**PERLİT MİNERALİNİN İÇERDİĞİ NADİR TOPRAK ELEMENTLERİNİN ZENGİNLEŞME SEVİYELERİNİN BELİRLENMESİ**

**Prof. Dr. Aybaba HANÇERLİOĞULLARI**

 Kastamonu University, Faculty of Science, Department of Physics, 37150 Kuzeykent, Kastamonu

**ORCID ID:** 0000-0000-1700-8480

**Prof. Dr. Şeref TURHAN**

 Kastamonu University, Faculty of Science, Department of Physics, 37150 Kuzeykent, Kastamonu

**ORCID ID:** 0000-0001-5303-3680

**Prof. Dr. Aslı KURNAZ**

 Kastamonu University, Faculty of Science, Department of Physics, 37150 Kuzeykent, Kastamonu

 **ORCID ID:** 0000-0002-7910-3461

**ÖZET**

Nadir toprak elementleri (NTE), lantanitler (on beş metalik element) skandiyum ve itriyum metalik elementlerden oluşmaktadır. NTE'ler, bilgisayar sabit diskleri, cep telefonları, elektrikli ve hibrit araçlar ve düz ekran monitörler ve televizyonlar gibi yüksek teknolojili tüketici ürünleri olmak üzere geniş bir uygulama yelpazesinde iki yüzden fazla ürünün gerekli bileşenleridir. NTE'lerin kullanıldığı önemli savunma uygulamaları arasında elektronik ekranlar, yönlendirme sistemleri, lazerler, radar ve sonar sistemleri bulunmaktadır. Bu tür teknolojik ve elektronik ürünlerde kullanılan NTE miktarı, ağırlık, değer veya hacim olarak o ürünün önemli bir kısmı olmasa da, cihazın çalışması için gereklidir. NTE'ler yer kabuğunda doğal elementler olarak oluşmazlar ve fosfatlar, silikatlar, karbonatlar, oksitler ve halojenürler gibi mineraller formunda bulunurlar. NTE’lerin başlıca ekonomik kaynakları bastnasit, monazit ve loparit mineralleri ve lateritik iyon adsorpsiyon killeridir. Gelecekte NTE'lere olan bu muazzam talebi karşılamak için potansiyel ikincil kaynakların araştırılması önem arz etmektedir. Bu yüzden bu çalışmanın amacı, ikincil NTE kaynaklarını araştırma amacıyla perlit mineralinin NTE potansiyelini ve bunların zenginleşme seviyelerini araştırmaktır. Perlit minerali, içyapısında nispeten yüksek su bulunan asit bileşimli amorf bir volkanik camdır. Perlit, doğal olarak oluşur ve yeterince ısıtıldığında büyük ölçüde genişleme gibi olağandışı bir özelliğe sahiptir. Ham perlit kimyasal bileşimi itibariyle silisli ve alüminyumlu bileşikler içerdiğinden kalsiyum esaslı bağlayıcılar ile kimyasal reaksiyona girerek hidrolik aktivite gösterir. Perlit minerali, inşaat, tarım, gıda, ilaç, kimya, seramik ve cam endüstrisinde katkı maddesi olarak kullanılmaktadır. Bu çalışmada, Türkiye'nin farklı şehirlerinde yer alan ocaklarından toplanan perlit örneklerindeki NTE'ler (Y, La, Ce, Pr ve Nd) enerji dağılımlı X-ışını floresans spektrometresi kullanılarak analiz edildi. Analiz sonuçlarına dayanarak, zenginleştirme faktörü (EF) ve referans olarak Sr elementi kullanılarak NTE'lerin zenginleştirme seviyeleri hesaplandı. Perlit örneklerinde analiz edilen Y, La, Ce, Pr ve Nd derişimleri, sırasıyla 11-26 mg/kg, 52-120 mg/kg, 10-168 mg/kg, 3-39 mg/kg ve 27-94 mg/kg aralığında değişti. Y, La, Ce, Pr ve Nd için hesaplanan EF’nin ortalama değerleri, sırasıyla 13, 55, 25, 40 ve 27 olarak hesaplandı. EF değerleri, söz konusu edilen NTE’lerin önemli ölçüde zenginleştiğini göstermektedir.

**Anahtar kelimeler:** Perlit, nadir toprak elementi, zenginleştirme faktörü, EDXRF

**DETERMINATION OF THE ENRICHMENT LEVELS OF RARE EARTH ELEMENTS IN PERLITE MINERALS**

**ABSTRACT**

Rare earth elements (REEs) involve lanthanides (fifteen metallic elements), scandium, and yttrium metallic elements. REEs are essential components of more than two hundred products in a wide range of applications, including computer hard drives, mobile phones, electric and hybrid vehicles, and high-tech consumer products such as flat-screen monitors and televisions. Important defense applications where REEs are utilized contain guidance systems, electronic displays, lasers, sonar, and radar systems. Although the amount of REE in such technological and electronic products may not be a significant part of that product in terms of weight, value, or volume, it is very necessary for the operation of the device. REEs do not occur as natural elements in the earth's crust and exist in the form of minerals such as phosphates, silicates, carbonates, oxides, and halides. The main economic sources of REEs are bastnasite, monazite, loparite minerals, and lateritic ion adsorption clays. It is important to investigate potential secondary resources to meet this enormous demand for REEs in the future. Therefore, this study aims to investigate the REE potential of perlite minerals and their enrichment levels. Perlite mineral is an amorphous volcanic glass with an acid composition and relatively high water content in its internal structure. Perlite occurs naturally and has the unusual property of expanding greatly when heated sufficiently. Since raw perlite contains siliceous and aluminum compounds in its chemical composition, it shows hydraulic activity by chemically reacting with calcium-based binders. Perlite mineral is used as an additive in the construction, agriculture, food, pharmaceutical, chemical, ceramic, and glass industries. In this study, the concentrations of REEs (Y, La, Ce, Pr, and Nd) in perlite samples collected from quarries in different cities of Turkey were analyzed using energy-dispersive X-ray fluorescence spectrometry. Based on the analysis results, the enrichment levels of REEs were calculated using the enrichment factor (EF) and the Sr element as a reference. The concentrations of Y, La, Ce, Pr and Nd analyzed in perlite samples varied from 11 to 26, 52 to 120, 10 to168, 3 to 39 and 27 to 94 mg/kg, respectively. The average values of EF calculated for Y, La, Ce, Pr and Nd were found as 13, 55, 25, 40 and 27, respectively. EF values show that the REEs in question are significantly enriched.

**Keywords**: Perlite, rare earth element, enrichment factor, EDXRF

**1. INTRODUCTION**

Rare earth elements (REEs) are utilized in a variety of industrial, commercial, medical, space, and military applications due to their unique chemical, electromagnetic and magnetic properties (Jha 2014). The use of rare earth elements or oxides has led to significant improvements in the performance of these applications, including efficiency, longevity, and reliability, in addition to a significant reduction in the weight and size of components and/or overall systems (Jha 2014). Rare earth materials are often characterized by various names, such as REEs, rare earth metals (REMs), rare earth oxides, or yttrium-based rare earth material (Jha 2014). Essentially, REEs fall into two different groups: light rare earth elements (LREEs), which is known as the cerium (Ce) group including lanthanum (La)-europium (Eu), and heavy rare earth elements (HREEs), also known as the yttrium (Y) group including gadolinium (Ga)-lutetium (Lu)-Y elements. REEs consist of 17 chemical elements including 15 lanthanides plus scandium (Sc) and Y (Jha 2014).

 Commercial applications of REEs are summarized in Table 1 (Jha 2014). REEs are widely used in nuclear power reactors, aerospace systems and components, jet engines, scramjets, battery electrodes for high-power batteries, and many other aerospace products. Samarium-cobalt magnets are best suited for high-power radiofrequency sources and microwave filters (Jha 2014). Yttrium-iron-garnet filters are widely used in satellite and airborne systems where a sharp cutoff frequency, minimal pass-band loss, and high attenuation in the stop-band regions are essential design requirements. High-performance diode-pumped solid-state infrared lasers use rare earth elements such as holmium, thulium, yttrium, and erbium to achieve superior laser performance at infrared frequencies.

**Table 1**. Examples of commercial products utilizing rare earth element

|  |
| --- |
|  |

|  |  |
| --- | --- |
| REE  | Commercial product |
| Neodymium (Nd), praseodymium (Pr), terbium (Tb) dysprosium (Dy) | Mobile phones, computer hard drives, cameras |
| Nd, Pr, Dy, La, Ce | Hybrid electric vehicles, high-capacity batteries, infrared lasers |
| Eu, Y, Tb, La | Energy-efficient light bulbs |
| Ce, La, neodymium (Nd), Eu  | Glass additives |
| Eu, Y, Er | Fiber-optic lines, fiber-optic amplifiers |
| Promethium (Pm) | Portable x-ray equipment |
| Scandium (Sc) | High-intensity flood lights for stadiums |
| Samarium (Sm)-cobalt (Co) | Permanent magnets for electric motors, widely deployed in hybrid electric vehicles |

The diversity and importance of high-tech and energy applications of REEs have increased dramatically since the 1960s (Jha 2014). Furthermore, because many of these applications are highly specific and substitutes for REEs are of lower quality or unknown, REEs have achieved a much higher level of technological importance than would be expected from their relative obscurity (Jha 2014). Although they are more abundant than similar industrial metals, rare earth elements are less likely to be concentrated in exploitable ore deposits. As a result, most of the world's REE supply comes from only a few sources that can be consumed in a short period. For example, the United States had a generally adequate supply of REEs for several decades but has since become dependent on imports from China, changing the strategic situation. Therefore, to meet the demand for REEs, developed countries try to explore potential secondary REE resources such as different industrial wastes (phosphogypsum, red mud, fly ash, etc.) and minerals.

Perlite is one of the natural volcanic aluminosilicate glasses formed by the rapid cooling of viscous rocks in lava or magma (Reka et al. 2019). Perlite is a volcanic glass with an acidic character. In this study, REEs (Y, La, Ce, Pr, and Nd) in 33 perlite samples collected from quarries in different cities of Türkiye (Erzurum, Erzincan, Nevşehir and Ankara) were analyzed using an energy-dispersive X-ray fluorescence (EDXRF) spectrometry. Based on the analysis results, the enrichment levels of REEs were calculated using the enrichment factor (EF) and strontium (Sr) reference elements.

**2. MATERIAL AND METHODS**

**2.1. Collection, preparation and analysis**

A total of 33 perlite samples were collected from perlite quarries located in Erzurum, Erzincan, Nevşehir, and Ankara provinces and brought to the sample preparation laboratory in plastic bags. Perlite samples were crushed, powdered, and dried to make them fit the calibrated powder geometry in the EDXRF spectrometer. Analysis of REEs in perlite samples was carried out by using an EDXRF spectrometer (Spectro Xepos, Ametek) with a thick binary Pd/Co alloy anode X-ray tube (50 kV, 60 W), in the Central Research Laboratory of Kastamonu University. The EDXRF spectrometer was equipped with a thick binary Pd/Co end-window tube (50 W, 60 kV) and a Peltier-cooled Si drift detector. The EDXRF spectrometer uses the “standardless” calibration based on the Fundamental Parameters method. (Turhan et al. 2020; Turhan et al. 2022). Perlite samples were placed in the automatic sampler and counted once for two hours, and the analysis processes were completed.

**2.2. Enrichment factor**

Enrichment factor (EF) was utilized to determine the contamination level and infer the distribution of elements of anthropogenic or natural origin from positions determined by individual elements in environmental samples. EF was calculated as follows (Parvez et al. 2023):

 (1)

where Cn is the concentration of REE and CRef is the concentration of a reference element. There are various elements (Ca, Al, Ti, Sc, Mn, Sr, Zr, and Fe) that can be used as reference materials in calculating EF (Poh and Tahi 2017; Parvez et al. 2023). In this study, Sr was selected to see how the enrichment states of REEs were analyzed in perlite samples. Sr is one of the main components of the Earth's crust and its concentration in the soil is related to the matrix (Poh and Tahi 2017). According to EF values, five categories of pollution (or contamination) are classified as given in Table 2 (Turhan et al. 2020).

# Table 2. Contamination categories related to the values of the enrichment factor

|  |  |  |
| --- | --- | --- |
|  | Value | Contamination category  |
|  | EF < 2 | Deficiency to minimal enrichment |
|  | 2 ≤ EF< 5 | Moderate enrichment |
| Enrichment factor | 5 ≤ EF < 20 | Significant enrichment |
|  | 20 ≤ EF < 40 | Very high enrichment  |
|   | EF ≥ 40 | Extremely enrichment |

**3. RESULTS AND DISCUSSION**

The concentrations of REEs analyzed in the perlite samples are given in Table 3. EF values calculated according to the reference elements are presented in Table 4. From Table 3, REEs analyzed in perlite samples are listed as Y < Pr < Nd < La < Ce according to their average concentration.

 The Ce concentrations analyzed in the perlite samples varied from 10 to 168 mg/kg with an average value of 91 mg/kg, which is higher than the Earth's crust average of 70 mg/kg (Yaroshevsky 2006). It can be seen from Table 4 that the values of EF varied from 3 (moderate enrichment) to 99 (extreme enrichment) with an average value of 25. According to the average values of the EF, it is seen that the perlite samples are much enriched with Ce.

**Table 3.** Concentration of REE in perlite samples

|  |  |
| --- | --- |
| Sample code  | The concentration of REE (mg/kg) |
| Y | La | Ce | Pr | Nd |
| P1 | 26.1 | 54.4 | 125.0 | 21.9 | 53.7 |
| P2 | 23.8 | 85.2 | 74.9 | 21.9 | 45.7 |
| P3 | 26.1 | 113.5 | 142.0 | 20.8 | 52.9 |
| P4 | 25.3 | 76.3 | 136.0 | 22.7 | 46.7 |
| P5 | 14.3 | 108.1 | 42.7 | 11.6 | 29.8 |
| P6 | 15.7 | 84.9 | 12.2 | 14.1 | 39.9 |
| P7 | 14.8 | 69.1 | 108.4 | 9.3 | 27.0 |
| P8 | 16.4 | 119.6 | 10.2 | 17.2 | 48.1 |
| P9 | 14.3 | 61.9 | 108.8 | 12.9 | 60.8 |
| P10 | 15.5 | 61.1 | 79.3 | 28.3 | 75.2 |
| P11 | 15.6 | 55.3 | 168.0 | 13.4 | 61.2 |
| P12 | 15.7 | 82.8 | 138.0 | 15.5 | 67.7 |
| P13 | 14.8 | 84.3 | 52.1 | 27.2 | 69.4 |
| P14 | 13.2 | 92.0 | 121.0 | 17.9 | 58.9 |
| P15 | 11.9 | 59.6 | 110.1 | 17.7 | 49.9 |
| P16 | 16.3 | 79.6 | 23.9 | 16.0 | 32.6 |
| P17 | 22.4 | 93.4 | 15.4 | 14.3 | 46.4 |
| P18 | 15.2 | 88.1 | 99.4 | 26.8 | 51.2 |
| P19 | 17.1 | 68.7 | 89.8 | 26.4 | 59.5 |
| P20 | 17.4 | 102.8 | 74.5 | 29.7 | 65.7 |
| P21 | 15.8 | 71.6 | 127.8 | 8.0 | 55.3 |
| P22 | 13.6 | 63.4 | 97.4 | 6.8 | 42.9 |
| P23 | 15.7 | 52.7 | 93.4 | 25.0 | 56.2 |
| P24 | 15.0 | 59.9 | 99.3 | 38.5 | 81.1 |
| P25 | 10.8 | 99.4 | 117.5 | 24.9 | 46.5 |
| P26 | 14.2 | 59.9 | 55.5 | 22.9 | 75.4 |
| P27 | 13.7 | 51.6 | 115.9 | 23.5 | 87.6 |
| P28 | 13.5 | 109.5 | 125.2 | 3.4 | 73.8 |
| P29 | 16.1 | 74.8 | 109.9 | 28.8 | 92.5 |
| P30 | 16.7 | 80.7 | 101.2 | 19.4 | 86.4 |
| P31 | 16.1 | 81.1 | 60.9 | 23.6 | 94.2 |
| P32 | 16.2 | 52.8 | 72.4 | 12.5 | 85.1 |
| P33 | 16.1 | 62.4 | 80.2 | 6.8 | 89.0 |

**Table 4.** EF values calculated for REE in perlite elements

|  |
| --- |
| Enrichment factor |
| Y | La | Ce | Pr | Nd |
| 40.3 | 83.9 | 79.9 | 108.9 | 64.9 |
| 41.6 | 149.1 | 54.3 | 123.5 | 62.7 |
| 43.7 | 190.1 | 98.5 | 112.3 | 69.4 |
| 41.8 | 126.0 | 93.0 | 120.8 | 60.4 |
| 12.1 | 91.8 | 15.0 | 31.8 | 19.8 |
| 10.1 | 54.4 | 3.2 | 29.1 | 20.0 |
| 12.6 | 58.7 | 38.2 | 25.5 | 18.0 |
| 11.2 | 82.0 | 2.9 | 38.0 | 25.8 |
| 11.0 | 47.7 | 34.8 | 32.1 | 36.8 |
| 10.8 | 42.6 | 22.9 | 63.6 | 41.1 |
| 11.6 | 41.3 | 52.0 | 32.2 | 35.8 |
| 11.7 | 61.8 | 42.7 | 37.3 | 39.6 |
| 5.9 | 33.4 | 8.5 | 34.7 | 21.5 |
| 6.2 | 43.3 | 23.6 | 27.2 | 21.7 |
| 6.7 | 33.8 | 25.8 | 32.3 | 22.2 |
| 40.7 | 198.6 | 24.7 | 128.6 | 63.7 |
| 38.6 | 161.0 | 11.0 | 79.4 | 62.7 |
| 3.6 | 21.0 | 9.8 | 20.6 | 9.6 |
| 3.2 | 13.0 | 7.1 | 16.1 | 8.8 |
| 3.2 | 19.0 | 5.7 | 17.7 | 9.5 |
| 9.9 | 44.9 | 33.2 | 16.2 | 27.2 |
| 10.6 | 49.2 | 31.3 | 17.0 | 26.1 |
| 10.1 | 33.9 | 24.9 | 51.9 | 28.4 |
| 4.2 | 17.0 | 11.7 | 35.1 | 18.0 |
| 5.5 | 50.2 | 24.6 | 40.5 | 18.4 |
| 1.8 | 7.8 | 3.0 | 9.6 | 7.7 |
| 1.8 | 6.9 | 6.5 | 10.2 | 9.2 |
| 1.8 | 14.7 | 7.0 | 1.5 | 7.8 |
| 1.8 | 8.3 | 5.1 | 10.3 | 8.0 |
| 1.8 | 8.7 | 4.5 | 6.7 | 7.3 |
| 1.8 | 9.2 | 2.9 | 8.7 | 8.4 |
| 1.8 | 5.9 | 3.4 | 4.5 | 7.5 |
| 1.8 | 7.0 | 3.7 | 2.4 | 7.8 |

 The La concentrations analyzed in the perlite samples varied from 52 to 120 mg/kg with an average value of 78 mg/kg, which is approximately 3 times higher than the Earth's crust average of 29 mg/kg (Yaroshevsky 2006). The values of EF varied from 6 (significant enrichment) to 199 (extreme enrichment) with an average value of 55. According to the average values of the EF, it is seen that the perlite samples are extremely enriched with La.

 The most important use of Nd is as an alloy containing iron and boron to make very strong permanent magnets. The Nd concentrations analyzed in the perlite samples varied from 27 to 94 mg/kg with an average value of 61 mg/kg, which is approximately 2 times higher than the Earth's crust average of 37 mg/kg (Yaroshevsky 2006). The values of EF varied from 7 (significant enrichment) to 69 (extreme enrichment) with an average value of 27. According to the average values of the EF, it is seen that the perlite samples are much enriched with Nd.

 The Pr concentrations analyzed in the perlite samples varied from 3 to 39 mg/kg with an average value of 19 mg/kg, which is lower than the Earth's crust average of 29 mg/kg (Yaroshevsky 2006). The values of EF varied from 2 (deficiency to minimal enrichment) to 129 (extreme enrichment) with an average value of 40. According to the average values of the EF, it is seen that the perlite samples are extremely enriched with Pr.

 Y is used in radar technology and often as an additive in alloys. Y is also used in white LED lights. The Y concentrations analyzed in the perlite samples varied from 11 to 26 mg/kg with an average value of 17 mg/kg, which is lower than the Earth's crust average of 29 mg/kg (Yaroshevsky 2006). The values of EF varied from 2 (deficiency to minimal enrichment) to 44 (extreme enrichment) with an average value of 13. According to the average values of the EF, it is seen that the perlite samples are significantly enriched with Y.

**4. Conclusions**

This study is aimed at identifying secondary REE resources in Turkey. According to our literature review, this is the first study to determine the enrichment levels of REEs in perlite samples. The study showed that the concentrations of six REEs (Ce, Nd, and La) analyzed with the EDXRF technique in perlite samples were significantly higher than the Earth's crust average values. However, only five REEs could be analyzed with the EXRF technique. Going forward, analysis techniques such as ICP-OES, ICP-MS, etc. will be used to analyze other REEs contained in perlite samples.

**REFERENCES**

Jha AR. Rare Earth Materials. Properties and Applications. (2014). CRC PressTaylor & Francis Group. Boca Raton. ISBN: 13: 978-1-4665-6403-9 (eBook - PDF).

Parvez MS, Nawshin S, Sultana S, Hossain MS, Rashid Khan MH, Habib MA, Nijhum ZT, Khan R. (2023). Evaluation of heavy metal contamination in soil samples around Rampal, Bangladesh. ACS Omega 8(18), 15990**–**15999.

Poh SC, Tahi NM. (2017). The common pitfall of using enrichment factor in assessing soil heavy metal pollution. Malaysian Journal of Analytical Sciences 21(1), 52–59.

Reka AA, Pavlovski B, Lisichkov K, Jashari A, Boev B, Boev I, Lazarova M, Eskizeybek V, Oral A, Jovanovski G, Makreski P. 2019. Chemical, mineralogical and structural features of native and expanded perlite from Macedonia Geologia Croatica 72(3), 215-221.

Turhan Ş, Garad, AMK, Hançerlioğulları A, Kurnaz A, Gören E, Duran C, Karataşlı M, Altıkulaç A, Savacı G, Aydın A. (2020). Ecological assessment of heavy metals in soil around a coal-fired thermal power plant in Turkey. Environmental Earth Sciences 79(6), 1–15.

Turhan Ş, Tokat S, Kurnaz A, Altıkulaç A. (2022). Distribution of elemental compositions of zeolite quarries and calculation of radiogenic heat generation. International Journal of Environmental Analytical Chemistry 109(19), 7851–7862.

# Yaroshevsky AA. (2006). Abundances of chemical elements in the Earth’s crust. Geochemistry International 44(1), 48–55.