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Evaluation of Rare Earth Elements in Black Sand and Phosphate ores, EGYPT

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Abstract

The rare earth elements (REEs), uranium (U) and thorium (Th) isotopes found naturally in soil, rock, water and plant. About 20 samples of Black sand and phosphate were collected from different locations in the Rashid city , Egypt. All the collected samples were prepared and chemically treated using different acids and microwave, then analyzed using ICP-MS. The present work was conducted to identify and evaluate the compositional trends of REEs, U and Th in the samples in terms of distribution patterns and indicator ratios. The results revealed that the black sand and phosphate ores are rich as natural sources of U, Th and other rare earth elements. The elements' concentrations in black sands and phosphate ores were found higher than the world average crust soil.

Keywords: Type your keywords here, separated by semicolons ; REEs, Lanthanides, Actinides, Uranium, Thorium, Treatment, ICP-MS

1. Introduction

Rare Earth Elements (REEs) are relatively abundant in the earth's crust, but discovered economic concentrations are less common than for most other ores. REEs consist of a coherent group of elements (lanthanide series) with similar chemical properties[1]. They can be divided into light rare earth elements (LREE) which include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), plus samarium (Sm); and Heavy rare earth elements (HREE) which include europium (Eu), gadolinium (Gd), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) ytterbium (Yb), lutetium (Lu), plus yttrium(Y) [2].The demand for rare earth elements has increased substantially owing to their unique physical ,chemical and light emitting properties [3].Some of such elements (Y, Nb , Ta , Zr , Hf, and Sc) are used in wide range of new technologies with which they are closely associated in many deposits, while others such as Nd, ,Dy, Eu, Tb, and Y are considered critical rare earth in terms of their importance to clean energy economy and the risk of supply disruption [4]. The source of REEs deposition into the environment, local in its influence, is from industrial plants extracting and processing phosphoric raw materials, which result in geological and chemical anomalies in aerosols, soils, crops, aqueous systems and living organisms[5]. The naturally existing radio nuclides like Uranium (^{238}U) and Thorium (^{232}Th) are present everywhere in the Earth's crust[6]. The abundance of thorium is about four times that of uranium in the earth crust. The U content in soils is usually about 1 ppm, it can be as high as 8 ppm, means while Th contents are usually about 5 ppm, but can be as high as 50 ppm.

In fact, the general distribution of U in soils is very similar to that in stream sediments[7]. In addition, the detection of U in soil and water is of great interest in biological and environmental science due to its radioactivity[8].

The Egyptian black sand along the Mediterranean coast comprise huge reserves of several common economic minerals. The Rosetta black sands have been the subject of many articles and dissertations, as well as technical reports by private firms[9].Beach sand deposits are mostly rich sources of industrial minerals [10].

Phosphate rocks of sedimentary origin contain ^{238}U and ^{232}Th and its decay products in addition to phosphate minerals .Considerable variations are found in the chemical composition of rock phosphate from different mining areas. In general, sedimentary

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phosphate rocks, or phosphorites, originated in a marine environment, are characterized by activity concentrations of U much higher than those of volcanic and biological rocks [11].Phosphorus fertilizers contain varying amounts of heavy metals and other REEs as contaminants from either phosphate rock ores or other ingredients used in the phosphate fertilizer industry[12]. As some heavy metals are potentially unsafe to human health, attention is being given to its way of entry into the human food chain. Uptake of such elements by plants consumed directly or indirectly by humans is one path of entry, so the effects of heavy metal contaminants in phosphate fertilizers are of concern[5, 13]. In this study destructive technique ICP-MS is selected to be used to determine the concentrations of U, Th and REEs. ICP-MS technique is an effective device for its high accuracy of the detection of the trace elements. The aim from this work can be given as follows: i) quantification of REE, Th, and U in black sands and phosphate ores using ICP-MS, and ii) obtain the baseline information about the content of REE, Th, and U in black sands and phosphate ores.

2. Experimental work

2.1. Materials and Methods

All reagents and used materials were of high analytical grade (Merck PA, Accustandard® and Sartorius®).All samples under investigation have been collected from different locations in Egypt as follows: Ten samples of black sand from different locations along the Rashid city at the Mediterranean seacoast, they represent the raw black sand in 1.5 km^2 stretch and the width is variable from few meters up to 70 meters and ten phosphate samples were collected from Abu El Mahameed area. These samples were air dried and sieved on a 2-mm mesh nylon sieve and then ground in an agate mortar and passed through a stainless steel 0.3-mm mesh sieve to homogenize them. one g of sample was digested in Teflon vessels with 4 ml of 65 % nitric acid (HNO_3) and 4 ml of 48 % hydrofluoric acid (HF) in a microwave oven[14]. The extracts were transferred to 25-ml certified flasks (NBR ISO/IEC) filled with ultrapure water (Millipore Direct-Q System) and filtered in filter paper (Sartorius®).

A Four-point calibration curve for the U, Th and REEs from a standard solution containing 10 µg/ml multi-element calibration standard (Accustandard ®) was prepared. Then analysis with the coefficient of determination (r2) of the calibration curve more than 0.990 was performed. Analytical data quality and standard process measures such as curve recalibration, analyses of blanks for the acid digestion procedure; were conducted. Based on this method of digestion the collected samples are verified and validated by using IAEA- 313 and IAEA -375 soil standard reference material (SRM).All of the analyses were carried out in duplicate using ICP-MS[15, 16].

2.2. ICP-MS setup:

In this study destructive technique ICP-MS (Agilent 7700) is calibrated to determine the concentrations of U, Th, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu, Dy, Er, Ho, Tb, and Tm in black sands and phosphate samples using ICP-MS. The most important operating standard tune parameters and plasma Radiofrequency ICP-MS is given in Table 1.

Table .1. Operating conditions and ICP-MS settings:

ICP-MS operating conditions		Mass Spectrometer acquisition setting	
plasma radiofrequency power	1550 W	mass gain	139
plasma radiofrequency power matching	1.8 V	mass offset	127
carrier gas	0.99 L/min	Dwell time	50ms
Tourch axis	-0.3 H and -0.5 V	Sweeps per reading	20
Interface cones	Nickle	Replicates	3
Lense setting	Auto Lense	Reading per peak	1
electron multiplier (EM) discriminator	4.5 mV	Scan mode	Peak hopping
analog	2665V	Detector mode	dual
pulse			1666 V
plasma carrier gas offset			-0.06L/min

3. RESULTS AND DISCUSSION:

3.1. Uranium and thorium in black sand samples:

Table (2) shows the concentration of uranium, thorium in different Black sand samples collected from different places in the Rashid area in Egypt .The average concentration of U and Th were 18.62ppm and 82.67 ppm, respectively. The average concentrations are higher than the average world crust soil especially for thorium.

The concentration ratios in black sand samples to the world average crustal soil varied as, U: 4.9 ppm and Th: 5.3ppm[17]**.** The black sand contains more Th (82.67 ppm) than U (18.62ppm). The concentration of Uranium and Thorium decreases as we approach the beach starting from sample (BS1) this may be due to the effect of water currents as shown in Figure.1.

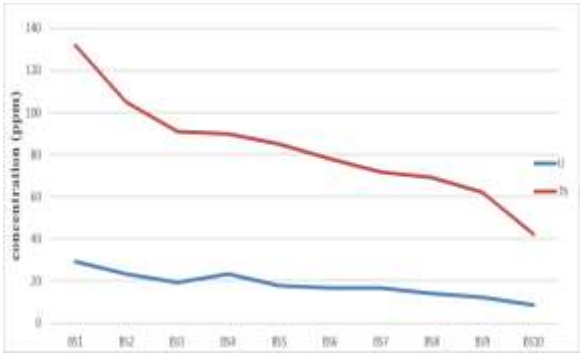

Figure 1 .Variation of concentrations for Th and U of beach black sand samples.

3.2. REEs in Black sand samples:

The rare earth elements are significant tracers and used in modeling of assorted geochemical processes. In our samples, the average concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Th, Yb and Lu were found 80.84, 42.95, 37.95, 88.44, 7.84, 29.607.05, 1.69, 8.41, 1.41, 8.29, 1.73, 5.57, 6.44 and 1.1 ppm, respectively as shown in **table (3)**. We also quantified the fractionation of LREEs and HREEs according to the La_N/Sm_N and Gd_N/Yb_N ratios, respectively, to interpret the REE patterns. Cerium [Cerium $[Ce_N / (La_N * Pr_N)^{0.5}]$ Eu anomalies $[Eu_N / (Sm_N * Gd_N)^{0.5}]$ were calculated [18], where N implies normalized values .

The average ΣREE concentrations in black sand were higher than the values reported for Brazil, Japan, China, Swedish, Europe, and the Earth's crust. As well, the average ΣHREE and ΣLREE concentrations were much higher in black sand than elsewhere except world earth crust. All of the REEs U and Th exhibited concentrations higher than those found in the average Earth's crust except for Nd, Pr and Eu. The experimental data for elemental content in our samples were compared with the similar black sand beach in other studies using instrumental neutron activation analysis (INAA) as shown in (Table 4).

Rare earth element' concentrations tend to decrease with increasing atomic number according to the Oddo Harkins rule [19]: Ce > Nd >La > Pr > Sm > Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm > Lu. In general, the average REE concentrations in this study exhibited a comparable ordering: Ce > La > Nd > Gd > Dy >Pr >Sm > Yb > Er > Tb > Ho > Eu >Lu > Tm . The concentrations distribution of REE elements in black sand samples are shown in Figure. 2(a,b).

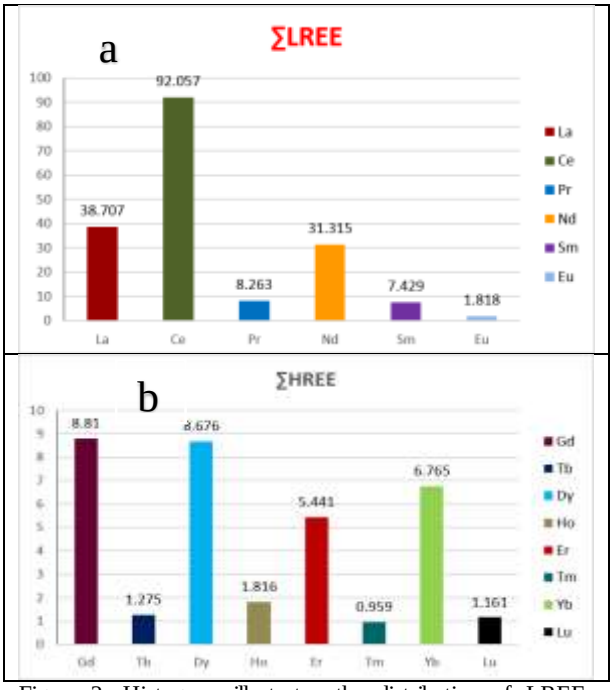

Figure 2. Histogram illustrates the distribution of LREEs and HREEs in beach black sand samples

Figure. 3 shows the proportions, in percent, of the concentrations of REE, LREE, and HREE in the studied area. LREEs comprised approximately 81% and HREEs 19% of the total REE concentrations.

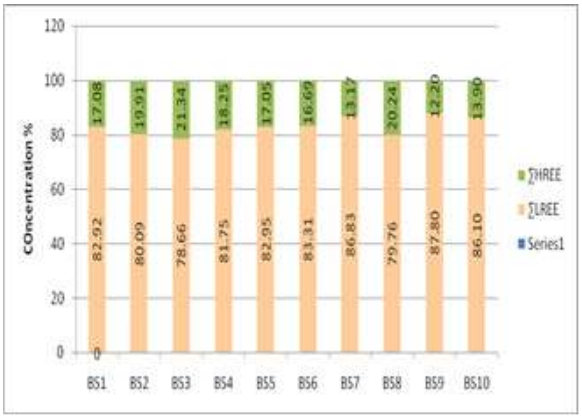

Figure3. Histogram illustrates the proportions of REE in Black sand samples.

Table .2: Concentrations of uranium and thorium in Black sand sample in ppm:

	Concentrations (ppm)										
element	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10	Ave
U	12.3	29.23	19.13	23.42	17.62	16.54	25.32	16.54	14.02	8.5	18.62

Th	62.23	132.11	91.02	90.01	85.21	78.11	105.01	71.74	69.12	42.21	82.67

a BS black sand sample are ordered according to the latitude. b ppm : part per million

Table 3: Elemental composition determined in beach black sand samples in ppm

	concentrations (ppm)										
element	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10	Ave
Sc	109	100	131	121	120	118	2.65	146	55.3	14.5	80.84
Y	19.3	61.7	49.2	57.4	45.4	47.7	3.21	53.3	55.3	56.3	42.95
La	15.4	46.6	27.5	43	32.3	39	33.77	32.6	41.9	75	37.16
Ce	36.1	69	55.8	90	89	94	82.27	64.4	176	164	88.44
Pr	4.17	10.4	6.83	10.7	7.89	9.59	7.08	7.8	9.86	8.31	7.84
Nd	17.1	41.6	28.3	41	29.5	35.2	28.35	31.2	38.9	22	29.60
Sm	3.7	8.57	6.4	8.71	6.2	7.37	4.85	6.6	8.19	13.7	7.05
Eu	1.27	2.16	1.82	1.94	1.45	1.74	1.2	1.83	1.75	3.02	1.69
Gd	3.99	9.09	7.02	11.6	9.4	11.4	8.82	7.42	8.92	10.39	8.41
Tb	0.59	1.49	1.2	1.61	1.23	1.42	1.13	1.23	1.41	1.45	1.41
Dy	3.78	10	8.22	9.65	7.27	8.07	6.83	8.36	9.08	15.5	8.29
Ho	0.83	2.31	1.84	2.12	1.64	1.75	1.17	1.93	2.01	2.57	1.73
Er	2.62	7.74	6.08	6.91	5.39	5.64	4.49	6.35	6.45	6.75	5.57
Tm	0.42	1.33	1.02	1.15	0.9	0.91	0.87	1.11	1.05	0.85	0.91
Yb	3.21	10.51	7.86	9.01	7.11	7.06	0.5	8.68	8.13	5.77	6.44
Lu	0.57	1.87	1.32	1.56	1.24	1.19	0.08	1.56	1.34	0.88	1.10
∑REE	93.75	222.6	161.0	238.9	200.5	224.3	181.4	181.0	315.0	330.1	205.7
∑LREE	77.74	178.3	126.6	195.3	166.3	186.9	157.5	144.4	276.6	286.0	171.8
∑HREE	16.01	44.33	34.36	43.6	34.18	37.44	23.89	36.64	38.42	44.16	33.90
Ce/Ce*	4.50	3.13	4.07	4.20	5.58	4.86	5.32	4.04	8.66	6.57	6.57
Eu/Eu*	0.33	0.24	0.27	0.19	0.19	0.19	0.18	0.26	0.20	0.25	0.25
Eu/Sm	0.343	0.252	0.284	0.222	0.233	0.236	0.247	0.277	0.213	0.220	0.239
Ce/La	2.344	1.480	2.029	2.093	2.755	2.410	2.436	1.975	4.200	2.186	2.379
La/Yb	4.797	4.438	3.580	4.772	4.542	5.524	67.54	3.755	5.153	12.99	5.767

[a] *To calculate Ce/Ce* and Eu/Eu* (McDonough and Sun, 1995).* *B ppm: part per million*

Table. 4: Descriptive statistics of the concentrations of REE, ∑REE, ∑LREE and ∑HREE of black sand (in ppm) the obtained results are compared with national and international soil data and Earth crust.

Element	mean	SD	median	min	max	P value	Egypt Black sand	Brazil	Japan	China	Swedish	Europe	Earth's crust
U	18.262	6.26	17.08	8.5	29.23	0.000	16.32	ND	ND	ND	ND	ND	3.3
Th	82.6771	24.61	81.66	42.21	132.11	0.000	78.84	ND	ND	ND	ND	ND	12.1
La	38.707	15.56	36.385	15.4	75	0.305	29.4	20.8	18.0	37.4	17.4	25.9	35.0
Ce	92.057	44.82	85.635	36.1	176	0.009	44.1	43.5	40.0	64.7	37.7	52.2	66.0
Pr	8.263	1.98	8.1	4.17	10.7	0.047	ND	9.61	4.53	6.67	4.10	6.02	9.10
Nd	31.31	8.04	30.35	17.1	41.6	0.083	35	17.7	18.0	25.1	15.1	22.4	40.0
Sm	7.429	2.72	6.985	3.7	13.7	0.030	31.32	3.37	3.74	4.94	2.98	4.28	7.00
Eu	1.818	0.52	1.785	1.2	3.02	0.051	7.52	0.600	1.03	0.980	0.650	0.850	2.10
Gd	8.81	2.26	9.03	3.99	11.6	0.124	8.54	2.32	3.72	4.38	3.07	4.20	6.10
Tb	1.275	0.28	1.315	0.59	1.61	0.593	3.625	0.500	1.22	0.580	0.490	0.640	1.20
Dy	8.676	2.97	8.29	3.78	15.5	0.253	ND	0.930	3.33	3.93	2.95	3.58	4.50
Ho	1.816	0.51	1.885	0.83	2.57	0.289	ND	0.17	0.71	0.830	0.610	0.720	1.30
Er	5.441	1.31	5.69	2.62	6.9	0.206	ND	0.59	2.02	2.42	1.88	2.10	3.50
Tm	0.959	0.24	0.955	0.42	1.33	0.036	ND	nd	0.29	0.24	0.36	0.33	0.33
Yb	6.765	2.95	7.395	0.5	10.5	0.124	31.12	0.670	2.01	2.32	2.01	2.09	3.10
Lu	1.161	0.53	1.28	0.08	1.87	0.174	3.3	0.050	0.34	0.35	0.300	0.300	0.800
∑LREE	179.589	63.35	172.335	77.74	286.03	0.273	147	95.6	85.2	140	78.0	112	159
∑HREE	34.903	8.91	36.04	16.01	44.16	0.0329	46	12.0	13.2	14.8	11.3	13.6	51.5
∑REE	214.492	70.09	210.59	93.75	330.19	0.014	193	108	98.4	155	89.3	125	211

References	This study	A. Ali et al.(2018)	Silva et al. (2016)	Yoshida et al. (1998)	Wei et al. (1991)	Sadeghi et al. (2013)	Sadeghi et al. (2013)	Tyler and Olsson (2002)

3.3. Uranium and thorium in phosphate samples:

Most Phosphate rocks contain between 30 and 200 ppm U and less than 10 ppm Th [20] .Table (5) shows the concentrations of U and Th in phosphate samples. The average concentrations of U and Th were 127.26 and 22.94 ppm, respectively. These concentrations are higher than the average world crust soil [17, 20] especially for U (10%).

In the present study, the average concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Th, Yb and Lu were found 4.24, 53.81, 39.80, 58.74, 7.43, 31.13,5.80, 1.691.55, 6.9.2, 1.14, 6.75, 1.7,1.46, 4.75, and 0.84 respectively as shown in table (6).

Figure 4. Shows the proportions, in percent, of the concentrations of REE, LREE, and HREE in the studied area. LREEs comprised approximately 84% and HREEs 16% of the total REE concentration. The average ΣREE, ΣLREE and ΣHREE concentrations in phosphate samples were lower than the values reported for the Earth's crust.

The average concentrations of U and Th were higher than the values reported for the Earth's crust Table (7).on the other hand, the average concentrations of ΣREE, ΣHREE and ΣLREE were lower than the world earth crust . Other international studies for estimation of such elements in phosphate ores are scarce and conducting using different techniques [20-22].The previous studies in Egypt evaluated the radioactivity of phosphate using instrumental neutron activation analysis[23-25].

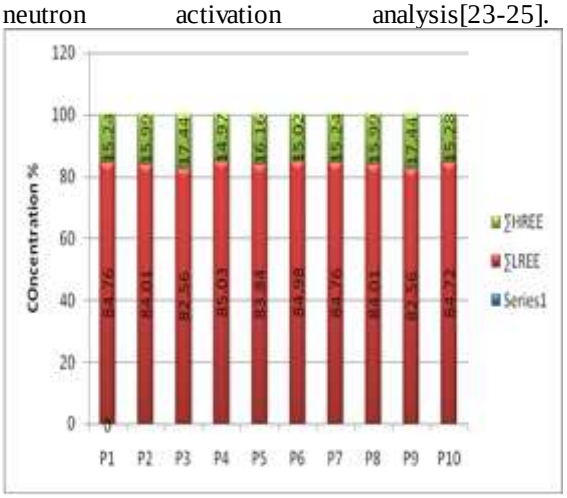

Figure4. Histogram illustrates the proportions of REE in phosphate samples.

4. CONCLUSION

In general, the Egyptian black sand contains several economic minerals. It is a promising source of REEs; Th and U. Based on this work, the baseline information concerning the content of Th, and U in the analyzed black sand and phosphate ores are obtained. It was observed that the average concentrations of U and Th in the samples were found to be higher than the average world level (4.9, 5.3%). The ratios of Eu / Sm and Ce/La values are almost the same as that presented in the literature, which confirms the precision of the ICP-MS analytical techniques applied in this work. The black sands in Rashid city are not recommended to be used in building materials due to the high content of Th and U. The measured REEs elements have many applications in medical, biological, industrial and nuclear fields.

5. Conflicts of interest

There is No conflict of interest.

Table .5: Concentrations of Uranium and thorium in Phosphate samples

	concentrations(ppm)										
Element	P1	P2	*P3*	*P4*	*P5*	P6	P7	P8	P9	P10	Ave
U	139.92	144.01	145.2	136	136.89	141.24	148.34	144	137.24	139.75	127.26
Th	25.213	25.33	26.34	21.03	23.57	27.34	28.23	29.34	21.3	26.94	22.942

Table .6: Concentrations of REEs in Phosphate samples.

Elements	concentrations(ppm)										ave
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	
Sc	5.32	2.74	2.58	3.98	7.56	6.32	5.22	2.78	2.88	3.08	3.7148
Y	70.69	40.10	52.55	50.87	43.08	67.11	70.69	50.10	42.55	50.40	46.745
La	49.78	33.02	35.33	39.89	32.13	50.65	49.87	33.02	35.33	38.89	34.813
Ce	69.92	44.69	69.21	51.67	40.66	74.76	69.92	44.69	69.21	52.71	51.752
Pr	8.44	5.55	8.04	6.34	8.20	9.19	8.44	5.55	8.04	6.59	6.594
Nd	35.52	23.49	32.23	26.01	36.22	38.58	35.52	23.49	32.23	28.01	27.578
Sm	6.81	4.61	6.58	5.42	3.61	7.56	6.81	4.61	6.58	5.47	5.125
Eu	1.92	1.29	1.57	1.34	1.01	2.08	1.92	1.29	1.57	1.52	1.359
Gd	8.31	5.66	7.15	5.46	6.20	8.88	8.31	5.66	7.15	6.49	6.096
Tb	1.21	0.82	1.18	0.91	1.86	1.31	1.21	0.82	1.18	0.93	1.022
Dy	7.73	5.27	7.8	5.93	5.86	8.14	7.73	5.27	7.80	5.98	5.978
Ho	1.74	1.21	1.71	1.31	0.87	1.80	1.74	1.21	1.71	1.34	1.29
Er	5.33	3.73	5.51	4.33	4.53	5.41	5.33	3.73	5.51	4.10	4.217
Tm	0.75	0.53	0.91	0.68	0.38	0.76	0.75	0.53	0.91	0.58	0.603
Yb	5.12	3.63	6.95	3.76	2.47	5.19	5.12	3.63	6.95	3.96	4.166
Lu	0.83	0.59	1.11	0.63	1.31	0.82	0.83	0.59	1.11	0.65	0.764
∑REE	203.5	134.09	185.28	153.67	145.31	215.13	203.5	134.09	185.28	157.2	151.3
∑LREE	172.4	112.6	152.9	130.6	121.83	182.8	172.4	112.65	152.96	133.1	127.2
∑HREE	31.02	21.44	32.32	23	23.48	32.31	31.02	21.44	32.32	24.03	24.13
Eu/Sm	0.281	0.279	0.238	0.247	0.279	0.275	0.281	0.279	0.238	0.27	0.265
Ce/La	1.40	1.353	1.958	1.295	1.265	1.476	1.40	1.353	1.958	1.3	1.48
La/Yb	9.740	9.096	5.083	10.609	13.0081	9.759	9.740	9.096	5.083	9.820	8.3567

Table. 7:Descriptive statistics of the concentrations of REE, ∑REE, ∑LREE and ∑HREE of phosphate samples (in ppm) the obtained results are compared with the Earth crust.

Element	mean	SD	median	min	max	P value	Earth's crust
U	73.26	4.05	80.58	76.00	88.34	0.000	3.3
Th	22.94	2.79	25.84	21.03	29.34	0.000	12.1
La	34.81	7.54	37.11	32.13	88.34	0.305	35.0
Ce	51.75	13.06	60.96	40.66	50.65	0.009	66.0
Pr	6.59	1.31	8.04	5.55	74.76	0.047	9.10
Nd	27.57	5.53	32.23	23.49	9.19	0.083	40.0
Sm	5.12	1.26	6.03	3.61	38.58	0.030	7.00
Eu	1.35	0.34	1.55	1.01	7.56	0.051	2.10
Gd	6.09	1.24	6.82	5.46	2.08	0.124	6.10
Tb	1.02	0.31	1.18	0.82	8.88	0.593	1.20
Dy	5.97	1.18	6.86	5.27	1.86	0.253	4.50
Ho	1.29	0.32	1.53	0.87	8.14	0.289	1.30
Er	4.21	0.75	4.93	3.73	1.80	0.206	3.50
Tm	0.60	0.17	0.72	0.38	5.51	0.036	0.33
Yb	4.16	1.47	4.54	2.47	0.91	0.124	3.10
Lu	0.76	0.25	0.83	0.59	6.95	0.174	0.800
∑REE	151.35	30.44	171.25	134.09	1.31	0.273	211
∑LREE	127.22	25.90	143.08	112.65	215.13	0.0329	159
∑HREE	24.13	4.89	27.53	21.44	182.82	0.014	51.5
References	This study						Tyler and Olsson (2002)

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