Rare Earth Element Geochemistry of Soils in Southwestern Part of Sheet 272 Katsina-Ala SE, North Central Nigeria

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DOI: 10.56201/ijaes.v10.no5.2024.pg285.300

Abstract
Following a reported enrichment of Rare Earth Elements (REE) from a regional stream sediment survey in parts of north central Nigeria, a medium density geochemical soil survey was carried out around Ushongo area of Benue State, Nigeria. This was with a view to assessing the REE mineralization potential of the study area. A detailed geological fieldwork was carried out in which three (3) rock types were identified - medium grained granite, amphibolite and migmatite gneiss. Sixty (60) soil samples were collected within the delineated area and analysed using the ICP-MS method. The soil geochemical data obtained were subjected to statistical analysis involving Pearson correlation and R-mode varimax rotated factor analysis techniques. The element distribution and trend maps were plotted using ArcGIS software. The total REE in ppm ranges from 232.7 to 1092.7. The REE concentrations (in ppm) revealed higher concentrations of the light REEs (216 – 1041 ppm) compared to the heavy REEs (12.61 – 52.67 ppm). Within the REE's; Ce, La, Nd, Th, Pr, Sm, shows positive correlation between each other with a significant value of 0.5 and above which interprets a strong association and a possibility of a common source of mineralization. The factor analysis enabled separation of elements into three factors and of the three associations only the Ce-La-Nd-Pr-Sm-Th (factor 2) is considered related to metallic mineralization. Furthermore, the aforementioned associated elements (Ce, La, Nd, Th, Pr, Sm) showed significant anomalous values when interpreted which were considered to be derived from primary mineralization of these elements. The concentration maps of these light REE's reveals a pattern that shows a similar trend of high concentration (670ppm, 232ppm, 213ppm,etc) and coupled with their strong correlation, a critical observation suggest a possible mineralization of Monazite (Ce, La, Nd, Th)(PO_4,SiO_4).

***Keywords**: REEs, enrichment, mineralization, exploration.*

I INTRODUCTION

The rare earth elements (REE) which are sometimes referred to as rare earth metals are a group of 17 chemically similar metallic elements, including 15 lanthanides, scandium and yttrium. The lanthanides are elements spanning atomic numbers from 57 (lanthanum, La) to 71 (lutetium, Lu). Scandium and Yttrium are considered as REE owing to their similar chemical and physical properties. The REE can easily substitute for each other due to their chemical similarity and this makes refinement to pure metal a bit difficult. Within the earth crust, the REE are relatively plentiful as individual REE varies widely from cerium the most abundant (43ppm) to thulium (0.28ppm) (Taylor and Mclennan, 1985; Ruchick et al.2003). As refined metals, the REE are lustrous, iron grey to silvery in appearance. They are

characteristically soft, malleable, ductile and typically reactive. Their electron structure gives them some unusual magnetic and optical properties. The melting points of the REE increase across the series from 798^0C (cerium) to 1663^0C (lutetium). With the exception of Sc, Y, La, Yb and Lu, the REE are strongly paramagnetic and have strong magnetic anisotropy (Gupta et al., 2005). In terms of mineralogy, it's a known fact that REE does not occur naturally as metallic element but in a wide range of mineral types including the halides, carbonates, oxides, phosphates and silicates. They are mostly hosted by rock forming minerals where they substitute for major ions while higher concentration of REE are required to form their own minerals (Moller, 1986). Worthy of note is the fact that the vast majority of resources are associated with just three minerals; Bastnaesite, Monazite and Xenotime. Bastnasite and Monazite are the primary sources of the LREE, mainly Ce, La and Nd. Monazite contains less of La and more of Nd, HREE and contains the radioactive element thorium while the Xenotime is dominated by the HREE including Y, Dy, Er, Yb and Ho (Harben 2002).

II STUDY AREA

The study area is bounded by Latitude 7^0 00'00''N to 7^0 05'00N and Longitude 9^0 16'00''E to 9^0 18'30''E and span an area of 4.5 km by 9.0 km within topographic Sheet 272, Katsina-Ala SE. It is located in Ushongo Local Government Area of Benue State in North Central part of Nigeria (**Figure 1**). The region is located in West Africa's Savannah belt, which is known for its grasslands and sparse shrubbery. In the region, tall grass grows to its fullest extent from September to December. The vegetation is tropical, and is characterized by alternating rainy and dry seasons. During the dry season, there are intermittent showers. The North-East trade winds (harmattan)" keep the humidity incredibly low from December through January. The average yearly rainfall ranges from 750 to 1120 millimeters. The area is underlained by the Basement Complex of Nigeria which consist of the Migmatite-Gneiss Complex (MGC); the Upper Proterozoic supracrustal rocks known as the Schist belts and the Syn

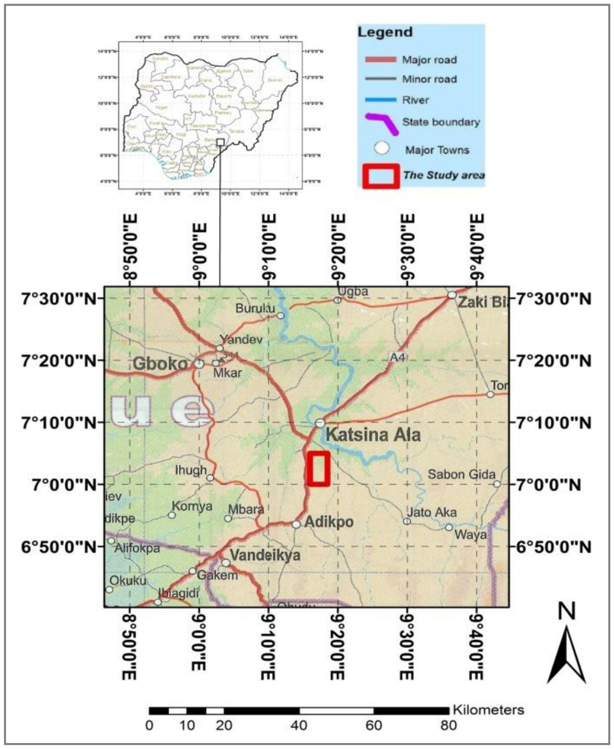


Figure 1 showing the location map of the study area

to late tectonic granitic rocks which intruded the MGC and the Schist belts that are pan-African in age (Obaje, 2009).

III MATERIAL AND METHODS

The material used in this study includes soil samples obtained at insitu within the study area. A total number of sixty (60) soil samples were analysed for rare earth element (REE) research.

♦ Geological Mapping

Detailed geological mapping was carried out within the study area on a scale of 1:25,000 using the Katsina-Ala Sheet 272 SE as a base map. Representative samples of rock were collected. Outcrops within the study area were located using a Global Positioning System (GPS) and each of them was examined and described base on appearance, macroscopic nature of the mineral constituents, structures and geologic relations with adjoining rock types. Structural elements such as joints, strike and dip were measured using a compass clinometer. Geologic map of the study area was produced by plotting the aforementioned information on the base map.

♦ **Soil sampling**

A systematic soil sampling was carried out within the delineated area from geological mapping. The delineated area was gridded into six (6) profiles with an average of 250m spacing between each profile and 250m spacing between each sampling point. At each sampling point, samples were collected from the B – horizon (zone of illuviation) which is preferred in most soil surveys owing to its high accumulation of trace elements. The sampling depth varies from 0.5 to 1m depending on the thickness of the horizons. At the end of the exercise, a total number of sixty (60) soil samples were collected and prepared for laboratory analysis.

♦ **Laboratory Analysis**

The laboratory analysis which involved a number of procedures was carried out at ***ALS Chimex Laboratories, South Africa*** for a detailed laboratory analysis using the Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for a multielement analysis. Stages of laboratory analysis involve sample drying and homogenization, sample digestion and sample analysis of the digested soil samples.

IV RESULTS AND DISCUSSION

Geology - Lithologically, the area of study is underlained by the migmatite gneiss, amphibolite and medium grained granite which intruded the aforementioned **(figure 2).** Others include the late felsic in-fills comprising of pegmatites and quartzo-feldspathics. The migmatite gneiss constitute the largest lithologic unit mapped covering about 70% within the study area. It displayed a mixture of the unmelted metamorphic part with the recrystallized igneous part resulting into formation of diatexite with swell and pinch structure. The strike of foliation assumes a general trend in a NE/SW direction. The Amphibolite represents the metavolcanic member of schist belt and was encountered at the central-west of the study area outcropping in a low lying, bouldery nature. Texturally, it is fine grained and dark grey in color which is an indication of the presence of high amount of mafic minerals over the felsic ones. Field evidences reveals that medium grained granite intruded the migmatite gneiss as contacts were established and relics of the older rocks (gneisses) were seen in some of the outcrops which actually shows an incomplete assimilation of the granitic melt. The felsic dykes/veins comprises of the pegmatites, aplite and quartzo-feldspathics which were observed within the gneiss and granite. They vary in width from few centimeters to a meter, trending almost concordant to the host rock while some discordant. The structural trend analysis of the tectonic and surface features of the study area reveals various trends in NE-SW and NW-SE directions with principal structural trend being in the NE/SW as indicated on the rose plot **(figure.3)**

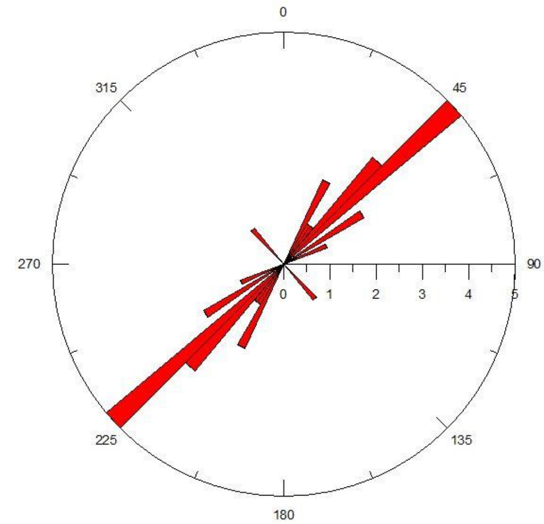
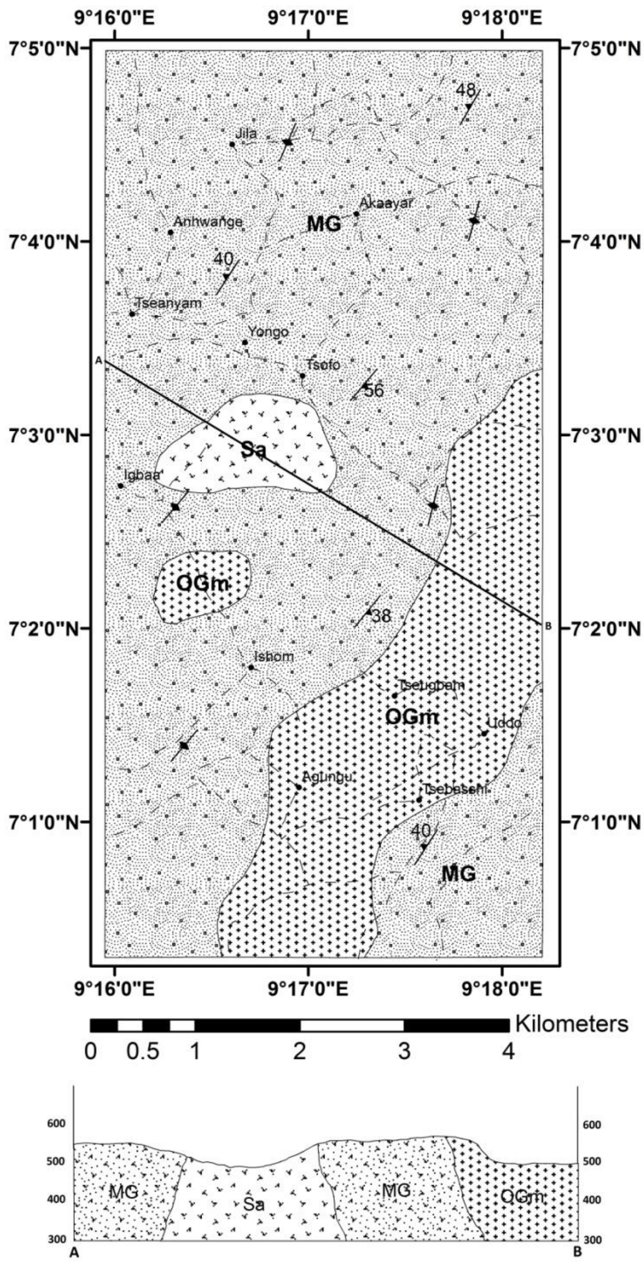


Figure 3. Rose diagram representing the structural orientation of the study area



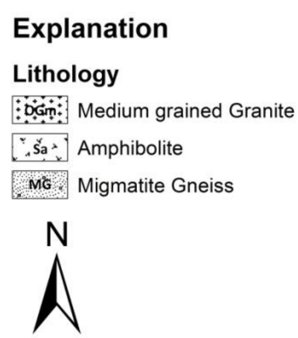


Figure 2. Geologic Map of the study area

<u>Soil Geochemistry</u> – results of the Rare Earth Elements (REEs) analyses are shown in Table 1. The result show the average concentrations of the REEs in decreasing order as Ce>la>Nd>Y>Pr>Sm>Gd>Dy>Yb>Er>Tb>Ho>Eu>Lu>Tm. This depicts high values in the light REE over the heavy REE (figure 3)

Table 1. Summary of Soil Sample Geochemical data for REE

Elements (ppm)	N	Min	Max	Background (median)	Average	Standard Deviation	Median Absolute Deviation	Threshold
Ce	60	115	670	250.5	260.7333	100.5463662	58	366.5
Dy	60	3.26	12.45	6.55	7.025833	2.180878607	1.23	9.01
Er	60	1.81	7.02	3.225	3.557833	1.211378388	0.705	4.635
Eu	60	0.58	2.16	0.985	1.092333	0.353468847	0.155	1.295
Gd	60	3.97	25.3	11.275	11.47333	3.865079062	2.525	16.325
Ho	60	0.57	2.3	1.165	1.265333	0.411501866	0.225	1.615
La	60	32.5	232	105.25	106.9167	38.32337503	22.8	150.85
Lu	60	0.27	1.06	0.5	0.558333	0.192346498	0.12	0.74
Nd	60	25.7	213	92.15	93.79	34.59916576	22.6	137.35
Pr	60	7.11	56.3	25.6	25.1065	9.206863288	6.35	38.3
Sm	60	5.5	36.7	16.875	16.4435	5.989682888	3.825	24.525
Tb	60	0.54	2.48	1.25	1.340167	0.409280028	0.23	1.71
Tm	60	0.25	1.01	0.46	0.519	0.17602677	0.09	0.64
Y	60	15.2	70.7	33.3	34.97833	11.71474649	8	49.3
Yb	60	1.82	7.06	3.25	3.562	1.230680947	0.75	4.75

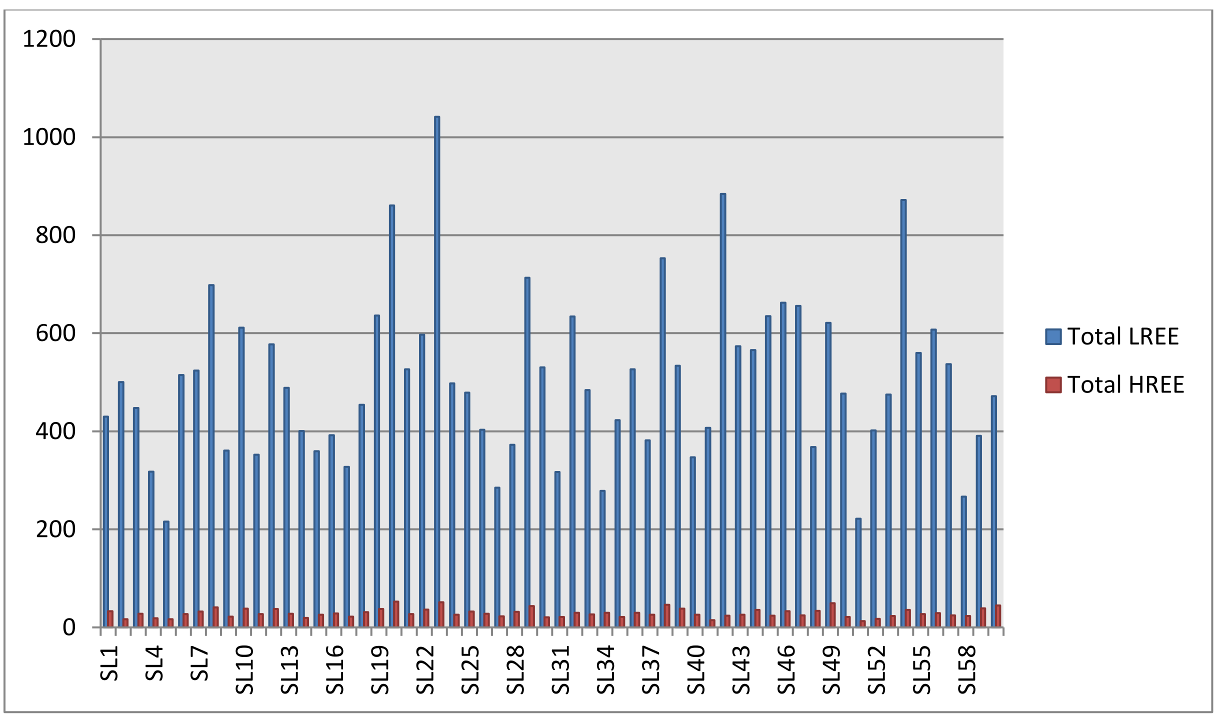


Figure 3. Histogram plot of LREE against HREE

REE Mineralization Potential of the study area - The mineralization potential of the study area (table 2) was determined by dividing the average analysed values of the REEs in the study area by their respective abundance in the upper crust after Dushyanthal et. al. 2020. This generated the enrichment status of each REE using a threshold of 2.0. The following elements show significant enrichment status; Ce, La, Nd, Pr, Gd and Sm which is an indication of a potential mineralization of the light REE Ore.

REE distribution pattern - The result of the analysis was used to prepare concentration maps in form of a point symbol map which is superimposed on the trend map and geology. To identify regions favorable for mineralization, background value and threshold were established as computed in Table 1. The threshold value of each of the element analysed was determined by using ***Median + 2 x Median absolute deviation*** *(Clemens Reimann, Patrice de Caritat, 2017)*

In interpreting element's concentration in earth's sampled materials and considering its significance in the study area, a basis of comparison is required. The average crustal abundance of elements in the earth and the calculated threshold serves that purpose in this study since our sampling media is an insitu soil derived from the bedrock. The summary is presented in table 3 and the distribution maps of the selected elements are herein presented in figures 4.

Table 2. REE Mineralization Potentials of the study Area (Enrichment factor = 2.0; Dushyanthal , 2020)

Elements	Average analysed value	Crustal abundance, Dushyantha et al (2020)	Enrichment ratio	Enrichment Status
Ce	260.7333	63	4.139	Enriched
Dy	7.025833	3.9	1.801	Not Enriched
Er	3.557833	2.3	1.547	Not Enriched
Eu	1.092333	1	1.092	Not Enriched
Gd	11.47333	4	2.868	Enriched
Ho	1.265333	0.83	1.524	Not Enriched
La	106.9167	31	3.449	Enriched
Lu	0.558333	0.31	1.801	Not Enriched
Nd	93.79	27	3.474	Enriched
Pr	25.1065	9.2	2.729	Enriched
Sm	16.4435	4.7	3.499	Enriched
Tb	1.340167	0.7	1.915	Not Enriched
Tm	0.519	0.3	1.730	Not Enriched
Y	34.97833	21	1.666	Not Enriched
Yb	3.562	2.2	1.619	Not Enriched

Table 3. Showing the relative abundance of the REE within the study area

Elements (ppm)	Background Value	Crustal Abundance, Dushyantha et al (2020)	Threshold	Anomalous points	Relative Abundance
Ce	250.5	63	366.5	8	High
Dy	6.55	3.9	9.01	12	Moderately high
Er	3.225	2.3	4.635	12	Moderate
Eu	0.985	1	1.295	17	low
Gd	11.275	4	16.325	6	High
Ho	1.165	0.83	1.615	15	Moderate
La	105.25	31	150.85	6	High
Lu	0.5	0.31	0.74	12	low
Nd	92.15	27	137.35	4	High
Pr	25.6	9.2	38.3	4	High
Sm	16.875	4.7	24.525	3	High
Tb	1.25	0.7	1.71	9	Moderate
Tm	0.46	0.3	0.64	15	Moderate
Y	33.3	21	49.3	6	High
Yb	3.25	2.2	4.75	11	Moderate

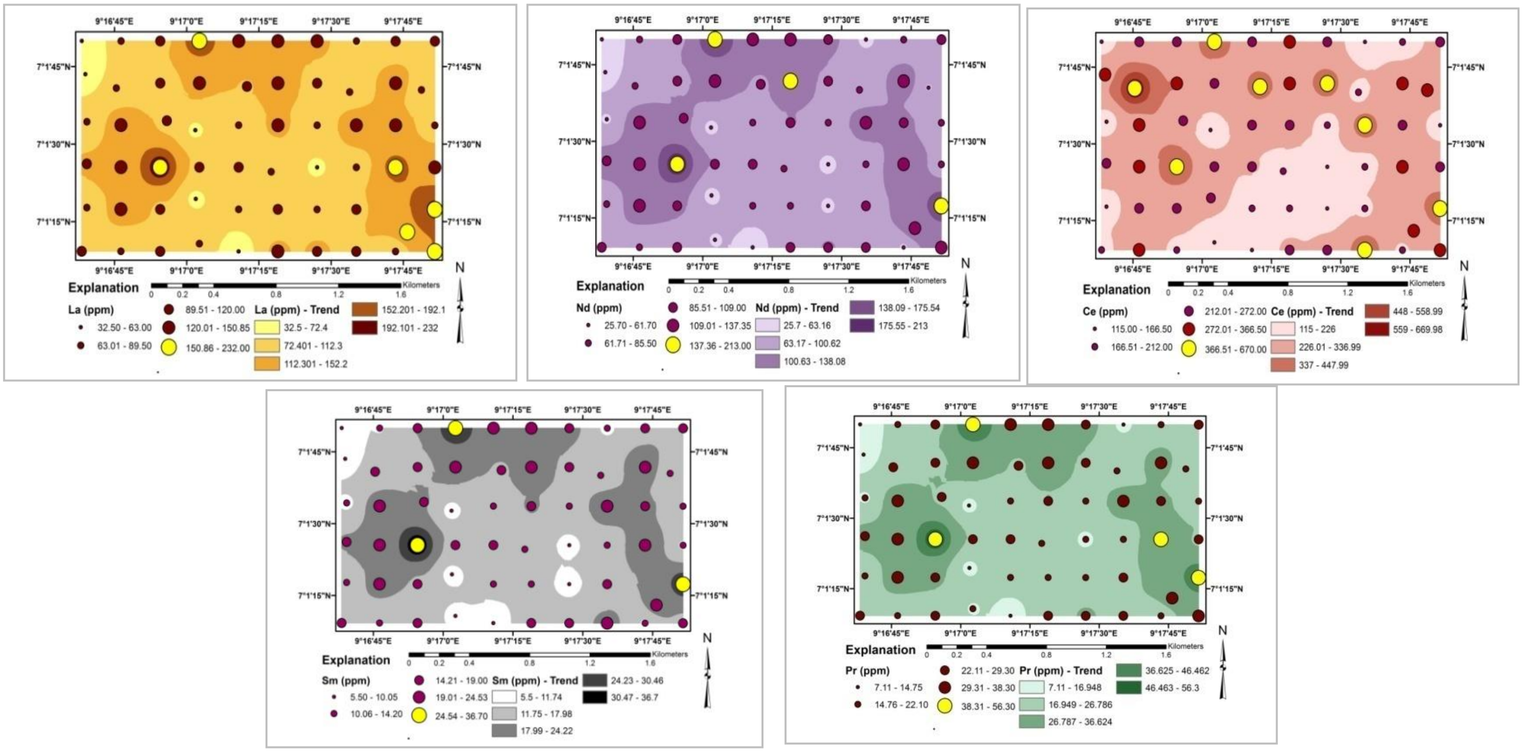


Figure 4. Showing the distribution patterns for the light REEs

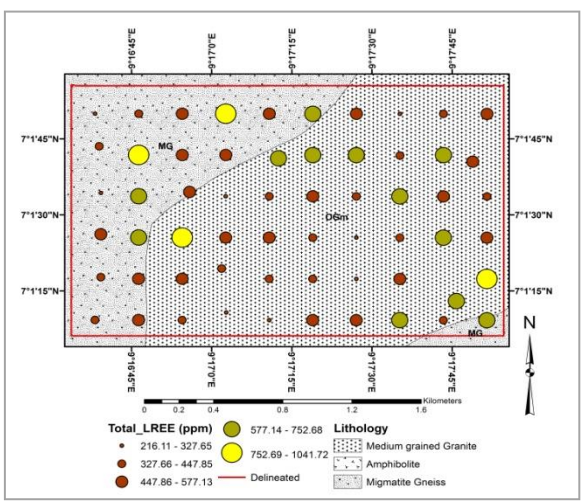


Figure 5. Point symbols of the LREE superimposed on the geology

Statistical Evaluation (Correlation Coefficient and Inter-Elemental Relationships) - The computation of the Pearson correlation coefficient for all pairs of elements is one of the first steps in carrying out multivariate analysis. Certain elements tend more or less to be associated with another element or group of elements (Goldschmidt, 1954) so that different types of bedrock or mineralization are determined by specific elemental associations. It is also performed to uncover inter-element relationships or association inherent in the geochemical data that could be interpreted as characteristic of the geological or geochemical processes operating in the study area. Pearson's correlation coefficient method is used in order to delineate the inter-elemental relationships. The coefficient measures the strength of linear relationship between any two variables. Correlation coefficients were also determined to identify the relationship between different geochemical factors that often influence the concentrations and associations of elements using SPSS 16.0 (Statistical Program for the Social Sciences). This computer software package is used to calculate the correlation coefficient and determine the inter-elemental relationship.

Certain groups of elements respond more or less similarly to a given set of environmental conditions. Consequently, mutual correlations between different elements serve to identify more clearly the variations present in the geochemical landscape (Levinson, 1974). The correlation matrix for the data obtained in this study (Table 4) was generated with the use of statistical package for social sciences (SPSS) and it shows both negative and positive correlation.

Factor analysis (R – mode) - The R-mode factor analytical technique is the commonly used in geochemical exploration. It assists in grouping the multi-element geochemical data into metal associations, which characterize specific geological processes, thereby improving the interpretation of the data.

The R-mode factor analysis using the varimax rotation method with Kaiser Normalization was employed in this study. The data were log-transformed before being analyzed and the factor solutions provide information on loading and Eigen values. In this analysis, three factor models is considered in view of the known geology of the study area.

Table 4: ***Pearson correlation matrix of soil geochemical data from the study area showing significance at 0.5 and above.***

	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Th	Tm	Y
Ce	1														
Dy	0.302	1													
Er	0.124	0.935	1												
Eu	0.082	0.71	0.752	1											
Gd	0.538	0.833	0.651	0.464	1										
Ho	0.193	0.973	0.979	0.762	0.732	1									
La	0.56	0.663	0.491	0.323	0.902	0.564	1								
Lu	0.128	0.901	0.969	0.729	0.609	0.946	0.483	1							
Nd	0.59	0.656	0.438	0.276	0.936	0.53	0.967	0.422	1						
Pr	0.594	0.648	0.429	0.274	0.928	0.52	0.977	0.42	0.997	1					
Sm	0.595	0.706	0.486	0.303	0.962	0.578	0.932	0.447	0.984	0.975	1				
Tb	0.439	0.947	0.831	0.632	0.947	0.887	0.808	0.788	0.812	0.807	0.855	1			
Th	0.612	0.337	0.077	-0.059	0.727	0.184	0.817	0.061	0.871	0.879	0.846	0.541	1		
Tm	0.097	0.909	0.981	0.749	0.625	0.966	0.495	0.976	0.429	0.423	0.459	0.8	0.066	1	
Y	0.165	0.965	0.979	0.726	0.711	0.985	0.567	0.953	0.529	0.519	0.573	0.866	0.172	0.963	1
Yb	0.113	0.903	0.982	0.726	0.6	0.955	0.462	0.986	0.398	0.393	0.434	0.789	0.043	0.983	0.962

Some of the elements have fairly strong to strong positive correlation with each other and weak negative to positive correlations with some other elements. Moreover, the strong positive correlation between some of the elements, notably, Ce/La, La/Nd, Ce/Pr, Ce/Sm, Nd/Pr, Nd/Sm, Lu/Tm, Nd/Yb just to mention a few may be indicative of a common source of mineralization or concentration.

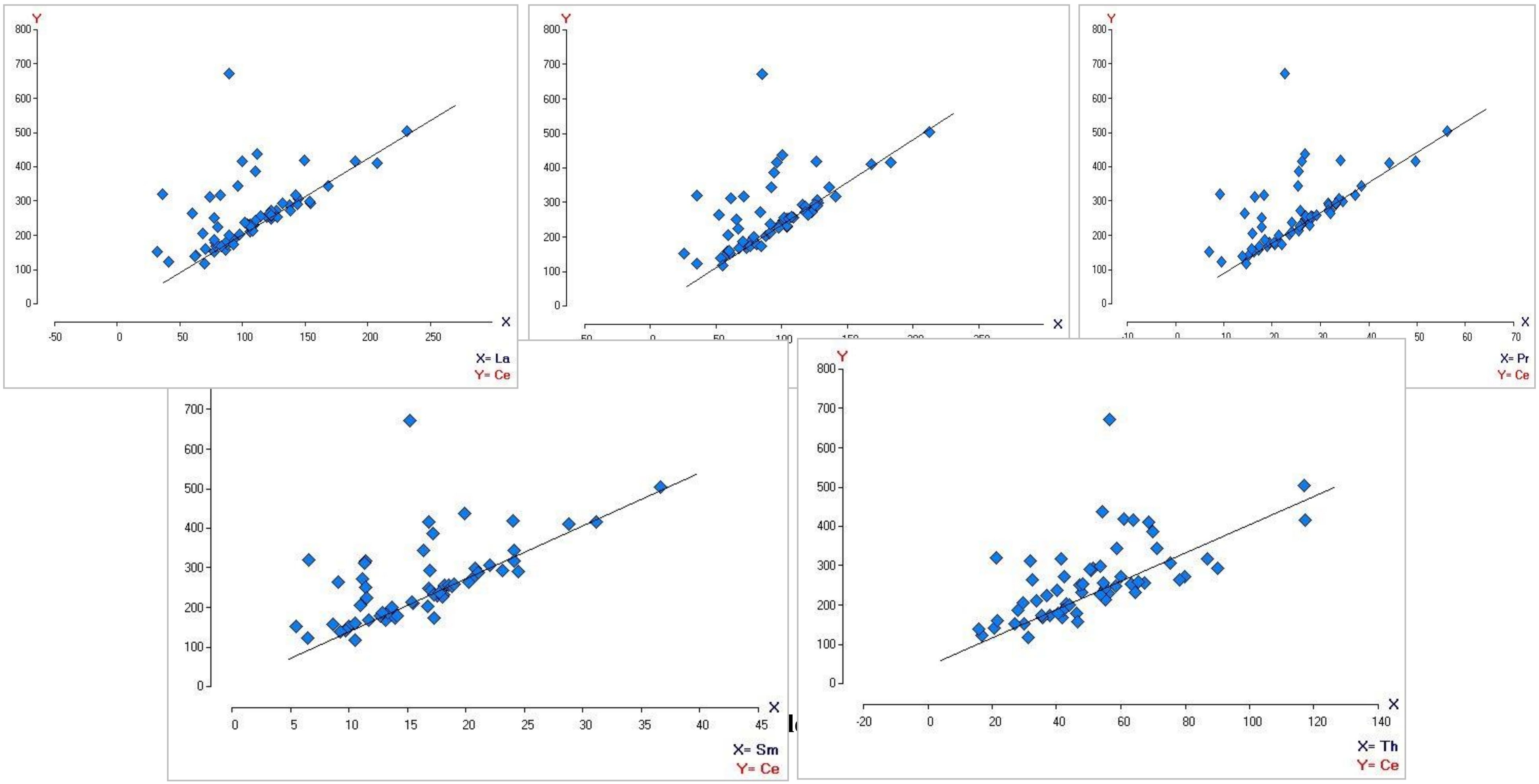

X= La
Y= Ce
X= Pr
Y= Ce
X= Sm
Y= Ce
X= Th
Y= Ce

Table 5. Component factor matrix for geochemical result of soil samples for REE prospection in the study area

Elements	Factor 1	Factor 2	Factor 3
Ce	0.4244	0.5675	0.6928
Dy	0.9635	-0.195	0.0031
Er	0.8777	-0.46	0.0025
Eu	0.6652	-0.463	0.1944
Gd	0.9204	0.3349	-0.0498
Ho	0.9227	-0.362	0.0038
La	0.8224	0.4964	-0.102
Lu	0.855	-0.468	0.0195
Nd	0.8059	0.5716	-0.104
Pr	0.8011	0.5787	-0.101
Sm	0.8315	0.5288	-0.0782
Tb	0.9785	0.0591	-0.0036
Th	0.5099	0.8141	-0.0966
Tm	0.8641	-0.472	-0.0203
Y	0.9152	-0.367	-0.038
Yb	0.8496	-0.491	0.0185
Eigen Values	**10.933**	**3.7**	**0.57**
% of Variance	**68.333**	**23.126**	**3.561**
Cumulative %	**68.333**	**91.459**	**95.019**

Table 6: Elemental Association of the Three Factor Model

Factors	Elements	% of variance
1	Dy,Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Th, Tm, Y, Yb	68.333
2	Ce, La, Nd, Pr, Sm, Th	23.126
3	Ce	3.561

Factor 1: shows a high metallic association and accounts for 68.33% of data variability in the area. As the most pronounced factor and the crop of elements associated, this probably defined a combination of both mineralization and lithology. The strong association between the REE elements in this factor perhaps represents granitic lithological units characterized with veins and dykes. **Factor 2:** This accounts for 23.126% of data variability in the area. The strong positively correlated variables among Ce-La-Nd-Pr-Sm and Th suggested the presence and influence of a granitic lithology. This association could probably be suggesting the presence of a ***monazite*** mineralization.

V CONCLUSION & RECOMMENDATION

The results from the laboratory analysis, with emphasis on the rare earth elements reveal the concentration of the total REE in ppm ranges from 232.7 to 1092.71. From interpretation, it is observed that the concentration is enhanced in the light REE than in the heavy REE, this pattern is typical of granitic (felsic) rocks. The correlation plots and correlation table for the REE's shows a strong association existing especially amongst the light REE including thorium. Within the REEs; *Ce, La, Nd, Pr, Sm, and Th* shows positive correlation between each other with a significant value of 0.5 and above which interprets a strong association and a possibility of a common source of mineralization. This is also corroborated in the factor analysis in the factor 2 association. Furthermore, the aforementioned associated elements showed significant anomalous values when interpreted which were suspected to be derived from primary mineralization.

In addition, the trend maps of the aforementioned light REE reveals a pattern that shows a similar trend of high concentration and coupled with their strong correlation, a critical observation suggest a possible mineralization of Monazite (Ce, La, Nd, Th)(PO_4,SiO_4).

In the light of the results obtained from the analysis and with critical observation from the interpretation, it shows an indication of the presence of light REE ore; it is therefore recommended that further exploration work such as whole rock geochemistry, ground geophysics and possibly drilling be carried out within the area of study to establish the REE ore mineralization.

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