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Measurement of rare earths elements in Kakul phosphorite deposits of Pakistan using instrumental neutron activation analysis

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Abstract The rare earth elements (REEs) content of Kakul phosphate rock (PR) from different localities of the main Hazara deposits of Pakistan were determined using instrumental neutron activation analysis (INAA). 25 phosphorite samples were collected from different phosphorite sites and 6 samples representing different batches from the crushing plant near Kakul Mine. Concentrations of seven REEs (Ce, Eu, La, Lu, Sm, Tb and Yb) were determined in the PR samples. The highest amounts of Heavy and light rare earth elements (HREE and LREE) were quantified in the PR samples collected at the Phosphate Rock Crushing Plant while the lowest amounts of these REEs were measured in the Lambidogi Phosphorite deposit samples. Comparison with global data showed the REEs content of the studied PRs show lower range for all REEs and mostly comparable to the data reported by Israel and Syria. Calculated chondrite ratio for these elements depicts enrichment of LREEs in all phosphorite deposits.

Keywords Instrumental neutron activation analysis (INAA) technique · Phosphate rock · Rare earth elements (REEs) · Chondrite ratio

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Introduction

Rare earth elements (REEs) include 15 chemically similar metallic elements of the lanthanide series from La to Lu. The REEs have less mobility and fractionation during weathering and sedimentation processes [1]; therefore they are widely used as tracers to investigate environmental changes and in studies related to the origin of sediments especially of anthropogenic origin [2–7]. REEs can also be used in manufacturing environmental protection and pollution-control systems (Ce), as cracking agents in petroleum refinery (La), in permanent magnets (Nd), and in phosphors for colour television and fluorescent lighting (Eu) etc. REEs can also occur in phosphorous fertilizers in trace amounts [8, 9]. The major source of the REEs is phosphate rock (PR) from which the specific fertilizer is made, or they can originate in the fertilizer from the ingredients used in fertilizer industry.

Phosphate fertilizers have been extensively used in agriculture for years and it is possible that their use will increase in the coming decades. Therefore even low accumulation rate of REEs in soil may finally reach undesired values. This risk may be higher to soils where there is extensive use of fertilizers with high REEs contents [10]. There are some reports in which REE accumulation and their effects on crops and soils after different concentrations of REE application have been studied [11–13]. A study by Diatloff and Smith [14] showed that REEs were toxic to plants. A 50% reduction in corn root elongation was evident with 4.8–7.1 μmol L^{-1} La or 12.2 μmol L^{-1} Ce in solution culture. In another study it was also indicated that rice straw weight and total grain weight were significantly decreased with high La concentration ($\geq$1.5 mg L^{-1}) in solution [15]. Exposure to excess amounts of REEs can cause notably harmful effects on the function of the immune, circulatory, digestive, and nervous systems of humans. This can affect the Intelligence Quotient (IQ), physical growth, and development of children, and can even cause cancer [16]. Therefore, extensive use of PR increases their REEs accumulation in the environment and may cause threat to the environment and finally human beings. So the ecological risk of the use of REEs has to be assessed and managed by drawing limits accordingly. Conversely REEs have been occasionally added as micronutrient in fertilizers for soil nutrient enhancement. In China, REEs are being applied to soil to increase crop yields since 1972 [17, 18]. Their use increased to few thousands tons per year in the early 1980s. Nowadays REEs complex fertilizers with La and Ce as their major components are extensively applied to the soil [19]. Such compound fertilizers include urea, organic compounds and carbon ammonium mixed with REEs [20, 21].

Hazara phosphorites are the only known commercially available deposits of phosphate in Pakistan. These deposits occur within 10 km from Abbottabad city. Out of these only Kakul Phosphate Mine is producing 60,000 ton of phosphate rock per year. These ore reserves are being exploited in manufacturing single super phosphate (SSP) at fertilizer plants in Pakistan [22]. The present study was undertaken to determine the REEs content of phosphate rock samples collected from Kakul mines of Pakistan. A total of 7 rare earth elements were quantified using Instrumental Neutron Activation Analysis technique (INAA).

Experimental

Sample collection

A total of 31 PR samples were collected from the major phosphorite deposits of Hazara in the North West Frontier Province (NWFP). The deposits occur in an area of about 30 km linear dimension within latitude of 34°5′–34°30′ N. Figure 1 shows location map of the phosphate rock deposits of the study area. Sample collection sites include Kakul Mines, Kakul West Open Pits (north, middle and south points), Lambidogi Open Pit and Sarhad Development Authority (SDA) Plant for crushing and milling the phosphate rock at Kakul. Twenty five samples were collected from various sections of each mine including Hanging Wall (i.e. formation immediately above the main phosphorite body), main phosphorite formation and Foot Wall (i.e. formation immediately below the main phosphorite body). Six samples were collected from Phosphate Rock Crushing Plant. These sites contain P_2O_5 content ranging from 30 to 38%. Details of samples collected are given in Table 1.

About 1 kg of each rock sample was collected and packed in labeled polythene bags. All the samples were taken to the Geochemistry Laboratory at the Pakistan Institute of Engineering and Applied Sciences (PIEAS) where the PR samples were washed and sun dried. All the samples were crushed and ground using a Tungsten Carbide crusher and the powder was dried at 110 °C for 20 h.

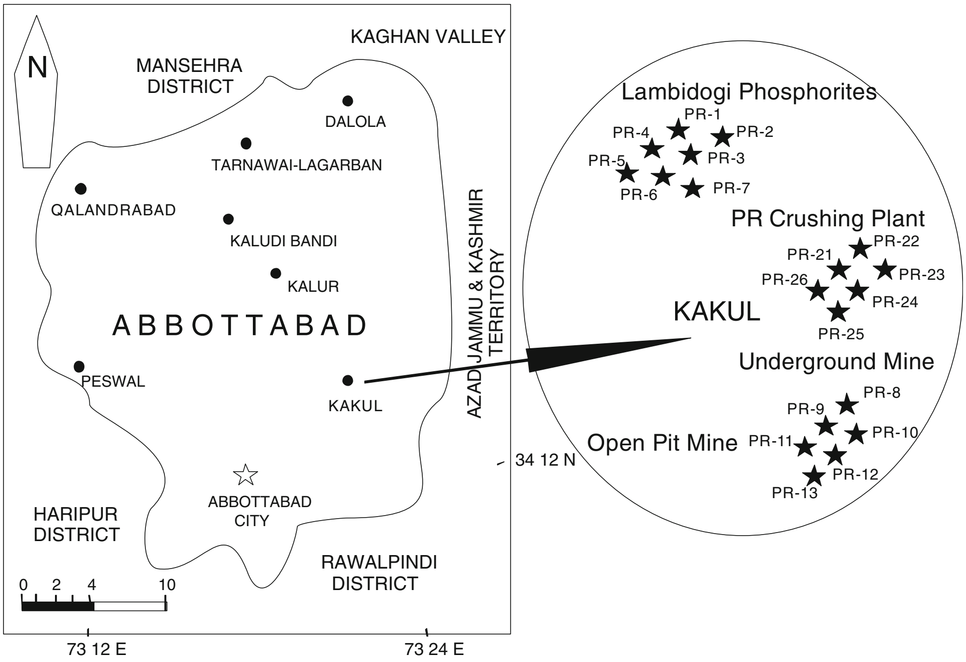


Fig. 1 Location map of the phosphate rock deposits of the study area

Table 1 Sample description

Sample number	Sample details
A. Lambidogi Phosphorite	
PR-1	Main rock body
PR-2	Main rock body
PR-3	Main rock body
PR-4	Main rock body
PR-5	Main rock body
PR-6	Hanging wall
PR-7	Foot wall
B. Kakul Mine (under ground) Phosphorite	
PR-8	Main rock body
PR-9	Main rock body
PR-10	Main rock body
PR-11	Main rock body
PR-12	Hanging wall
PR-13	Foot wall
C. Kakul West Open Pit Mine Phosphorite	
PR-14	Main rock body
PR-15	Main rock body
PR-16	Main rock body
PR-17	Main rock body
PR-18	Main rock body
PR-19	Hanging wall
PR-20	Foot wall
D. Kakul Phosphate Rock Crushing Plant	
PR-21	Phosphorite
PR-22	Phosphorite
PR-23	Phosphorite
PR-24	Phosphorite
PR-25	Phosphorite
PR-26	Phosphorite

Target preparation and radioassay

A synthetic multi-element comparison standard was prepared as mentioned in our earlier works [23, 24]. By taking optimum amounts of specpure elemental salts from Johnson and Matthey and dissolving in ultra-pure aqueous acid mixture from E. Merck. 100 μL of the aliquot was then dried on filter paper and used as a comparative standard throughout this work. In order to ensure accurate and precise analytical results, quality assurance was performed and the concurrent analyses of IAEA SL-1 (Lake Sediment) and GSJ-JR-1 (Rhyolite) reference materials was done using the multi-element comparator base by adopting the same irradiation, cooling and counting protocols as for the sample. Multiple batches of about 100 mg of sample in triplicate, synthetic multi-element comparison base and reference materials (RMs) were packed in clean polyethylene capsules. The samples were thermally sealed and each batch was then packed in reactor rabbit and labeled prior to irradiation. The prepared targets were subjected to different irradiation protocols. The different irradiation protocols used to determine REEs of various half lives are presented in our earlier publication [25–27].

NAA instrumentation

The sealed targets were irradiated in the periphery of the core of the Pakistan Atomic Research Reactor (PARR-2) which is a miniature neutron source reactor (MNSR). The reactor power is 27 kW with a thermal flux of 1×10^{12} n cm^{-2} s^{-1}. Before counting, the samples were transferred to pre-cleaned and pre-weighed polyethylene capsules for counting. The measurement system consisted of a Canberra model (AL-30) high purity Germanium detector (HPGe) attached to a PC-based multi-channel analyzer (MCA), (Inter-Technique model pro-286e) through a sensitive spectroscopy amplifier (Ortec model 2010). The resolution of the system was 1.9 keV for 1,332.5 keV ^{60}Co peak with a peak to Compton ratio of 40:1. Intergamma version 5.03 software was used for data acquisition. For calculations our indigenously developed computer program for activity and concentration calculations was used. All corrections for background and any required decay factors are incorporated in this program called “GammaCal”.

Results and discussion

Analysis of rare earth content of phosphate rock samples collected from the Hazara phosphate deposits of Pakistan was carried out using INAA. Two different irradiation protocols were adopted for the quantification of ten REEs using the PARR 2 irradiation facility. Irradiation protocol 1 comprising of intermediate lived isotopes (^{140}La, ^{153}Sm and ^{175}Yb) were measured after 1 h irradiation and cooling times of 1–2 days while in irradiation protocol 2, the long lived isotopes (^{141}Ce, ^{152}Eu, ^{177}Lu, and ^{160}Tb) were quantified through irradiation for 5 h and decay time of 2–3 weeks. All possible spectral interferences for the REEs were corrected. The full energy peak area for ^{141}Ce at 145.5 keV was determined by subtracting contribution from ^{59}Fe at 142.5 keV [24–28]. Furthermore, to avoid elemental interferences, the gamma-peaks used for the quantification of most of the REEs were carefully selected. To measure ^{152}Eu the high abundance clear peaks at 344.3 and 1,408 keV were selected for quantification. Interference free photo peaks at 1,596.5 keV for ^{140}La and 396.3 keV for ^{175}Yb using irradiation protocol 1 were considered for the measurement of these two elements.

Table 2 INAA of REEs in IAEA lake sediment and GSJ rhyolite

Element	IAEA SL-1 (lake sediment)[a]		GSJ-JR-1 (rhyolite)[b]	
	Our value	Certified value	Our value	Certified value
Ce	115 ± 7	117 ± 17	47.0 ± 2.8	47.2 ± 4.3
Eu	1.50 ± 0.12	(1.60)	0.33 ± 0.03	0.31 ± 0.04
La	51.2 ± 4.1	52.6 ± 3.1	20.1 ± 1.2	19.7 ± 1.8
Lu	0.53 ± 0.05	(0.54)	0.68 ± 0.07	0.71 ± 0.08
Sm	9.50 ± 0.50	9.25 ± 0.51	5.90 ± 0.30	6.03 ± 0.81
Tb	1.36 ± 0.14	(1.40)	1.09 ± 0.11	1.01 ± 0.20
Yb	3.50 ± 0.30	3.42 ± 0.64	4.70 ± 0.40	4.55 ± 0.46

() Information value

Source: [a] International Atomic Energy Commission (IAEA)

[b] Geological Survey of Japan (GSJ)

However ^{177}Lu and ^{175}Yb interference was encountered at 112.9 keV and dealt with as mentioned in our earlier work [26, 27]. The results for the two RMs (IAEA-SL-1 and GSJ-JR-1) are shown in Table 2. This shows that the results obtained correspond very well with the certified values for the quantified REEs [29, 30].

Concentrations of 7 REEs in phosphate rock samples analyzed using NAA technique are presented in Table 3. Ce, Eu, La, Lu, Sm, Tb and Yb, were determined using intermediate and long irradiation protocols. The detection limits in µg/g for each element are presented in parenthesis. Each elemental concentration is reported on dry weight basis and their associated uncertainties in µg/g. Average values and ranges for the REEs in all samples collected at each site are also given in this table. At site A (Lambidogi Phosphorite) the main rock body samples show a close concentration range for most of the quantified REEs with the exception of sample PR-2 that shows very high concentration of Light REEs (LREE) i.e. Ce, La and Sm. The same sample shows slightly elevated levels of Middle REEs (MREE) i.e. Eu and Tb while Heavy REEs (HREE) i.e. Lu and Yb are in comparable range to other samples of the same site. Sample PR-6 (hanging wall) from the same site has lower concentration for all REEs while sample PR-7 (foot wall) shows least concentration for these elements. The site B (Underground Phosphorite) shows all detected REEs in the main rock body have a large variation in concentration except for Eu. Sample PR-9 has very high concentration of all elements whereas PR-10 was quantified with very low levels of MREEs and very high concentration levels of LREE and HREE. Similar to site A this site also indicates lower concentrations of all REEs in hanging wall (PR-12) and foot wall (PR-13) samples. Lu in samples PR-10, PR-11 and PR-12 could not be quantified due to concentration levels below the minimum detectable limits. Site C represents open pit Phosphorite mine. Sample PR-15 shows maximum variation and high concentration range for Ce, La, Lu, Sm, Tb and Yb while Eu is lower than in sample PR-16. The rest of the REEs except for Lu are also comparably high in this sample. A closer inspection of the data shows that at sites A (Lambidogi Phosphorite) and B (Kakul Mines) the concentrations of the REEs determined are lower for the hanging wall (PR-6 and PR-7) and foot wall (PR-12 and PR-13) samples and respectively, whereas for site C (Kakul West [Open Pit Mine] Phosphorite deposits) the amounts of REEs determined in the hanging wall and foot wall samples are variable and generally higher than the main rock body. The hanging wall and foot wall are defined on the P_2O_5 content therefore the amounts of REEs may be higher or lower in the PR samples collected at these sites as compared to the main rock body. The variations in concentration of the REEs determined may be due to geological differences between sites. Characterization of REEs in Phosphorite samples collected from six different batches at the Kakul phosphorite rock crushing plant (D) show that these elements are in close range in all samples. However relatively high La in PR-21 and Lu contents in PR-24 were observed. Sample PR-26 however show lowest levels of these elements. This variation in concentration range could be due to the different batches collected from different locations of the same mine. The variation in REEs concentration in all phosphorite sites could be due to the topography of the area and some geological processes for the formation of phosphorite rocks that result in depletion and enrichment of the REEs [31].

In order to compare the REEs content of local phosphate rocks with global results the concentration range of REEs in all of the PR samples studied in this work (data for the main rock formations only) is presented along with global data in Table 4 [32–35]. The comparison shows that the PR deposits of Russia depict highest concentration values for LREE with Ce (3,420 µg/g), La (2,150 µg/g), Sm (131 µg/g) and MREEs with Eu (45 µg/g), and Tb (9.6 µg/g). However low concentration levels of all REEs of Ce (22 µg/g), Eu (1.02 µg/g), La (34 µg/g), Lu (0.8 µg/g), Sm (5.2 µg/g), Tb (0.50 µg/g) and Yb (4.6 µg/g) were reported for Israel phosphate rocks. The reported concentration ranges for HREEs (Lu, and Yb) and MREEs (Eu and Tb) in this work are compatible to the lower values cited in Table 4. However the Ce concentration in the PR of the Hazara area is comparable to Morocco, Syria and Tunis whereas Sm concentration to all reported countries except Russia. Tb concentration range for Pakistan is similar to Morocco, Syria, Tunis and USA. On the whole the REEs content of Pakistani PR are closet to the data cited for Israel and Syria.

The Chondrite ratio plot shown in Fig. 2, which has been obtained for the average REEs content of PR samples

Table 3 Concentration of rare earth elements in Kakul phosphate rocks using INAA (all concentrations expressed in μg/g)

Sample number	Elements						
	Ce (0.3)	Eu (0.01)	La (0.2)	Lu (0.003)	Sm (0.02)	Tb (0.03)	Yb (0.1)
A. Lambidogi Phosphorite							
PR-1	45.1 ± 10.9	1.6 ± 0.3	39.7 ± 6.3	0.4 ± 0.1	10.2 ± 2.4	1.6 ± 0.4	5.1 ± 1.2
PR-2	53.9 ± 13.0	2.5 ± 0.6	62.6 ± 10.7	0.3 ± 0.1	65.3 ± 14.7	1.9 ± 0.5	5.1 ± 1.1
PR-3	32.1 ± 7.4	1.2 ± 0.4	44.2 ± 7.5	0.8 ± 0.2	37.6 ± 8.2	1.3 ± 0.4	3.4 ± 0.7
PR-4	48.7 ± 12.6	2.3 ± 0.6	57.2 ± 8.9	0.4 ± 0.1	13.2 ± 3.5	1.6 ± 0.4	4.8 ± 1.1
PR-5	47.4 ± 10.7	1.5 ± 0.4	54.4 ± 9.2	0.3 ± 0.1	12.8 ± 3.0	1.6 ± 0.5	6.9 ± 1.3
PR-6	15.3 ± 3.6	0.3 ± 0.1	12.9 ± 2.1	0.10 ± 0.01	9.5 ± 2.1	0.2 ± 0.1	0.7 ± 0.1
PR-7	2.2 ± 0.6	0.03 ± 0.01	1.3 ± 0.2	0.10 ± 0.03	0.4 ± 0.1	0.04 ± 0.01	0.2 ± 0.03
Mean ± SD	34.9 ± 8.4	1.35 ± 0.34	38.9 ± 6.4	0.34 ± 0.09	21.3 ± 4.8	1.17 ± 0.33	3.74 ± 0.79
Range	2.2–53.9	0.03–2.50	1.36–62.60	0.1–0.8	0.4–65.3	0.04–1.90	0.2–6.9
B. Kakul Mines (underground) Phosphorite							
PR-8	53.9 ± 13.0	1.7 ± 0.4	52.1 ± 8.8	0.4 ± 0.1	12.2 ± 3.0	1.6 ± 0.5	4.2 ± 1.0
PR-9	70.6 ± 15.9	1.7 ± 0.3	57.5 ± 10.8	0.6 ± 0.1	16.6 ± 4.0	2.2 ± 0.7	6.8 ± 1.5
PR-10	15.7 ± 3.6	1.3 ± 0.3	12.7 ± 2.5	–	3.6 ± 1.0	0.5 ± 0.1	1.5 ± 0.4
PR-11	40.5 ± 9.6	1.4 ± 0.3	39.1 ± 6.7	–	10.3 ± 2.4	1.3 ± 0.4	2.7 ± 0.5
PR-12	6.6 ± 1.6	0.10 ± 0.04	4.4 ± 0.8	–	1.0 ± 0.3	0.2 ± 0.1	0.3 ± 0.1
PR-13	5.1 ± 1.4	0.20 ± 0.04	2.5 ± 0.4	0.04 ± 0.01	0.7 ± 0.2	0.10 ± 0.02	0.3 ± 0.1
Mean ± SD	32.1 ± 7.5	1.06 ± 0.23	28.1 ± 5.0	0.35 ± 0.07	7.4 ± 1.8	0.98 ± 0.30	2.6 ± 0.6
Range	5.1–70.6	0.1–1.7	2.5–57.5	0.04–0.60	0.7–16.6	0.1–2.2	0.3–6.8
C. Kakul West (open pit mine) Phosphorite							
PR-14	4.5 ± 1.1	0.10 ± 0.03	2.9 ± 0.6	0.4 ± 0.1	0.8 ± 0.2	0.2 ± 0.1	0.3 ± 0.1
PR-15	111 ± 30.2	1.3 ± 0.5	155.6 ± 67.6	1.23 ± 0.3	17.0 ± 4.1	3.8 ± 1.1	10.1 ± 2.0
PR-16	49.9 ± 12.0	1.7 ± 0.3	44.7 ± 12.6	0.20 ± 0.04	11.1 ± 2.5	1.3 ± 0.4	2.8 ± 0.7
PR-17	5.0 ± 1.3	0.10 ± 0.04	3.0 ± 1.0	0.10 ± 0.02	0.8 ± 0.2	0.2 ± 0.1	0.5 ± 0.1
PR-18	5.2 ± 1.4	0.20 ± 0.04	2.9 ± 0.9	0.03 ± 0.01	1.1 ± 0.2	0.2 ± 0.1	0.4 ± 0.1
PR-19	54.9 ± 15.2	0.9 ± 0.2	37.7 ± 7.5	0.3 ± 0.1	10.8 ± 2.4	1.3 ± 0.4	3.0 ± 1.0
PR-20	46.5 ± 10.9	1.4 ± 0.4	49.3 ± 11.0	0.20 ± 0.04	9.8 ± 2.2	1.2 ± 0.4	2.6 ± 0.5
Mean ± SD	39.7 ± 12.5	0.8 ± 0.2	42.3 ± 14.5	0.4 ± 0.1	7.3 ± 1.7	1.2 ± 0.4	2.8 ± 0.6
Range	4.5–111.3	0.1–1.7	2.9–155.6	0.10–1.23	0.8–17.0	0.2–3.8	0.3–10.1
D. Kakul Phosphate Rock Crushing plant							
PR-21	66.9 ± 15.1	2.2 ± 0.5	85.2 ± 18.2	0.4 ± 0.1	13.1 ± 2.9	2.1 ± 0.6	5.4 ± 1.0
PR-22	51.9 ± 12.2	1.3 ± 0.3	27.5 ± 4.3	0.4 ± 0.1	7.4 ± 1.7	1.2 ± 0.3	3.5 ± 1.0
PR-23	35.6 ± 8.5	1.5 ± 0.3	32.4 ± 5.3	0.3 ± 0.1	8.1 ± 2.1	1.3 ± 0.4	3.1 ± 0.6
PR-24	59.9 ± 13.5	2.3 ± 0.6	43.5 ± 7.3	0.9 ± 0.2	13.1 ± 3.3	2.3 ± 0.6	5.7 ± 1.1
PR-25	54.9 ± 12.5	1.5 ± 0.5	36.2 ± 6.0	0.7 ± 0.1	11.9 ± 3.0	1.4 ± 0.4	5.4 ± 1.2
PR-26	11.4 ± 3.1	0.4 ± 0.1	5.3 ± 1.0	0.03 ± 0.01	1.3 ± 0.3	0.2 ± 0.1	0.7 ± 0.1
Mean ± SD	46.7 ± 10.8	1.5 ± 0.4	38.3 ± 7.0	0.45 ± 0.10	9.2 ± 2.2	1.4 ± 0.4	3.9 ± 0.8
Range	11.4–66.9	0.4–2.3	5.3–85.2	0.03–0.90	1.3–13.1	0.2–2.3	0.7–5.7

at each site, follows the same trend as the data for REEs concentrations; i.e. the Chondrite ratios in PR samples being highest at site D and lowest at site B. The Plot also confirms high enrichment of LREEs (Ce, La and Sm) at all sites. However the major difference between the Chondrite ratios plots for the PR samples is that La at site C and Sm at site A has the highest Chondrite ratio.

Further research is in progress to investigate REEs and other trace elements in phosphate fertilizers and the uptake of these elements by some of the crops. These studies would hopefully provide more quantitative information regarding accumulation of REEs in the specific crop and risks assessment of large-scale application of REE fertilizers.

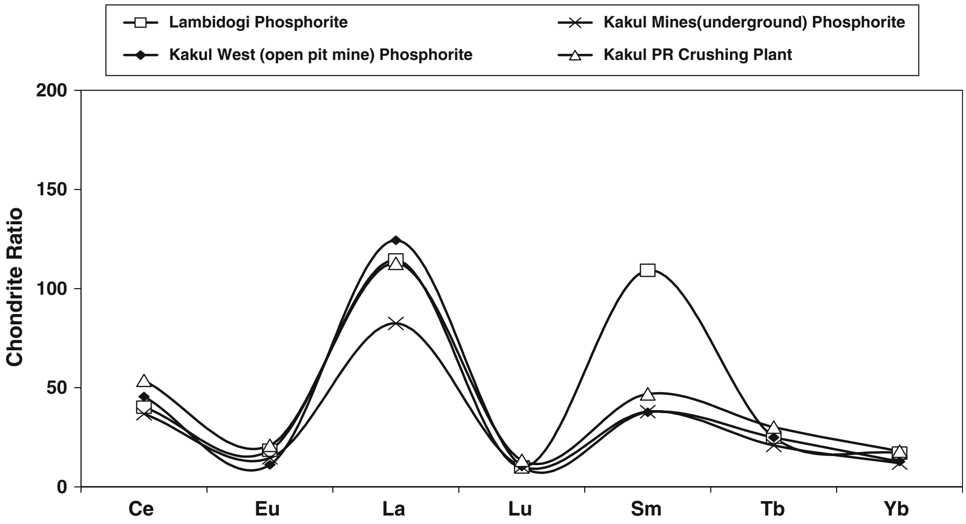
Table 4 Global pattern of rare earth elements (μg/g) in phosphate rocks

Elements	Ce	Eu	La	Lu	Sm	Tb	Yb
Algeria[a]	290 ± 4	8.7 ± 0.2	191 ± 2	2.4 ± 0.1	36 ± 1	3.5 ± 0.3	16.5 ± 0.6
Israel[b]	22 ± 4	1.02 ± 0.03	34 ± 1	0.8 ± 0.1	5.2 ± 0.1	0.50 ± 0.01	4.6 ± 0.2
Morocco[a]	46 ± 3	3.9 ± 0.1	109 ± 2	2.7 ± 0.1	12.9 ± 0.2	2.3 ± 0.2	14.5 ± 0.6
Nigeria[c]	474 ± 2	13.8 ± 0.2	243 ± 04	3.4 ± 0.1	56 ± 1	9.4 ± 0.1	29 ± 4
Russia[b]	3420 ± 37	45 ± 1	2150 ± 20	0.9 ± 0.1	131 ± 2	9.6 ± 0.7	10.9 ± 0.4
Syria[d]	41 ± 3	1.70 ± 0.04	46 ± 1	0.9 ± 0.1	9.3 ± 0.1	0.90 ± 0.07	5.0 ± 0.3
Togo[b]	225 ± 2	7.6 ± 0.1	120 ± 1	1.2 ± 0.1	25 ± 0.5	3.8 ± 0.2	7.9 ± 0.1
Tunis[a]	44 ± 3	3.8 ± 0.1	100 ± 2	1.3 ± 0.1	15.5 ± 0.2	1.6 ± 0.1	8.5 ± 0.2
USA[b]	114 ± 3	3.2 ± 0.1	78 ± 2	1.3 ± 0.1	14.9 ± 0.2	1.9 ± 0.1	8.4 ± 0.4
Present study[e]	15.7–10.3	1.2–2.5	12.7–62.6	0.3–0.8	3.6–65.3	0.5–2.2	1.5–6.8

[a] Ref. [32], [b] [33], [c] [34], [d] [35]

[e] Overall ranges obtained for all PR samples (main rock formations only) studied in this work

Fig. 2 Chondrite ratio of all the samples analyzed using INAA



Conclusion

The raw material used for the production of phosphate fertilizers is basically phosphate rock, which contains significant amount of REEs. In the present study phosphate rock samples from Kakul were analyzed for their rare earth content employing INAA. Seven REEs namely Ce, Eu, La, Lu, Sm, Tb and Yb were quantified in the samples collected from four different locations. The highest amounts of REEs (LREE and HREE) were quantified in the PR samples collected at site D (Kakul Phosphate Rock Crushing Plant) while the lowest amounts of REEs (LREE and HREE) were measured in PR samples from the Lambidogi Phosphorite Mines. The amounts of most of these REEs were found to be comparable to the lower values cited in the literature for Israel and Syria. Chondrite ratio for the PR samples show enrichment of LREE in all Kakul phosphorite sample.

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