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Explanation of the Sutlegen Bauxites to Some REE Contents by Statistical Approach and Inequality Expressions

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Keywords

Bauxite

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Abstract

Bauxite formation is usually possible in humid and tropical weather conditions with the enrichment of minerals containing Al_2O_3 in the environment. These minerals are found in chemical compositions that are rich in major and trace elements, and REEs. Karst-type bauxites have different characteristics in terms of REE and trace elements since they undergo alteration processes. Various correlations can be evaluated using geostatistical methods to reveal the behavior of these elements in bauxitization processes. The REE contents of the Sutlegen bauxite deposits were obtained by conducting ICP-MS analysis. The inequality expressions of the La element, which is in the lanthanide group of the periodic table and is included in the light rare earth elements, with Y element, the heavy and transition metal, has provided information about the formation conditions of bauxite. The arithmetic mean of the La/Y ratios of bauxites was found to be 0.25, and the ore formation condition was interpreted as acidic. Therefore, ∑REE concentrations of the Sutlegen bauxite deposits were associated with ∑LREE/HREE and La/Y ratios. ∑REE concentration was found to be positively correlated with the ∑LREE/HREE and La/Y ratios, and the correlation coefficients were found to be 0.89 and 0.44, respectively. The positive correlation between ∑REE concentration and La/Y ratio can be interpreted that the pH in the bauxite formation environment has a positive effect on REEs. Under the acidic conditions of ore formation, the bauxites were enriched in REEs.

Cite

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1. INTRODUCTION

In bauxite formation processes, the rare earth element (REE) concentrations, as well as the characteristics of the environment, vary due to chemical alteration processes (Maksimovic & Panto, 1991; Yalcin & Temur, 2006; Yalcin & Ilhan, 2008; 2013; Kansun et al., 2010; Nyamsari & Yalcin, 2017; Nyamsari et al., 2019; 2020; Sidibe & Yalcin, 2019; Yalcin et al., 2012; 2016a). Rare earth elements are studied under two groups: light rare earth elements (LREEs) and heavy rare earth elements (HREEs). Bauxite formation depends on ambient conditions (Atakoglu & Yalcin, 2021). For bauxite formation, the upper soil horizon is enriched with trace elements such as Fe, Al. Acidic or alkaline conditions with pH varying between 4-5 are provided (Yang et al., 2019). With the effect of erosion, the chemical decomposition of the elements in the soil increases, trace and REE group elements decrease or increase, thus providing acidic or alkaline conditions. In order to understand these conditions that develop in the bauxite formation environment, the concentrations and ratios of some REE and trace elements should be looked at. The relationship of Y element, one of the transition metals, with lanthanides provides information about the pH conditions in the formation of bauxite (Maksimovic & Panto, 1991). In bauxite formation processes, chemical decomposition reactions and the concentrations of REEs are affected by the other major and trace elements (Yalcin & Ilhan, 2013; Yalcin et al., 2013; 2015; 2019a; 2020;

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Ozer & Yalcin, 2019; 2020). Several studies in the literature on associating the behavior of REEs with the ore formation environment are as follows:

In the study conducted in four selected bauxite deposits in former Yugoslavia and Greece, the La, Y, and REE concentrations were determined by Maksimovic & Panto (1991). The characteristics of the ore formation environment were revealed using the La/Y ratios, and the findings were evaluated using the ∑REE concentrations. REE concentrations and the values of the elements of Y and La-Lu were analyzed for 4 different karstic bauxite deposits in former Yugoslavia and Greece. The formation patterns in bauxite deposits were suggested based on the values of the chemical concentrations (Maksimovic & Panto, 1991).

In the study conducted on Henan Baofeng bauxite deposit in China, major elements, trace elements, and REE concentrations were analyzed. The value of La/Y inequality was investigated to interpret the conditions of the ore formation environment. The rare earth element behavior of the ore, whose formation environment was interpreted, was associated with the value of La/Y inequality (Yang et al., 2019).

In the study on the Mandan and Deh-Now bauxite deposits, the REE concentrations were revealed and correlated with the pH conditions of the environment. According to the results of the study, the relationships between the major and trace elements and REEs that played a role in the formation were evaluated, and the sedimentary environment conditions were interpreted (Zarasvandi et al., 2012).

The study area covers the Sutlegen bauxite deposits in the Kas district of the province of Antalya. Interpretation of the origin and formation conditions is important for the bauxite raw material, which has economic value. Therefore, the formation conditions of bauxite were interpreted using the inequality expressions in the present study.

In the literature, no study was found on the interpretation of the ore deposit formation conditions using statistical approaches. In this context, the study was carried out for the statistical explanation of the correlation between the La/Y ratios and REE concentrations of the bauxite deposits. Besides, the correlation between pH conditions and REE concentrations was also evaluated statistically in the study.

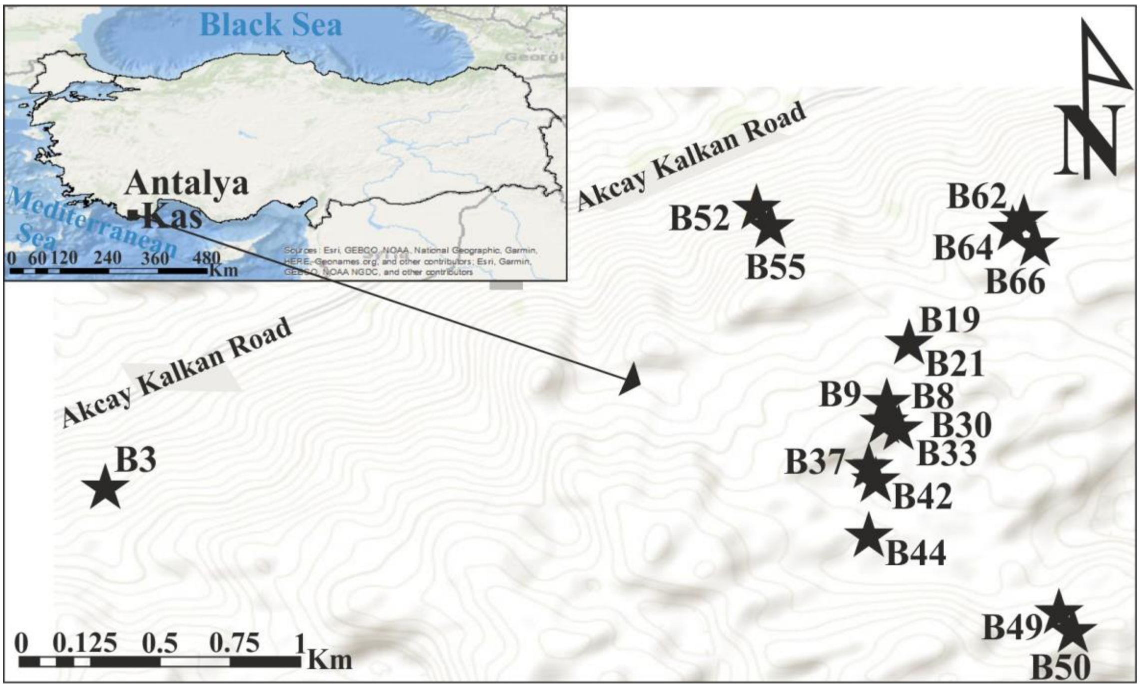

***Figure 1.** Site Location Map of the Study Area*

2. MATERIAL AND METHOD

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method was used to determine La, Y and REE concentrations of the Sutlegen bauxite deposits. Then, the statistical analysis of the findings of the ICP-MS method was conducted using the SPSS23 software package. The coordinate information of the samples collected from the Sutlegen was processed on the Turkey map using Arcmap 10.7 program and distribution maps were created.

3. REGIONAL GEOLOGY

The study area is located within the boundaries of Beydaglari carbonate rock association and Katran Mountain (Figure 2). Beydaglari autochthonous, which is composed of rocks showing angular unconformity, consists of neritic limestones and clastic units deposited in the Upper Cretaceous-Miocene age range (Keser & Ozel, 2008). The units belonging to the Beydaglari autochthon on the exposed surfaces of the study area are listed as follows; Beydaglari formation consisting of Jurassic-Upper Cretaceous neritic limestones, Gomuce member which is Burdigalian aged algal unit, Caybogazi member as Burdigalian aged clayey unit, Kibrisdere member consisting of clayey limestones, Sinekci formation which is Burdigalian aged consisting of claystones, Kasaba formation which is Upper Burdigalian-Lower Langhian sandstone and conglomerate, Felenkdagi conglomerate which is Upper Langhian-Serravallian aged siltstone unit (Keser & Ozel, 2008). Allochthonous units in tectonic relationship on Beydaglari are Elmali formation consisting of Upper Lutetian-Lower Burdigalian aged neritic limestones and Mandirkaya formation consisting of Liassic-Upper-Cretaceous clastic units. The youngest units in the region are represented by alluvium and slope debris (Keser & Ozel, 2008) (Figure 3).

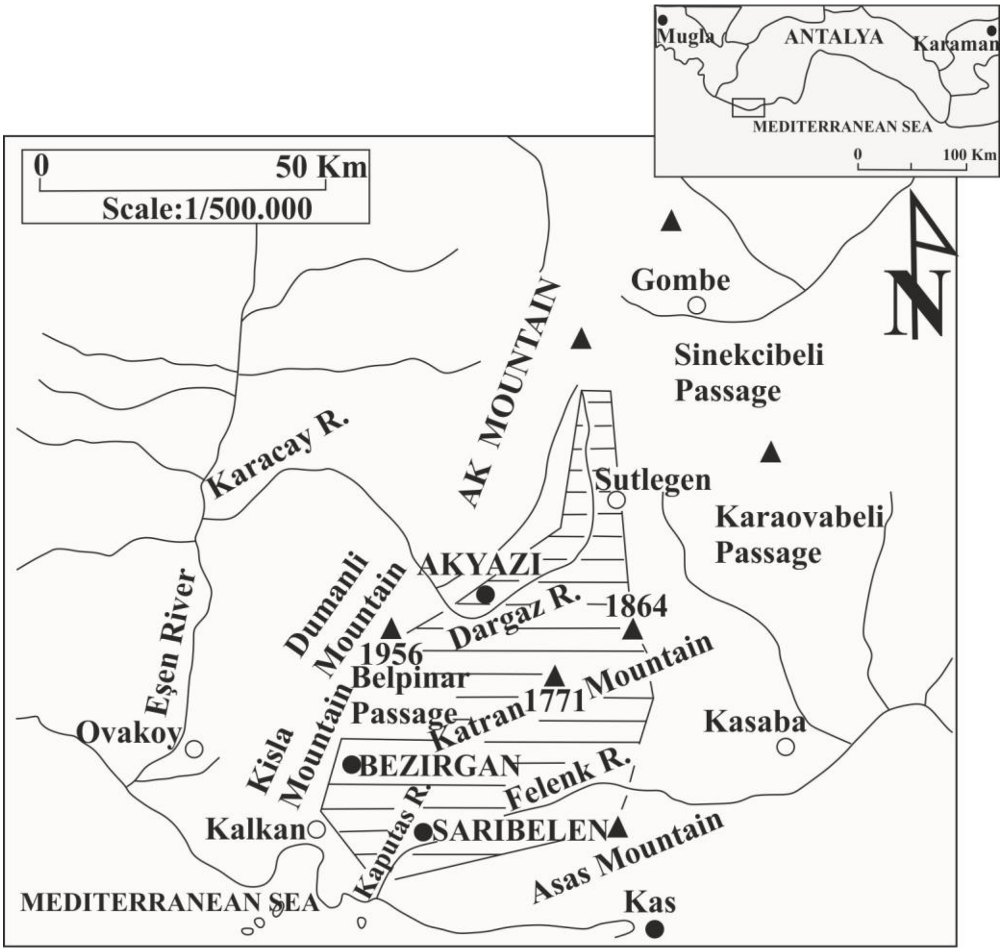

Figure 2. *Boundaries Map of the Study Area (modified after Keser & Ozel, 2008)*

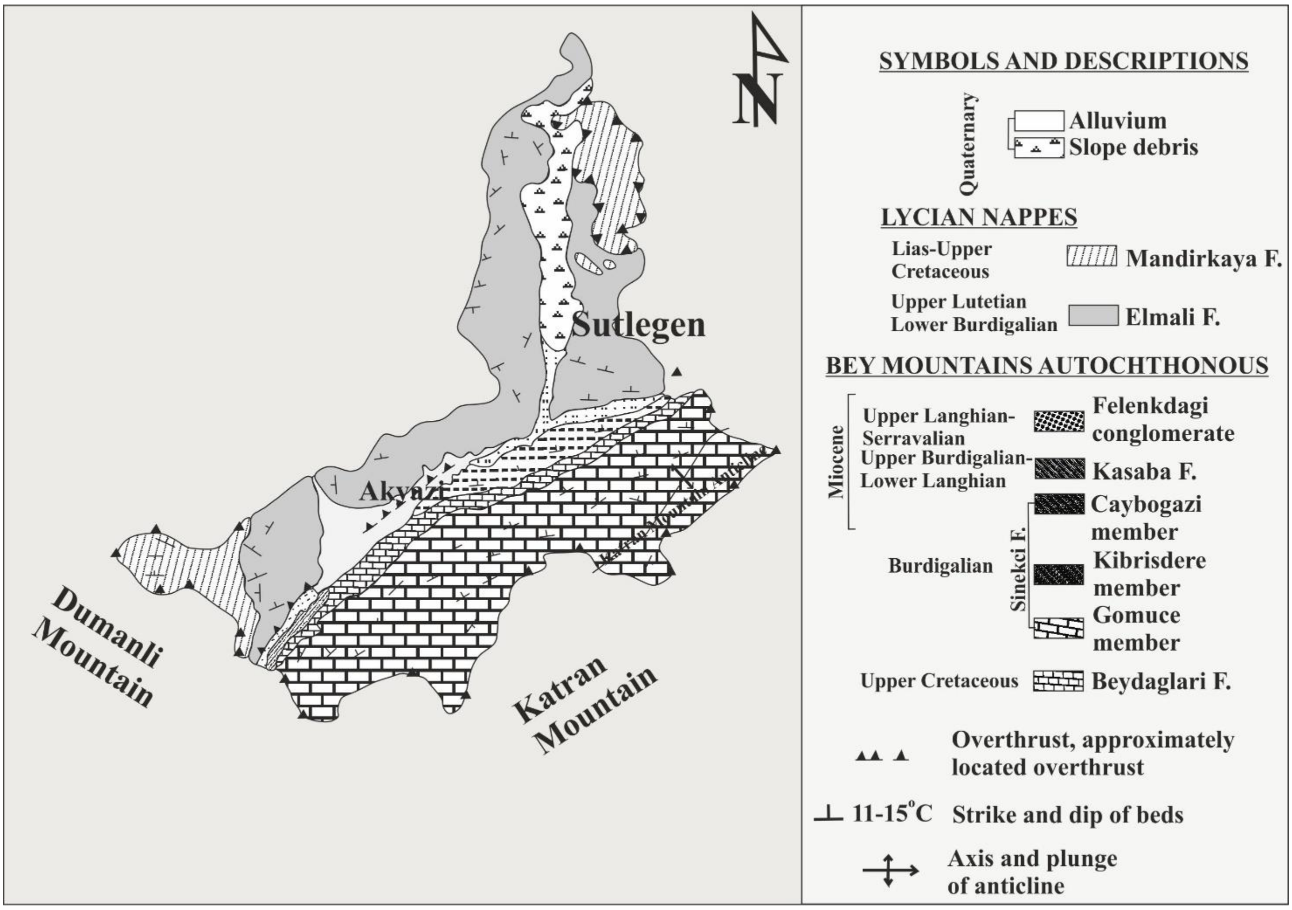

Figure 3. *Regional Geologic Map of the Study Area (modified after Keser & Ozel, 2008)*

4. RESULTS AND DISCUSSION

REE element contents of 17 samples collected from the study area were revealed by conducting ICP-MS analysis (Table 1). The inequality expressions suggested for the La/Y concentrations by Maksimovic & Panto (1991) and Zarasvandi et al. (2012) are as follows (1), (2):

$$La/Y < \text{Acidic conditions} \quad (1)$$

$$La/Y > \text{Alkaline conditions} \quad (2)$$

The findings were compared with the values of other karstic-type bauxite deposits in the literature. On the other hand, in the study conducted on the Henan karstic-type bauxite deposits in China, the bauxite formation condition was found to be generally alkaline (Yang et al., 2019). The La/Y ratio of the Grebnik karstic bauxite deposit was found to vary between 0.5 and 4; thus, it was interpreted that the transition from acidic to alkaline conditions could be possible by a carbonate contact (Maksimovic & Panto, 1991). The box plot used for descriptive statistics is given in Figure 4.

ΣREE, ΣLREE (La-Sm), ΣHREE (Gd-Lu), and ΣLREE/HREE values are given in Table 2. In the study conducted on Baofeng bauxite deposits, the value of the coefficient of determination (R^2) of the model which was designed to explain ∑REE using the ∑LREE/∑HREE ratio was found to be 0.57. On the other hand, the R^2 value of the model which was established to explain ∑REE using the La/Y ratio was found to be 0.55. The positive correlation found was associated with source rocks that played a role in the ore formation. It was interpreted that pH played a critical role in ∑REEs, and it increased in total ∑REE concentration under alkaline conditions (Yang et al., 2019).

Table 1. *REE Elements Results and La/Y Ratios of the Sutlegen Bauxites (ppm) (Ozer, 2020)*

Sample Code	Latitude	Longitude	Ce	Dy	Er	Eu	Gd	Hf	Ho	La	Lu	Nd	Pr	Sc	Sm	Tb	Th	Tm	U	Y	Yb	La/Y
B3	36.3928	29.5553	81.80	21.30	11.40	3.90	17.70	1.90	4.30	22.00	1.60	70.00	11.80	26.40	18.60	3.30	2.60	1.80	1.50	104.30	10.20	0.21
B8	36.5591	29.5628	52.10	14.70	7.90	2.80	13.40	5.10	2.90	9.10	1.20	46.50	7.70	36.60	11.50	2.40	20.60	1.10	3.50	138.80	7.10	0.06
B9	36.5591	29.5628	20.90	15.80	8.00	3.20	16.10	1.60	3.20	9.80	1.10	52.50	6.90	20.40	14.50	2.60	22.70	1.20	5.00	85.60	7.10	0.19
B19	36.3995	29.5928	48.40	21.20	12.60	2.80	13.20	3.50	4.60	17.60	1.80	19.30	3.40	24.40	10.20	3.00	31.30	2.10	4.70	88.40	11.20	0.11
B21	36.3995	29.5928	6.20	4.00	2.50	0.40	2.40	2.70	0.80	5.20	0.40	4.20	0.90	21.70	1.20	0.50	20.60	0.40	6.10	17.90	2.70	0.72
B30	36.3959	29.5917	13.70	2.70	1.90	0.30	1.50	1.50	0.70	4.60	0.30	5.30	1.20	10.20	1.40	0.40	15.30	0.30	2.90	11.90	2.20	0.29
B33	36.3956	29.5922	60.80	14.30	8.40	2.30	9.70	2.60	3.00	12.40	1.30	27.40	4.40	19.50	9.20	2.00	24.40	1.40	2.20	58.70	8.60	0.21
B37	36.3938	29.5908	46.30	23.60	13.10	3.70	18.80	3.60	5.00	12.50	1.80	32.50	4.20	25.40	14.00	3.50	28.20	2.10	2.70	130.40	11.60	0.05
B42	36.3936	29.5908	9.00	6.30	4.10	0.80	4.60	0.90	1.50	2.90	0.50	5.70	0.90	14.00	2.80	0.90	8.30	0.60	4.20	50.10	3.40	0.37
B44	36.3906	29.5908	45.00	9.30	5.60	1.60	6.30	2.70	1.90	11.80	1.00	22.30	3.50	24.10	7.40	1.40	21.80	1.00	4.30	31.60	6.60	0.48
B49	36.3870	29.5997	39.20	4.10	2.40	0.70	2.70	6.50	0.80	4.90	0.60	9.50	1.60	26.80	3.20	0.50	15.60	0.40	2.10	19.10	2.90	0.25
B50	36.3870	29.5997	31.70	4.60	2.90	0.80	2.90	2.80	1.00	9.30	0.60	12.60	2.50	23.90	3.60	0.60	28.10	0.60	3.00	19.00	4.00	0.09
B52	36.4058	29.5856	10.40	15.30	9.70	1.70	9.10	4.00	3.40	8.30	1.50	9.10	1.70	21.50	5.20	2.10	33.60	1.60	3.90	73.40	9.50	0.46
B55	36.4058	29.5856	10.00	10.60	6.60	1.10	6.00	3.10	2.40	8.00	1.00	7.40	1.40	25.90	3.40	1.40	27.90	1.10	8.50	71.10	6.80	0.24
B62	36.4053	29.5981	5.20	1.10	0.60	0.20	0.90	1.50	0.20	2.70	<0.1	3.70	0.70	10.10	1.10	0.20	27.50	<0.1	2.10	3.70	0.60	0.11
B64	36.4053	29.5981	105.10	16.10	8.40	3.40	14.60	2.80	3.20	22.50	1.20	64.10	11.70	18.50	16.30	2.60	26.80	1.40	2.60	48.10	8.10	0.38
B66	36.4053	29.5981	104.50	20.20	10.10	3.90	16.80	3.10	3.90	18.00	1.40	64.10	11.20	20.50	18.00	3.20	28.20	1.70	2.20	73.80	9.50	0.11
Mean																						0.25
Std. Deviation																						0.18

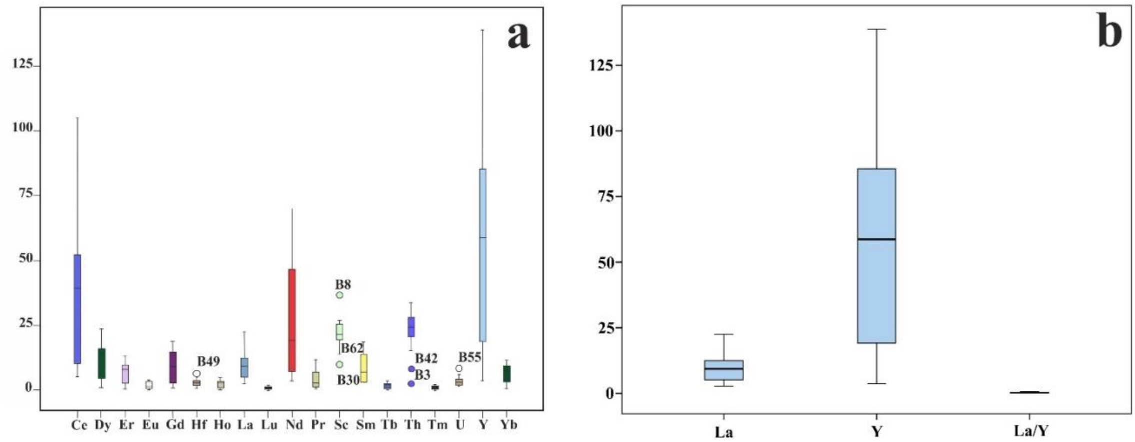

Figure 4*. Box Plot of the* ***a)*** *REE of Bauxite Samples,* ***b)*** *La, Y and La/Y*

As seen in Figure 5, the REE content was found to have a positive correlation with the ∑LREE/HREE ratio, and the correlation coefficient was calculated as 0.89. The ∑REE behavior was observed to increase based on the ∑LREE content. Furthermore, it was observed that the ∑REE contents were positively correlated also with La/Y ratios, and the coefficient of correlation was found to be 0.44 (Figure 6).

The explained variance (coefficient of correlation) (R^2) of the model that was designed to explain ∑REE values using La/Y and ∑LREE/∑HREE ratios was found to be 0.57 (Table 3). In other words, it is possible to explain about 57% of the variability of ∑REE with La/Y and ∑LREE/∑HREE ratios. In addition, the error rate of this model was found to be 0 (Table 4). Therefore, explaining ∑REE with La/Y and ∑LREE/∑HREE ratios is statistically significant (Ozer & Yalcin, 2019; 2020; Aydin et al., 2020; Ozer et al., 2020, Atakoglu et al., 2021; Ince et al., 2021; Yalcin et al., 2021).

Table 2. *The Results of ΣREE, ΣLREE, ΣHREE and ΣLREE/ΣHREE Calculations of the Bauxite Samples in the Study Area (Atakoglu & Yalcin, 2021)*

Sample Code	**∑REE**	**∑LREE**	**∑HREE**	**∑LREE/∑HREE**
B3	295.9	185.6	103.4	1794.00
B8	209.9	115.4	93.6	12329.00
B19	184.6	88.7	101.6	0.87303
B55	86.3	44069	71.4	0.3753501
B62	44038	43902	16.00	0.76875
B21	50.8	43967	41.9	0.3937947
B33	176.1	105	72.7	14442916
B42	54.6	4396	40.9	0.4523227
B44	142.2	82.6	63.1	13090333
B50	97.6	56.1	44.9	12494432
B49	97.4	55.2	44	12545455
B37	206,00	95.5	111	0.85
B64	289.1	203.4	80.1	25393258
B66	297.5	197.8	93.4	2117773
B52	100.6	43980	79.3	0.372005
B30	44.5	440670	43944	10598291
B9	176.2	90.1	83.7	10764636
Mean	14920	82576	685117	11277575
Std. Dvd.	8981668	6347113	28885240	0.6123101

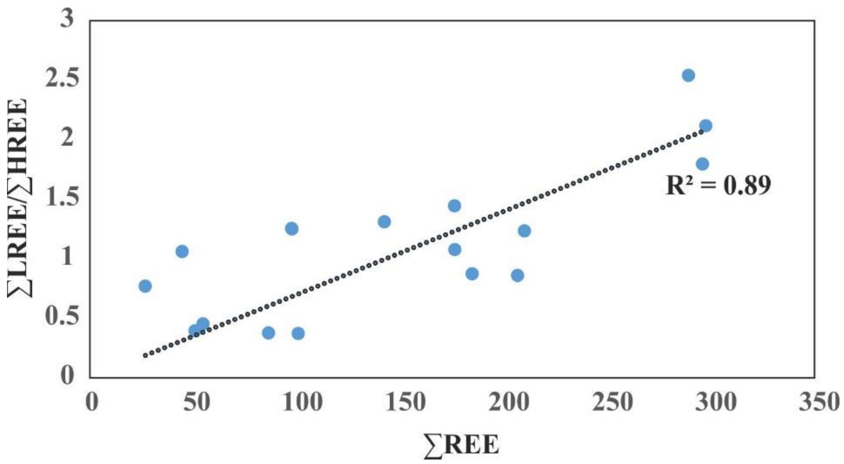

Figure 5. *Simple Regression Scatter Diagrams of ΣREE versus ΣLREE/ΣHREE Ratio*

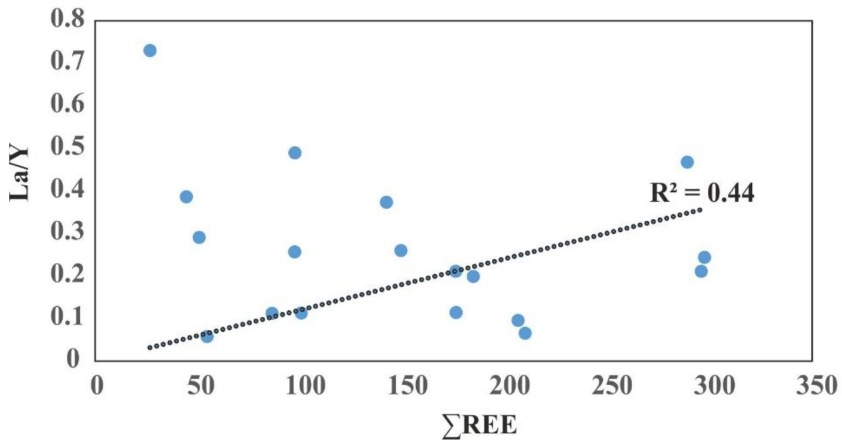

Figure 6. *Simple Regression Scatter Diagrams of ΣREE versus the La/Y Ratio*

Table 3. *Determination Coefficient of the Model Explaining ΣREE using the ΣLREE/ΣHREE and La/Y Ratios*

Model Summary[b]				
Model	R	**R Square**	Adjusted R Square	Std. Error of the Estimate
1	0.76[a]	**0.57**	0.51	0.12
a. Predictors: (Constant), ∑REE, ∑LREE b. Dependent Variable: La/Y				

Table 4. *Error Data of the Model Explaining ΣREE using the ΣLREE/ΣHREE and La/Y Ratios*

ANOVA[a]						
Model		Sum of Squares	df	Mean Square	F	**P-value**
1	Regression	0.30	2	0.15	0.63	**0**[b]
	Residual	0.22	14	0.01		
	Total	0.52	16			
a. Dependent Variable: La/Y b. Predictors: (Constant), ∑REE, ∑LREE						

The results of the correlation analysis performed according to La, Y and La/Y values are given in Table 5. Factor analysis was performed to determine the variance ratios of La, Y and La/Y values and to understand the relationships they established (Yalcin & Unal, 2018; Ozer et al., 2019; Tarinc et al., 2019a, b; Yalcin et al., 2007; 2008; 2019b; Yazici et al., 2021) (Table 6).

Table 5. *Pearson's Correlation Coefficients Calculated using the Results of La, Y and La/Y*

	La	**Y**	**La/Y**
La	1		
Y	0.463	1	
La/Y	-0.060	-0.719**	1

Table 6. *Total Variance Explained According to Factor Analysis*

Total Variance Explained						
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	**Cumulative %**
1	**1.88**	62.78	62.78	1.88	62.78	**62.78**
2	0.94	31.51	94.29			
3	0.17	5.70	100			
Extraction Method: Principal Component Analysis.						

The province polygon with the coordinates was selected and converted to raster data format in Arcmap 10.7 program. Distribution maps were created using the Krigging interpolation method with La, Y and the calculated La/Y ratio values from REE group elements in raster data format (Yalcin et al., 2016b, c, d) (Figure 7).

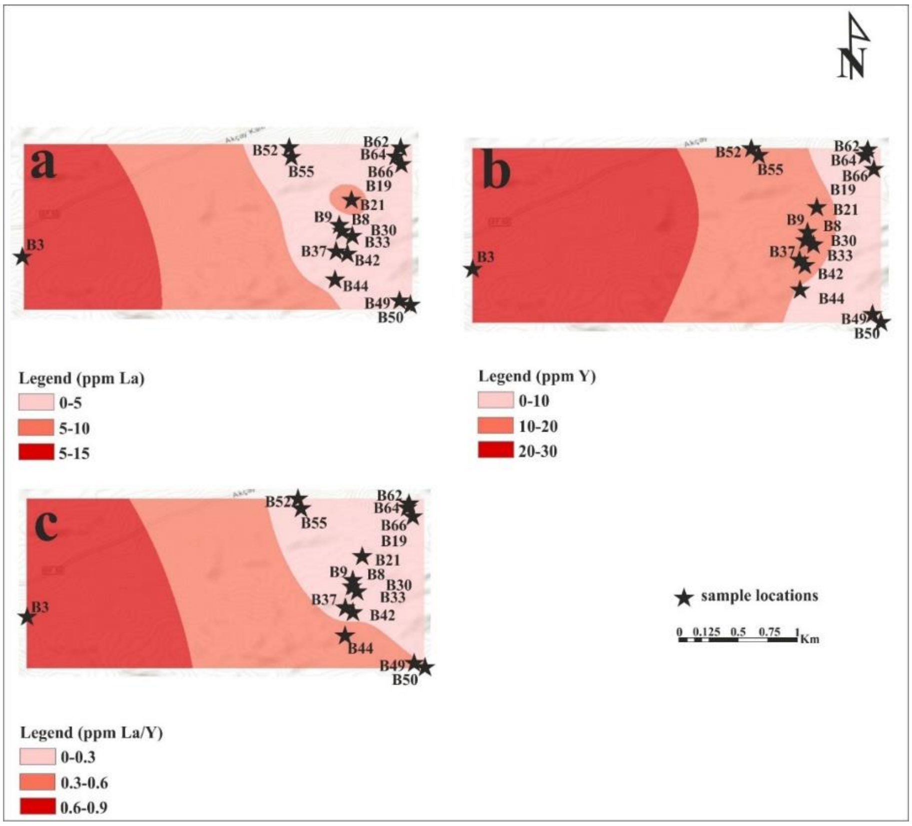

Figure 7. *Spatial Distribution Maps of* ***a)*** *La,* ***b)*** *Y,* ***c)*** *La/Y*

5. CONCLUSION

In this study, the arithmetic mean of La/Y ratios for the Sutlegen bauxites was calculated as 0.25 while the standard deviation was found to be 0.18. It was interpreted that the formation conditions of bauxites were acidic. The positive correlation of La/Y ratios, which were associated with the pH values of the ore formation environment, with ∑REE provided the information that bauxites that were formed under acidic conditions were also enriched in REEs. The positive correlation of La/Y ratios, which were associated with the pH values of the ore formation environment, with ∑REE provided the information that bauxites that were formed under acidic conditions were also enriched in REEs. In the case of the Sutlegen bauxites, it was found that the ∑REE concentrations increased under acidic conditions (pH <1), and the established model was statistically significant. According to the correlation analysis, there is a high-order negative-intermediate correlation between Y and La/Y. The data were collected under 1 factor with an eigenvalue greater than 1, and it was seen that the 1st factor explained 62.78% of the total variance.

The distribution maps obtained by the Krigging interpolation method; La and Y distributions of REE group elements are similar in the study area. The distribution of the La/Y ratio calculated in this context is similar in the study area.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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