Rare earth element abundances in some A-type Pan-African granitoids of Karbi Hills, North East India

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This is a preliminary report of the rare earth metal abundances in certain Pan-African granitoids of Karbi Hills, Assam, North East India. Higher abundance of rare earth metals is apparently related to the mineralogical abundance of certain key rare earth element (REE)-bearing accessory minerals like allanite, xenotime, bastnaesite, apatite, zircon and monazite. The bulk chemistry of the granitoids suggests their A-type, calcium-deficient but alkali-rich, anomalous, anorogenic, within-plate granitoid character. Textural variants considered for the present study are: (1) porphyritic to sub-porphyritic, medium to fine-grained, mylonitized grey and pink-coloured granitoids of the Panbari–Geleki area in northern Karbi Hills, and (2) the non-porphyritic, medium to fine-grained granitoids of Kathalguri area in north-western Karbi Hills. Compositionally, the plutons are granitic to granodioritic in composition. The study reveals that the grey porphyritic granitoids are poor in REE, but the pink porphyry/sub-porphyry variety is enriched in REE. The pink granitoids show richness in La (average 1086 ppm) and Ce (average 2329 ppm) in particular. The average LREE content in the non-porphyritic Kathalguri granitoids is 607.46 ppm, but their HREE content is slightly higher (average 26.50 ppm) than normal granitoids. Chondrite normalized LREE–HREE profile and ratios of Ce_N/Yb_N, La_N/Yb_N, La_N/Sm_N and Tb_N/Yb_N of individual plutons indicate co-magmatic derivation of magmatic masses from the lower crust.

Keywords: Granitoids, mineralogical abundance, plutons, rare earth elements.

THE Karbi Hills of Assam (KHC) are comprised of Precambrian basement rocks similar to those found in the Dharwar and Singhbhum belts of the Indian Peninsula. The basement has witnessed episodic magmatic activities since the Proterozoic, producing polyphase granitoids, greenstones, mafic intrusives (doleritic dykes) and extrusives and carbonatite complexes. It is suggested that the evolutionary trend of the basement in this plateau is similar in many respect to the rest of the Indian Pan-African terrains, viz. Dharwar, Singhbhum, Bhandara, Bundelkhand and Aravalli[1]. It is also considered that protocontinents formed between 3.5 and 2.5 Ga, were welded and accreted together to generate the Mesoproterozoic (2.0–1.6 Ga) terrain of the Indian Peninsula, paving the way for subsequently formed super continental assembly of Rodinia and Gondwana[2]. The geology of KHC has not received much research attention till recent times. Earlier workers studied the Neoproterozoic intrusive granites of the adjacent Meghalaya plateau and provided general descriptions[3,4]. Significantly, the present data gap on various geological issues such as establishing geochronology of the lithostratigraphic units, appraisal on tectono-evolutionary history and metallogenic appraisal would be the major area of future research.

This study examines the issue of abnormally high rare earth metal abundances in certain granitoids of the Karbi Hills as a part of metallogenic appraisal, inviting the attention of the exploration agencies. Published geological notes on intrusive granites and carbonatites of Karbi Hills in recent times provide preliminary information on the status of magma evolution and rare earth element (REE) enrichment[5–7].

A preliminary study was undertaken to evaluate the REE distribution in certain moderately to highly evolved polyphase granitoids of KHC. The areas studied include the granitoids in the Kathalguri (KG) locality of the extended Dizo Valley (long. 92°52′24″E; lat. 26°22′10″N) in the NW Karbi Hills. Both grey and pink coloured Panbari–Geleki (PG) sub-porphyritic plutons (long. 93°29′41″E; lat. 26°36′12″N) occur in the central northern part under Kaziranga magmatic suite (Figure 1). The PG granitoids were emplaced around 1953 ± 39 Ma (ref. 8) whereas the Kathalguri pluton has been assigned an age of 500 ± 50 Ma (ref. 3) akin to those that occur in other proven Pan-African segments of India, e.g. Kerala (740–550 Ma)[9].

The dependence of REE distribution in relation to the structural elements present in the study area is of much interest. In the Kaziranga suite, a NNE–SSW trending dextral strike–slip shear zone transects the different lithologies, including PG granitoids with a maximum width of about 440 m, measured from LISS III imagery. The KG pluton occurs in a plunging anticline, the axis of which trends N 35°E and plunges toward 225°. It is cut by a thin E–W striking shear zone that shows a dislocation of <50 m at its northern end. Shearing is accompanied by brittle–ductile deformation of the granitoids and has given rise to mylonites in which minerals like quartz, mica and feldspar have undergone recrystallization. Formation of quartz ribbons, mica fish and slip in the feldspar twining have all been observed.

The present study chiefly focuses on the petrography and REE geochemistry of two separate granitic plutons which possess erratic but high concentrations of REE. The aim of the study is to generate more data and obtain an understanding of the origin and evolution of magmatic rocks in a breakaway segment of Pan-African continent.

Thirty-one samples were analysed for major element oxides using XRF (PAN analytical-make, model Axios)

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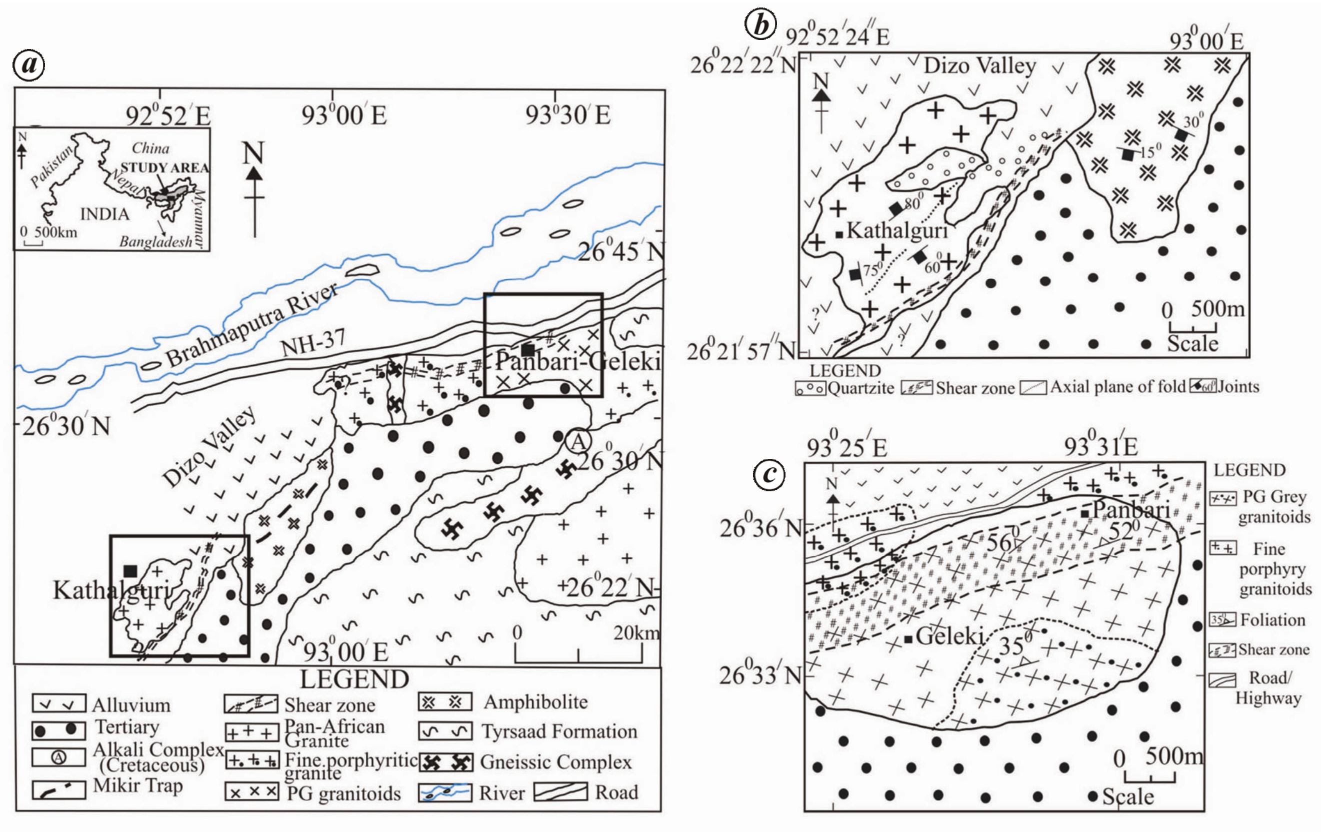

Figure 1. ***a***, Regional geological map of a part of Karbi Hills. ***b***, Map of Kathalguri locality. ***c***, Panbari–Geleki locality.

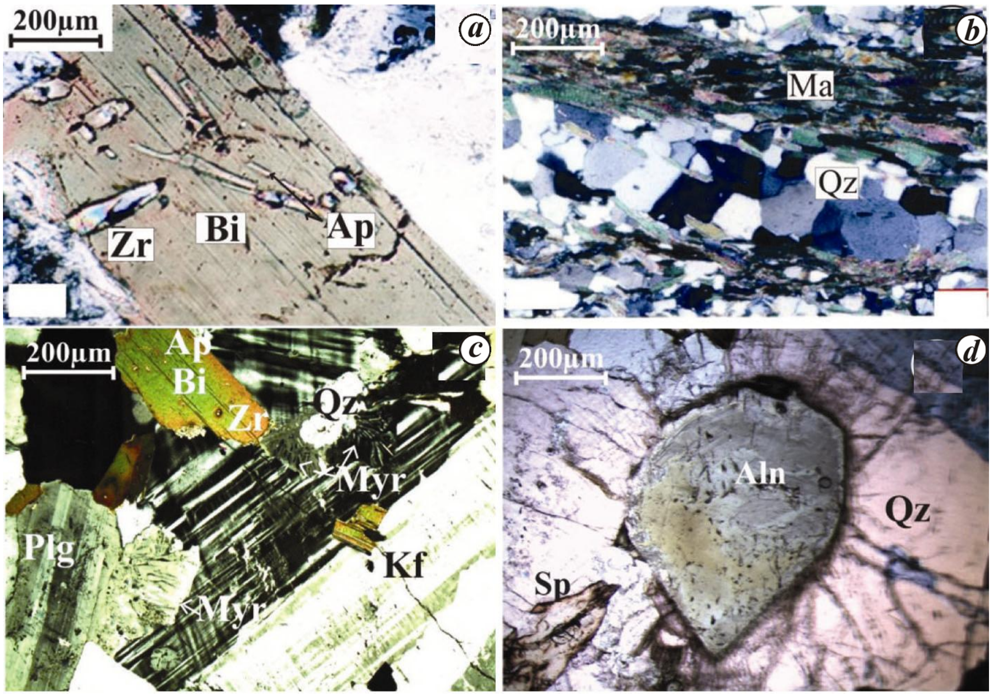

Figure 2. Photomicrographs of the studied Panbari–Geleki (PG) and Kathalguri (KG) granitoids. ***a***, Zircon (Zr) and apatite (Ap) inclusions in biotite (Bi) flakes of PG granitoids. ***b***, Alternating bands of recrystallized quartz (Qz) and muscovite/biotite (Ma) in sheared PG granitoids. ***c***, ***d***, REE-bearing accessory mineral phases, viz. allanite (Aln) and sphene (Sp) dominate the KG granitoids showing hypidiomorphic texture. Myrmekites (Myr) are occasionally seen in petrographic sections of KG.

Table 1. Chemical composition of granitoids of the study area. Major oxides are in wt%

	Kathalguri granitoids	Panbari–Geleki granitoids (suborphyritic)	
Major oxides	Average non-porphyry (*n* = 20)	Average pink (*n* = 3)	Average grey (*n* = 12)
SiO_2	66.58	73.1	62.63
TiO_2	0.82	0.53	0.925
Fe_2O_3 (T)	4.39	3.33	6.96
MgO	2.95	1.1	2.73
Al_2O_3	13.17	12.43	12.82
Na_2O	2.07	2.93	2.60
K_2O	5.06	3.46	3.125
MnO	0.10	0.1	0.125
CaO	3.07	2.16	3.66
P_2O_5	0.64	0.2	0.275
A/CNK	0.89	0.77	0.73
Agpaitic index	2.15	1.34	1.54
K_2O/Na_2O	4.98	1.22	1.24
CIPW norm			
Q	26.64	36.43	25.7
Or	29.90	20.7	19.25
Ab	10.67	25	21.71
An	14.11	9.76	14.38
Hy	7.86	3.4	7.95
Mt	1.77	2.06	4.56
Ilm	0.79	0.96	1.84
Ap	1.52	0.36	0.69
	(*n* = 13)	(*n* = 3)	(*n* = 3)
Cr	8.85	21.5	7.91
Ni	8.80	25.8	4.7
Co	16.26	21.2	8.7
Sc	6.59	5.4	8.3
V	12.10	14.9	10.0
Cu	3.86	2.6	2.4
Pb	52.40	54.1	25.9
Zn	61.03	62.0	91.9
Rb	289.02	306.3	29.7
Cs	10.79	9.4	8.5
Ba	1,376.24	13,550.0	2,722.0
Sr	300.43	3,264.7	944.5
Ga	22.54	21.1	22.5
Ta	8.61	1.0	1.3
Nb	52.87	31.8	41.8
Hf	7.14	5.4	3.8
Zr	229.45	156.5	495.6
Y	65.45	48.6	61.4
Th	48.85	68.3	15.4
U	8.71	7.1	4.7
Zr/Hf	32.13	29.0	131.4
Nb/Ta	6.14	31.7	33.0
Rb/Sr	0.96	0.09	0.03
Ba/Rb	4.98	44.56	92.77
K/Rb	137.13	93.20	885.46

at the University Sophisticated Instrumentation Centre, Gauhati University. Beads for XRF analyses were prepared by fusing a mixture of 1 g each of the powdered rock samples with 4 g lithium tetraborate and 1 g lithium carbonate in Au–Pt crucibles at 1100°C. Analytical software X-40 was utilized for data management. REE analyses were performed for 15 samples at the Geochemistry Laboratory, National Geophysical Research Institute (NGRI), Hyderabad using inductively coupled plasma-mass spectrometer (ICP-MS; Perkin Elmer SCIEX-make model Elan DRCII-ICP). All quantitative measurements were made using instrument software, and knowledge-driven routines in combination with numerical calculations to perform an automated interpretation of the whole spectrum. The GCD Kit 2.3 software was used for data management and interpretation.

Petrographically, PG granitoids are medium to fine-grained, either grey or pink coloured, subporphyritic, consisting of quartz, alkali feldspar, minor oligoclase and biotite (often altered to chlorite). The rock is sheared in parts, where it shows development of mylonitic fabric with evidence of recrystallization of mainly quartz grains. Modally, PG grey granitoids are quartz-poor (15.9–26.7%), but feldspar and biotite-rich (37.0–57.1% and 13.1–24.0% respectively). Plagioclase feldspar dominates over K-feldspar in PG grey granitoids. The pink granitoids are quartz- and K-feldspar-rich (33.0–42.6% and 23.3–44.1% respectively) and contain good percentage of zircon, sphene and monazite, whereas the grey varieties are poor in these minerals (Figure 2 *a* and *b*). QAP plot after IUGS for the PG granitoids (Figure 3) suggests a composition range from granite to granodiorite, with a little affinity to alkali granite[10].

KG granitoids are medium to coarse-grained, non-porphyritic, hypidiomorphic showing salt and pepper-like texture. They are mostly hypersolvus; essentially composed of quartz (average 51.17%), K-feldspar (average 20.40%), biotite and muscovite (average 11.6%), plagioclase (average 8.5%) and REE-bearing accessory minerals like zircon, allanite, sphene, xenotime, bastnaesite and apatite, constituting about 8.2%. The QAP classification for KG reveals a true granitic composition, although some sodic granites (alaskite) occur as apophyses (Figure 3). Euhedral grains of plagioclase with distinct zoning and randomly oriented primary mineral inclusions are commonly found in KG granitoids. Mineralogically, high-temperature ferro-magnesian minerals are replaced by quartz and high-temperature more calcic plagioclases are replaced by K-feldspar or more sodic plagioclases and myrmekite; coarseness of quartz vermicules in myrmekite at plagioclase/K-feldspar boundary with occasional vermicular quartz intergrowth in K-feldspar when plagioclase replaces the latter (Figure 2 *c* and *d*).

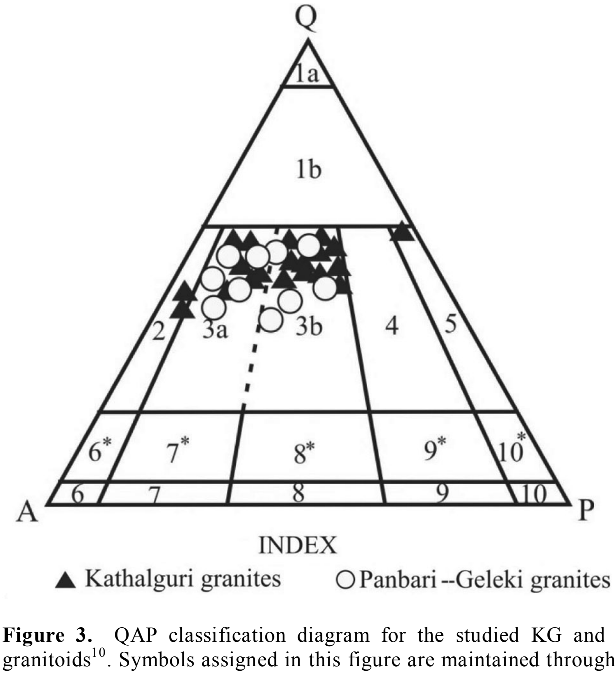

Figure 3. QAP classification diagram for the studied KG and PG granitoids[10]. Symbols assigned in this figure are maintained throughout the text. Effective fields are: 2 – alkali feldspar granite, including alaskite; 3 – granite and 5 – tonalite.

The whole-rock average geochemical data comprising major oxides, selected trace elemental composition and CIPW norms of the representative granitoid samples from Kathalguri and Panbari–Geleki area are presented in Table 1. Table 2 gives the REE composition of the plutons along with a generalized concentration found in average leucogranite[11].

Amongst the major oxides, the average SiO_2 content of PG pink granitoid is higher (average 73.1%) than PG grey (average 62.63%); but for KG, it is 66.58%; PG pink and KG are $Fe_2O_{3(T)}$-deficient (4.39% and 3.33% respectively) than PG grey (average 6.96%). Al_2O_3 in all the three studied varieties does not vary much (>12%), but MgO and CaO are less in PG pink (1.1% and 2.16% respectively) than in KG (2.95% and 3.07% respectively). The PG grey granitoids are however, MgO (2.73%) and CaO-rich (3.66%); K_2O in PG pink is about 3.46% and in KG, it is 5.06%. The sodic granitoids are relatively poor in Ca, Al and Mg, marked mineralogically by low anorthite content and plagioclase is mostly albite. The K_2O/Na_2O of all the granitoids studied shows a normal calc-alkaline trend in the AFM diagram[12] (Figure 4), which can be attributed to the crystal fractionation phenomenon as a major process in the extraction of the granitic melt from the original magma. The KG granitoid compositions, however, vary from granite-adamelite to granodiorite[13] (Figure 5). These are characteristically metaluminous, A-type and plot in the field of within-plate-granite (WPG) field[16] (Figures 6 and 7).

One of the many significant features of granites with high concentration of REE is the extreme degree of chemical fractionation of the parent magma. Chemical

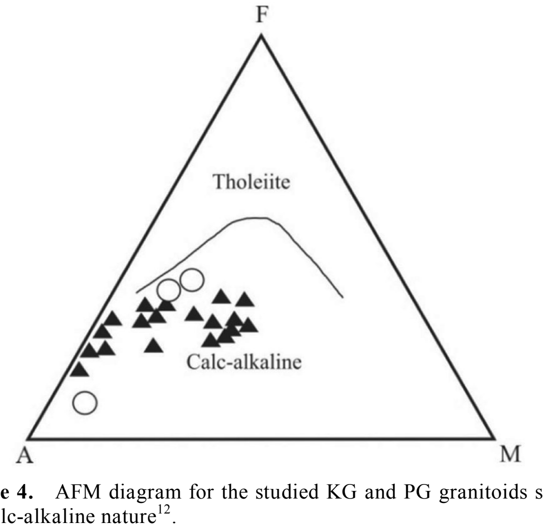

Figure 4. AFM diagram for the studied KG and PG granitoids showing calc-alkaline nature[12].

Table 2. Rare earth element data of the studied granitoids (ppm)

	Average non-porphyry granitoids of Kathalguri ($n = 13$)	Panbari-Geleki granitoids		
		Average pink ($n = 3$)	Average grey ($n = 3$)	Leucogranite*
La	100.56	1,086.1	41.3	17
Ce	380.63	2,329.0	93.0	31.5
Pr	22.30	36.6	10.9	5.2
Nd	84.48	133.6	45.4	17
Sm	14.53	21.1	9.6	11.2
Eu	2.00	3.5	2.2	0.17
Gd	12.61	14.0	8.4	6.8
Tb	1.84	1.8	1.4	1.6
Dy	10.87	9.5	10.4	–
Ho	1.38	0.9	1.2	2.4
Er	4.69	3.0	6.5	5.9
Tm	0.65	0.3	0.5	0.66
Yb	6.10	3.3	5.4	5.4
Lu	0.98	0.5	0.9	–
ΣREE	643.62	3,643.2	237.1	105.0
Y	65.45	48.6	61.4	46.0
ΣREE + Y	709.6	3,691.7	298.5	151.0
ΣLREE	607.46	3,609.8	202.4	81.9
ΣHREE	26.50	32.8	33.8	23.38
ΣLR/ΣHR	22.59	109.9	6.0	3.50
(La/Yb)N	14.08	225.1	5.13	–
(La/Sm)N	4.20	31.97	2.68	–
(Ce/Yb)N	14.13	182.97	4.39	–
(Tb/Yb)N	1.63	5.76	3.75	–
Eu/Eu*	0.49	0.70	0.88	–

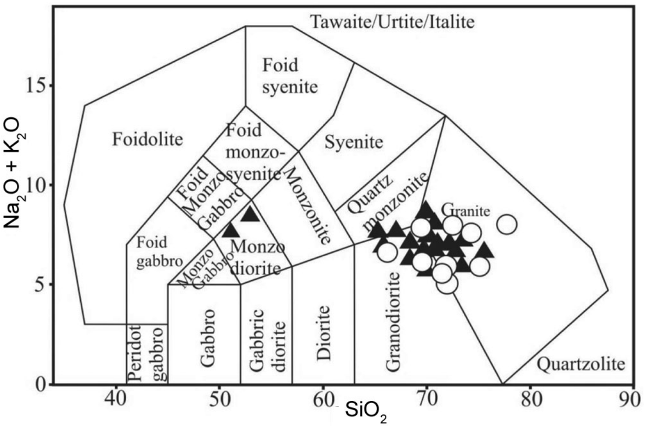

Figure 5. SiO_2–$Na_2O + K_2O$ plot showing dominance of granitic-granodioritic composition for the studied granitoids[13].

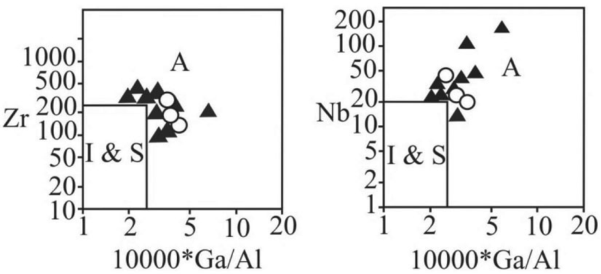

Figure 6. Binary plots of the studied granitoids which clearly fall in the A-type granite field[15].

fractionation led to the abundance of large ion lithofile elements (LILE) including REE. For assessing REE prospectivity in PG pink and KG granitoids, the concentration of three important LILE, Ba, Rb and Sr, and their ratios have been considered[17,18]. Results indicate that the PG pink is characterized by extremely high values of Ba (13,550 ppm), Sr (3264.7 ppm) and Rb (306.3 ppm). KG is characterized by lower values of all three LILE components of Ba (1376.4 ppm), Sr (300.43 ppm) and Rb (289.2 ppm). Abundance of LILE such as Rb and Ba is more pronounced in the PG pink granitoids, but they show Sr depletion. Th and Ce contents are, however, enriched in them. The studied KG granitoids have variable Ba/Rb ratio, maximum up to 17.02, while Rb/Sr ratio is low (up to 2.88) but their Ba/Rb ratio is high (up to 6.44).

Besides, Ba, Rb and Sr abundance, there is the predominance of high field strength elements (HFSE), e.g. Zr, Hf, Nb, Ta, Th and U. These are concentrated in REE-bearing mineral phases sphene, zircon and apatite. Concentrations of these elements found in PG pink and KG are high such as Zr (average 156.5 ppm for PG pink and 229.45 ppm for KG); Nb (average 31.8 ppm for PG pink; 52.87 ppm for KG), Ta (average 1.0 ppm for PG pink; 8.61 ppm for KG) and Y (average 48.6 ppm for PG pink; 65.45 for KG). Hafnium (Hf) has a close geochemical affinity for zirconium and the same bears an enriched value ranging from 3.8 to 7.14 ppm in granitoids of both localities.

The REE data for the studied PG pink and KG granitoids show enrichment in total REE (average 3643.2 ppm for PG pink; 643.2 ppm for KG) compared to the average REE of about 250 ppm in normal granites[19]. Abundance of LREE + Y (average 709.6 ppm) and relatively low HREE indicates partial melting of lower crust producing calc-alkaline melt possessing high values of REE, a feature especially found in KG granitoids. It is stated that LREE enrichment is common in calc-alkaline rocks[20]. The attribute of chondrite-normalized REE plots both for PG pink and KG granitoids indicates the following: (i) predominance of light rare earth elements (LREE) over heavy rare earth elements (HREE); (ii) steeper slopes from La to Sm; (iii) relatively flat pattern or slight depression from Gd through Lu, and (iv) general parallelism of the REE patterns with negative Eu anomalies. The PG pink granitoids, however, are significantly enriched in first two REE, viz. La and Ce (average 1086 ppm and 2329 ppm respectively). Moderate degree of HREE fractionation in these granitoids is indicated by $Tb_N/Yb_N > 1$. The negative Eu anomaly in chondrite-normalized REE[21] is attributed to the fractionation of plagioclase (Figure 8).

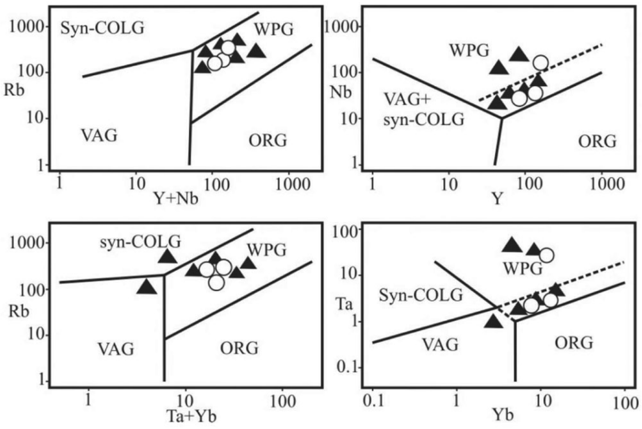

Figure 7. Binary plots of the studied granitoids showing within-plate character for most of the samples[16].

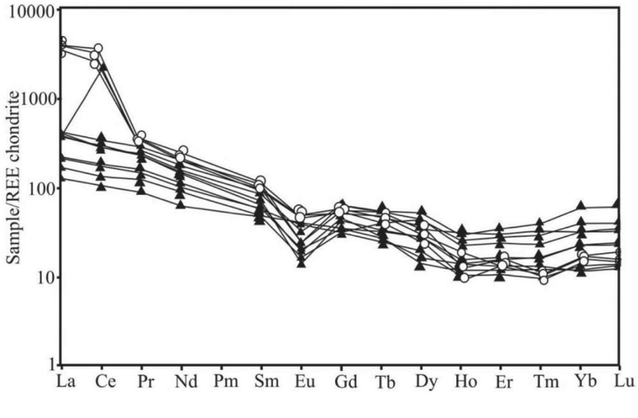

Figure 8. Chondrite-normalized REE patterns for the studied granitoids[21] indicating steeper slopes for LREE and trough-like HREE pattern with variable negative Eu anomaly.

High values of REE elements in non-porphyritic granites of Nongpoh area of Meghalaya Plateau have been reported recently[22], where LREE (>663 ppm) and HREE (>56 ppm) with prominent negative Eu anomaly have been shown. These values are similar to the studied KG granitoids.

The REE distribution in PG and KG granitoids has certain relation to the existing shear dislocations in the area. This is more pronounced in PG pink than in KG, as shearing in KG is relatively less intense; however, samples collected nearer to the fold axis in KG graitoids show slightly higher REE values. Apart from general abundance of REE, there is an increase in total REE value for KG as depth increases. This is substantiated by an increase in REE-bearing minerals with depth. It is attributed to the evolved status of magma, which led to high levels of REE fractionation and differentiation at greater depth. Early removal of plagioclase during the process of fractionation led to lower europium concentrations in the melt[23]. The observed ratios of La_N/Sm_N (average 4.20), La_N/Yb_N (average 14.08) and Ce_N/Yb_N (average 14.13) are indicative of higher levels of REE fractionation and differentiation. Similar trend is found in many calc-alkaline Pan-African granitoids[24]. The observed Eu/Eu* in this study (0.49 for KG and 0.70 for PG pink) is indicative of high fO_2 of crystallizing magma[25].

Summarizing, the present study of rare earth metal resources in granitoids of Karbi Hills has shown results comparable to the status of Nonpoh Pluton of the adjacent Meghalaya Plateau[22]. The distribution of precious REE is not only anomalous, but is indicative of good prospect as it is found with greater homogeneity even outside the shear zone and fold hinge zone. High and variable concentrations of La and Ce noted in limited number of PG pink granitoids (average 3643 ppm) are certainly encouraging. In KG granitoids, the total LREE content is high (average 643.62 ppm; normal value is 250 ppm in low Ca granite), while HREE shows marginally high value. It can thus be predicted that a potential resource of rare earth metals and rare earths exists in the area. It is regrettable that such a potential REE resource is being extracted for stone and stone metal for construction purposes.

In conclusion, the combined petrological–geochemical parameters of the granitoids under reference indicate good concentration of accessory minerals, e.g. xenotime, allanite, monazite, sphene, bastnaesite, apatite and zircon. The evolved status of the magma is found to be similar to A2-type granites formed in a post-orogenic extensional setting. Variability in the normalized ratios, for example, Ce_N/Yb_N, La_N/Yb_N, La_N/Sm_N and Tb_N/Yb_N are consistent with high degree of differentiation leading to REE enrichment after parent magmas were generated due to anatexis of older crust.

In view of present findings, undertaking a detailed regional exploration programme for REE is called for.

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Carbonate formation of the Lower Carboniferous in central part of Volga–Ural basin

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Carbonate rocks of the Lower Carboniferous (Tournaisian stage) of the central Volga–Ural basin (the eastern portion of the East European platform) are of practical scientific interest to geologists, particularly because they contain large reserves of oil. Although such layers have been studied, various questions pertaining to development of sedimentation schemes for the rocks have not been answered. We have attempted to resolve these by studying a wealth of drill core materials. The study involved structural and genetic analysis of rocks and facies reconstructions. The rocks are mainly represented by different types of shallow-water limestone. The thickness of coeval layers and their lithological structures changes from well to well within an oilfield, primarily due to the different environments of sedimentation during the Tournaisian

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