Distribution of Rare Earth Elements in the Metamorphic Rocks of the Paleoproterozoic Nyong Unit (Congo Craton, South – Cameroon)

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Abstract— We reported for the first time the geochemistry of rare earth elements (REE) for the metamorphic rocks of the Paleoproterozoic Nyong unit situated at the west of Congo craton in Cameroon. Rare earth elements, define a group of fifteen chemical elements from lanthanum to lutetium (atomic numbers 57-71) characterized by similar chemical properties. To study their distribution in the metamorphic rocks of the Nyong unit, 24 representative samples were selected. The selected samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Rocks are strongly enriched in REE (especially LREE) and these rare earths set up a complex group. The abundance of REE suggests the presence of REE-rich minerals such as monazite and this monazite should be rich in LREE (La, Ce, Nd, Sm). The variations of the REE fractionation in the studied rocks is explained by different degrees of partial melting of the protolith and by variable enrichment of the source. REE concentrations in the rocks were of geogenic origins and not influenced by anthropogenic sources. LREE enrichment result in geochemical distribution of these elements in the area and good correlation between them. The unusually high contents of REE and unusually high contents of light rare earths enrichment compared to heavy rare earths is highlighted in biotite-gneisses, garnet-micaschists and garnet charnockitic gneisses. Chondrite normalization patterns are parallel; they show high La_N/Yb_N ratios which reflect highly fractioned REE compositions displaying a W-profile and a strong Eu anomaly for meta-igneous unit; zigzag-profile with a marked negative Ce anomaly and a pronounced positive Eu anomaly for metasediments. REE residence includes major minerals (feldspar, garnet, amphibole, biotites, clinopyroxene, epidote) and accessory minerals (phosphates such as monazite). The REE of Edea region can be economically exploitable.

Keywords— Rare earth elements, Paleoproterozoic Nyong unit, Congo craton, major minerals, accessory minerals.

I. **Introduction**

The rare earth elements (REE), from lanthanum (La, Z = 57) to lutetium (Lu, Z = 71) are a geochemical group of elements characterized by a single oxidation state: REE (III) except cerium and europium; promethium has naturally-occurring isotopes. The lanthanides have three valence electrons, the three valence electrons causes the REE^{3+} to be the most stable ions found in nature except for europium, which is mostly as Eu^{2+}, and cerium which may be partially oxidized to Ce^{4+} [1]. The entry of new electrons in the 4f orbitals, when the atoms have fully occupied the 6s orbital increases the electrostatic attraction between the N shell and the nucleus. This leads to a reduction of the REE^{3+} ionic radius with increasing Z, a phenomenon which is known as Lanthanide contraction [1], [2]. According to the International Union of Pure and Applied Chemistry (IUPAC), REE consist of a group of 17 elements with a similar geochemical behavior comprising the lanthanides, yttrium (Y, Z = 39) and scandium (Sc, Z = 21, [2]). The rare earth elements group show identical physical and chemical properties making them useful probes of low temperature geochemical reactions [3]. The REE range from La-Sm is classified as light rare earth elements (LREE) also known as cerium earths and Gd-Lu consist of heavy rare earth elements (HREE) also called yttrium earths. The middle members of the group, Sm to Ho are known as the middle rare earth elements (MREE).

During the last few decades, REE have become important geochemical tracers in order to understand and describe the chemical evolution of the earth's continental crust [4], [5], [6], [7]. Rare earth elements have been used, as analogues for actinide elements, in studies related to radioactive waste disposal in order to demonstrate their general immobility in weathering environments [8]. The comparison among REE facilitates the normalization of analyses to reference standards such as chondrite [9]. Technological developments have increased the use of REE in the defense, aerospace, medical and automotive industries. Also, REE are essential components of catalysts, high-strength magnets, super-alloys, display technology and lasers [10], [2], [11]. REE concentration has been proven to occur in a wide range of geological settings [12] and [13].

This work is carry out in Edea region situated within the Paleoproterozoic Nyong unit or Nyong serie also known as Lower Nyong unit, and this unit is located NW corner of Congo craton in Cameroon. Metamorphic rocks in this area include meta-igneous rocks and metasedimentary rocks [14]. The aim of this work is to study the distribution of REE in meta-igneous and metasedimentary rock samples collected in the Nyong serie at Edea region.

II. **Geological Setting**

The Congo craton is a large sub-circular mass of about 5,711,000 km^2 in area, and has a diameter of about 2500 km, comprising Archaean crust, early to mid-Proterozoic fold belt and Proterozoic cover [15]. The northwestern margin of the Archaean Congo craton in Southern Cameroon is represented by the Ntem complex [16], [17], [18], which is bordered in the north by the Yaoundé Group [19], [20], [21], [22], of the Pan-African orogenic belt in Central Africa (Fig. 1).

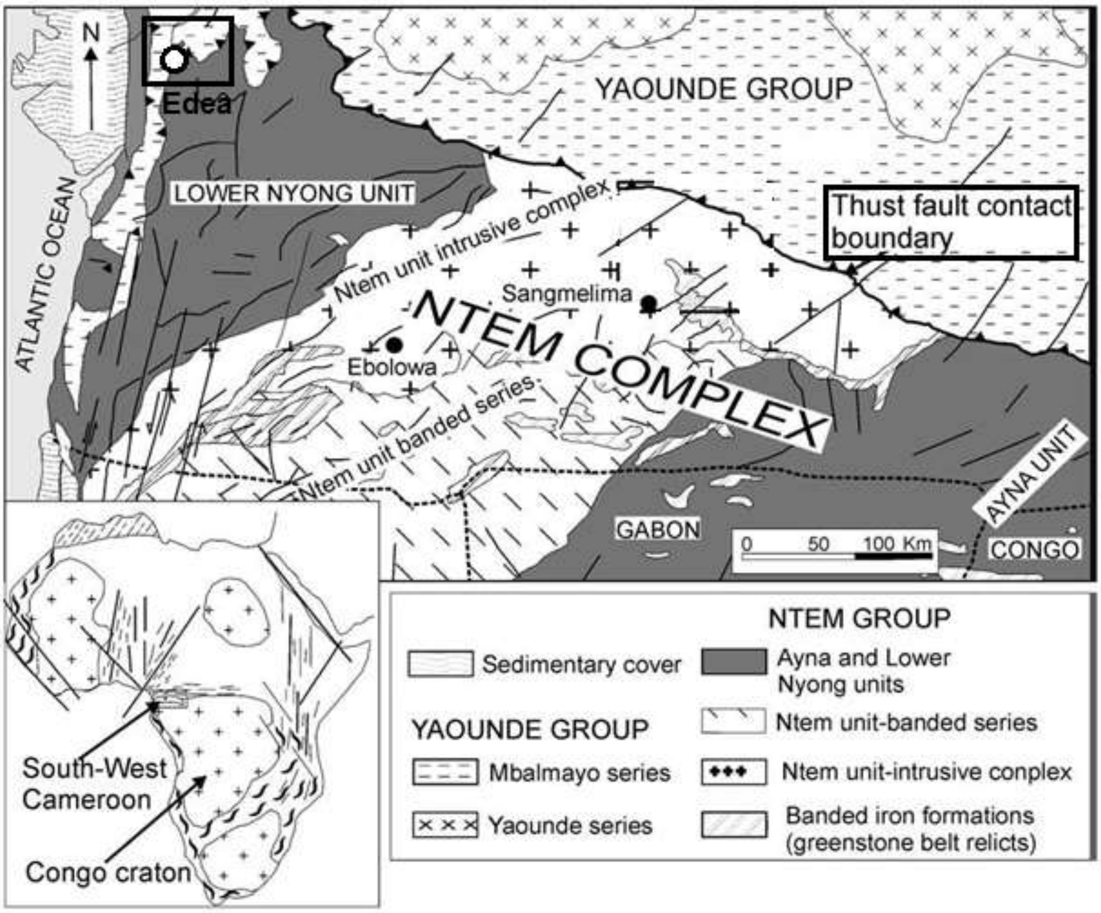


Fig. 1. Geologic map of South-West Cameroon [15], [14] as modified from [17] showing the lithologic units of Ntem Complex or Congo craton in Cameroon and the studied area (Edea).

The Ntem Complex is divided into two main structural domains: the Nyong serie or Nyong unit, to the northwest end, and the Ntem unit, in the south-central area. The Ntem unit is dominated by massive and banded plutonic rocks of the charnockite suite and by intrusive tonalites, trondhjemites and granodiorites (TTG). Some of these rocks were dated at 2.9 Ga [23], [24], [25]. The igneous bodies contain large xenoliths of supracrustal rocks interpreted as remnants of greenstone belts and dated at 3.1 Ga [26]. The studied areas, Edéa (Fig 1) belong to the Nyong serie. This serie consists of metasedimentary and metavolcanic rocks, syn-to late-tectonic granitoids and syenites [14], [27]. It displays three groups of ages [24], [28], [25],[29]: (1) Archaean ages (2500–2900 Ma); (2) Palaeoproterozoic (2050 Ma), Palaeoproterozoic ages of the granulitic metamorphism comprised between 1734 ± 22 Ma and 1893 ± 43 Ma (Th-U-Pb EMP-dating on monazites) are contemporaneous to the melting responsible to the charnockitisation and the emplacement of the igneous protoliths in the Nyong serie [30]; (3) Neoproterozoic ages (626 ± 26 Ma). Pan-African ages for the amphibolite metamorphic facies range between 577 ± 2 Ma-677 ± 36 Ma (Th-U-Pb, EMP-dating on monazites, [30] correspond to the melt and the emplacement of the sedimentary protoliths in the Nyong series. The Nyong unit includes some Archaean parts of the Ntem Complex that were reworked during a Palaeoproterozoic event, and new Palaeoproterozoic material that was accreted to the Archaean craton.

III. **Analytical Methods**

Fresh rock samples of metasediments and meta-igneous were collected from which 24 representative samples were selected for chemical analysis. Rare earth elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) on a VG-Plasma Quad STE ICP mass spectrometer at the Institute of Mineralogy and Geochemistry of the University of Lausanne in Switzerland. The samples were dissolved in a Teflon pressure bomb, using a 1:1 mixture of HF and $HClO_4$ at 180°C, and then taken up in HNO_3 solution with an internal standard. After dissolution in HF-$HClO_4$, the samples were taken up in a mixture of HNO_3, 6N HCL and HF and diluted. Analysis precision for rare earth elements is estimated at 5% for concentrations > 10 ppm and 10% when lower.

IV. **RESULTS**

Litologically, the study area is made up of meta-igneous and metasedimentary rock units. Meta-igneous rocks include pyroxene-gneisses, garnet-charnockitic gneisses, charnockitic gneisses, pyribolites, amphibolites, amphibole-biotite gneisses, biotite-gneisses. Pyroxene-gneisses, garnet-charnockitic gneisses and amphibole-biotite gneisses are the dominant rock types of this group. Metasedimentary rock unit is composed of garnet-micaschists mainly.

A. Meta-Igneous Rock Units

- Pyroxene-gneisses are mainly distributed in the study area; they are well-layered and interbedded with pyribolites layers of varying thickness. Charnockitic gneisses also occur within this rock type as leucocratic rocks with relict of pyroxene, biotite and amphibole. Pyroxene-gneisses samples exhibit strongly varying REE contents with ΣREE in the range of 97.31 to 852.17 ppm with an average of 322 ppm (Table 1). LREE varying from 86.19 to 765.63 ppm (av. = 288.64 ppm) are strongly enriched compared to HREE (23–96 ppm) with 33.37 ppm as average. The rock yield heterogeneous LREE/HREE ratios between 7 to 10 (av. = 8.43). The concentrations of the 14 REE in pyroxene-gneisses follow the order of La (av. = 158.64 ppm) > Pr > Ce > Lu >Eu > Tb > Ho > Sm > Tm > Nd> Dy > Gd > Yb > Er (av. = 1.12 ppm). REE patterns (Fig. 2a) are parallel and display a W-profile, they are very strongly fractionated (La_N/Yb_N = 6.49-344, av. = 192.80) with LREE enrichment (Ce_N/Sm_N = 0.79-2.10), HREE enrichment (Gd_N/Yb_N = 1.54-2.33) and a higher positive Eu anomaly (Eu/Eu* = 0.89-17.80). All these features are due to the accumulation of pyroxenes. The analysis of the correlation matrix (Table 4) puts in evidence two groups: (1) in the first group the majority of LREE (from La to Sm) have strong positive correlations with the other REE (from Nd-Lu) and (r = 0.62-0.99); (2) perfectly positive correlation is dominated in the second group where r = 1; HREE (from Tb to Yb) are perfectly correlated with MREE (from Eu to Er). Alongside of the two groups, there are some isolated cases of notable positive correlations (r = 0.49-0.59) between La and Nd, Sm; Ce, Ho; Pr and Sm; Dy and Ho, Tm. Less positive correlations (r = 0.1-0.48) are recorded between La and Ce, Gd, Dy, Er, Yb; Ce and Pr, Eu, Tb, Tm, Lu; Pr and Gd, Dy, Er, Yb; Nd and Lu; Sm and Lu. Lu displays a less negative correlation with Gd, Dy, Er, Yb (r = -0.01 to -0.18; Fig. 3a).

Table I. Rare Earth Element concentrations of Pyroxene-Gneisses and Garnet-Charnockitic Gneisses

	Pyroxene-gneisses								Garnet-charnockitic gneisses									
Samples	**ED1**	**ED1B**	**ED1C**	**ED3B**	**ED3E**	**Min**	**Max**	**Mean**	**ED1D**	**ED1A**	**ED3A**	**ED3C**	**ED4C**	**ED3D**	**ED4B**	**Min**	**Max**	**Mean**
La (ppm)	52.00	80.97	205.05	427.18	28.03	28.03	427.18	158.64	164.95	181.16	275.15	230.03	297.25	393.84	420.29	164.95	420.29	280.33
Ce	5.44	8.23	22.06	52.78	58.24	5.44	58.24	29.35	15.75	17.89	26.50	21.52	26.23	38.30	37.51	15.75	38.30	26.24
Pr	20.31	29.20	77.92	207.65	7.59	7.59	207.65	68.53	54.11	63.08	89.73	74.71	76.88	127.04	113.03	54.11	127.04	85.51
Nd	3.77	5.06	12.67	38.10	30.55	3.77	38.10	18.03	8.01	9.02	15.02	16.25	9.57	20.97	16.35	8.01	20.97	13.60
Sm	1.62	1.95	2.67	7.52	6.54	1.62	7.52	4.06	2.35	2.10	5.48	5.05	4.32	6.32	4.72	2.10	6.32	4.33
Eu	3.05	3.80	9.06	32.40	1.78	1.78	32.40	10.02	5.47	6.27	16.00	20.00	5.79	20.01	14.36	5.47	20.01	12.55
Gd	0.38	0.41	1.14	4.20	5.82	0.38	5.82	2.39	0.69	0.77	2.71	3.51	0.73	3.11	2.15	0.69	3.51	1.95
Tb	2.52	2.96	5.91	26.07	0.82	0.82	26.07	7.66	3.45	4.10	18.65	22.43	4.69	17.83	14.88	3.45	22.43	12.29
Dy	0.46	0.51	1.14	4.96	5.31	0.46	5.31	2.48	0.69	0.64	3.76	4.32	1.12	3.37	2.99	0.64	4.32	2.41
Ho	1.32	1.44	2.88	13.75	1.08	1.08	13.75	4.09	1.84	1.78	10.16	11.88	3.28	9.02	8.60	1.78	11.88	6.65
Er	0.19	0.18	0.41	1.98	2.84	0.18	2.84	1.12	0.23	0.20	1.44	1.79	0.63	1.19	1.32	0.20	1.79	0.97
Tm	1.28	1.49	2.66	13.94	0.44	0.44	13.94	3.96	1.59	1.45	10.00	10.94	4.43	8.60	8.32	1.45	10.94	6.47
Yb	0.15	0.21	0.39	2.18	2.84	0.15	2.84	1.15	0.21	0.20	1.45	1.61	0.66	1.23	1.24	0.20	1.61	0.95
Lu	4.82	6.14	21.75	19.47	0.44	0.44	21.75	10.52	1.85	1.37	62.50	57.75	46.54	19.87	20.33	1.37	62.50	30.03
ΣREE	97.31	142.54	365.70	852.17	152.30	97.31	852.17	322.01	261.18	290.02	538.54	481.79	482.12	670.71	666.10	261.18	670.71	484.35
ΣLREE (La-Eu)	86.19	129.20	329.43	765.63	132.73	86.19	765.63	288.64	250.63	279.51	427.88	367.57	420.04	606.49	606.26	250.63	606.49	422.62
ΣHREE(Gd-Lu)	11.12	13.34	36.28	86.55	19.57	11.12	86.55	33.37	10.55	10.51	110.66	114.22	62.09	64.23	59.84	10.51	114.22	61.73
ΣLREE/ΣHREE	7.75	9.68	9.08	8.85	6.78	6.78	9.68	8.43	23.76	26.60	3.87	3.22	6.77	9.44	10.13	3.22	26.60	11.97
(La/Yb)N	228.02	256.46	344.09	128.92	6.49	6.49	344.09	192.80	519.97	582.23	125.05	94.22	294.32	210.97	223.08	94.22	582.23	292.83
(Ce/Sm)N	0.79	1.00	1.95	1.66	2.10	0.79	2.10	1.50	1.58	2.01	1.14	1.00	1.43	1.43	1.88	1.00	2.01	1.50
(Gd/Yb)N	2.05	1.58	2.33	1.54	1.64	1.54	2.33	1.83	2.66	3.00	1.50	1.75	0.88	2.03	1.39	0.88	3.00	1.89
Eu/Eu*	11.97	13.12	16.03	17.80	0.89	0.89	17.80	11.96	13.23	15.27	12.83	14.67	10.06	13.93	13.92	10.06	15.27	13.42

- According to the results of correlation analysis (Fig. 3b) that exhibits an unusually case, all the REE correlate positively with their respective correspondent. Higher positive correlations with r values ranging from 0.60-0.99 are noticeable. They consist of two groups: (1) MREE to HREE (from Gd-Lu) correlate higher positive with Pr to Yb (r = 0.60-0.99) and (2) LREE (from La to Eu) have good correlations with LREE (from La to Sm) with r = 0.68-0.99. La and Ce have notable positive correlations with MREE and HREE from Eu to Yb (r = 0.44-0.58). They are also notable positive correlations between Lu and Eu (r = 0.49) and between Lu and Gd (r = 0.56). Less positive correlation (r = 0.13 to 0.33) is observed between Lu and LREE (from La to Nd).

- Biotite-gneisses interbed with amphibole-biotite gneisses. Biotite gneisses exhibit a predominance of the REE (Table 2) with an unusually high contents of ΣREE (10,903.96 to 1,659.54 ppm, av. = 6,281.75 ppm) and the unusually high contents of La (7,284.25-981.91 ppm, av. = 4,133 ppm) usually the dominant REE followed by Pr (2,307.39-377.89 ppm, av. = 1,342 ppm) and Ce (725.57-112.54 ppm, av. = 419,06 ppm). They also display higher LREE/HREE (17.93-46; average = 31.96) ratios. Ce (725.57-112.54 ppm) and Nd (237.97-54.71 ppm) contents are higher compared with those of pyroxene-gneisses (Ce = 8.23-58.24 ppm; Nd = 3.77-38 ppm) and garnet-charnockitic gneisses (Ce = 15.75-38.3 ppm; Nd = 8-20.97 ppm). REE distributions follow the order of La > Pr > Ce > Nd >Lu > Eu > Tb > Sm > Ho> Tm > Gd > Dy > Yb > Er (Table 2). The chondrite- normalized REE plot (Fig. 2c) reveals broadly similar distribution patterns, displaying higher LREE enrichment ((La_N/Yb_N =

415.45-4989.46; av. = 2702.46), relative HREE enrichment (Gd_N/Yb_N = 2-6.17) with a pronounced positive Eu anomaly (Eu/Eu* = 18.53-26.78). The correlation matrix (Fig. 3c) displays an unusually correlation. The coefficient returns a value between -1 and 1 that represents the limits of correlation from (1) a full negative correlation (r = -1) to (2) a full positive correlation (r = 1). **e.g.** LREE to MREE (from La to Tb) show full positive or perfectly positive correlations with LREE to MREE (from La to Dy); Lu correlates full positively with LREE to MREE (from La-Dy), and Yb has positive correlations with Ho, Er and Tm. Also Tm correlates with Er. MREE to HREE (from Ho to Yb) display full negative correlations with LREE to MREE (La to Dy) and Lu correlates full negatively with HREE (Ho to Yb).

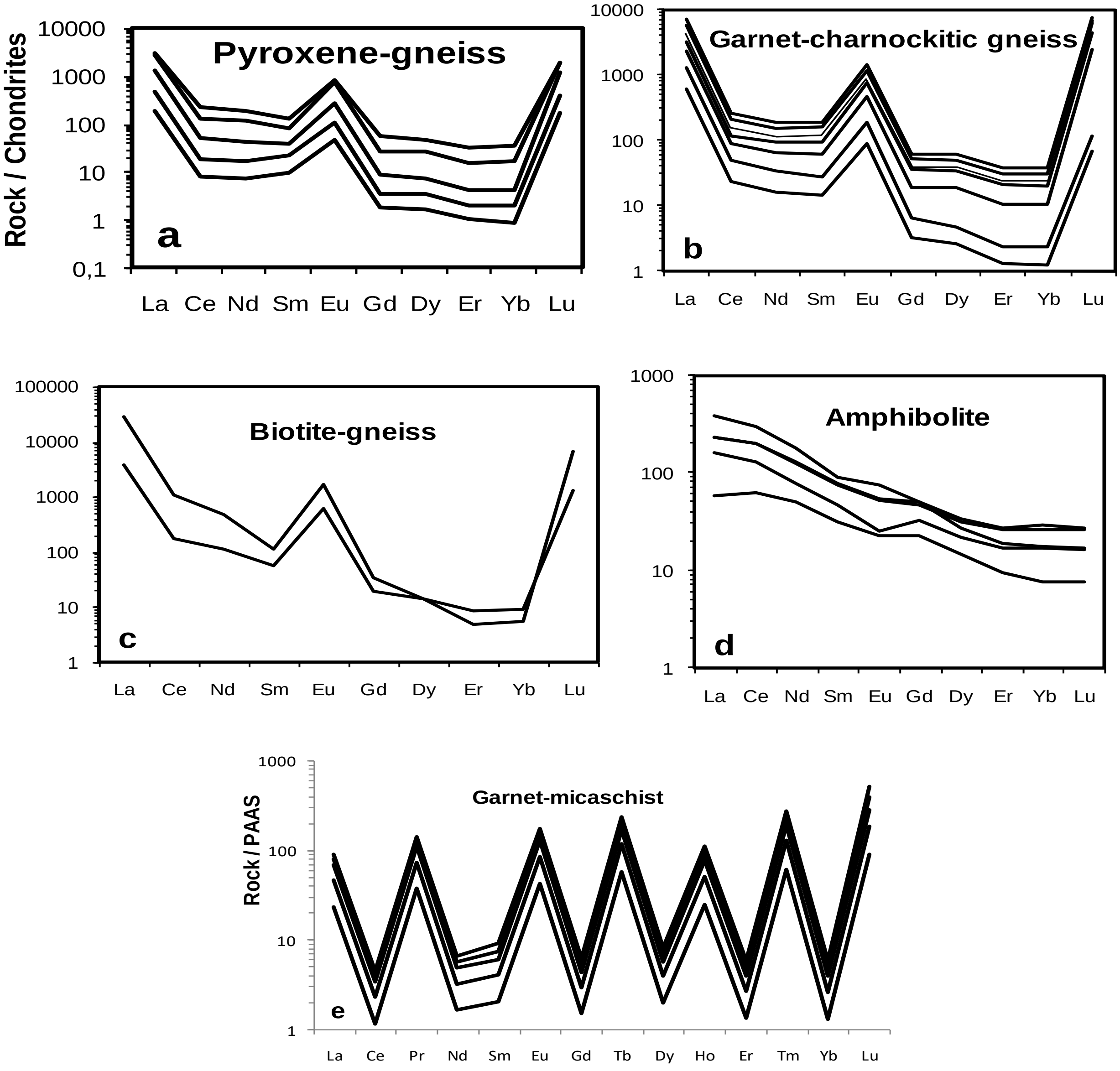
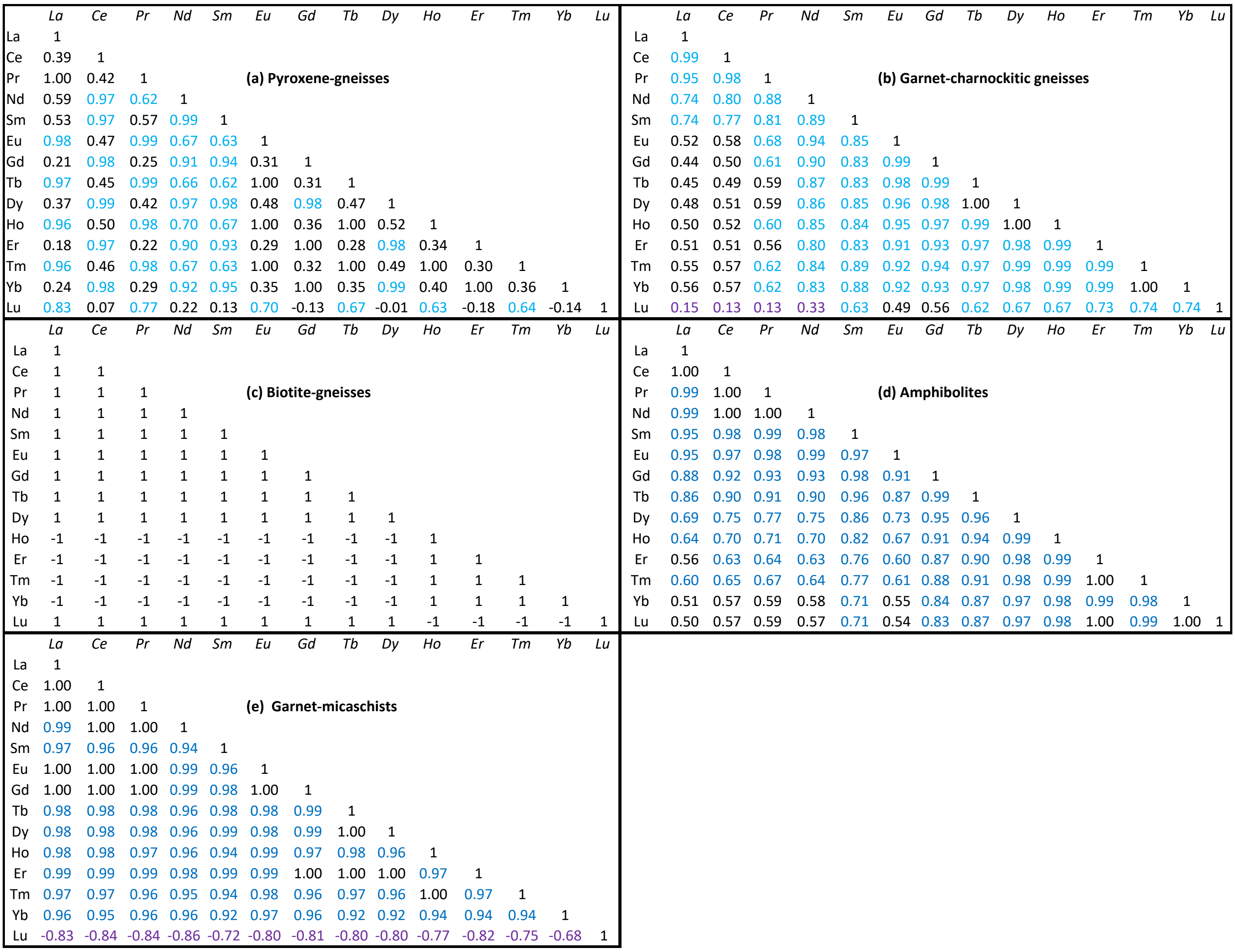


Fig. 2. Chondrite normalized REE patterns of] meta igneous rocks (normalizing values are according to [31] and metasediments (normalizing values are those of [7]. **a**: pyroxene-gneiss, **b**: garnet-charnockitic gneiss, **c**: biotite-gneiss, **d**: amphibolites and **e**: garnet-micaschist.



(a) Pyroxene-gneisses

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	0.39	1												
Pr	1.00	0.42	1											
Nd	0.59	0.97	0.62	1										
Sm	0.53	0.97	0.57	0.99	1									
Eu	0.98	0.47	0.99	0.67	0.63	1								
Gd	0.21	0.98	0.25	0.91	0.94	0.31	1							
Tb	0.97	0.45	0.99	0.66	0.62	1.00	0.31	1						
Dy	0.37	0.99	0.42	0.97	0.98	0.48	0.98	0.47	1					
Ho	0.96	0.50	0.98	0.70	0.67	1.00	0.36	1.00	0.52	1				
Er	0.18	0.97	0.22	0.90	0.93	0.29	1.00	0.28	0.98	0.34	1			
Tm	0.96	0.46	0.98	0.67	0.63	1.00	0.32	1.00	0.49	1.00	0.30	1		
Yb	0.24	0.98	0.29	0.92	0.95	0.35	1.00	0.35	0.99	0.40	1.00	0.36	1	
Lu	0.83	0.07	0.77	0.22	0.13	0.70	-0.13	0.67	-0.01	0.63	-0.18	0.64	-0.14	1

(b) Garnet-charnockitic gneisses

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	0.99	1												
Pr	0.95	0.98	1											
Nd	0.74	0.80	0.88	1										
Sm	0.74	0.77	0.81	0.89	1									
Eu	0.52	0.58	0.68	0.94	0.85	1								
Gd	0.44	0.50	0.61	0.90	0.83	0.99	1							
Tb	0.45	0.49	0.59	0.87	0.83	0.98	0.99	1						
Dy	0.48	0.51	0.59	0.86	0.85	0.96	0.98	1.00	1					
Ho	0.50	0.52	0.60	0.85	0.84	0.95	0.97	0.99	1.00	1				
Er	0.51	0.51	0.56	0.80	0.83	0.91	0.93	0.97	0.98	0.99	1			
Tm	0.55	0.57	0.62	0.84	0.89	0.92	0.94	0.97	0.99	0.99	0.99	1		
Yb	0.56	0.57	0.62	0.83	0.88	0.92	0.93	0.97	0.98	0.99	0.99	1.00	1	
Lu	0.15	0.13	0.13	0.33	0.63	0.49	0.56	0.62	0.67	0.67	0.73	0.74	0.74	1

(c) Biotite-gneisses

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	1	1												
Pr	1	1	1											
Nd	1	1	1	1										
Sm	1	1	1	1	1									
Eu	1	1	1	1	1	1								
Gd	1	1	1	1	1	1	1							
Tb	1	1	1	1	1	1	1	1						
Dy	1	1	1	1	1	1	1	1	1					
Ho	-1	-1	-1	-1	-1	-1	-1	-1	-1	1				
Er	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1			
Tm	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1		
Yb	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	
Lu	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	1

(d) Amphibolites

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	1.00	1												
Pr	0.99	1.00	1											
Nd	0.99	1.00	1.00	1										
Sm	0.95	0.98	0.99	0.98	1									
Eu	0.95	0.97	0.98	0.99	0.97	1								
Gd	0.88	0.92	0.93	0.93	0.98	0.91	1							
Tb	0.86	0.90	0.91	0.90	0.96	0.87	0.99	1						
Dy	0.69	0.75	0.77	0.75	0.86	0.73	0.95	0.96	1					
Ho	0.64	0.70	0.71	0.70	0.82	0.67	0.91	0.94	0.99	1				
Er	0.56	0.63	0.64	0.63	0.76	0.60	0.87	0.90	0.98	0.99	1			
Tm	0.60	0.65	0.67	0.64	0.77	0.61	0.88	0.91	0.98	0.99	1.00	1		
Yb	0.51	0.57	0.59	0.58	0.71	0.55	0.84	0.87	0.97	0.98	0.99	0.98	1	
Lu	0.50	0.57	0.59	0.57	0.71	0.54	0.83	0.87	0.97	0.98	1.00	0.99	1.00	1

(e) Garnet-micaschists

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1													
Ce	1.00	1												
Pr	1.00	1.00	1											
Nd	0.99	1.00	1.00	1										
Sm	0.97	0.96	0.96	0.94	1									
Eu	1.00	1.00	1.00	0.99	0.96	1								
Gd	1.00	1.00	1.00	0.99	0.98	1.00	1							
Tb	0.98	0.98	0.98	0.96	0.98	0.98	0.99	1						
Dy	0.98	0.98	0.98	0.96	0.99	0.98	0.99	1.00	1					
Ho	0.98	0.98	0.97	0.96	0.94	0.99	0.97	0.98	0.96	1				
Er	0.99	0.99	0.99	0.98	0.99	0.99	1.00	1.00	1.00	0.97	1			
Tm	0.97	0.97	0.96	0.95	0.94	0.98	0.96	0.97	0.96	1.00	0.97	1		
Yb	0.96	0.95	0.96	0.96	0.92	0.97	0.96	0.92	0.92	0.94	0.94	0.94	1	
Lu	-0.83	-0.84	-0.84	-0.86	-0.72	-0.80	-0.81	-0.80	-0.80	-0.77	-0.82	-0.75	-0.68	1

Fig. 3. Correlation matrix (a) pyroxene-gneisses, (b) Garnet-charnockitic gneisses, (c) Biotite-gneisses, (d) Amphibolite and (e) Garnet-micaschists.

- Amphibolites are relatively REE-rich with a total of ΣREE ranges from 369.18 to 534.31 ppm with an average of 431.27 ppm (Table 2). Chondrite normalization showed high La_N/Yb_N ratios (7.13-22.3) which reflect highly fractioned REE compositions. Gd_N/Yb_N ratio was calculated to investigate the relative depletion of HREE and the chondrite normalized value shows low Gd_N/Yb_N ratios (1.3-3.12). All these features are illustrated by a negative slope and parallel REE pattern (Fig. 2c). This slope is referred as the ratio La_N/Yb_N (7.13-22.3) or La_N/Lu_N (7.58-22.25). REE show a continue fractionation from the LREE to the HREE with a slightly negative Eu anomaly (Eu/Eu* = 0.45-0.69). REEs contents follow the trend of Ce >La >Nd >Pr >Sm >Gd >Dy > Yb >Er >Eu >Ho >Tb >Lu >Tm. The correlation matrix of (Fig. 3d) exhibits an unusually case where all the REE exhibit positive correlations (r = 06-0.99) with their respective correspondents, meanwhile Yb and Lu show notable positive correlations with LREE (La to Nd; r = 0.50-0.59) and with Eu (r = 0.54-0.55).

B. Metasedimentary Rock Units

Garnet-micaschists represent the main rock type of this group. They exhibit higher La (398.21-900.11 ppm; av. = 699.45 ppm) amount and the unusually high contents of REE (ΣREE = 765.21 to 1,595.44 ppm; av. = 1,265.79 ppm; Table 3). Ce (40.33-92.52 ppm; av. 71.45 ppm) contents are depleted relative to La (398.21-900.11.52 ppm; av. 699.45 ppm) and Pr (143.82-331.92 ppm; av. 253.87 ppm) concentrations. REE show an overall order of abundance such as: light rare earth elements > high rare earth elements (LREE/HREE = 4.91-9.17, av. = 7.38). The concentrations of the REE in garnet micaschists follow the order of La >Pr >Ce >Lu >Nd >Eu >Tb >Tm>Ho >Sm>Dy >Gd >Er = Yb. The PAAS normalized patterns of REE (Fig. 2e) also show enrichment of LREE (La_N/Yb_N of 11.22-17.92, av. = 15.11) over HREE with Gd_N/Yb_N of 0.96-1.15 illustrated by a zigzag or multi folded and parallel REE pattern (Fig. 2e) displaying a pronounced negative Eu anomaly (Eu/Eu* = 20.29-25.55; av = 23) and a marked negative and constant Ce anomaly (Ce_N/Ce^* = 0.04). Also Nd anomaly (0.15-0.20) is negative. In the correlation matrix (Fig. 3e), all the REE show higher positive correlations (r = 0.92-0.99), except Lu which shows a higher negative correlation with all the REE (r = -0.68-0.84).

Table II. Rare Earth Element concentrations of Biotite-Gneisses and and Amphibolites

	Biotite-gneisses					**Amphibolites**							
Samples	A4B	B1	Min	Max	Mean	P1	P2	P3	P4	P5	Min	Max	Mean
La (ppm)	7284.25	981.91	981.91	7284.25	4133.08	15.27	61.82	101.17	61.91	42.01	15.27	101.17	56.43
Ce	725.57	112.54	112.54	725.57	419.06	42.27	136.15	200.53	137.29	88.04	42.27	200.53	120.85
Pr	2307.39	377.89	377.89	2307.39	1342.64	5.62	16.08	22.53	15.93	9.75	5.62	22.53	13.98
Nd	237.97	54.71	54.71	237.97	146.34	24.79	64.41	89.93	62.69	38.46	89.93	24.79	56.05
Sm	17.65	8.89	8.89	17.65	13.27	4.96	12.43	14.77	12.15	7.51	4.96	14.77	10.37
Eu	99.13	35.91	35.91	99.13	67.52	1.38	3.32	4.61	3.17	1.52	1.38	4.61	2.80
Gd	7.40	4.03	4.03	7.40	5.72	4.90	10.77	10.86	10.19	6.92	4.90	10.86	8.73
Tb	27.52	23.00	23.00	27.52	25.26	0.65	1.40	1.39	1.38	0.97	0.65	1.40	1.16
Dy	3.81	3.70	3.70	3.81	3.75	3.94	9.07	7.47	8.59	5.82	3.94	9.07	6.98
Ho	8.13	10.20	8.13	10.20	9.16	0.70	1.70	1.36	1.72	1.11	0.70	1.72	1.32
Er	0.88	1.49	0.88	1.49	1.18	1.69	4.83	3.42	4.69	3.00	1.69	4.83	3.53
Tm	5.61	9.44	5.61	9.44	7.52	0.23	0.68	0.51	0.69	0.45	0.23	0.69	0.51
Yb	0.96	1.55	0.96	1.55	1.26	1.33	5.06	3.11	4.54	2.87	1.33	5.06	3.38
Lu	177.69	34.27	34.27	177.69	105.98	0.74	0.74	0.47	0.71	0.44	0.21	0.74	0.62
ΣREE	10903.96	1659.54	1652.43	10911.07	6281.75	107.94	328.45	462.13	325.63	208.86	107.94	462.13	286.60
ΣLREE (La-Eu)	10671.96	1571.86	1571.86	10671.96	6121.91	94.29	294.20	433.54	293.13	187.28	94.29	433.54	260.49
ΣHREE (Gd-Lu)	232.00	87.68	87.68	232.00	159.84	13.65	34.25	28.59	32.50	21.58	13.64	34.25	26.11
ΣLREE/ΣHREE	46.00	17.93	17.93	46.00	31.96	6.91	8.59	15.17	9.02	8.68	6.91	15.17	9.67
(La/Yb)N	4989.46	415.45	415.45	4989.46	2702.46	7.56	8.04	21.40	8.98	9.63	7.56	21.40	11.12
(Ce/Sm)N	9.70	2.99	2.989	9.70	6.34	2.00	2.58	3.20	2.67	2.77	2.01	3.20	2.65
(Gd/Yb)N	6.17	2.08	2.08	6.17	4.12	2.96	1.71	2.80	1.80	1.93	1.71	2.96	2.24
Eu/Eu*	26.78	18.53	26.78	18.53	22.65	0.87	0.88	1.12	0.88	0.65	0.65	1.12	0.88

Table III. Rare Earth Element concentrations of Garnet-Micaschists

Garnet-micaschists								
Samples	M4	M4+	M4++	M5	M5*	Min	Max	Mean
La	900.11	885.12	887.91	398.21	425.90	398.21	900.11	699.45
Ce	92.52	92.17	91.30	40.33	40.92	40.33	92.52	71.45
Pr	331.92	322.23	324.07	143.81	147.31	143.81	331.92	253.87
Nd	56.53	54.02	57.41	27.83	25.99	25.99	57.41	44.36
Sm	11.57	11.32	10.82	8.30	9.19	8.30	11.57	10.24
Eu	45.96	46.84	46.71	25.54	27.53	25.54	46.84	38.52
Gd	7.07	6.84	6.85	4.09	4.44	4.09	7.07	5.86
Tb	44.76	45.76	41.44	26.96	29.05	26.96	45.76	37.59
Dy	9.30	9.14	8.47	5.47	5.99	5.47	9.30	7.67
Ho	24.30	26.88	25.39	16.28	17.35	16.28	26.88	22.04
Er	3.90	3.87	3.68	2.51	2.65	2.51	3.90	3.32
Tm	24.61	27.46	25.90	17.13	18.45	17.13	27.46	22.71
Yb	3.71	3.65	4.03	2.41	2.80	2.41	4.03	3.32
Lu	39.19	41.38	42.44	46.84	57.16	39.19	57.16	45.40
ΣREE	1595.44	1576.67	1576.41	765.69	814.73	765.69	1595.44	1265.79
ΣLREE (La-Eu)	1438.61	1411.70	1418.22	644.01	676.85	644.01	1438.61	1117.88
ΣHREE (Gd-Lu)	156.83	164.97	158.19	121.69	137.88	121.69	164.97	147.91
ΣLREE/ΣHREE	9.17	8.56	8.97	5.29	4.91	4.91	9.17	7.38
(La/Yb)N	17.92	17.92	16.27	12.19	11.22	11.22	17.92	15.11
(Ce/Sm)N	0.56	0.57	0.589	0.34	0.31	0.31	0.59	0.47
(Gd/Yb)N	1.15	1.14	1.03	1.03	0.96	0.96	1.15	1.06
Eu/Eu*	23.93	25.07	25.55	20.64	20.29	20.29	25.55	23.10
Ce/Ce*	0.04	0.04	0.04	0.04	0,04	0.04	0.04	0.04
Nd-anomaly	0.19	0.18	0.20	0.17	0.15	0.15	0.20	0.18

V. **Discussion**

Rare earth elements are more abundant than other better known, but more conspicuous elements such as lead, tin, gold. They are lithophile refractory elements and their relative proportions in the silicate earth are identical to the proportions found in the carbonaceous chondrites [1]. The proportion enrichment of REE in the study area is still remained similar with increasing atomic number. The enrichment patterns of LREE in Edea is due to the fact that HREE are more soluble and more complex than middle or light REE and are more strongly absorbed on most substrates [32]. The variations of the REE fractionation in the studied rocks is explained by different degrees of partial melting of the protolith and by variable enrichment of the source.

The abundance of REE suggests the presence of REE-rich minerals such as monazite and xenotime. According to [33] total REE in excess of 50-100 ppm precipitates as monazite or xenotime (on the basis of monazite saturation values of 50-100 ppm RE_2O_3 at 750 °C [34], [35], [36]. Monazite is a monoclinic Ce-phosphate mineral with the ideal formula $CePO_4$, where Ce can be replaced by the other light rare earth elements in any proportion [37], whilst xenotime (YPO_4) or ($[YHREE]PO_4$) according to [37] refers to a tetragonal Y-phosphate mineral, with a REE coordination number of 8, so that it prefers the HREE with smaller ionic radii. Considering the two definitions, the result of this study points the presence of monazite in the study area, because monazite is characterized by LREE enrichment compared to HREE, and the compositions of the natural monazites vary in LREE, Th, Y, Ca and Si [38]. This monazite should be rich in La, Ce, Nd, and Sm.

REE values and geochemical trends were used to determine genetic relations of these elements. Based on average values (Tables 1, 2, 3), REE are more abundant in biotite-gneisses (6281.75 ppm), followed by garnet-micaschists (1265.79 ppm), garnet-charnockitic gneisses (422.62 ppm), pyroxene-gneisses (288.64 ppm) and amphibolites (286.60 ppm). This comparison indicates that REE concentrations are controlled by Biotite-gneisses. The wide range of REE concentrations in the examined samples is indicative of lithological variations of these rocks because lithological characteristics influence REE concentrations. The fact that the relative higher LREE/HREE (4.91-9.17, av. = 7.38) ratio is found in garnet-micaschists indicates the presence of a clay fraction [39] and [40] in metasedimentary rocks. These ratios are similar to average terrigeneous and to the values given for continental or near-shore argillaceous and arenaceous sediments [41].

The concentrations of the REE in rock samples follow different order trends according to the rocks types showing after [42] that the rare earths set up a complex group. In the amphibolites the distribution of REE follow the order of Ce >La >Nd >Pr >Sm >Gd >Dy > Yb >Er >Eu >Ho >Tb >Lu >Tm which is relatively similar to the mean REE values in Terengganu Coastal Waters [43], similar to the mean REE values in oceanic crust proposed by [44] and those of the study in South China Sea reported by [45]. Chondrite normalization (Fig. 2) of meta-igneous rocks (except for the amphibolites, La_N/Yb_N = 7.13-22.3, av. = 11.12; Fig. 2d) show the variables and the unusually high La_N/Yb_N ratios; that is La_N/Yb_N = 6.49-344, av. = 193 for pyroxene-gneisses; La_N/Yb_N = 94.21-598.23, av. = 293 for garnet-charnockitic gneisses and, La_N/Yb_N = 415.45-4989.46, av. = 2702.46 for biotite-gneisses which reflect highly fractioned REE compositions. This observation illustrates that the studied meta-igneous rocks result from diverse protoliths. According to [14], they derive from (1) intermediate to basic tholeiitic rocks with high TiO_2 (0.6-3.47%) contents compatible with the extensive orogenic domain and (2) calc-alkaline protolith display high FeO*/MgO (1.5-3.31) ratios which is in accordance with the typical domain of collisional orogeny. Contrary, chondrite normalization of metasediments (Fig. 2e) show low La_N/Yb_N ratios (11.22-17.92, av = 15.11) which are in agreement with the composition of Post-Archaean Australian sedimentary rocks (PAAS; [7] that La_N/Yb_N = 13.55. Therefore the standardized spectra of rare earth of the studied metasediment samples are equivalent to that of the PAAS as a whole. This confirms the result of [14] demonstrating that chemical patterns of metasedimentary rocks from the Nyong Serie are those of shale and the fractioned REE patterns suggest that the contribution of alkaline vulcanite and a continental environment can be envisaged for these rocks.

The application of the equation $Eu/Eu^* = Eu_N/[(Sm_N)(Gd_N)]^{1/2}$ reveals positive Eu anomalies for most of the rocks suggesting cumulative or fractionation. The positive anomaly of Eu is also reported by [27] for Archaean crustal accretion of Congo craton and by [43] for the geochemistry of the rare earth elements distribution in Terengganu Coastal Waters. The positive Eu anomalies are due to cumulative feldspar or to the fractionation of the garnet/amphibole ± pyroxene [46]. In general, the feldspars have a marked preference for the lightest $LREE^{3+}$ and Eu^{2+} whereas the ferromagnesian minerals either prefer the $HREE^{3+}$ (garnet, zircon) or are little selective (amphibole, clinopyroxene). Hence, the REE except Eu tends to form minerals of their own, phosphates, silicates, niobotantalates, carbonates [1].

Alongside of Eu anomalies, metasediments display a negative and constant Ce anomaly (Ce_N/Ce^* = 0.04) and a negative Nd anomaly (0.15-0.20). The cerium anomaly confirms that Ce concentration is depleted in rock relative to La and Pr, and it indicates that Ce is partially oxidized to Ce^{4+} ($Ce^{3+} \leftrightarrow Ce^{4+}$). The negative Ce anomaly might also partially due to early stage weathering which led to less pronounced REE fractionation [47]. The Negative Nd anomaly according to [1] is related to extreme monazite fractionation.

Correlation trends mostly exhibit to groups for each rock sample (Fig. 3a to 3e) where positive correlations (higher positive, notable positive, less positive and unusually perfectly positive) dominated among REE and their correspondents. However some few correlations are negatives. This variability of correlation also confirms that the rare earths set up a complex group. The strong correlations between REE and their correspondents indicate that REE concentrations in the study area were of geogenic origins and not influenced by anthropogenic sources. LREE enrichment in the study region could be resulted in geochemical distribution of elements; this is supported by the works of [48] where LREE enrichment resulted in geochemical distribution of these elements and good correlation between them. There is a strong negative correlation between Lu and other REE in garnet-micaschists (Fig. 3e). Furthermore, the overall enrichment in REE (and especially in biotite-gneisses) compared to the other rock types samples has to be highlighted.

Another important point of this work is to know which minerals contain REE. Petrographically the studied rocks [30] and [14] contain major minerals and accessory minerals (Table 4). These minerals could constitute the REE residence in the study area. This result is in accordance with the studies of [49] and [50] indicating that the sources of rare earth elements and phosphorus in metamorphic monazite are major minerals or former accessory REE-minerals of the original rock, although migration of rare earth elements may also occur [51]. Major minerals and minor minerals are also reported by [1] as REE-residence for the geochemistry of the Lanthanide Elements.

Table II. REE Residence for the Metamorphic Rocks of Edea Region

Rock types	**Major minerals**	**Accessory minerals**
Pyroxene-gneiss	Feldspar, garnet	Phosphates, such as monazite
Amphibolite	Amphibole, clinopyroxene, feldspar	
Garnet-charnockitic gneiss	Garnet, feldspar, clinopyroxene, biotite	
Biotite-gneiss	Epidote, feldspar, biotite	
Garnet micaschist	Garnet, feldspar, biotite	

In Edea, major and accessory minerals (Table 4) can contain detectable amounts of REE (Table 1 to 3) that can be economically exploitable. The few economically exploitable deposits are known as rare earth minerals [52]. In most cases, REE are randomly trapped in silicate minerals where they are incompatible [53]. The distribution of LREE and HREE shows an interesting difference exemplified by La with contents are highest and Ytterbium which display low contents.

VI. **CONCLUSION**

In this work, we used the inductively coupled plasma mass spectrometry (ICP-MS) analysis to study the distribution of rare earths elements in the metamorphic rock samples of the Paleoproterozoic Nyong unit. This study shows that the rocks are strongly enriched in REE (especially LREE) and these rare earths set up a complex group. The abundance of REE suggests the presence of REE-rich minerals such as monazite and this monazite should be rich in LREE (La, Ce, Nd, Sm). REE concentrations were of geogenic origins and not influenced by anthropogenic sources. LREE enrichment resulted in geochemical distribution of these elements in the area and good correlation between them. The unusually high contents of REE and unusually high contents of light rare earths enrichment compare to heavy rare earths is highlighted in biotite-gneisses, garnet-micaschists and garnet charnockitic gneisses. In general, chondrite normalizations pattern are parallel, they show high La_N/Yb_N ratios which reflect highly fractioned REE compositions displaying a W-profile and a strong Eu anomaly for meta-igneous unit, and zigzag-profile with a marked negative Ce anomaly and a pronounced positive Eu anomaly for metasediments. This illustrates that meta-igneous rocks result from diverse protoliths. REE residence includes major minerals (feldspar, garnet, amphibole, clinopyroxene, biotite, epidote) and accessory minerals phosphates (such as monazite). The REE from Edea can be economically exploitable and the distribution of LREE and HREE shows an interesting difference exemplified by La with contents are highest and Ytterbium which display low contents.

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