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## Rare earth element (REE) resources of Turkey: An overview of their characteristics and origin

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Research Article

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### ABSTRACT

The Rare Earth Elements (REE) deposits and mineralization of Turkey can be divided into four types based on their geological setting and origin. First are deposits associated with carbonatite-alkaline magmatic rocks, rich in Light Rare Earth Elements (LREE). The best known examples are the Kızılcaören (Eskişehir) and Kuluncak (Malatya) deposits with TREE grades of 2.9% and 0.7% respectively, and typical enrichment of La-Ce. Lower grade REE mineralization at Keban (0.05% TREE) and Divriği (0.13% TREE) is associated with abundant fluorite and all four occurrences show similar ranges for homogenization temperatures and salinities for fluid inclusions in fluorite and REE profiles. The second type are Triassic shales and the bauxites formed from them in the Bolkardağı region. Enrichment of Heavy REE (HREE) is typical and TREE grades are about 0.15% in bauxites and its protolith. These occurrences are geochemically similar to “ion adsorption type” deposits associated with lateritic clay on the weathered granitic rocks of China. Third is the placer type, represented by the Çanaklı (Burdur) deposit which is enriched in U, Th and HREE and heavy minerals such as; magnetite, zircon and rutile and has an average grade of about 0.08% TREE. The fourth potential source of REE is phosphorites. These rocks host the world’s largest resources elsewhere, however the Cretaceous Mazıdağ deposits in Turkey are very low grade (40ppm TREE) and clearly uneconomic. Consideration of the environmental and health issues associated with exploitation and processing of REE has identified the more favorable outcomes associated with exploitation of the ion adsorption type of deposits and justification for further evaluation of the resources and processing technologies that would enable exploitation of REE-enriched bauxites in the Bolkardağı region.

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## 1. Introduction

The Rare Earth Elements (REE) consist of a total of 17 elements, including 14 natural and 1 artificial element known as the Lanthanides (La) starting from the mass number of 57 up to Lutetium (Lu) with mass number of 71, plus Y and Sc, due to their similar geochemical properties. In this REE group

where the ion charge is usually +3 valence; La, Ce, Pr, Nd and Sm elements are called as the LREE, and Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y elements are called as the HREE. Because of its geochemical characteristics, the REE group is widely used for the analysis of geotectonic-petrogenetic environment, the interpretation of physicochemical conditions and for many other geological problems. However, more

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importantly, the REE mining has gained extraordinary importance in the world over the last fifty years due to demand from the electronics and defense industries.

Some raw materials are regarded as strategic and critical according to their supply risk and economic importance ([http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical\\_en](http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en)) and the REEs are at the top of these critical raw materials (Figure 1). Eighty-five percent of the total REE of 140 thousand tons produced per year in the world is realized by China. China supplies 65% of its production from bastnasite, the main mineral of hydrothermal deposits associated with carbonatites, and the remaining from clays formed by supergene processes.

The reason why China is the main leader in the world's REE production is not only the rarity of deposits elsewhere in the world, but also the usual presence of high levels of radioactive elements, such as Th and U, which in turn limits the production. Exposure to radiation during production, processing, and storage of waste containing U and Th, can result

in a serious health threat both to workers and for all post-production environmental damage.

The world's major REE resources include (i) bastnasites (REE, Ce(CO<sub>3</sub>)F) in carbonatites (eg, Mt Pass Deposit USA) Hewett (1954), Bayan Obo Deposit China, Xu et al. (2012) (ii) monazites located in the ocean shore placers (REEPO<sub>4</sub>) (eg, Indian and Australian shores) Paleparthi et al. (2017), (iii) xenotime (Y, REEPO<sub>4</sub>), a byproduct of Ti, Zr, Sn deposits, (iv) sedimentary phosphate deposits (Emsbo et al., 2015), (v) bauxites (Deady et al., 2016b), and (vi) ion adsorption clays - type deposits result from deep tropical weathering of granites (Voßenkaul et al., 2015), where the combination of high precipitation and temperature decomposes the REE-bearing minerals (Sanematsu and Watanabe, 2016). Following their exploitation in China, similar deposits were discovered in Madagascar and Brazil (Rocha et al., 2013).

Except for REE resources associated with monazite and xenotime, the geological environments

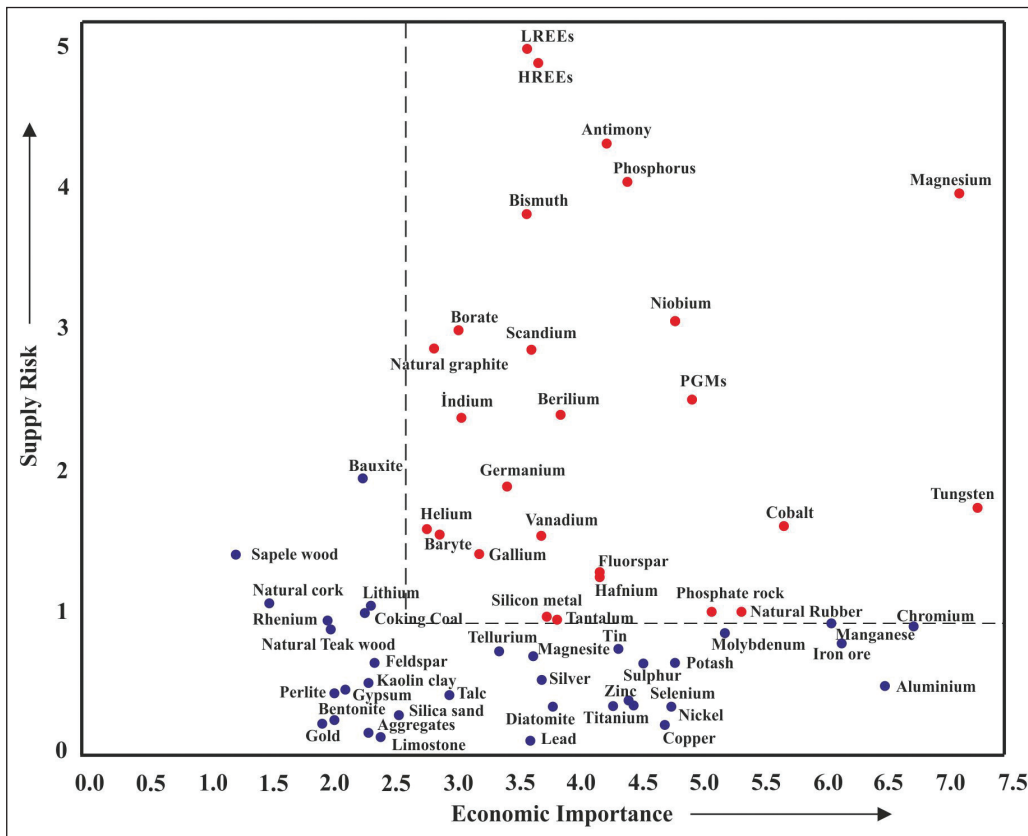


Figure 1- Position of the raw materials critical to the EU Commission for the year 2017 according to the threshold of supply risk and economic importance (see upper right-hand region, [http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical\\_en](http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en)).

and formations for the other types of REE deposits are observed in Turkey (Figure 2). The geological setting, mineralogy, trace element and REE geochemistry and fluid inclusion properties of these deposits and occurrences will be discussed in this article.

## 2. Method

In this study, a total of 44 ore samples were taken from the deposits and mineralization with REE potential from different geological environments in Turkey (sample numbers of deposits and mineralization are seen in Tables 1 and 2). Their mineralogical, petrographical, geochemical (REE, major oxide and trace element geochemistry) and fluid inclusion properties were studied, with geochemical analyses carried out in Canada at the ACME Laboratories using ICP-AES for main oxides and the loss on ignition, and ICP-MS for the other elements. Boynton (1984) values were used in the chondrite normalization. Fluid inclusion analyzes were carried out on the Linkham THMG-600 instrument at the Geological Engineering Department of Istanbul University- Cerrahpaşa. In this study, the fluid inclusion data are given as a summary and results relating to the REE geochemistry are discussed. As REE is transported in the form of fluorine complexes in hydrothermal systems (Migdisov et al., 2009), the REE geochemistry and fluid inclusion

properties of all fluorite deposits in Turkey were examined. However, only the mineralizations that show REE enrichment were introduced among fluorite deposits of Turkey.

## 3. REE Sources Associated with Carbonatite and Alkaline Magmatic Rocks

REE enrichment associated with carbonatites occur at Kızılcaören (Eskişehir) and Kuluncak-Başören (Malatya). Alkaline magmatic rocks-related REE-bearing fluorite deposits occur at Keban (Elazığ) and Divriği (Sivas). All these deposits are always associated with fluorite. This is due to the fact that REE is transported by the fluorine forming complex ions (Migdisov et al., 2009). The most important example of carbonatite-hosted deposit in Turkey is Kızılcaören (Eskişehir) (Kaplan, 1977a; Stumpel and Kırınkoğlu, 1985; Nikiforov et al., 2014). This deposit also contains Th which has strategic significance. Apart from Kızılcaören, the Kuluncak Fluorite-REE mineralization in the vicinity of the Başören village (Kuluncak-Malatya) has been studied by MTA with a similar interest in terms of Th (Özgenç and Kibici, 1994). The MTA has also conducted a research on the Cu-F mineralization of Divriği (Sivas) for uranium, and the high REE content of the mineralization will be presented in this study for the first time.

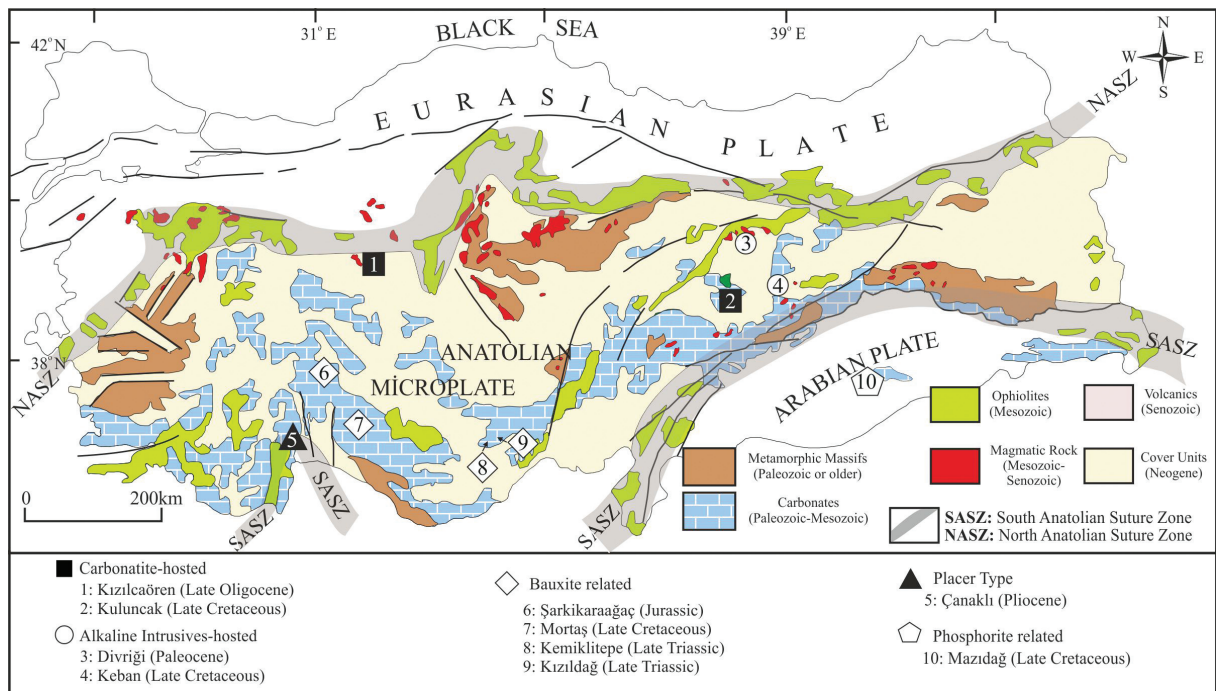


Figure 2- Geological settings of the deposits and mineralization with REE potential in Turkey.

Table 1- The REE+Y, Th, U contents of REE deposits and the rocks that have potential for REE of Turkey. Kızıldağ shale (protolith of bauxites), Kemikli Tepe and Mortaş bauxite data are from Haniçli (2013), the red mud data is from Deady et al. (2016b), the Canaklı placer data is from Cox et al. (2013), the ion absorption clay deposit data of China is from Voßenkaul et al. (2015) and the Seydişehir phyllite data is from Karadağ et al. (2009). The other data are produced in this study (n.d: no data; Please see table 2 for sample locations).

NTE Resource	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣNTE	Y	U	Th
Kızılcaören Carbonatite (n=10)	9380	15070	1234	3584	289	57	224	15	66	9,4	25	3,9	23	2,9	29982	331,7	123	1072
Kuluncak Carbonatite (n=6)	2919	3317,1	248,8	598,4	48,8	8,7	43,1	5,4	29	5,8	16	2,2	11	1	7254,7	214,6	14,4	297,5
Divriği Alkali Magmatite (n=6)	299,7	507,6	62,4	237,8	58,8	7,3	61,2	9,4	53	9,9	27	3,8	22	2,6	1362,9	698,5	116	2,8
Keban Alkali Magmatite (n=10)	219,2	247,2	19,3	42,4	3,5	0,8	3,2	0,4	2,2	0,4	1	0,1	0,8	0,1	540,5	13,2	46	8,8
Çanaklı (Placer)	191	325	34	120	16	4,1	11,1	1,4	6,7	1,1	3,3	0,5	3,2	0,5	717,2	37	10,4	49
Kemiklitepe Bauxite (n=2)	337,1	635,7	91,8	376,1	71,9	15	65,2	8	42	7,2	19	2,9	18	2,7	1693,1	126,2	15,6	47,7
Kızıldağ Shale (n=3)	398,9	467,7	96,5	361,1	65,8	13	58,7	8	39	6,7	16	2,3	14	2,1	1548,5	125,2	10,2	26,4
Mortaş Bauxite (n=1)	39,5	191,6	10,5	38	8,6	1,8	7,8	1,5	11	2,1	6,9	1,1	8	1,2	329,2	49,7	6	47,8
Red mud (Bauxite waste, Seydişehir)	356,2	728,5	102,7	346,7	67,9	14	8,2	52	43	8,2	22	3,3	22	3,3	1777,4	180,2	vy	vy
Seydişehir (Phyllite)	58,1	124,6	13,7	54	10,1	2,0	8,5	1,4	7,8	1,5	4,5	0,7	4,3	0,7	292,0	vy	vy	vy
Şarkikaraağaç Bauxite (n=2)	44,6	110	13,6	63,4	16,3	5,5	14,5	2	10	2	4,9	0,8	4,4	0,6	293	42,4	1,3	4,5
Şarkikaraağaç (Bauxite-protolith is basalt)	17,2	33,4	4,21	18,0	4,11	1,32	4,45	0,71	4,18	0,72	1,9	0,3	1,67	0,24	92,41	18,6	0,5	2,3
Mazıdağı phosphorite (n=4)	15,1	5	1,51	6,2	1,12	0,3	1,67	0,2	2,3	0,7	2,2	0,2	2	0,4	39	45,3	71,8	<0,2
Ganzhou (China clay deposit)	287	311	65	278	44	8	36	5	26	5	14	2	11	2	1094	157	vy	vy

### 3.1. Kızılcaören REE Deposit

The Kızılcaören deposit is the biggest REE deposit in Turkey and also the largest occurrence of F-Ba-Th. It consists of sub-horizontal banded ore and sub-vertical vein-type mineralization within steeply dipping Permo-Triassic conglomerates, sandstones and schists (Figure 3). The sub-horizontal mineralization shows variation between the bands and individual

bands can be rich in either fluorite, manganese oxide, barite or fine-grained silica. These banded ores are coarse grained but have a soft and earthy features. The sub-vertical veins lack banding and this harder mineralization is finer grained and includes locally flow structures. Alkali metasomatism is indicated by widespread fenite veins of K-feldspar and alkali amphiboles that sometimes form small outcrops and feldspathic bands within the deposit.

Table 2- Major oxide and trace element contents of the REE deposits and probable REE sources of Turkey. Data of Bayan Obo deposit from Yang et al. (2003) (**KO**: Kızılcaören deposit; **KUL**: Kuluncak mineralization; **DIV**: Divriği mineralization, **KB**: Keban mineralization; **KM**: Kemikli tepe bauxite deposits, **KD**: Kızıldağ protholith, **MR**: Mortaş bauxite deposit, **SK**: Şarkikaraağaç iron-rich bauxite deposit, **MD**: Mazıdağı phosphorites).

	Deposits	KO	KUL	DIV	KB	KM	KD	MR	SK	MD	Bayan Obo
	Sheet and Coordinate	İ26c4 Y: 60195 X: 85070	K39a2 Y: 83370 X: 12620	J40a2 Y: 31124 X: 66040	K41a3 Y: 96750 X: 76300	N32c2 Y: 88220 X: 09990	N32c1 Y: 13247 X: 11735	N27b3 Y: 01005 X: 27500	M26b2 Y: 65030 X: 06563	N44b1 Y: 15840 X: 50023	
		(n=10)	(n=6)	(n=6)	(n=10)	(n=2)	(n=3)	(n=1)	(n=2)	(n=4)	Yang vd.,2003
Major Oxides (%)	SiO <sub>2</sub>	2,22	6,12	11,11	7,08	3,50	9,60	8,91	11,265	0,37	1,64
	Al <sub>2</sub> O <sub>3</sub>	0,95	1,38	0,39	2,07	57,90	49,70	56,89	12,9	0,02	0,29
	Fe <sub>2</sub> O <sub>3</sub>	4,23	1,65	16,16	2,58	22,90	26,50	17,31	55,735	0,07	11,78
	MgO	0,15	0,27	0,05	1,52	0,10	0,40	0,15	0,97	0,18	9,23
	CaO	37,63	56,97	45,23	53,18	0,10	0,10	0,13	0,305	55,72	23,92
	Na <sub>2</sub> O	0,06	0,09	0,01	0,07	0,10	0,10	0,03	0,03	0,67	0,02
	K <sub>2</sub> O	0,08	1,21	0,09	1,31	0,00	0,20	0,22	0,19	-	0,09
	TiO <sub>2</sub>	0,05	0,33	0,01	0,06	2,90	2,60	2,52	0,53	-	0,30
	MnO	0,44	0,17	0,07	0,15	0,10	0,10	-	12,485	-	1,58
	P <sub>2</sub> O <sub>5</sub>	0,49	0,53	0,01	0,08	0,00	0,10	-	0,03	30,60	0,26
	LOI	4,46	8,55	5,55	13,84	11,70	8,10	13,60	5,3	12,10	
	<b>Total</b>	<b>50,76</b>	<b>77,27</b>	<b>78,68</b>	<b>81,94</b>	<b>99,40</b>	<b>97,60</b>	<b>99,76</b>	<b>99,74</b>	<b>99,71</b>	
Trace Elements (ppm)	Ba	>50000,00	226,80	9,20	1505,90	24,00	55,00	36,00	313	103,50	1089,00
	Rb	3,00	61,30	4,20	73,00	1,10	7,90	11,80	4,55	-	5,00
	Sr	3290,00	1474,70	39,70	880,40	56,20	40,30	13,40	104,95	1424,35	1621,00
	Th	1071,60	297,50	2,80	8,80	47,70	45,60	47,80	8,9	-	
	U	123,20	14,40	116,30	46,00	15,60	20,60	6,00	4,25	65,88	
	V	334,10	16,80	8,70	22,10	501,00	579,00	241,00	77	97,50	44,00
	Zr	21,30	360,40	12,50	15,30	612,10	619,60	464,10	114,6	12,25	1,00
	Y	331,70	214,60	698,50	13,20	191,50	87,40	49,70	30,2	41,95	132,00
	Nb	56,00	312,90	21,30	7,90	71,00	74,60	43,20	10,35	0,10	340,00
	Ga	3,30	11,10	2,90	4,60	71,10	61,80	50,90	28	-	
	Hf	0,60	2,80	0,60	0,50	16,90	17,50	13,60	3,05	0,10	
	Ta	0,96	2,66	0,76	0,18	5,00	5,00	3,50	0,75	-	
	Mo	56,00	3,80	11,90	1594,10	0,90	1,10	7,70	3,2	1,03	
	Cu	3,40	8,50	9160,50	291,80	13,10	18,20	3,30	35,25	27,05	13,00
	Pb	520,00	457,50	177,70	6661,60	61,30	17,20	57,50	197,7	6,15	
Zn	244,50	219,00	484,80	1832,90	97,00	50,30	7,00	328,5	509,00	81,00	
Ni	21,10	108,00	385,30	177,20	83,90	73,60	66,20	78,85	12,38	5,00	

K/Ar radiometric dating of the phonolites and alkali vein rocks in the deposit indicates that the mineralization is Upper Oligocene (23 Ma, Nikiforov et al., 2014).

Exploratory drilling by MTA at Kızılcaören indicates reserves of 0,38 million tons of ore with a grade of 0,212 % ThO<sub>2</sub> and 4,78 million tons ore with an average grade of 2,78% NTE (Ce + La + Nd + Y) (Kaplan 1977a, b). MTA also identifies the potential

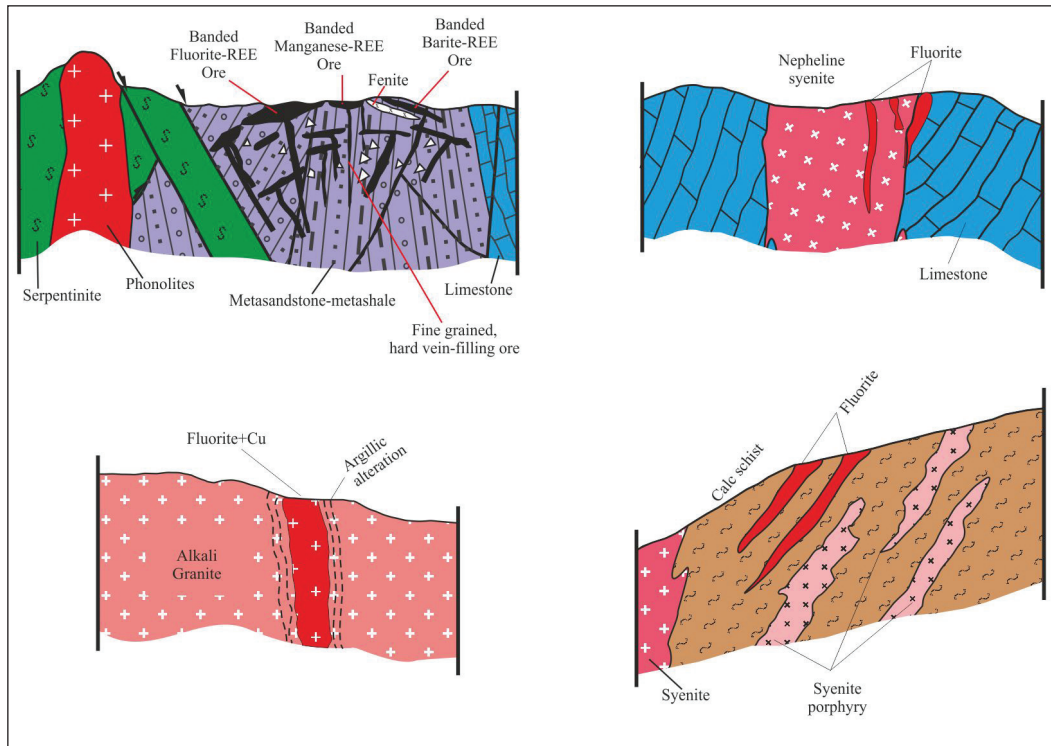


Figure 3- Sections showing the wall rock relationships of the carbonatite-hosted Kızılcaören REE-F-Ba-Th deposit and the carbonatite-nepheline syenite-hosted Kuluncak REE-bearing fluorite and the Keban and Divriği Fluorite-REE mineralization associated with alkaline intrusives (not to scale).

for ten million tons of fluoride and barite (Kaplan, 1997b). The current license holder, Eti Mining, carried out a detailed study between 2015-2017 related to resources and technological studies on the recovery of barite, fluorite and thorium.

The main REE mineral is bastnasite (Kaplan 1977a, Özgenç, 1993) and microprobe data indicates that it also contains thorium (Nikiforov et al., 2014). Studies indicate that fluorite, barite, pyrite and Mn-carbonate minerals are paragenetically linked to bastnasite with oxidation of carbonates and pyrite leading to Fe and Mn oxides. Enrichment of La and Ce enrichment is typical, and the chondrite normalized REE pattern shows a strong decrease from LREE towards HREE (Figure 4).

Fluid inclusion studies indicate multiple phases of mineralization. For example, purple and green fluorites contain both two phase and three phase inclusions with homogenization temperatures of between 150-394°C. Salinities are about 11% for two-phase inclusions and 32% (NaCl weight equivalent) for three-phase inclusions (Altuncu, 2009) and the results from fluid inclusion studies at Kızılcaören resemble those for the Kuluncak, Divriği and Keban mineralization.

Fluoride minerals expand during fluid inclusion measurements, which cause higher homogenization values to be measured than the actual homogenization temperature. For this reason, it should be taken into consideration that the homogenization temperatures obtained from fluoride minerals may be higher than actual temperatures.

### 3.2. Kuluncak REE-bearing Fluorite Mineralization

The Kuluncak REE - bearing Fluorite mineralization is located near the Başaören village of Kuluncak district in Malatya within a license held by MTA which is undertaking intensive exploration. The mineralization is observed in the Upper Cretaceous-Paleocene (Leo et al., 1974) nepheline syenite and in narrow zones at the contacts with Cretaceous limestone within an ophiolitic mélange setting. Purple fluorites are the main ore mineral and compared to other formations except the REE high Nb and Ta are observed in the chemical analyzes carried out in the mineralization. The TREE value in the fluorite ore is 7254,7 ppm. A typical decrease in the chondrite normalized pattern is observed from LREE towards HREE. The Ce and Th-rich mineral, britholite was

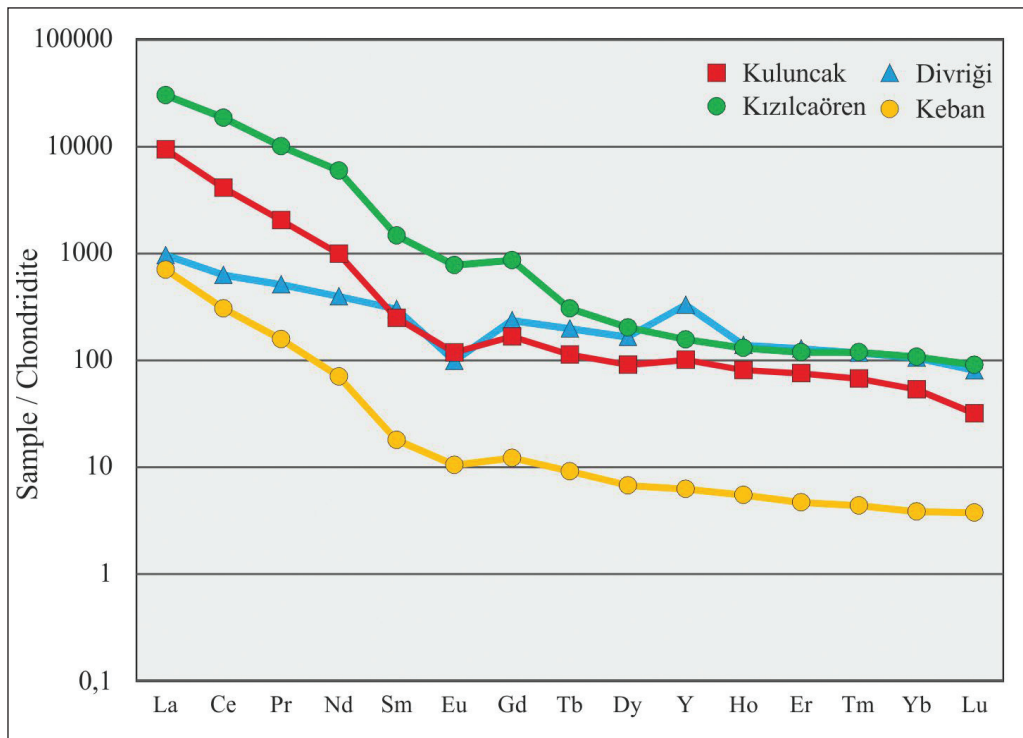


Figure 4- Chondrite normalized REE patterns of Kızılcaören, Kuluncak, Keban and Divriği Fluorite-REE mineralization. A decrease from LREE to HREE is clearly seen in the chondrite normalized patterns of the four deposits.

detected by Özgenç and Kibici (1994). Fluid inclusion data for the Kuluncak fluorites give homogenization temperatures ranging from 145-600°C with salinities between 4-64 % NaCl equivalent, broadly similar to results for the Kızılcaören deposit (Altuncu, 2009).

### 3.3. Divriği Fluorite-REE-Cu Mineralization

The mineralization in Divriği district of Sivas province is located within the Efendi River at elevations of 1600 m in Paleocene-Eocene (Boztuğ et al., 2007) alkali granites (Figure 3). The mineralised zone has a thickness ranging from 0,6 to 1 m at the surface and a length of approximately 300 m. It was discovered in 1958 by MTA during uranium exploration where investigations, including drilling, revealed 50m long galleries and an estimated 35,000 tons of Cu-fluorite mineralization. The center of the ore vein is green fluorite and the wall zones are rich in chalcopyrite, galena and sphalerite. The ore also includes arsenopyrite, pyrite, bismutinite, covellite, chalcocite calcite, quartz, clay (possibly kaolinite) and limonites after pyrite.

The average TREE value of 6 fluorite-rich samples is 1363 ppm (Table 1), and the REE pattern dominated

by LREE is typical. The ore samples contain very high levels of Y with an average of 698,5 ppm (Table 1). Fluid inclusion studies on fluorite indicate hydrothermal solutions at temperatures ranging from 190-455 °C and salinity ranges between 10-32% (NaCl weight equivalent) (Altuncu, 2009).

### 3.4. Keban Fluorite-REE Mineralization

Keban Fluorite-REE mineralization occurs as veins within Permo-Triassic calcareous schists. The schists are cut by the Upper Cretaceous Keban syenites (Kuşcu et al., 2013) and numerous syenite porphyry dykes and Fluorite-REE mineralizations are common in the region. Fluorite mineralizations consist of stockwork veins reaching one meter in thickness and contain 540 ppm TREE in average (Table 1). The amount of Pb and Zn is higher among the trace elements (Table 2). Fluorite specimens contain fluid inclusions with two and three phases and homogenization temperatures range from 125-600°C with salinities from 7-61% (NaCl equivalent) (Altuncu, 2009). The three-phase fluid inclusions show resemblance with Kızılcaören, Kuluncak and Divriği ores. The REE pattern of the Keban mineralization is enriched in LREE, similar to three deposits described above (Figure 4).

#### 4. Bauxite Deposits and REE Contents of Source Rocks

All bauxite deposits in Turkey are located in the Taurus belt except for the Kokaksu (Zonguldak) deposit (Figure 1). Some of these bauxite deposits and their source rocks (protoliths) contain significant REE and therefore may be a potential source, given Chinese production of REE from clays in the ion adsorption deposits. Therefore, we have investigated the chemistry of the bauxite deposits and their source rocks in the Taurus belt to enable comparison with both bauxite and protolith compositions for the REE deposits in China (Tables 1 and 2). Some data were taken from Karadağ et al. (2006) and Haniççi (2013).

REE contents and chemical composition of bauxite deposits in Turkey are recorded in tables 1 and 2. This data includes: bauxite and phyllitic source rocks in the Seydişehir region by Karadağ et al. (2009); red mud waste from the Seydişehir bauxite deposits, by Karadağ et al. (2006) and Deady et al. (2016b); the Kemiklitepe and Kızıldağ bauxites and the slate protoliths of Kızıldağ bauxites in the Bolkardağı region by Haniççi (2013); and the Yalvaç-Şarkikaraağaç bauxites and basaltic protolith in the Isparta region (this study). REE analyses indicate wide variation with highest REE values in the bauxites and protolith of the Bolkardağı region, comparable to the values for the REE deposits of the Ganzhou region in China (Table 1). The REE contents of bauxite and protoliths of Bolkardağı region are largely similar to REE elements in Ganzhou region clays in China (Figure 5).

##### 4.1. Mortaş and Doğankuzu Bauxites

The Mortaş-Doğankuz bauxite deposits are located in the discordance line Cenomanian-Turonian of the Upper Cretaceous limestones (Karadağ, 1987; Öztürk et al., 2002, Figure 6a). The provide ore is for the Seydişehir alumina smelter. At the bottom and top of the bauxites, and also along internal fracture lines, are greenish-colored zones rich in fine grained pyrite and marcasite. The TREE values of the Mortaş bauxites range between 282-986 ppm (Karadağ et al., 2006). The red mud waste from alumina production contains approximately 80 ppm Y and 1777 ppm TREE (Deady et al., 2016b) (Table 1). However, analysis by Karadağ et al. (2006), gave 1966 ppm TREE, including both Y and Sc.

##### 4.2. Yalvaç-Şarkikaraağaç Bauxites

The Yalvaç-Şarkikaraağaç bauxites are observed in three main zones within Upper Jurassic units in the Isparta region that extend for tens of kilometers (Ayhan and Karadağ, 1985). Each zone developed from weathering of Jurassic basalt with the transition from basalt to bauxite clearly evident, as shown in figure 6b. These bauxites are the only deposits identified on basalt protolith within the Taurus belt and their iron-rich character has prevented production, despite large reserves. The low TREE value of 293 ppm and uranium content of 1 ppm, 10 times less than other bauxites, reflects the low values within the basalt protolith (Table 1).

##### 4.3. REE Content of the Bolkardağı Bauxites and Source Rocks

The geology and geochemistry of the bauxites in the Bolkardağı region and protoliths were detailed by Haniççi (2013). These bauxites developed on Lower and Upper Triassic shales (Figures 2 and 7) and show enrichment in REE. Among bauxites in the region, especially the shales, which are the source rock (protolith) of the Kızıldağ bauxites, and the Kemiklitepe bauxites show enrichment in terms of HREE and their average TREE values are 1545 and 1693 ppm, respectively (Table 1). The REE composition of the Kemiklitepe bauxite deposit and the Lower Triassic shales which are the source rocks of the Kızıldağ bauxite mineralization, show one to one resemblance with REE values of the Guangzhou clays in China (Table 1). The low U and Th contents of the clays, bauxites and bauxite protoliths when the compared to hydrothermal and placer type REE mineralization (Table 1) provides a significant advantage in processing due to minimal radioactive waste.

The Lower Triassic shales forming the protolith of bauxites in the Bolkardağı region were probably derived from the Ordovician Seydişehir schists because of the similarity of REE patterns and absence of granite or aluminosilicatic metamorphic rocks in the region. The bauxites developed in the Upper Triassic-Aalenian (Middle Jurassic) period (Haniççi, 2013), when the pre-Aalenian Tauride Anatolide continent should have been located in tropical latitudes suitable for lateritic soil development. As a result, it is likely that significant REE resources would have been stored in the Upper Triassic clays of the Tauride-Anatolide



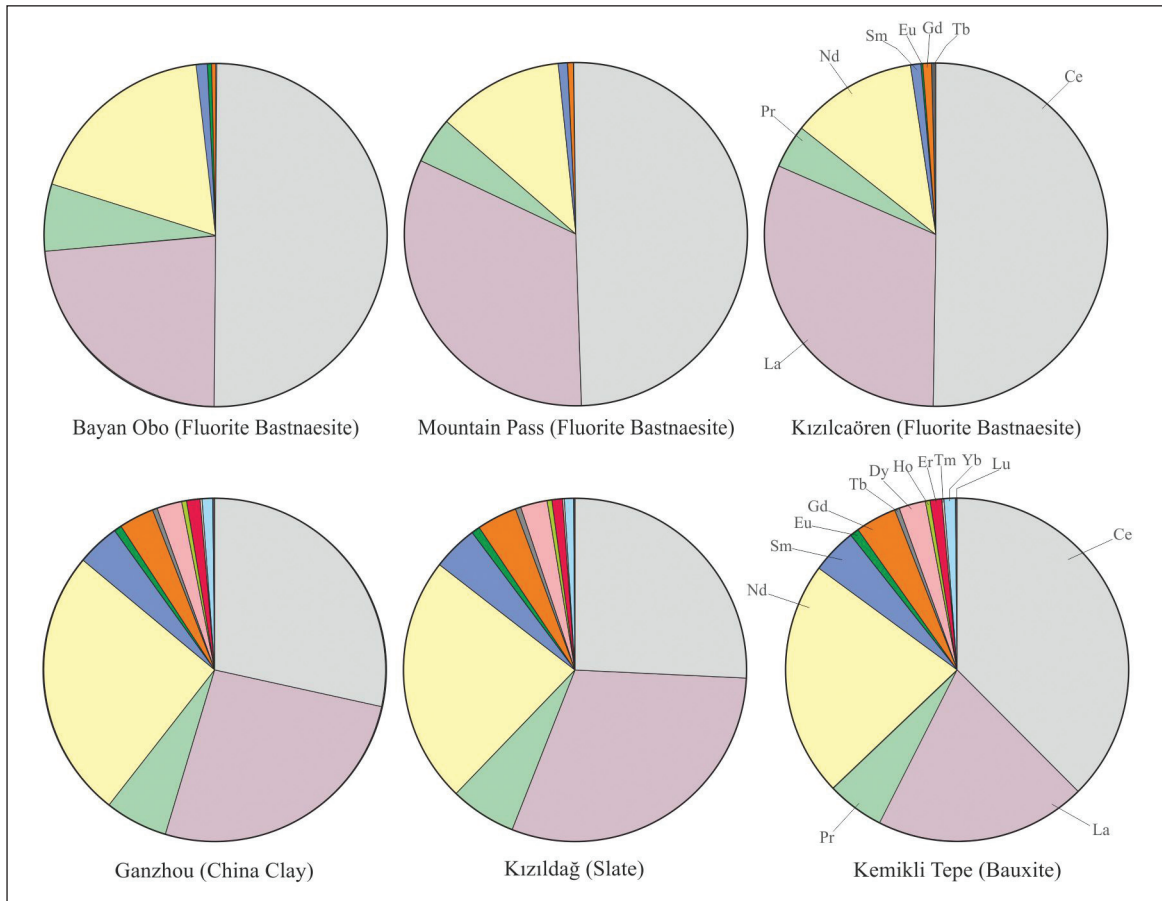


Figure 5- Comparison of REE abundance in the Bayan Obo (China), Mt. Pass (USA) and Kızılcaören REE deposits associated with carbonatite-alkaline magmatic rocks (top row), and the clay based Ganzhou region deposits with the Lower Triassic slate protoliths of the Kızıldağ bauxites and Kemikli Tepe bauxites (bottom row). Data for Bayan Obo and Mt. Pass deposits from Haque et al. (2014); for Kızıldağ and Kemikli Tepe from Haniççi (2013). The REE composition, the Kızılcaören deposit resembles the well-known carbonatite deposits (Mt Pass, USA and Bayan Obo, China), while the REE profile and abundances for bauxite and Triassic slate protoliths from the Bolcardağı region resemble deposits of the Ganzhou province in China.

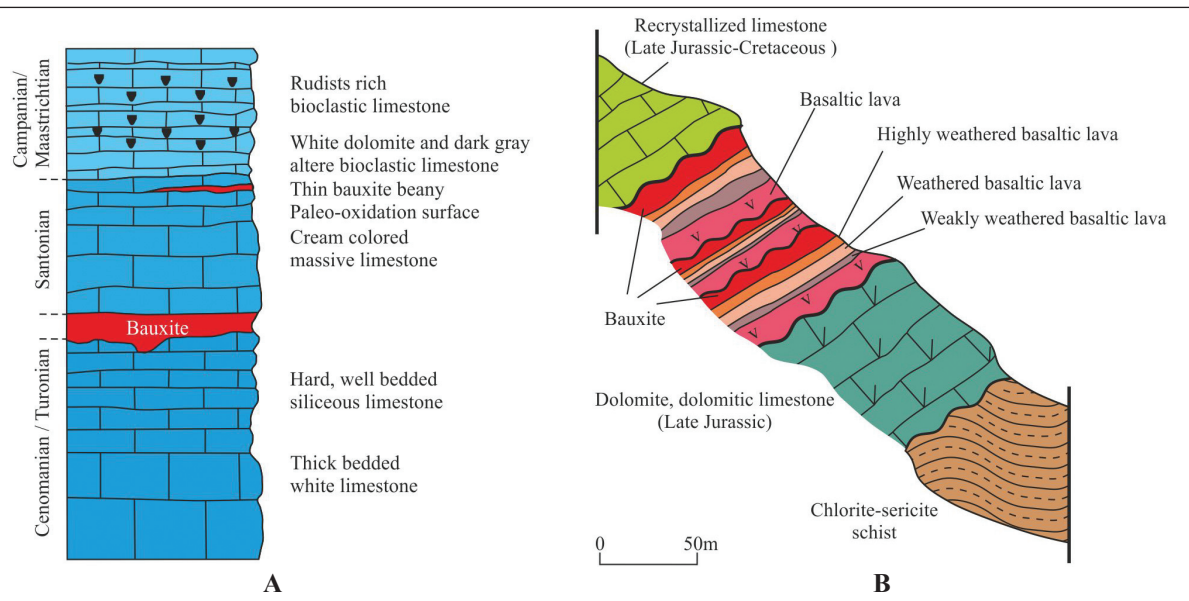


Figure 6- Section showing wall rock relationships of (a) Mortaş and Doğankuzu bauxite deposits, and (b) Yalvaç-Şarkikaraağaç bauxites. The different REE contents of both bauxite deposits (see table 1) clearly indicates their different source rocks.

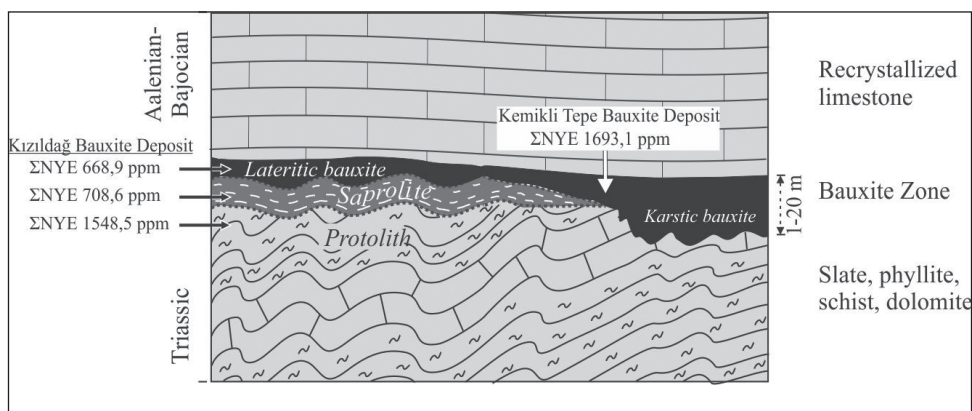


Figure 7- Relationship of the Triassic shales which are source rocks (protolith) of bauxite and the bauxites in Bolkardağı province (Hanilçi, 2013).

belt. Clay grains formed during lateritic weathering will balance any electrostatic charge deficit at their outer margins with ions of  $\text{Ca}^{+2}$ ,  $\text{Na}^{+1}$ ,  $\text{NTE}^{-3}$  etc. leading to enrichment by adsorption on to their outer surface. This process can lead to REE enrichment in clays and their subsequent incorporation into bauxites.

## 5. REE and Heavy Mineral - Bearing Placer Formations

The Çanaklı REE and heavy mineral-bearing mineralization in the Burdur region (Figure 2) is a unique placer formation that is relatively HREE -rich. The mineralization is a terrestrial accumulation of the Plio-quaternary limestones. Drillings has defined reserve of 80 million tons in the Canaklı-1 area with approximately 808 ppm TREE, and grades of 0.72%  $\text{TiO}_2$  and 490 ppm  $\text{ZrO}_2$  and 414 million tons of reserve with 627 ppm TREE, and grades of 0.7%  $\text{TiO}_2$  and 404 ppm  $\text{ZrO}_2$  in the Çanaklı-2 region (Cox et al., 2013; Deady et al., 2016a). The major minerals containing REE are allanite, celvkinite, titanite and apatite, and the minerals containing thorium and uranium are torite, uranotorite and betafite. It was reported that this mineralization was the result of terrestrial decomposition of a Pliocene alkaline volcanic eruption (Cox et al., 2013)

## 6. Sedimentary Phosphorites

Marine sedimentary phosphorite deposits are regarded as the world's most abundant and clean REE mineral deposits (Emsbo et al., 2015). TREE values of the phosphorites in different age ranges ranging from Paleozoic to recent in different regions of the world reached 1200 ppm (0.12%). REE substitutes

for Ca in flour-apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) as does Sr and U. Within Paleozoic phosphate deposits in the USA, there are varying amounts of TREE (900-1200 ppm) and HREE (400-600 ppm). According to Emsbo et al. (2015), these HREE values are higher than in deposits currently operated by China (50-200 ppm). The phosphorites are likened to REE of the deep sea muds (Kato et al., 2011) both because of their negative Ce pattern and high values (Emsbo et al., 2015).

Phosphate deposits are located in cherty levels of the Upper Cretaceous limestones around Mazıdağ (Mardin) in Turkey. This deposit is made up of three main mineralized zones called Taşıt at the bottom, Kasrik in the middle and Şemikan at the top. Etibank identified total reserves of 330 million tons (Apaydın and Erseçen, 1981) with 270 million tons at a grade of 10-12%  $\text{P}_2\text{O}_5$ , 30 million tons with a grade of 22%  $\text{P}_2\text{O}_5$  and 30 million tons of calcareous ore requiring calcination with a grade of 14%  $\text{P}_2\text{O}_5$ .

The Eti Bakır Company has initiated work to build a modern plant for phosphate production and carried out additional drilling studies in the deposit since 2013. The most important mineralization is the upper Şemikan phosphate zone (Imamoğlu et al., 2009) and REE analyses were carried out on four specimens taken from this zone. It consists of 1,5-2 m thick, massive phosphate ore with shark teeth fossils, overlain by two or three thin phosphate levels (10-20 cm) among thin chert bands and white massive chert (Figure 8). TREE values are extremely low at 40 ppm (excluding Y), similar to the lateral equivalent of the Jordan deposit (Al-Shereideh et al., 2010), with a typical negative Ce anomaly. Uranium values are relatively high at 71 ppm (Table 1).

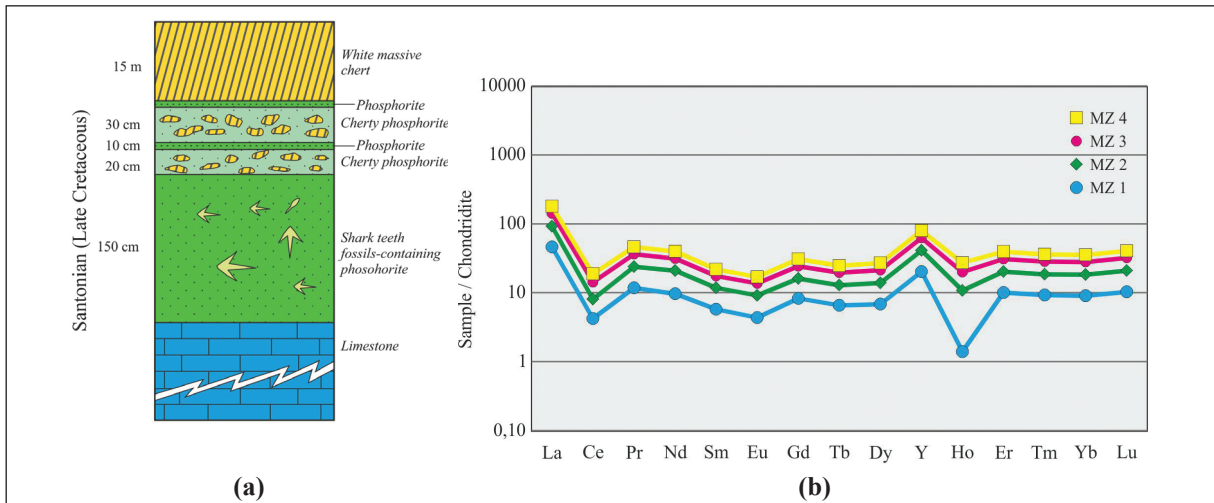


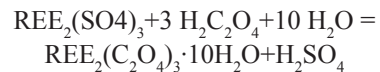
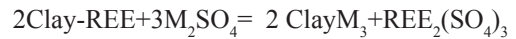
Figure 8- (a) Stratigraphic position and (b) the chondrite normalized REE pattern of the Mazıdağ phosphorites. The horizontal REE pattern indicates that HREE and LREE did not differentiate. Mazıdağ phosphorites with their strong negative Ce and Ho and positive Y anomaly and low REE pattern resemble the Jordanian phosphorites.

### 7. Discussion and Results

REE deposits associated with carbonatite-alkaline magmatism in Turkey are in the form of vein type hydrothermal-pegmatitic fillings and rich in LREE like La and Ce. They exhibit mineralogic and geochemical similarities to USA’s Mt. Pass and China’s Bayan Obo deposits. At the same time, the Kızılcaören REE-Ba-F-Th deposit is also contains significant levels of Th with 10 samples averaging 1072 ppm Th. Due to radioactive elements such as Th and U in these deposits they can often be detected with relative ease, however their exploitation and processing can result in environmental and public health problems occurs during the REE production. Similar problems are to be expected from exploitation of placer deposits linked to alkaline magmatism, such as Canaklı.

In contrast, the clay-based HREE deposits contain minimal radioactivity and can be exploited with blasting and rock breaking, resulting in lower mining costs. In this context, it is necessary to seriously consider the recovery of REE from the HREE-rich shales and clayey schists of the Bolkardağı region. For example, mining operations at more than 200 deposits located at 24° northern latitudes in Jiangxi province, southern China, REEs are stripped from the exterior of clays by ion exchange. The recovery rate of TREEs from these deposits ranges from 40% to 85% with an average of about 70%. TREEs of the deposits (including Y) range between 300-6500 ppm (Roskill, 2011) and their average is around 1500 ppm. In ore recovery, the application of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> leads to NH<sub>4</sub><sup>+</sup> entering the

clay with REE being adsorbed to form REE<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Wu et al., 1990, Chi and Tian, 2008). Addition of oxalic acid forms REE oxalate (REE<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>) precipitate that is heated to 900°C to leave a REE oxide residue (Papangelakis and Moldoveanu, 2014). These REE oxides are then subject to individual REE element separation. According to Papangelakis and Moldoveanu (2014), the recovery of REE from clays occurs in the following reactions:



REE recovery can proceed by tank leach or heap leach, with NaCl used in previous times because of its ability to ion exchange, instead of ammonium sulfate. The production from clay based REE deposits in China constituted 26% of China’s total REE production between 1988 and 2007, and has increased to 36% after 2009 (Yang et al., 2013). Recovery of the HREEs is lower due to their stronger bond with clays. The very low level of U and Th eliminates any problems linked to radiation and REE acquisition from clays is increasingly preferred.

In Turkey, shales rich in REE occur on the Tauride-Anatolide platform and include the Ordovician Seydişehir schists (Monod, 1967) with TREE of 300 ppm (Karadağ et al., 2009) and the Lower Triassic shale-slates in the Bolkardağı region contain much

higher TREE (Table 1, and Haniççi, 2013). Figure 9 shows the similarity between chondrite-normalized patterns of the Triassic shale-slates and Seydişehir phyllites. Under tropical weathering conditions during the Triassic, it is likely that clays developed on the Seydişehir phyllites contained TREE of between 500-1800 ppm, based on REE enrichment in China. If these REE-enriched clays were eroded into a sedimentary basin during the Triassic, it could explain the similarity between the chondrite-normalised REE patterns of the Ordovician Phyllites and Triassic shales-slates. Subsequent exposure and tropical weathering of these Triassic sediments would then give rise to the bauxites in the Bolkardağı region with relatively high REE content. The Triassic bauxite and shales were subsequently covered by marine carbonates in the Jurassic and metamorphosed to lower greenschist facies during Cretaceous-Eocene orogenesis (Haniççi, 2013).

Our study indicates that the occurrence of REE-enriched Triassic shales and slates, and potentially economic REE deposits in the some Triassic-Jurassic bauxites of the Bolkardağı region can be explained by the REE content of the Ordovician Seydişehir phyllites and their exposure to tropical weathering during the Triassic. Interestingly, the chondrite-normalized

REE patterns in the deposits of the Ganzhou region in China are similar to the REE patterns of bauxite and its source rocks in the Bolkardağı region (Figure 9). In addition, the clay-based REE deposits in China are enriched by a factor of six compared with the REE content of the Mesozoic peraluminous granites (average 350 ppm TREE) which form the protolith. This REE enrichment factor is comparable to the difference between the REE content of the Seydişehir phyllites and Triassic shales-slates (Table 1). These comparisons indicate that the Triassic shales-slates of the Tauride belt warrant further investigation for bauxite-associated REE deposits.

Operating deposits in the Ganzhou region of China have TREE grades (including Y) > 500 ppm. Deposits with reserves >0.5 million tons are classified as large, and between 0.5-0.05 million tons are medium-size (Sanematsu and Watanabe, 2016). Ore zones are usually 6-10 meters thick, locally 30 m, and rarely reaching 60 m (Yang et al., 1981; Chen, 2011). The protolith is mainly ilmenite type granite, and very rarely on phyllites (Zhang, 1990). The estimated reserve of REE deposits in China (excluding potential resources) is around 15 million tons (Sanematsu and Watanabe, 2016). Factors such as degree of weathering and the specific REE-bearing mineralogy (bastnasite,

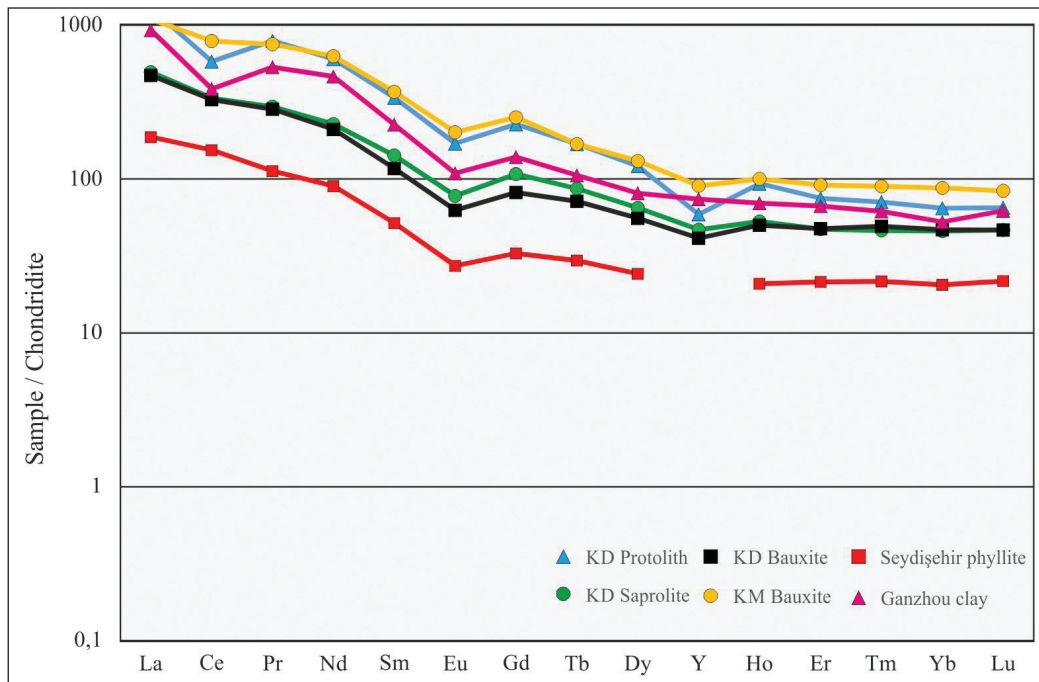


Figure 9- Comparison of chondrite normalized REE patterns of the clays from which REE is produced in the Ganzhou region of China and bauxite in the Taurus belt and its possible source rocks (KD: Kızıldağ, KD Pro: Kızıldağ protolith, KD Sap: Kızıldağ saprolite, KM: Kemiklitepe).

fluorite, apatite, allanite, xenotime etc.) determine the activation and fractionation of REE (Yusoff et al., 2013). For example, in the uppermost soil zone there is a positive Ce anomaly, due to oxidation of Ce from +3 to +4 and accumulation in the form of  $CeO_2$  with a corresponding Ce depletion in the REE accumulation zone beneath it (Berger et al., 2014). Whilst there are similarities between the Triassic shales and bauxites of Turkey and the chondrite normalized patterns and REE contents of the “Ion Adsorption Type” ore in China, there are significant differences to be considered in evaluating the potential of the Bolcardağı region bauxites. For example, with granitic protolith REE can be transported at surface conditions by bonding with carbonates and bicarbonates ( $REECO_3^+$ ,  $REEHCO_3^{2+}$ ; see Liu and Byrae, 1998), and also fluorides and organic complexes (Chen et al., 2001) when HREE bond more strongly with organic complexes. In addition, the host mineralogy can be more important than the chemical complex. Whereas REE are adsorbed on the outside of clays in China and can yield high recoveries in processing, in Turkey the bauxites have experienced low grade metamorphism and REE are more likely to be hosted within the crystal lattice and yield lower recoveries. Therefore, any new evaluation of the bauxite-related REE potential in the Bolcardağı region and Tauride belt will need to understand these differences and their potential impact on the size of the resource base required for viable operations.

In contrast the Cretaceous phosphorite occurrences in Turkey contain only one twentieth of the REE content of the REE-rich phosphorite deposits elsewhere in the world and are clearly uneconomic as a source of REE. Nevertheless, investigation of the REE potential of phosphatic sediments in the Lower Paleozoic belt in Turkey should not be ignored.

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