16	22.84	2.63	72.55	5.95	2.59	0.38	4.37
T5	49.10	35	11.3	13.9	14.4	16.9	3.10	53.00	8.33	2.40	0.32	2.80
T6	39.77	31.38	4.56	10.62	12.84	16.31	6.88	39.77	4.83	1.95	0.15	3.83
T7	97.00	76.1	11.61	25.99	31.97	39.04	6.55	97.00	4.97	1.89	0.15	9.29
T8	119.30	102.37	8.92	26.17	38.49	54.64	11.48	119.30	7.17	1.86	0.09	8.01
T9	127.51	105.76	11.88	30.38	45.52	51.61	8.90	127.51	6.96	1.72	0.11	9.87
T10	22.21	15.68	5.342	7.63	5.70	8.882	2.94	22.21	6.63	1.42	0.34	1.19
T11	49.00	29.11	17.29	15.48	11.66	15.03	1.68	55.83	6.64	1.57	0.59	2.60
T12	26.10	15.92	8.84	7.92	6.38	8	1.80	29.90	7.29	1.82	0.56	1.34
T13	59.83	30.8	25.98	17.52	12.47	15.98	1.19	73.69	5.79	1.49	0.84	3.05
T14	18.69	10.11	7.54	6.1	4.03	5.42	1.34	21.83	6.55	0.82	0.75	1.04
T15	72.37	49.3	19.05	22.55	18.57	25.39	2.59	78.23	6.62	2.02	0.39	4.02
T16	70.80	47.8	18.1	22.3	19.1	25	2.64	75.20	5.71	1.83	0.38	4.90
T17	69.15	48.73	16.56	23.33	19.3	23.07	2.94	72.60	8.29	2.34	0.34	3.86
T18	124.27	94.5	18.81	35.41	39.15	42.11	5.02	131.87	8.14	4.71	0.20	10.96
T19	41.73	22.55	17.11	12.78	8.67	11.5	1.32	50.51	6.84	2.08	0.76	2.07
T20	29.91	19.4	8.82	9.63	7.58	10.11	2.20	32.50	6.51	2.14	0.45	1.69
T21	41.64	28.78	10.61	12.19	10.87	15.05	2.71	45.17	6.71	2.02	0.37	2.25
T22	177.20	113.8	51.4	65.4	43.7	60.1	2.21	185.20	4.81	1.83	0.45	12.00
T23	109.40	74.2	28.9	30.6	28.7	38.1	2.57	121.40	6.79	2.08	0.39	6.30
T24	79.40	58.3	16.4	23.2	21.5	30.3	3.55	83.80	6.36	2.50	0.28	4.70
T25	125.60	87.4	26.9	51.4	57.7	10	3.25	132.10	7.22	3.29	0.31	11.30
T26	28.64	17.26	9.25	10.51	6.24	9.39	1.87	31.14	6.79	1.03	0.54	2.13

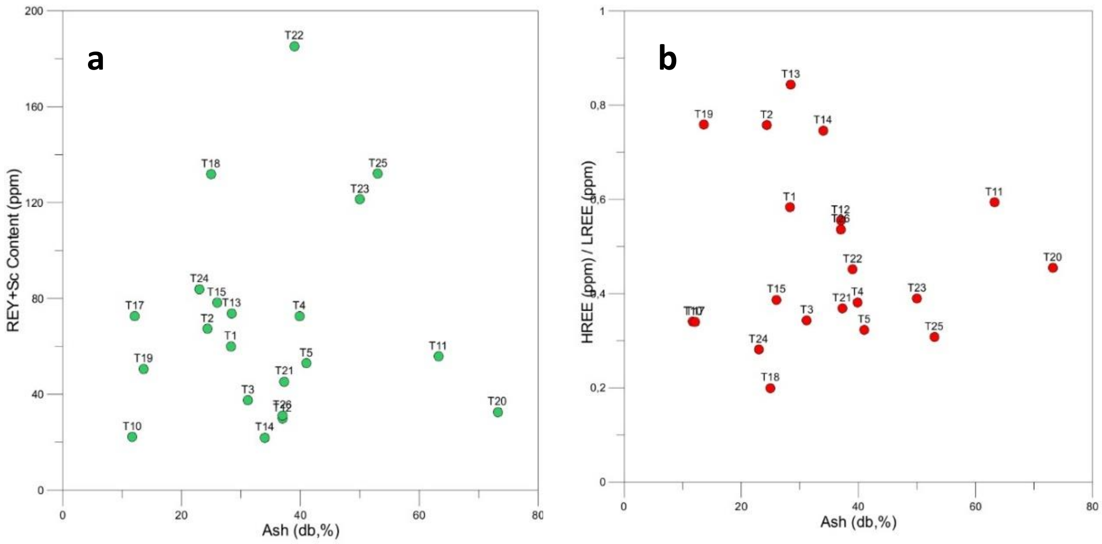

Figure 3a. REY+Sc Content **b)** HREE/LREE Ratios For Investigated Coal Samples As A Function Of Coal Ash Yield On The Bulk Analysis.

Table 3. Correlation Coefficients of Rare-Earth Elements (REE, whole coal basis) With Other Elements In Investigated Coal Area Samples.

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Sc																
Y	0.336															
La	0.346	0.591														
Ce	0.398	0.679	0.531													
Pr	0.348	0.672	0.992	0.573												
Nd	0.343	0.602	0.982	0.617	0.978											
Sm	0.369	0.785	0.955	0.641	0.982	0.952										
Eu	0.246	0.607	0.844	0.473	0.853	0.836	0.852									
Gd	0.363	0.520	0.850	0.730	0.841	0.929	0.829	0.697								
Tb	0.306	0.805	0.792	0.704	0.830	0.837	0.885	0.913	0.793							
Dy	0.261	0.796	0.595	0.604	0.628	0.634	0.708	0.547	0.660	0.724						
Ho	0.318	0.860	0.591	0.691	0.642	0.659	0.739	0.657	0.699	0.861	0.935					
Er	0.437	0.914	0.724	0.797	0.782	0.778	0.872	0.661	0.784	0.872	0.835	0.897				
Tm	0.193	0.705	0.512	0.662	0.571	0.590	0.652	0.600	0.629	0.773	0.613	0.735	0.762			
Yb	0.441	0.893	0.727	0.818	0.778	0.789	0.863	0.723	0.809	0.919	0.829	0.917	0.985	0.798		
Lu	0.341	0.830	0.599	0.748	0.657	0.679	0.747	0.713	0.718	0.906	0.737	0.890	0.888	0.927	0.934	
Ash	0.037	0.009	0.113	0.139	0.116	0.049	0.120	0.140	0.049	0.043	0.083	0.127	0.003	0.212	0.016	0.039

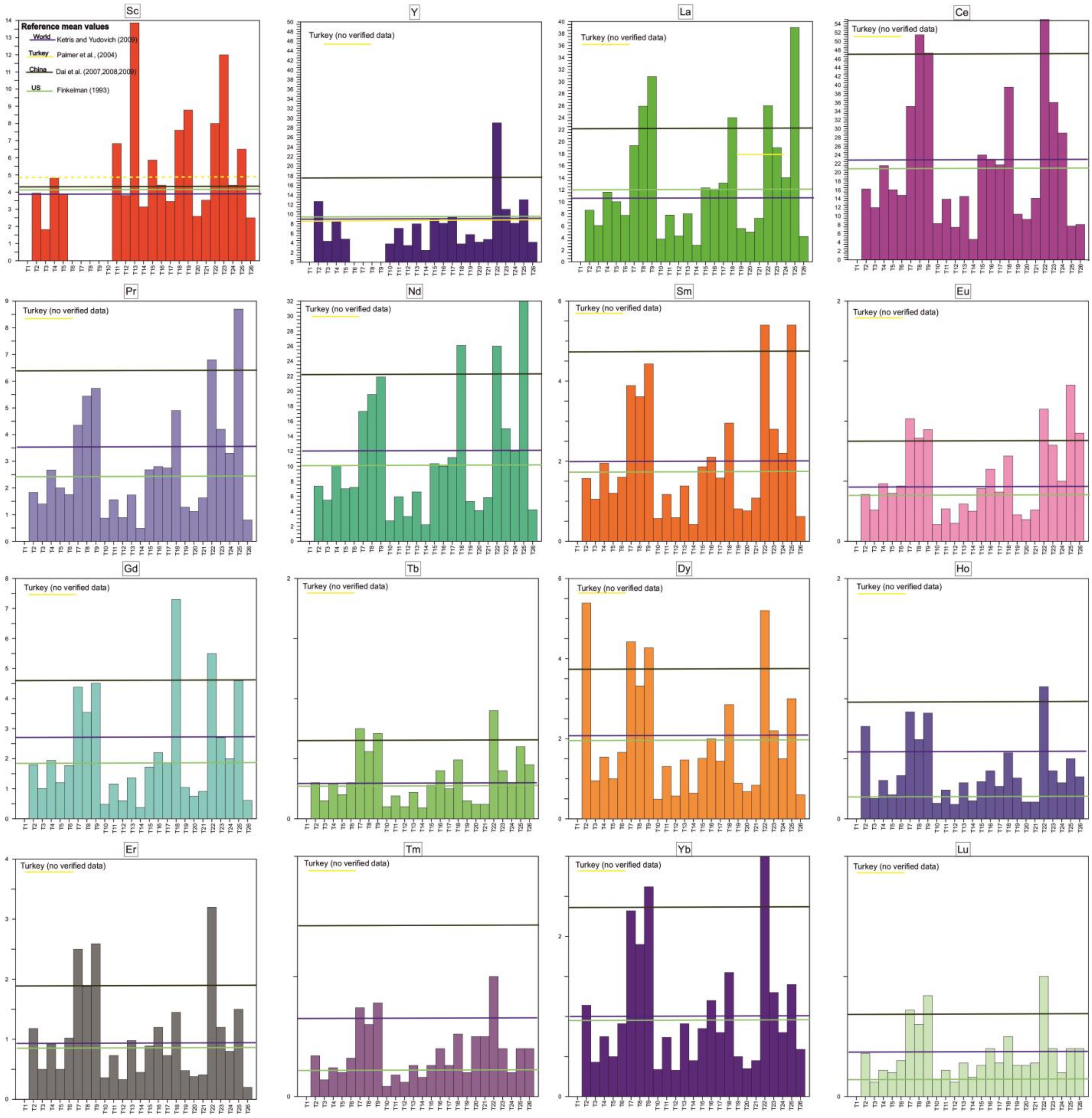

Figure 4. The Concentration Of Rare-Earth Elements (REE; whole coal basis, in ppm) In Investigated Different Turkish Coal Areas In Comparison With REE Contents Worldwide (Ketris & Yudovich, 2009), US (Finkelman, 1993), Chinese (Dai et al. 2012, 2008, 2007) and Turkish coal (Palmer et al. 2004) Average Ratios.

CONCLUSIONS

In this study, 26 coalfield samples from Tertiary coal basins in Turkey were examined, evaluated in terms of rare earth elements richness, and found that the ∑REE concentration based on of all coal varied between 18.69 and 177.2 ppm. It was determined that REE enrichment in the studied coal samples is related to both organic and inorganic materials of coal components. The most important result obtained from this study is that the coals in the Turkish Tertiary coal basins have an important richness in rare earth elements. For the analyzed coal samples, an average of 73.73 ppm REY + Sc abundance was determined based on dry whole coal. Also, there is no linear relationship between REY + Sc and sample ash yields. REE content normalized to the upper continental crust indicates that it is a similar origin for all investigated samples and one of the possible REE sources identified as volcanic ash. With the further development of extraction techniques for REE from coal, the increase in the

production of these elements and the widespread use of clean coal technologies may provide great environmental benefits.
Considering the environmental and industrial effects of coal and REE from coal and coal by-products, which are indispensable, reliable and, cheap energy resources for Turkey, it is very important to create technologies and methods that will provide selective production. The results of this study clearly show how important it is to conduct detailed research on the extraction process of Turkish lignite CFA. Coal and coal by-products are a potential source of REEs, but the concentration of REEs is currently very low compared to resources provided by REE and, production technologies need to be improved to have commercial value.

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