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Statistical Analysis of REE Contents in Felahiye (Kayseri) Fluorite Deposit

Felahiye (Kayseri) Florit Yatağındaki NTE İçeriklerinin İstatistiksel Analizi

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ABSTRACT

Geochemical data is applied to clarify many geological questions. One of the practical operations of these data is statistical approaches. As it is recognized, the geological characters of many mineral deposits are performed with the use of Rare Earth Elements (REE) they have. The formation environment and physicochemical properties, specifically in vein type fluorite deposits, are pointed out by the REE content. Hayriye (Felahiye-Kayseri) fluorites are in the form of veins and epigenetically formed within the syenites in the Central Anatolian Crystalline Complex. The Felahiye fluorite mineralization is poor in REE contents. The average F% value of fluorite mineral taken from this region and analyzed is 19.72. When the arithmetic means of REE values are examined, Y has a maximum value with 20.65 and Lu has a minimum value with 0.006. In correlation analysis, a high positive correlation is observed between Tb-Er, Tb-Sm, Tb-Eu, Gd-Yb, Tb-Tm and Tb-Yb respectively. Regression analysis shows that the% F values are directly related to REE amounts.

Key Words: REE, Correlation, Regression, Fluorite

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ÖZ

Jeokimyasal veriler birçok jeolojik problemin çözümünde kullanılır. Bu verilerin etkili kullanım alanlarından biri ise istatistiksel yaklaşımlardır. Bilindiği üzere birçok maden yatağının jeolojik özellikleri ihtiva ettikleri Nadir Toprak Elementleri (NTE) yardımıyla yapılır. Özellikle damar tipi florit yataklarında oluşum ortamı ve fizikokimyasal özellikler REE içeriği ile açıklanır. Hayriye (Felahiye-Kayseri) floritleri Orta Anadolu Kristalen Kompleksinde siyenitler içerisinde damar tipi şeklinde ve epijenetik oluşumludur. Felahiye florit zenginleşmesi, Nadir Toprak Elementleri (REE) içeriği bakımından fakirdir. Bu bölgeden alınan ve analiz edilen florit mineralinin ortalama % F değeri 19.72'dir. REE değerlerinin aritmetik ortalamaları incelendiğinde, Y 20.65 ile maksimum, Lu ise 0.006 ile minimum değere sahiptir. Korelasyon analizinde sırasıyla Tb-Er, Tb-Sm, Tb-Eu, Gd-Yb, Tb-Tm ve Tb-Yb arasında yüksek pozitif korelasyon gözlenmektedir. Regresyon analizi, % F değerlerinin doğrudan REE miktarları ile ilişkili olduğunu göstermektedir.

Anahtar Kelimeler: *NTE, korelasyon, Regresyon, Florit*

INTRODUCTION

Many researchers have tried to identify analytical and statistical explanations to adopt the geochemical analysis results further adequately (Cheng et al., 1994). These explanations involve numerous mathematical methods, consisting of traditional (Hawkes and Webb, 1963; Tennant and White, 1959; Tukey, 1970) and modern techniques (such as fractal/multifractal analysis) (Cheng, 1999; 2007; Carranza, 2009; Cheng et al., 1994, 2000; Li et al., 2003; Zuo and Wang, 2016; Zuo et al., 2019). Studies based on statistical parameters, mineralization, correlation and anomalies are presented to point out geological relations (Agterberg, 2012; Carranza, 2009; Cheng et al., 1994; Madani and Sadeghi, 2019).

Fluorite, which is formed as a gangue or ore mineral in many mineral deposits, is one of the minerals with the most diverse color range. Fluorite can be mineralized in mantle-based magmatic masses or in normal sea water due to evaporation. REE, are an important indicator in geological studies, reflect ore origin and crystalization conditions just like fluorite deposits.

Rare earth elements (REE) are an essential indicator utilized as indexes of the physicochemical conditions in which minerals are formed. Geochemical statistics was applied as an indicator for the fluorite-REE relation (Schneider et al., 1975; 1977; Marchand et al. 1976; Grappin et al., 1979). The extraordinary characters of REE distribution and patterns have been studied on many vein-type fluorite deposits. Thanks to these studies, geological problems such as genesis types of REE, depth, pH, and mineralization have been cleared up (Rub et al., 1986; 1987; Bredikhina et al., 1992; 2000).

The rare earth elements (REE)-fluorite relation benefits the formation of mineral deposits (Samson et al., 2004). The REE concentrations correlated with fluorite and the origin and formation type of fluorite are extremely significant for geochemical studies (Bau and Dulski, 1995; Grammaccioli et al., 1999; Irber et al., 1996, Möller et al., 1976; Möller et al., 1994; Schwinn and Markl, 2005; Kolonin and Shironosova, 2007). REE having fluorite was early outlined in the granite complex by Gahn and Berzelius in Sweden in 1814 (Pekov et al., 2009). In following studies, the fluorite-REE relation was checked out as an approach to solve many geochemical questions. Models are established for prognosis and uncertainty situations with geostatistical techniques. Statistical models based on random function or variable theory are involved in these models (Shaltami et al., 2021). Although geostatistics methods have been practiced frequently in reserve calculations from recent to present, they are still put for ore formation type and origin newly. Successful analyzes have been carried out with these applications, which are based on representing the relations of the geological structures (ore, fault, anomaly, etc.) examined with geostatistical methods. For example, Saein and Afzal (2017), as a result of the geostatistical analysis of the data gathered in the Kerman Magmatic Belt in Iran, declared that the Mo concentration is associated with faults. Lindagato et al., (2018) set up a correlation of NE-SW trending Au–As–Hg anomalies with faults related to Au mineralization by kriging and interpolation. For this reason, correlation and geostatistical analysis according to the results of geochemical analysis obtained from the field are one of the essential approach methods in problem solving.

Most of fluorite is associated alkaline magmatic rocks in Turkey, depending on the closure of Neo-Tethys (Kadıoğlu et al., 2006). Rocks are divided into three classes depending on the type of rare earth element-rich fluorite deposits in Turkey: (i) carbonatite, (ii) alkaline igneous rocks, and (iii) limestone (Altuncu, 2009). Öztürk et al. (2019) stated that these deposits developed in relation to post-collision magmatism and that ore-forming fluids were also fed from other sources.

Hayriye fluorite mineralization is observed in the Central Anatolian intrusive rocks (Uras et al., 2020). Geology, geochemistry and microthermometric studies have been carried out in fluorite deposits located in different regions within the Central Anatolian intrusive rocks (Yaman, 1985; Göncüoğlu et al., 1991; Genç, 2006; Uras, 2007; Şaşmaz and Yavuz, 2007; Koç et al., 2007; Coşanay et al., 2017; Uras et al., 2020). The aim of this study is to explain and reveal the basic relationships between the% F and REE values of 12 samples belonging to Hayriye fluorites.

METHOD

The study area is located in the Central Anatolian Crystalline Complex. (Figure 1). In this complex, metamorphic basement and igneous and ophiolite rocks are observed simultaneously. Hayriye fluorite mineralization is observed in Central Anatolian intrusive rocks. The mineralization observed in the form of veins in fractures and cracks in altered syenites is epigenetic in natüre (Figure 2a). The vein thicknesses range between 5 and 20 cm. The fluorites observed in this region are purple in color and pyrite minerals are still formed in places. The length of the ore vein does not exceed 1 meter (Uras et al., 2020). Carbonation and sericitization are common in thin sections (Figure 2b). Fluorites were formed in the fractures and cracks developed in the syenites during the hydrothermal phase.

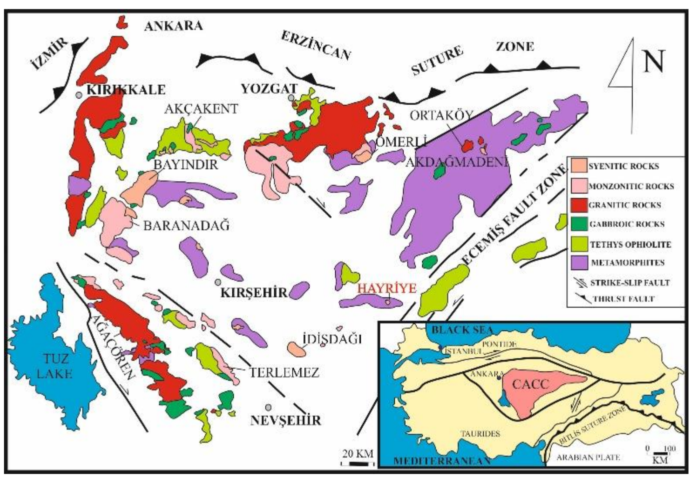

Figure 1. Geological map of the Central Anatolian Crystalline Complex (OAKK) and the location of the study area (modified from Kadıoğlu et al., 2006)

Şekil 1. Orta Anadolu Kristalen Karmaşığının (OAKK) jeoloji haritası ve inceleme alanının konumu (Kadıoğlu vd., (2006)'den değiştirilmiştir)

Fluorite samples were classified separately as pure fluorite and separated fluorite respectively in Hayriye region (Uras et al., 2020). The selected crystals were ground in agate mortar, packed in 5 grams. 12 samples were sent to Acme Laboratories (Vancouver-Canada) for rare earth element analyzes were made by LIBO2 fusion with ICP-MS method.

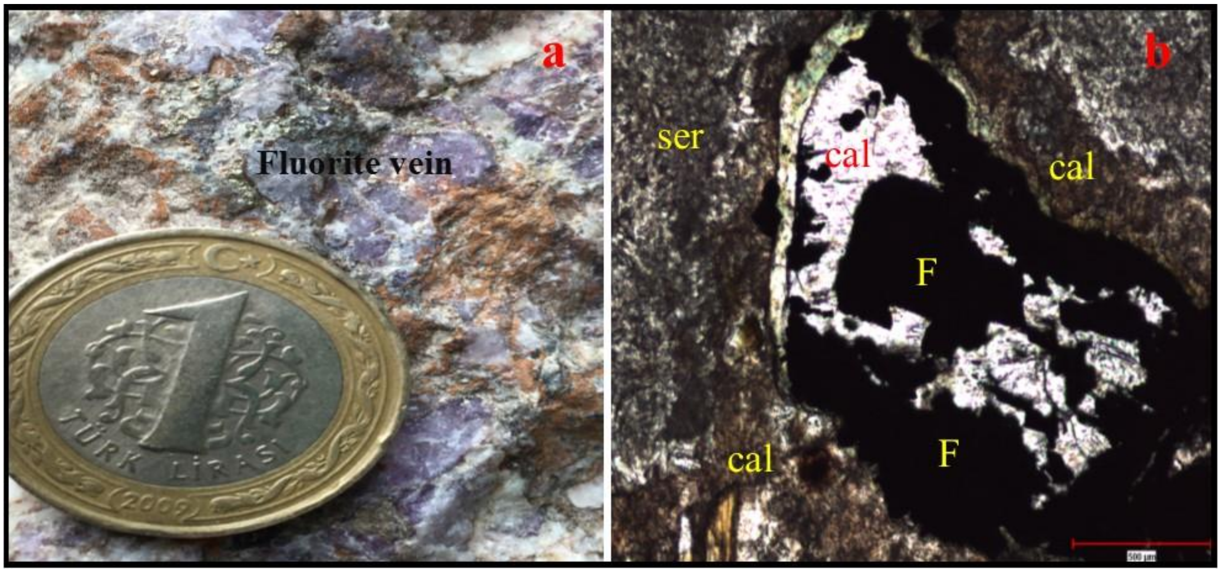

Figure 2. a. General view of fluorite vein, b. Polarizing microscope image of fluorite and host rocks; Abbreviatin: calcite (cal), fluorite (F), sericite (ser)

Şekil 2. a. Florit damarının görünümü, b. Florit ve yan kayacın polarizan mikroskop görüntüsü; Kısaltmalar: kalsit (cal), florit (F) serisit (ser)

% Fluorite and Rare Earth Element (REE) analysis values of 12 fluorite samples observed in the southern of Hayriye (Felahiye-Kayseri) were evaluated in correlation matrix and regression analysis with using Microsoft Excel.

Statistical Analysis

The average F% (Table 1) of Hayriye fluorites with F% values between 12.2-35.8 is 19.72. REE (Table 1) contents of fluorites vary between 0.02 and 8.2 ppm and there is 443.5 ppm ΣREE in total (Uras et al., 2020).

Table 1. % F and REE analyzes of Hayriye fluorites (from Uras et al., 2020).

Çizelge 1. Hayriye floritlerinin % F ve NTE analizleri (Uras vd.,, 2020'den alınmıştır).

SAMPLE	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**	**F9**	**F10**	**F11**	**F12**
F (%)	21.69	12.2	13.05	14.09	18.8	35.8	20	19.88	20.5	19.78	21.2	19.67
La (ppm)	3.4	5.1	4.6	4.2	4.9	5.3	2.8	2.6	3.7	2.3	2.9	3.4
Ce (ppm)	6	8.2	6	7	7.5	5.1	5.3	6.4	5.6	6.2	5.9	6.2
Pr (ppm)	0.97	1.12	0.91	0.82	1.09	0.84	0.85	0.9	0.9	0.84	0.99	0.87
Nd (ppm)	4.6	4.5	3.8	3.4	3.2	3.9	4.3	4.3	4.3	3.2	3.5	4.1
Sm (ppm)	1.26	0.84	0.72	0.82	0.71	1.11	1.11	1.29	1.06	1.27	1.33	1.32
Eu (ppm)	0.32	0.18	0.14	0.12	0.14	0.24	0.27	0.34	0.31	0.31	0.33	0.41
Gd (ppm)	1.85	0.9	0.75	0.82	0.78	1.44	1.64	1.74	1.53	1.58	1.59	1.61
Tb (ppm)	0.32	0.15	0.12	0.11	0.12	0.24	0.28	0.33	0.27	0.31	0.33	0.35
Dy (ppm)	2.02	0.91	0.79	0.64	0.74	1.47	1.6	2.16	1.69	2.12	3.1	3
Ho (ppm)	0.4	0.2	0.18	0.14	0.18	0.21	0.39	0.44	0.38	0.41	0.44	0.51
Er (ppm)	1.07	0.59	0.38	0.28	0.45	0.71	0.99	1.16	0.95	1.15	1.16	1.21
Tm(ppm)	0.12	0.05	0.05	0.05	0.06	0.1	0.1	0.12	0.1	0.11	0.13	0.15
Yb (ppm)	0.66	0.32	0.24	0.34	0.31	0.49	0.58	0.62	0.61	0.59	0.61	0.66
Lu (ppm)	0.08	0.04	0.03	0.02	0.09	0.07	0.07	0.08	0.07	0.09	0.1	0.08
Y (ppm)	25	14.3	13	12	13.2	24.3	24.5	25.8	22.2	24.4	25.5	23.6
Ce\Ce*	0.8	0.8	0.7	0.9	0.8	0.6	0.8	1.0	0.8	1.1	1.2	0.9
Eu/Eu*	0.6	0.6	0.5	0.4	0.5	0.5	0.6	0.6	0.7	0.6	0.7	0.8
ΣREE	44.67	32.3	27.11	26.56	28.57	40.22	41.98	45.68	39.97	42.58	33.85	40.01

When the arithmetic mean of REE are examined, Y has a maximum value with 20.65 and Lu has a minimum value with 0.006. This displays that the Hayriye fluorites are poor in terms of REE. The formation of fluorites according to REE chemistry shows hydrothermal waters circulating along the fracture lines. A limited amount of enrichment is observed in terms of Eu in Hayriye fluorites. Negative Ce anomaly means high oxygen fugacity (Uras et al., 2020).

REE analysis results of fluorites (Uras et al., 2020) were evaluated with the help of the correlation calculation function in the "Data Analysis" submenu of Microsoft Excel's "Tools" menu. As a result of this evaluation, it was determined that a high positive correlation was observed between Tb-Er, Tb-Sm, Tb-Eu, Gd-Yb, Tb-Tm and Tb-Yb respectively (Table 2).

Table 2. Correlation matrix of Hayriye fluorites according to REE results.

Çizelge 2. NTE sonuçlarına göre Hayriye floritlerinin korelasyon matrisi

REE	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Y**
La	1,00														
Ce	0,36	1,00													
Pr	0,39	0,68	1,00												
Nd	-0,02	-0,13	0,11	1,00											
Sm	-0,75	-0,51	-0,35	0,24	1,00										
Eu	-0,70	-0,47	-0,26	0,35	0,94	1,00									
Gd	-0,73	-0,62	-0,35	0,41	0,94	0,91	1,00								
Tb	-0,76	-0,54	-0,30	0,32	0,98	0,98	0,96	1,00							
Dy	-0,69	-0,43	-0,19	0,13	0,93	0,93	0,81	0,93	1,00						
Ho	-0,83	-0,43	-0,23	0,30	0,90	0,97	0,88	0,96	0,92	1,00					
Er	-0,79	-0,45	-0,20	0,30	0,95	0,97	0,93	0,98	0,92	0,97	1,00				
Tm	-0,67	-0,55	-0,31	0,22	0,95	0,97	0,91	0,97	0,95	0,93	0,94	1,00			
Yb	-0,75	-0,56	-0,35	0,34	0,95	0,95	0,97	0,97	0,86	0,92	0,94	0,94	1,00		
Lu	-0,51	-0,30	0,12	-0,11	0,68	0,68	0,66	0,72	0,71	0,69	0,75	0,74	0,69	1,00	
Y	-0,68	-0,67	-0,36	0,31	0,94	0,89	0,97	0,96	0,83	0,85	0,92	0,91	0,93	0,72	1,00

% F and REE were used for regression analysis. In the regression analysis, the standard error was 0, and it was determined that F% and REE results were directly related (Table 3).

RESULTS AND DISCUSSION

Yazıcı et al., (2021) established interpretations of the major and trace element contents prepared from marbles by applying the Pearson correlation coefficient. They still proved by regression analysis that CaO, which plays a significant role in the formation of marbles, has a strong negative correlation with SiO_2 and MgO. Atakoğlu and Yalçın (2021) explained the statistical properties of Sutlegen (Antalya) bauxite according to their REE content and set up thematic maps with the Krigging interpolation method.

Table 3. Regression analysis in Hayriye fluorites.

Çizelge 3. Yeşilyurt floritlerinin regresyon analizi.

Regression Statistics					
Sample Number	**R**	**R square**	**Adjusted R Square**	**Std. Error of the Estimate**	
12	1	1	65535	0	
ANOVA					
	df	**SS**	**MS**	**F**	**Sig.**
Regression	15	398,9387667	26,59591778	-	-
Residual	0	0	65535		
Total	15	398,9387667			

When the statistical results of F% and REE values of Felahiye (Kayseri) fluorites and correlation analysis of REEs are evaluated; Fluorites are poor in terms of REE. When the arithmetic means of REE values are examined, Y has a maximum value with 20.65, and Lu has a minimum value with 0.006 respectively. The standard error is 0 as a result of regression analysis. % F values are closely related to REE compositions, According to the correlation matrix results, it was determined that element Tb has high positive correlation with many elements.

Statistical approaches in terms of fluorite-REE relation will lead to subsequent studies. After the statistical evaluation of all geochemical analyzes, the fluorite-REE relations will be further acceptable with the creation of thematic maps.

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