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Content of rare earth elements in basalt aggregate from Winna Góra, Poland

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Abstract

Seek for new Rare Earth Elements (REE) sources encourage looking for easily available sources located in Europe. REE in evolved magmatic systems are predominantly associated with alkali environments. Therefore, it was decided to identify the content of REE in alkali igneous rocks of the Winna Góra basalt quarry located in Lower Silesia, Poland. In this study, a commercially available basalt aggregate from Winna Góra deposit located in the south-western part of Poland near Jawornik was examined for REE content. Mineral content and chemical composition were examined with a light microscope, XRD and XRF, whereas trace element content was measured with the ICP-MS technique. A new method of sample preparation for the purpose of REE identification in basalt aggregate based on pressure microwave mineralisation was developed. Mineral composition and TAS diagram classify aggregate as tephrite. The mineral composition of samples reflects typical mafic and ultramafic rocks. Quantitative mineralogical analysis by the Rietveld method showed that the main minerals are anorthite (46.7%) and augite (37.4%) with a minor content of forsterite (7.5%), nepheline (7.4%) and apatite below 1%. The total content of REE does not exceed 132 ppm. Chondrite normalised curves show the highest concentration of La and Pr. In the case of HREE, the majority of elements (Eu, Tb, Dy, Ho, Er, Yb) concentrations were below 1 ppm, a Tm and Lu were not detected. The low enrichment in HREE was also reflected in La/Gd ratios. Obtained results are comparable to the REE contents in the western part of the Cenozoic European Volcanic Province.

Keywords

basalt aggregate; Rare Earth Elements; chondrite patterns



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Introduction

The global need for a more efficient, sustainable management of natural resources has been the focus of attention in recent years. This is particularly important given the fact that some of the elements found in nature are crucial for the continuous development of civilisation and technology. Among them are Rare Earth Elements (REE). REE, in accordance with the classification of the International Union of Pure and Applied Chemistry (IUPAC), are a group of seventeen chemical elements in the periodic table, in particular, the fifteen lanthanides as well as yttrium and scandium. All these elements occur in nature but not in a pure state and, in most cases, need advanced processing methods to be extracted. Hence, the need for sustainable extractive methods and/or recovery and recycling of these elements (Likhachev, 2002; Kuric, 2011; Kuric et al., 2019). The problem with REE supply is due to the fact that these elements are never found in an equal or predictable distribution (Gupta and Krishnamurthy, 1992; Sága et al., 2019). There are three minerals abundant in REE that are commercially exploitable; these are bastnäsite, monazite and xenotime. Other sources of REE include ion-adsorbed clays, which are a very important source of heavy rare earth elements where up to 60% of Rare Earth Oxides (REO) content in these clays comes from yttrium group elements. These clays are easier to process since they require only hydrometallurgical processing (Jordens et al., 2013). Typical beneficiation methods of REE include processes such as gravity separation, magnetic separation, electrostatic separation and froth flotation. Global reserves of REE calculated as the REO equivalent and REE mine production is presented in Table 1. As it can be seen from the table, global mine production was estimated to have increased to 210000 tons of REO equivalent, and it indicates an 11% increase compared with that of 2018. In the United States, the production of mineral concentrates increased by 44% compared to 2018. Still, China dominates the global supply of REE, and it also has the largest reserves.

	Mine proc	Mine production [t]		
	2018	2019		
United States	18000	26000	1400000	
Australia	21000	21000	3300000	
Brazil	1100	1000	22000000	
Burma (Myanmar)	19000	22000	N/A	
Burundi	630	600	N/A	
Canada	-	-	830000	
China	120000	132000	44000000	
Greenland	-	-	1500000	
India	2900	2900	6900000	
Madagascar	2000	2000	N/A	
Russia	2700	2700	12000000	
South Africa	-	-	790000	
Tanzania	-	-	890000	
Thailand	1000	1000	N/A	
Vietnam	920	920	22000000	
Other Countries	60	-	310000	
World total (rounded)	190000	190000	120000000	

Table 1. REE mine production and reserves as of January 2020 (REO equivalent). Source: USGS, 2020

In European Union, the concept of critical raw materials was introduced in 2011 in the communication on raw materials of the European Commission (European Commission, 2011). Since then, two updated lists of critical raw materials have been published - in 2014 and 2017 (European Commission, 2014, 2017). In each list, as a critical raw material, REE were listed with division into Heavy Rare Earth Elements, i.e. Dysprosium, Erbium, Europium, Gadolinium, Holmium, Lutetium, Terbium, Thulium, Ytterbium, Yttrium and Light Earth Elements, i.e. Lanthanum, Cerium, Praseodymium, Neodymium, Samarium. Estimates of McLeod and Shaulis (2018) show that REEs constitute <0.022% of the elemental budget of Earth's upper crust but are intricately associated with specific geological environments. They point out that of the 799 REE deposits worldwide (including potential resources) for which REE-mineralogical data is currently available for, 122 are associated with evolved and/or alkaline igneous activity (not including carbonatites, of which there are 149). Alkaline igneous rocks host deposits of a variety of rare metals and industrial rocks and minerals. In most cases, these

rocks are used as industrial rocks and aggregates. Nevertheless, the potential of alkali igneous rocks as a source for REE has been highlighted in several publications (McLeod and Shaulis, 2018; Dostal, 2017; Goodenough et al., 2016; Lesnov, 2012). In general, REE in evolved magmatic systems are predominantly associated with alkali environments (McLeod and Shaulis, 2018). Therefore, it was decided to identify the content of REE in alkali igneous rocks of the Winna Góra basalt quarry located in Lower Silesia, Poland. Previous studies were focused on the xenoliths occurring in this province rather than host rocks (Dajek et al., 2015). The content of REE in these particular deposits has not been identified. Therefore, it is crucial to verify if these contents are relatively higher than the average abundances of REE in Earth's crust and contents in the Western part of the Cenozoic European Volcanic Province (Tab. 2).

	Abun	dance in Earth's c	rust	Chondritic abundance	Siebengebirge basanites	
Elements	Taylor and McLennan (1985)	Wedepohl (1995)	Lide and Frederikse (1997)	Pourmand, Dauphas and Ireland (2012)	(Germany) (Kolb et al. 2012)	
La	16.00	30.00	39.00	0.2469	52.40	
Ce	33.00	60.00	66.50	0.6321	100.88	
Pr	3.90	6.70	9.20	0.0959	11.26	
Nd	16.00	27.00	41.50	0.4854	44.26	
Sm	3.50	5.30	7.05	0.1556	8.26	
Eu	1.10	1.30	2.00	0.0599	2.53	
Gd	3.30	4.00	6.20	0.2093	7.06	
Tb	0.60	0.65	1.20	0.0378	1.00	
Dy	3.70	3.80	5.20	0.2577	5.33	
Но	0.80	0.80	1.30	0.0554	0.96	
Er	2.20	2.10	3.50	0.1667	2.35	
Tm	0.30	0.30	0.52	0.0261	0.31	
Yb	2.20	2.00	3.20	0.1694	1.86	
Lu	0.30	0.35	0.80	0.0256	0.26	
Y	20.00	24.00	33.00	1.3950	24.97	
Sc	30.00	16.00	22.00	5.4930	27.75	
Total	136.90	184.30	242.17	9.5118	291.42	

Tab. 2. Average abundance of REE (ppm) in Earth's crust and basanites from Siebengebirge Volcanic Field compared with chondritic

As part of this work, common analytical methods used to determine the content of REE in rocks were assessed. The selection was based on suitable detection limit and accuracy of obtained results (Cavalcante et al., 2014; Sindern, 2017; Wengi et al., 2010; Latacz, 2017; Wdowin and Franus, 2014).

The first method that is commonly used for the analysis of rare earth elements (REEs) is X-ray fluorescence spectroscopy (XRF) which is divided into the analysis of minors and traces in materials with natural origin and the analysis of industrial products containing REEs as the main, minor or trace components in solid material (Pauw et al., 2020). The XRF method is considered to be quick and not requiring any additional steps for the preparation of the sample, except the case when the material is powdered and needs to be compressed. However, its significant disadvantage is the high error of determination and a high average lower limit of detection (LLD) of about 1-10 µg/g (Schramm, 2016). An alternative method is mass spectrometry with an inductive coupling of plasma - ICP-MS, where spectrometric analyses of liquid samples mineralised in inorganic acids are analysed (Seregina, 2018). It is one of the very labour-intensive methods but characterised by higher sensitivity than XRF (Pinto et al., 2012). This method involves a more complex sample preparation process affecting the yield of analysed elements. Sample preparation is a wet open or closed process (Holubcik, M. et al., 2020). The most effective when analysing samples is a closed system, in which the digestion of the sample material is at elevated temperature and pressure. This allows for the reduction of contamination of the sample. Digestion of the sample in a closed system is carried out either by conventional or microwave heating. Microwave heating reduces digestion time which in the case of conventional heating may last up to dozens of hours (Kozak, 2012). Fluids used for the digestion of samples are selected based on the mineral composition of the sample and, in the case of a complex matrix with high content of SiO₂, except oxidising HNO₃ acid, the silica dissolving acid HF is necessary (Krishna, 2009). The important parameters of the mineralisation process include temperature, pressure, time and heating power. These parameters depend on the nature of the mineralised matrix and should be selected individually for each tested material based on preliminary tests. Other techniques used to detect REE are LA-ICP-MS analysis, where a pulsed high-energy laser beam is focused on the surface of a solid sample, which is placed in an air-tight sample chamber flushed with a carrier gas. Irradiation causes the release of aerosol particles from the sample surface, which are transported to the ICP ion source in which they are vaporised and finally ionised (Sindern, 2017).

The aim of this work was to identify and assess the potential of REE in the commercially developed basalt deposit of Winna Góra near Jawor in Poland with the use of the ICP-MS technique and microwave pressure microwave mineralisation.

Geological setting

The Winna Góra deposit is located in the South-Western part of Poland in Lower Silesia Voivodeship. Mineral reserves of this deposit are estimated at 11 246 000 tonnes with an average yearly production of approximately 500 000 t (Szuflicki et al., 2019). The tertiary mafic rock deposit belongs to the Polish part of Tertiary-Quaternary Cenozoic European Volcanic Province. The European Cenozoic volcanic province surrounds the Alps from South-West France and expands to Hungary and Czech Republic, with outcrops reaching the South-Western part of Poland (see Fig. 1). Basaltic volcanism in Lower Silesia, at the northern termination and eastern flanks of the Ohre Rift, spanned the Oligocene–Pliocene interval (Birkenmayer et al., 1970). In Lower Silesia, basalts are a common name of various alkaline igneous rocks with an aphanitic structure. The rocks found in these regions are basalt, trachyte, tephrite, basanite, phonolite basanite, quartz latite, foid-bearing basalt, nepheline syenite, dolerite, basanitoid, limburgite, ankarite, trachyandesite, trachyphonolite (Szuflicki et al., 2019).



Fig. 1. Geological setting of the Bohemian Massif and the Eger Rift (modified from Awdankiewicz et al., 2016) with the location of the study area – the Winna Góra volcanic rock outcrop. EFZ – Elbe Fault Zone, ER – Eger Rift, OFZ – Odra Fault Zone, SBF – Sudetic Boundary Fault.

Material and Methods

Rock samples were acquired from an active quarry. The raw material was a fine aggregate of size 0-2 mm. The total mass of samples was 50 kg. Samples were air-dried and quartered in a Jones splitter to obtain analytical samples. The condition of the basalt sample is shown in Fig. 2.



Fig. 2. The condition of the basalt sample.

In order to properly characterise basalt aggregate and assess REE potential, the following set of analyses was conducted:

- structural using light microscopy (LM),
- mineral composition-with the use of the X-ray diffraction (XRD) method,
- chemical composition-using the X-ray fluorescence method (XRF),
- trace element analysis with Inductively coupled plasma mass spectrometry (ICP-MS).

X-ray diffraction phase identification was carried out in Empyrian diffractometer manufactured by Panalytical equipped with a copper lamp at 40 kV and amperage of 30 mA. For quantitative phase analyses based on the Rietveld approach, HighScore plus software was used.

ZSX Primus II spectrometer manufactured by Rigaku was used for elemental analysis (from Be to U). The spectrometer uses an X-ray lamp with Rh anode 4,0 kW and amperage of 60kV and SDD detector. Internal reference materials were used for the tests. Phase and chemical analyses were conducted at the Silesian Centre for Education and Interdisciplinary Research in Chorzów (Poland).

REE content analysis using the ICP-MS was carried out in several stages. In the first one, the method was validated in terms of linearity, LOD detection limit and LOQ determination, as well as accuracy, repeatability and reproducibility. Due to the nature of basalt, an important part of REE content analysis was the sample preparation process using mineralisation in the Microwave Reaction System. Pressure microwave mineralisation was chosen as the preferred method due to the chemical composition of samples. In the next stage, in order to increase the recovery of determined REEs, the developed method was optimised in terms of:

- proportions and/or mixtures of acids used for mineralisation,
- changes in the conditions in which mineralisation is carried out, including increasing the temperature,
- elimination of non-spectral matrix interference caused by the presence of dissolved solids and viscosity change by the introduction of sample diluting.

The results of the optimisation of the method allowed to reduce the method's measuring range. The third stage consists of actual sample analysis based on the elaborated procedure. 0.2 g of each sample was mineralised in a closed system using 6 ml 65% HNO₃ and 2 ml 40% HF for 70 minutes at the temperature of 240°C, the pressure of 60 bar (0.5 bar/s increment) and 800W power. Once mineralisation was completed, the solution was complexed with 12 ml H₃PO₄ and topped up with demi water to 25 ml obtaining a clear and transparent solution. After that, REE content was measured in ICP-MS7900 manufactured by Agilent Technologies. Prior to ICP-MS analyses, the spectrometer was calibrated on certified reference materials and two reagent blanks. The calibration curve was prepared for the element concentration range from 0.005 to 1.8 mg/dm³. The calibration coefficient R for REE are given in Table 3, and the calibration curve for Y is in Fig. 3.

Element	Isotope	R
Sc	45	0.9998
Y	89	0.9999
La	139	0.9998
Ce	140	0.9998
Pr	141	0.9996
Nd	146	0.9998
Sm	147	0.9999
Eu	153	0.9999
Gd	157	0.9998
Tb	159	0.9998
Dy	163	0.9998
Но	165	0.9998
Er	166	0.9995
Tm	169	0.9998
Yb	172	0.9998
Lu	175	0.9998

Tab. 3. The values of the calibration coefficient R for REE.



The reagent blank was a mixture of digestion reagents at the concentrations used for sample mineralisation. Trial tests showed that the calibration curves were correct. REE content calculation was conducted with MassHunter 4.4 Workstation Software. Analyses were carried out on five aggregate samples marked as WG/P1-1, WG/P1-2, WG/P1-3, WG/P1-4, WG/P1-5. Each measurement was repeated five times per sample.

Results

Macroscopic observations using a light stereoscopic microscope show that basalt has a microporhyry structure consisting of olivine, rarely pyroxenes and occasionally plagioclaze. Olivine crystals are often corroded by magma (Fig. 4). Pyroxenes sometimes show zonal or polysynthetic-zonal structure (Fig. 5). Paleocrystals reach a size of up to 2 mm, and in the case of plagioclases, even up to 3 mm. The rock matrix consists of plagioclases, pyroxenes and also opaque minerals, probably magnetite. It should be noted that the arrangement of the plagioclase lamellae clearly indicates a parallel fluidised texture (Fig. 6). Lenticular clusters of pyroxene crystals with a size of up to 0.5 mm (larger than a rock matrix) are observed.

The rock exhibits slight carbonation, which is manifested by the presence of small clusters of carbonate minerals (probably calcite and dolomite) in the rock matrix and the carbonation of plagioclase, rarely olivine. (Fig. 7)



Fig. 4. Paleocrystals of olivine corroded by magma, crossed nicols, magnification 200x.



Fig. 5. Pyroxene crystal with polysynthetic-zonal structure, crossed nicols, magnification 200x.



Fig. 6. Parallel arrangement of the plagioclase lamellae indicating fluidised texture, single nicol, magnification 200x.



Fig. 7. Plagioclase precrystal carbonation, crossed nicols, magnification 200x.

Results of phase analysis with X-ray diffraction method revealed peaks of augite, anorthite forsterite, nepheline and apatite (see Fig. 8). Such mineral composition reflects typical mafic and ultramafic rocks. Quantitative mineralogical analysis by the Rietveld method showed that the main minerals are anorthite (46.7%) and augite (37.4%) with a minor content of forsterite (7.5%), nepheline (7.4%) and apatite below 1%.



Ol – olivine.

The chemical composition of basalt aggregate from Winna Góra (Tab. 4) show that the dominant compound is SiO₂ (43.54 wt%). Other compounds with high content are aluminium oxide Al₂O₃ (16.27 wt%), iron Fe₂O₃ (12.95 wt%), calcium oxide CaO (10.25 wt%), magnesia MgO (5.93 wt%) and sodium Na₂O (4.20 wt%). Compounds with lower concentration are titanium oxide TiO₂ (4.2 wt%) and potassium K₂O (1.42 wt%). Loss on ignition, which incorporates OH groups and CO₂, as expected, are low (1.42 wt%). The concentration of remaining compounds does not exceed 1 wt%. The chemical composition of basalt aggregate split into compounds with concentration over and below 1% is shown in Figure 9.

Tab. 4.	Chemical	composition	of basalt	aggregate	from	Winna	Góra
		• • · · · · · · · · · · · · · · · · · ·					

Compound	Content [wt%]				
SiO ₂	43.54				
TiO ₂	2.78				
Al_2O_3	16.27				
Fe ₂ O ₃	12.95				
MnO	0.25				
MgO	5.93				

CaO	10.25
Na ₂ O	4.20
K ₂ O	1.42
P_2O_5	0.76
VO_2	0.03
Cr_2O_3	0.05
CoO	0.01
NiO	0.02
CuO	0.01
ZnO	0.02
SrO	0.10
ZrO_2	0.05
Nb ₂ O ₅	0.01
Cl	0.10
LOI	1.26
Total	100.00

Since the concentration of olivine estimated based on the Rietveld method is 7.5 %, the TAS classification of igneous rocks (La Maitre et al., 1989) names the basalt aggregate as tephrite (see Fig. 10).



Fig. 9. The chemical composition of basalt aggregate from Winna Góra split into compounds with concentration over(left) and below (right) 1%.



Fig. 10. TAS Diagram with the Winna Góra basalt aggregate marked in red. Olivine is below 10%; therefore, samples can be classified as tephrite.

Results of REE abundances measured with ICP-MS are summarised in Table 5. The maximum concentrations do not exceed 50 ppm, and the highest concentration can be found for scandium, where in one sample, it reaches 45.6 ppm, yet on average, this value does not exceed 27 ppm. In the case of yttrium, concentration is even lower, and on average, it does not exceed 15.4 ppm with the maximum concentration of 22.3 ppm in one sample. For lanthanides, the concentrations of Eu, Tb, Dy, Ho, Er, Yb do not exceed 1 ppm, Tm and Lu do not occur. In the remaining six elements, the highest concentration was found for lanthanum, with the highest concentration of 20.9 ppm in sample WG/P1-1 (11 ppm on average). Cerium concentrations are 22.2 ppm on average, neodymium and samarium concentrations are 13 ppm and 8.1 ppm, respectively. Pr concentration does not exceed 10 ppm. Gadolinium concentration was low and did not exceed 8.5 ppm. La/Gd normalised ratios show Light REE enrichment over Heavy REE.

Tab. 5. REE abundances (ppm) in basalt aggregate from Winna Góra measured with ICP-MS.										
Element	WG/P1-1		WG/P1-2		WG/P1-3		WG/P1-4		WG/P1-5	
	Xa	S _x								
Sc	24.00	±0.81	17.85	±0.64	20.95	±1.20	23.55	±1.77	45.60	±0.42
Y	10.30	±0.44	8.84	±0.27	18.62	±0.86	22.27	±0.64	17.02	±0.62
La	20.91	±0.31	12.80	±0.42	7.02	±0.56	6.34	±0.36	7.85	±0.51
Ce	19.14	±3.26	12.71	±1.42	28.11	±0.72	24.41	±0.95	26.82	±1.12
Pr	-	-	9.72	±0.68	7.55	±1.37	6.28	±0.69	8.14	±1.37
Nd	21.66	±2.21	14.70	±0.28	13.55	±0.49	6.62	±0.59	8.20	±0.57
Sm	8.41	±0.33	8.30	±2.55	7.65	±0.21	6.55	±0.49	9.45	±0.92
Eu	-	-	0.25	±0.03	0.22	±0.03	0.21	±0.03	0.30	±0.02
Gd	8.11	±0.52	8.45	±1.34	7.00	±0.14	5.60	±0.42	7.05	±1.06
Tb	-	-	0.22	±0.01	0.02	±0.01	0.02	±0.01	0.02	±0.01
Dy	0.11	±0.01	0.73	±0.01	0.74	±0.02	0.62	±0.04	0.64	±0.05
Но	-	-	0.02	±0.01	0.03	±0.01	0.02	±0.01	-	-
Er	-	-	0.19	±0.01	0.22	±0.01	0.16	±0.02	0.14	±0.01
Tm	-	-	-	-	-	-	-	-	-	-
Yb	-	-	0.07	±0.02	0.09	±0.01	0.06	±0.02	0.02	±0.01
Lu	-	-	-	-	-	-	-	-	-	-
(La/Gd) _N	2.19		1.28		0.85		0.95		0.94	
Σ REE	112.64		94.85		111.77		102.09		131.25	
x _a – avera	ge									

 s_x – standard deviation

Chondrite normalised patterns for five REE with the highest abundances (Y, La, Ce, Nd, Sm, Gd and Pr) of the basalt aggregate are shown in Fig. 11. La varies from 25 to 85 ppm, Y is on average 15.4 ppm, whereas for Ce, Nd and Gd, the values are on average 22.2 ppm, 13 ppm and 8.1 ppm, respectively. Pr normalised concentration is relatively high, with 82.6 ppm on average.



Fig. 11. Chondrite-normalized (Pourmand et al., 2012) rare earth element (REE) patterns for Winna Góra basalt aggregate.

Discussion and conclusions

A basalt aggregate from Winna Góra deposit in Poland was examined in terms of chemical composition and REE content (Akatov et al., 2019). The purpose of this work was to verify if REE contents are of any importance when compared to the Western part of the Cenozoic European Volcanic Province (Pástor et al., 2020). Mineral composition and TAS diagram classify aggregate as tephrite. Five samples were tested to estimate REE potential of the basalt aggregate with the use of the ICP-MS method (Kuric, 2011). The total content of REE is 132 ppm and 111 ppm on average. Chondrite normalised curves show the highest concentration of La and Pr. In the case of HREE, the majority of elements (Eu, Tb, Dy, Ho, Er, Yb) concentrations were below 1 ppm, a Tm and Lu were not detected. Tm and Lu have very low concentrations, which are much below the ones found in Earth's crust and in the Western part of the Cenozoic European Volcanic Province (Kolb et al., 2012; Taylor and McLennan, 1985; Wedepohl, 1995; Lide and Frederikse, 1997; Pourmand et al., 2012). The low enrichment in HREE was also reflected in La/Gd ratios. In general, results are comparable to the REE contents in the western part of the Cenozoic European Volcanic Province (Kolb et al., 2012; Taylor and McLennan, 1985). This indicates its considerably low commercial potential in comparison to typical REE-bearing minerals such as bastnesite, monazite, and xenotime, which are the main rare earth minerals of commercial importance (Xie et al., 2014). On the other hand, the low content of REE and high content of metal oxides could be an advantage in agricultural use, and rock dust from Winna Góra basalt processing could be used for these purposes (Nunes et al., 2014; Dalmora et al., 2016; Ramos et al., 2017).

Accuracy of obtained results shows that the analytical method developed and employed to assess the REE content in basalt aggregate based on pressure microwave mineralisation can be successfully applied to other complex matrices with high silica content.

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