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Petrogenetic and Distribution of Trace and Rare-Earth Elements in the Marble from Igarra Area, Southwest Nigeria.

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ABSTRACT
A multivariate statistical and upper background methods were used to interpret geochemical data of the trace and rare earth elements in the marble from Igarra in order to determine the provenance and elemental mineralized anomalies. Correlation matrix showed that Th correlates positively with both the light and heavy rare earth elements as well as Pb. The presence of Th and Pb in the marble reflects their mutual association as light ion lithophile elements (LILE) that show radioactive mineralization . Most of the calculated trace element concentrations are within the background values except elements Ba, Sr and Zr whose contents in some samples exceed the upper background thresholds (UBT) of 68.77ppm, 1702ppm and 14.13ppm respectively. The rare earth elements (REEs) that exceed the UBT are La, Ce and Y. The viability of these anomalous elements is doubtful. The geochemical data reveal a depleted concentration of the heavy rare earth elements, (HREE) Eu (0.04-0.17ppm),Tb (0.01-0.2ppm), Er (0.09-0.7ppm) and Lu (0.03-0.1ppm) and an enriched light rare earth elements, (LREE), La(0.8-10ppm), Ce(1.4-11.6ppm), Pr(0.15-1.27ppm) and Na(0.5-4.3ppm). The marble contains measureable amounts of volatile materials represented by very high contents of loss on ignition (LOI). Enriched light rare earth elements (LREEs), incompatible elements Ba(24-122ppm), Sr(1076-2790) and Rb(1.95-7ppm) with high contents of volatile materials and depleted concentration of HREEs are characteristics suggestive of mantle- materials derived from metasedimentary rocks.
Keywords; Factor analysis, mantle material, multivariante and Provenance.

1.0 INTRODUCTION.

The Igarra area lies within the Pre-cambrian Basement complex of the Southwestern Nigeria. The geology has been studied by authors among which are Elueze,1980,1991; Turner, 1983; Rahaman,1992;Odeyemi,1988;Odeyemi *et al*.,1991;Ekwueme, 1990,2000 respectively.Trace element studies for the determination of the crust or mantle evolution process or tectonic setting of granitic rocks using variation and discrimination diagrams have been undertaken by early scholars such as Pearce and Cann, 1973; Floyd and Winchester, 1975; Pearce, 1975; Wood et al., 1979 and Shervais, 1982. The use of elemental and isotopic studies for marble provenance determinations started in the 1960s and by 1965 Rybach and Rissen made use of neutron activation analysis (NAA) to determine sodium and manganese contained in the marble. Since then many authors have progressively used different analytical techniques to measure isotope ratios of carbon and oxygen in an attempt to either characterize, discriminate or determine marble provenance (Craig and Craig 1972 ; Manfra *et al*., 1975, Herz, 1985, 1987; Van der Merwe *et al* ., 1995;Barbin *et al*.,1992; Jongste *et al*.,1992, and MeLoni *et al.,* 1995). A combination of data analysis using oxygen and carbon ratios and petrography is suggested for a successful provenance determination. However, a single approach of technique has been argued against stating that integrated methods would provide a successful marble provenance studies. A multivariate statistical method has been found to be very useful in data analyses especially in metal associations relating to possible mineralization.

McDough (1990) is of the opinion that a source of volatiles and incompatible elements is important in the upper mantle. Bell and Rossman, 1992 reveal that rocks such as garnet, or olivine in the upper mantle contains measurable amounts of volatiles (OH or H) and that oxygen fugacity of the upper mantle is sufficiently enough to stabilize carbonate minerals such as magnesite, $MgCO_3$ and dolomite, $CaMg(CO_3)$. Volatile-bearing minerals harbour most of the incompatible element K,Tc, Al, Rb, Ba, Sr, H, Cl, and light rare earth elements (LREES) (Baiky, 1970). Carbonate minerals contain volatiles that are enriched in incompatible elements, as well as light rare earth elements (LRREs).

Trace and rare earth elements data of marble from Igarra area are determined using the Inductively Coupled Plasma-Mass Spectrophotometry (ICP-MS) analytical method. The results are subjected to multivariate statistical analysis from which the elemental abundances, quantitative distributions and marble provenance are determined. This study is provoked by the fact that little or scanty work has been done on the use of trace and rare earth elements to determine their abundances and petrogenesis of marble in the study area.

2.0 Materials and Methods

2.1 Sample collection and preparation

Forty samples were collected from different quarry locations in Igarra area. Global positioning system instrument (GPS) was used to locate the northings (latitudes) and eastings (longitudes).The samples were then crushed to reduce the sizes and pulverized into powdered form. They were subsequently sent to Activation Laboratory (ACTLAB) in Ontario, Canada for geochemical analysis using the Inductively Coupled plasma-Mass Spectrometry (ICP-MS) Method. Details of the ICP-MS methods are given in Longerich *et al.*,1990.

The analysis provided data on the major, trace and rare earth elements (REE) from which the elements had been used for this work. Representatives of the trace and REEs were then used in all computations using the statistical package for the social sciences SPSS 19.software (Nie et al.,1975).Statistical method involving use of correlation analysis is accepted to explain and interpret the data in order to specify the elemental relationships while the factor analysis singles out variable elements that are mutually related into principal associations (factors) on the basis of their mutual correlation coefficient. These associations may now be interpreted to relate to lithology or mineralization or environmental issues. In the factor analysis, only elements with positive loadings greater than 0.40 are considered significant.

The upper background threshold (UBT) formula below as proposed by ȳoØa, FyPBHy (1964) was adopted in the calculations and determination of elemental anomalies .

UBTq= Md + 0.5 √3/q(Q3-Md)………….(1)

Where q= 0.05, Md=Median,Q=quartile

The UBT can also be determined by using the proposal of Van de Meent et al., (1990) by taking into account the percentile of 98p, 95p along the cumulative curve distribution of the element concentrations. However, in most determinations, the UBT is calculated by using the formula (1) stated above in the interpretation of elemental anomalies.

3.0 DISCUSSION.

The trace element chemistry for Igarra area as presented in Table1 shows that the marble hosts the following elements, V, Ba, Sr, Zr, Cr, Co, Rb, and Cs, trace metals, Ni, Cu and Zn at varying concentrations in parts per million (ppm). Ba contents vary from 24 to 122 ppm, Sr(1076-2790 ppm), Rb (1.95-7ppm), Pb (0.45-24 ppm) and U (0.9-1.5 ppm) respectively. Sr is relatively high and the marked enrichment suggests its association with feldspar. Sr and Ba have been reported high in carbonates elsewhere (Lonos et al., 1990). They are found in the same vertical column of the periodic table and are chemically alike. They are Lithophile elements, very compatible and they strongly partition into feldspar. Sr has an ionic radius of 1.12A^o and it lies between Ca and K whose ionic radii are 0.99A^o and 1.33A^o respectively. It is therefore expected to substitute for both elements in the rock due to the proximity of their ionic radii. Ca increases with the substitution while K decreases in the rock in most cases. Cu and Zn are naturally distributed in carbonates in concentrations of 4ppm and 20 ppm respectively (Turekian and Wedepohl, 1961). The concentrations of Ca and Zn in Table 1 show that their values range between 10 and 30 ppm and from < 30 ppm to 90 ppm respectively. Zircon content varies from < 4 to 23 ppm. The presence of zircon in carbonate rocks is an evidence that marble is derived from detrital grains during the formation of limestone. Zirconium (Zr) mineral, $ZnSiO_4$ is found as an accessory in detrital deposits. Carmichael et al., (1974) point out that the presence of zircon in rocks lead to depletion of heavy rare earth element (HREE).

Pb, Th and U (radioactive elements) are present in the marble. The source of Pb is doubtful but its high mobility potential is suggestive of extraneous input of material either during the formation of limestone from marls, argillaceous and detrital grains or metamorphism to marble. Limestone can easily take in Pb deposits. The presence of Pb, Th and U in the marble suggests a threat in the purity and use of the rock.

The marble contains the light rare earth elements (LREE) La, Ce, Pr, Nd and Sm and the heavy rare earth elements (HREE) Eu, Gd, Tb, Du, Er, Lu, Yb and Y (Table 2). The REEs are set of fifteen chemical elements in the periodic table with the elements from Lanthanum (La) to Lutetium (Lu). Phase elements have similar chemical prospective and are widely dispersed and enriched in crustal rock but are not seen in concentrations economically exploitable like other metal ores. The few economically exploitable deposits are known as rare earth minerals (Haxel el al., 2006). In most cases, however, REEs are randomly trapped in silicate minerals where they are incompatible. The distribution of LREE and HREE shows an interesting difference exemplified by La with contents ranging from 0.7 to 6.9 ppm and Ytterbium, Yb varying from 0.08 to 0.3 ppm .

Generally, the HREE elements in the marble display depleted concentrations as against the enriched LREEs. The Igarra marble contains very high contents of loss on ignition (LOI) (Obasi, 2012) and by implication contains measurable amounts of volatile materials (OH, CO_2 and H_2O).

In order to further establish the marble provenance and to identify the mineralized anomalies of these trace and REEs, a reliable interpretational multivariate statistical analysis is adopted.

4.0 Multivariate statistical analysis. (MSA)

The MSA techniques is hitherto applied to examine the inter element associations in the trace and rare earth elements in the marble using correlation, models and analysis. The analysis factors related variables into principal associations on the basis of their mutual correlation coefficients (Davis, 1973).

Tables 3 and 4 present the descriptive statistics of trace and REE elements of the marble.

The arithmetic mean, standard deviation, skewness, kurtosis, range and the upper background threshold (UBT_{005}) are summarized. …….. Ba and Sr have values that range between 24 and 122ppm and 1076-2790ppm with their mean values as 54.3 and 1649.4ppm respectively. Rb content varies from 1.95 to 7ppm. Ba, Sr and Rb are incompatible elements and they are enriched in the marble.

Figures1a,b and c show the histogramic distribution of Ba, Sr and Rb elements by skewness and kurtosis. The cumulative curves of the content distribution of these elements show that they are positively skewed an indication of their concentrative abundance as shown also in Table 3 .

The REE elements in Table 2 are characterized by relative abundance of the LREEs La(0.8- 10ppm), Ce(91.4-11.6ppm), Pr(0.15-1.27ppm), and Nd(0.5-4.3ppm) and low concentrations of HREEs, Eu(00.4 – 0.7ppm) and Lu(00.3 – 0.1ppm) respectively. Enriched incompatible elements of LREEs and depleted HREE in the presence of volatile materials in the opinion of Wood, (1979) and Pearce (1982) are characteristics of rocks that are of mantle sources .

The data in Tables 1 and 2 are lognormally transformed into Tables 5 and 6 respectively before the performance of the factor analysis models as proposed by Nie et al., (1975). Orthogonal transformation of the factor matrix has been carried out in line with Kaiser 1958 method.

The results from the factor matrix are summarized in Table 7 indicating the elements that are correlated in the trace and REE of the marble. Sr mutually correlates positively with Ba, just as Rb is associated together with V, Sr, and negatively with Zr, Co and Cu. This implies that Zr, Co and Cu cannot be in the same crystal lattice with the Rb. Zn correlates with Sr, Cr, Cu and negatively with Co. The correlation of Zn with Cu is a reflection of their chalcophile relationship and mineralogy.

Th correlates easily with both the LREE and the HREE as well as with Pb. The presence of Th and Pb in the marble reflects their mutual association as light ion Lithophile elements (LILE) that are usually mobile and radioactive.

The REEs show significant correlation that portrays their mineralogical relationship. Lanthanium, La occurs in all the associated elements (Table 7). La is compatible with Ce and Nd in partition coefficient (Rollinson, 1993). The REE elements present a systematic variation from LREE (La-Nd) to HREE (Sm- Lu) and most likely to suggest significant difference in their partition coefficient and behaviour.

The coefficient of correlation pattern for trace element in Fig 2 shows a visual idea of the spread of the data in the scattered diagram.

The scattering pattern is explained under the assumption that the greater the number of competing petrological processes, the greater the scatter on the elemental variation diagram. The scattering of the elements therefore is a significant evidence that geological and or environmental processes acted together to produce the marble at Igarra, Fig 3 presents the REE variation diagram in which almost all the samples of REE elemental concentration show a negative or downward slopes of the marble curves on Eu, Tb and Lu respectively .However, Lu presents a positive spike in Eu thus suggesting that during the metamorphism that produced marble in the study area, europium, Eu most likely substituted calcium in the plagioclase crystal lattice . Fowler and Doig, (1983) pointed out that during the crystallization of plagioclase europium is sequestered in its crystal lattice and in this case the REE plots will show a downward spike as is shown in Figure 3.The variability in their chemical behavior does not exclude the possibility of elemental association in the formation of marble during metamorphism. Fig 4 is a three principal component plot (PCP) in which both the light and the heavy rare earth elements cluster in one component displaying their mutual associations.

Table 8 presents a five-factor model cumulatively accounting for 87.002% of the total data variance. Factor 1 (Ba- Sr- Cr- Zn- Rb-Co) is heavily loaded with respect to Zn, Cr, Sr, and Rb. Other elements that have contributed to the loading significantly are Ba, and Co. The element Co displays a negatively high loading implying that the marble is depleted in Co. The factor accounts for 30.213% of the total variance of the 5-factor model. The high loading of the trace elements suggests their high mobility within the environment during the regional metamorphism of limestone to marble. The 30.213% of total variance suggests the significance of the elements in mineralization. Sr is associated with marble mineralization, strontianite ($SrCO_3$).

Factor 2 (Ba- Zr- Cr- Cu- Ag- Cs) accounts for almost 21.1% of total data variance. This element grouping reflects an environment for the mineralization of two associated minerals Cu and Ag with Zircon as an accessory mineral.

Factor 3 (V-Zr-Rb-Ag) accounts for 14.241% of total data variance with V and Ag elements contributing more loading and reflecting a lithological controlled formation. Factor 4 (Ba-Sr-Co) contributes about 12% of the total data variance. The association of Ba and Sr in this factor is an implication of their relationship to mineralization. The strong loading of Ba may be due to its association to marble and the formation of ($BaCO_3$) white mineral. Factor 5 has Zr and Ni .Zr is found in relationship with carbonate mineralization ($NiCO_{3)}$

Table 9 shows a three-factor model of the REEs that accounts for 92.2% of the total data cumulative variance. Factor 1 account for 69.9 % of the total data variance. This elemental grouping is heavily and positively loaded with respect to the LREE and HREE. The significant loading suggests mineralization that involved both the LREEs and HREEs in the marble. Factor 2 (Tb-Yb) accounts for 13.7% of the total data variance . This factor 2 is scarcely loaded as only Tb and Yb are mutually associated in the group. Factor 3 (Tb-Pb-Th) contributes about 8.7 % of the total data variance. The strong loading of Pb (0.607) and Th (0.616) in this factor establishes their mutual relationship to radioactive mineralization.

5.0 Upper Background Threshold.

The upper background threshold ($UBT_{0.05}$) values are calculated for the trace elements using the formula proposed by ÿòØa, TÿPBHÿ, (1964)

UBTq= Md + 0.5 √3/q(Q3-Md)………….(1)
Where q=0.05, Md= median, Q=quadrant

The values are presented in Tables 3. The UBT is the upper limit of element concentration above which the element is considered anomalous. Most of the trace elements calculated fall within the background values (Bgv) (Table 1) except Ba in samples7and, 8 , Sr(samples7,8,9), and Zr(sample 6) whose contents exceed the UBT [Ba(68.77ppm),Sr(1702ppm), Zr(14.13ppm)] respectively and are therefore anomalous. Similarly, most of the REE in Table 4 are within the background values except la (sample 6), Le (sample 5) and Y (samples5,7) that exceed the calculated UBT and are therefore considered anomalous. Pb is anomalous in samples 4,5,6 respectively. However, these anomalous elements are not viable enough to be exploited.

6.0 CONCLUSIONS

The factor analysis reveals a high loading of metal association of Zn,Cr and Pb. Th correlates positively with the light and heavy rare earth elements. Similarly Zn and Cu correlate thus reflecting their chacophile association and possible mineralization. The correlation of Pb and Th establishes possible occurrence of radioactivity within the marble environment. The marble contains measurable amounts of volatile materials represented by high LOI and hosts most of the enriched incompatible elements (Rb, Ba, Sr) as well as LREEs. The presence of volatile-bearing minerals, enriched incompatible elements coupled with enriched LREE with depleted HREEs are characteristics suggestive of mantle-derived carbonate.

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Table 1: Trace element chemistry of the Igarra marble (vol wt %)

Sample	1	2	3	4	5	6	7	8	9	10
V	4.52	4.8	4.9	4.85	4.8	4.95	4.92	7	4.95	4.86
Ba	36	60	24	26	33	69	122	47	58	68
Sr	1209	1076	1509	1695	1588	1255	2790	1768	1968	1606
Zr	6	18	3.95	3.98	4	23	3.96	8	3.88	4.98
Cr	19.5	19.5	19	19.9	19.85	19.92	19.94	19.94	19.98	19.86
Co	1	1	0.05	0.08	0.09	0.08	0.09	0.09	0.08	0.09
Ni	19.95	19.86	19.9	19.92	19.96	19.85	19.9	19.9	19.85	19.92
Cu	9.85	9.8	9.84	9.86	9.92	9.95	9.88	9.8	9.9	9.98
Zn	29.5	29.8	29.85	29.9	29.95	29.92	29.95	29.9	29.95	29.95
Rb	1.95	3	1.95	2	7	1.95	6	6	3	2
Ag	0.04	0.04	0.03	0.04	0.04	0.03	0.04	0.04	0.04	0.03
Cs	0.04	0.04	0.03	0.03	0.04	0.04	0.03	0.04	0.04	0.04

Table 2: Rare earth element (REE) characteristics of Igarra marble

Element	samples								
	1	2	3	4	5	6	7	8	9	10
La	2.1	2	1.1	2	4.7	6.9	0.8	2.3	1.4	2
Ce	2.7	3.7	1.9	3.6	8.7	11.6	1.4	4.2	2.5	3.2
Pr	0.26	0.42	0.21	0.39	1.05	1.27	0.15	0.45	0.27	0.35
Nd	1.6	1.5	0.7	1.4	4.3	4.6	0.5	1.5	0.9	1.4
Sm	0.2	0.4	0.2	0.3	1.1	1	0.1	0.3	0.2	0.3
Eu	0.04	0.07	0.04	0.045	0.17	0.35	0.035	0.08	0.04	0.04
Gd	0.2	0.3	0.2	0.2	1.2	0.9	0.1	0.3	0.1	0.2
Tb	0.08	0.07	0.01	0.01	0.2	0.1	0.01	0.01	0.01	0.01
Dy	0.3	0.3	0.2	0.3	1.3	0.7	0.1	0.3	0.2	0.2
Er	0.2	0.2	0.1	0.1	0.7	0.4	0.09	0.2	0.09	0.08
Yb	0.08	0.2	0.07	0.1	0.7	0.3	0.08	0.08	0.01	0.07
Lu	0.03	0.03	0.03	0.03	0.1	0.03	0.03	0.03	0.03	0.03
Y	1.52	1.68	1.95	1.9	7	5	1.95	1.95	1.96	1.98
Pb	0.48	0.45	0.48	21	17	24	0.45	16	5	2
Th	0.2	0.5	0.2	0.6	0.7	0.5	0.2	0.7	0.4	0.2
U	1.3	1.5	0.9	1.1	1.3	0.9	1.3	0.9	0.9	1.3

Table 3. Descriptive Statistics of trace elements from the Igarra marble

	N	Minimum	Maximum	Mean(MedianMd,50p),ppm	Std. Deviation	Percentile75 (quartile Q_3)	Skewness	Kurtosis	Upper Background Value(UBT)
V	10	4.52	7.00	5.0550	.69471	4.95	2.961	9.159	3. 775
Ba	10	24.00	122.00	54.3000	29.04804	68.25	1.414	2.679	68.77
Sr	10	1076.00	2790.00	1649.4000	486.51737	1840.50	1.425	2.960	1702.94
Zr	10	3.88	23.00	7.9750	6.83108	10.50	1.760	1.922	14.13
Cr	10	19.00	19.98	19.7390	.31356	19.94	-1.745	2.739	21.48
Co	10	.05	1.00	.2650	.38756	19.93	1.774	1.398	17.44
Ni	10	19.85	19.96	19.9010	.03872	9.93	.006	-.988	7.65
Cu	10	9.80	9.98	9.8780	.06015	29.95	.311	-.749	17.03
Zn	10	29.50	29.95	29.8670	.13825	6.00	-2.483	6.632	10.95
Rb	10	1.95	7.00	3.4850	2.02636	0.04	.962	-.985	-3.69
Ag	10	.03	.04	.0370	.00483	0.04	-1.035	-1.224	0.25
	10	.03	.04	.0370	.00483	18.00	-1.035	-1.224	16.45

Table 4: Descriptive Statistics for the rare earth elements.

	N	Minimum	Maximum	Mean	Std. Deviation	Variance		
	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic	Skewness	UBT
La	10	.80	6.90	2.5300	1.86193	3.467	1.799	4.95
Ce	10	1.40	11.60	4.3500	3.24320	10.518	1.669	8.12
Pr	10	.15	1.27	.4820	.37309	.139	1.583	1.81
Nd	10	.50	4.60	1.8400	1.42688	2.036	1.479	4.47
Sm	10	.10	1.10	.4100	.34785	.121	1.559	1.86
Eu	10	.04	.35	.0910	.09974	.010	2.387	0.46
Gd	10	.10	1.20	.3700	.37133	.138	1.793	1.47
Tb	10	.01	.20	.0510	.06315	.004	1.678	3.51
Dy	10	.10	1.30	.3900	.35730	.128	2.239	0.78
Er	10	.08	.70	.2160	.19608	.038	2.026	0.93
Yb	10	.01	.70	.1690	.20371	.041	2.359	1.13
Lu	10	.03	.10	.0370	.02214	.000	3.162	2.02
Y	10	1.52	7.00	2.6890	1.81369	3.289	2.034	3.1
Pb	10	.45	24.00	8.6860	9.64595	0.63	.596	-1.665
Th	10	.20	.70	.4200	.20976	1.30	.123	-1.769
U	10	.90	1.50	1.1400	.22706	0.32	.091	-1.655

Table 5 Correlation Matrix for trace elements.

	V	Ba	Sr	Zr	Cr	Co	Ni	Cu	Zn	Rb	Ag	Cs
V	1.000											
Ba	-.020	1.000										
Sr	.185	.629	1.000									
Zr	.023	.171	-.533	1.000								
Cr	.274	.437	.441	.028	1.000							
Co	-.292	-.100	-.540	.311	-.376	1.000						
Ni	-.121	-.359	.006	-.598	-.102	.060	1.000					
Cu	-.394	.259	.091	.002	.416	-.456	.058	1.000				
Zn	.244	.325	.496	-.055	.497	-.821	-.315	.411	1.000			
Rb	.446	.276	.523	-.244	.386	-.246	.276	-.137	.362	1.000		
Ag	.151	.015	.273	-.270	.321	.341	.196	-.520	-.198	.517	1.000	
Cs	.164	-.072	-.494	.405	.277	.341	-.101	.207	-.165	.057	.048	1.000

Table 6 : Correlation Matrix for Rare earth elements

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er	Yb	Lu	Y	Pb	Th	U
La	1.000															
Ce	.992	1.000														
Pr	.981	.997	1.000													
Nd	.972	.977	.983	1.000												
Sm	.924	.953	.973	.977	1.000											
Eu	.968	.961	.944	.903	.861	1.000										
Gd	.874	.906	.934	.955	.983	.803	1.000									
Tb	.031	.051	.068	.124	.131	-.114	.125	1.000								
Dy	.764	.804	.843	.890	.931	.652	.969	.261	1.000							
Er	.771	.806	.841	.891	.921	.675	.969	.174	.984	1.000						
Yb	.683	.734	.782	.827	.897	.586	.943	.262	.972	.967	1.000					
Lu	.825	.785	.742	.680	.596	.912	.501	-.228	.305	.330	.226	1.000				
Y	.810	.849	.884	.903	.947	.747	.973	.093	.960	.943	.935	.448	1.000			
Pb	.732	.762	.753	.697	.669	.690	.625	.368	.579	.524	.463	.558	.594	1.000		
Th	.479	.557	.577	.528	.576	.408	.565	.409	.596	.575	.547	.134	.501	.776	1.000	
U	-.166	-.166	-.135	-.040	-.006	-.262	.016	.307	.088	.124	.256	-.371	-.023	-.426	-.159	1.000

Table 7. Pearson correlated trace and REE.

Trace Elements	Rare Earth Elements(REE)
Sr correlates with Ba Cr ------ Ba,Sr Zn ------ Sr,Cr,Cu, -veCo Rb ----- V,Sr Ag ----- Rb Cs ----- Zr	Ce correlates with La Pr -- La,Ce Nd --La,Ce,Pr Sm -- La,Ce,Pr,Nd Eu -- La,Ce,Pr,Nd,Sm Gd -- La,Ce,Pr,Nd,Sm,Eu Dy -- La,Ce,Pr,Nd,Sm,Eu,Gd Er - La,Ce,Pr,Nd,Sm,Eu,Gd,Dy Yb - La,Ce,Pr,Nd,Sm,Eu,Gd,Dy,Er Lu - La,Ce,Pr,Nd,Sm,Eu,Gd Y - La,Ce,Pr,Nd,Sm,Eu,Gd,Dy,Er Pb -La,Ce,Pr,Nd,Sm,Eu,Gd,Dy,Er,Yb,Lu,Y, Th –La,Ce,Pr,Nd,Sm,Eu,Gd,Dy,Er,Yb,Y,Pb

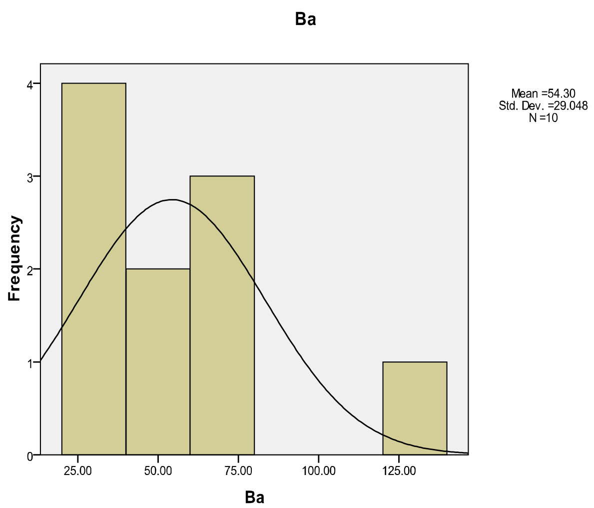
Table 8.Principal factors and Loadings for trace elements.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Loadings	Ba 483 Sr 850 Cr 653 Zn 825 Rb 587 Co -881	Ba 600 Zr 466 Cr 437 Cu 586 Ag 507	V 741 Rb 466 Zr 447 Ag 650	Ba 580 Sr 438 Co 432	Ni j783 Zr 495
Eigenvalue	3.626	2.529	1.709	1.429	1.147
Percent of data variance	30.213	21.079	14.241	11.911	9.558
Cumulative%	30.213	51.292	65.534	77.448	87.002

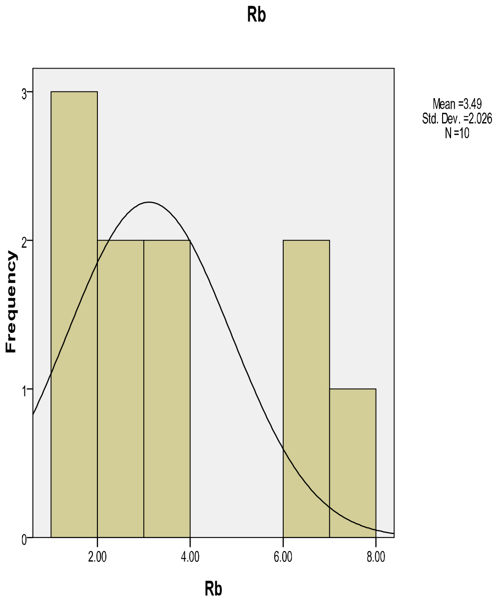
Table 9 : R mode varimax factor matrix for rare earth **element**

Principal factors and loadings of REE metals in Igarra marble Component			
	Factor 1	Factor 2	Factor 3
	La 0.949		Tb 0.593
			Pb 0.607
			Th 0.616
	Ce 0.969		
Loadings	Pr 0.983		
	Nd 0.990		
	Sm 0.993		
	Eu 0.895		
	Gd 0.981		
		Tb 0.655	
	Dy 0.919		
	Er 0.920		
	Yb 0.873	Yb 0.438	
	Lu 0.647		
	Y 0.944		
Eigenvalues	11.181	2.197	1.399
Total Variance %	69.883	13.731	8.746
Cumulative%	69.883	83.615	92.361

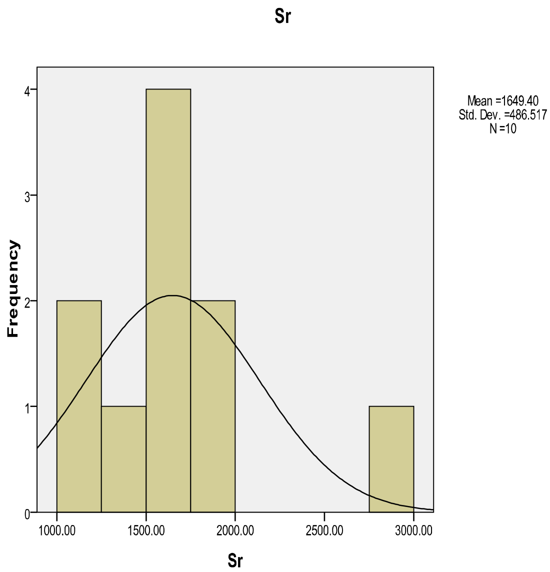
(a)



(b)



(c)



Figs 1 a, b and c. Cumulative curves of Ba, Sr and Rb.

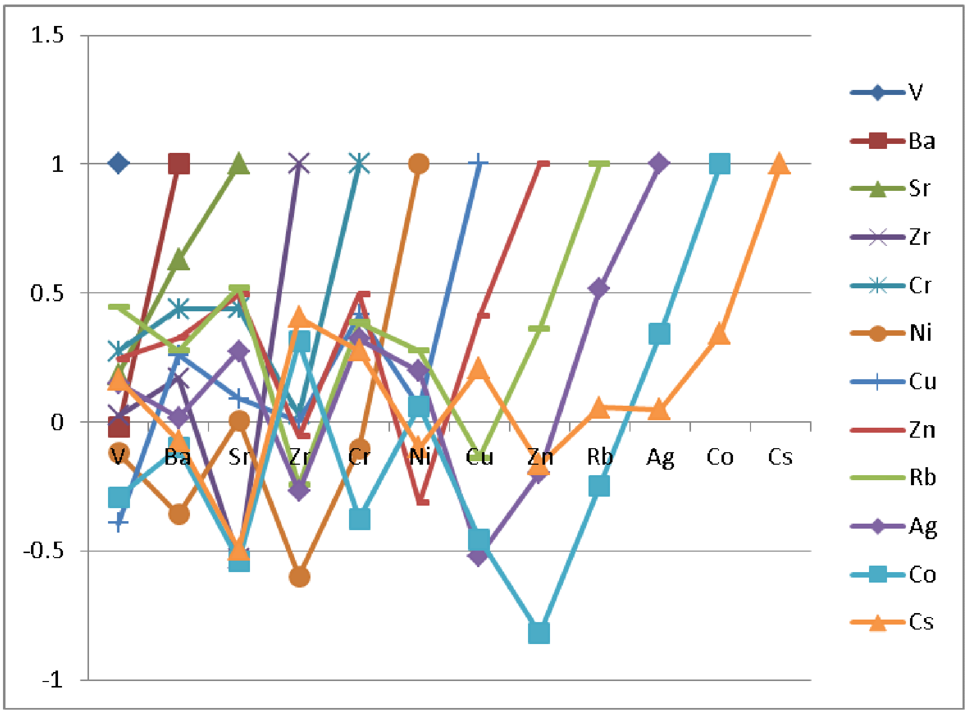


Fig.2. Coefficient of correlation pattern for trace elements

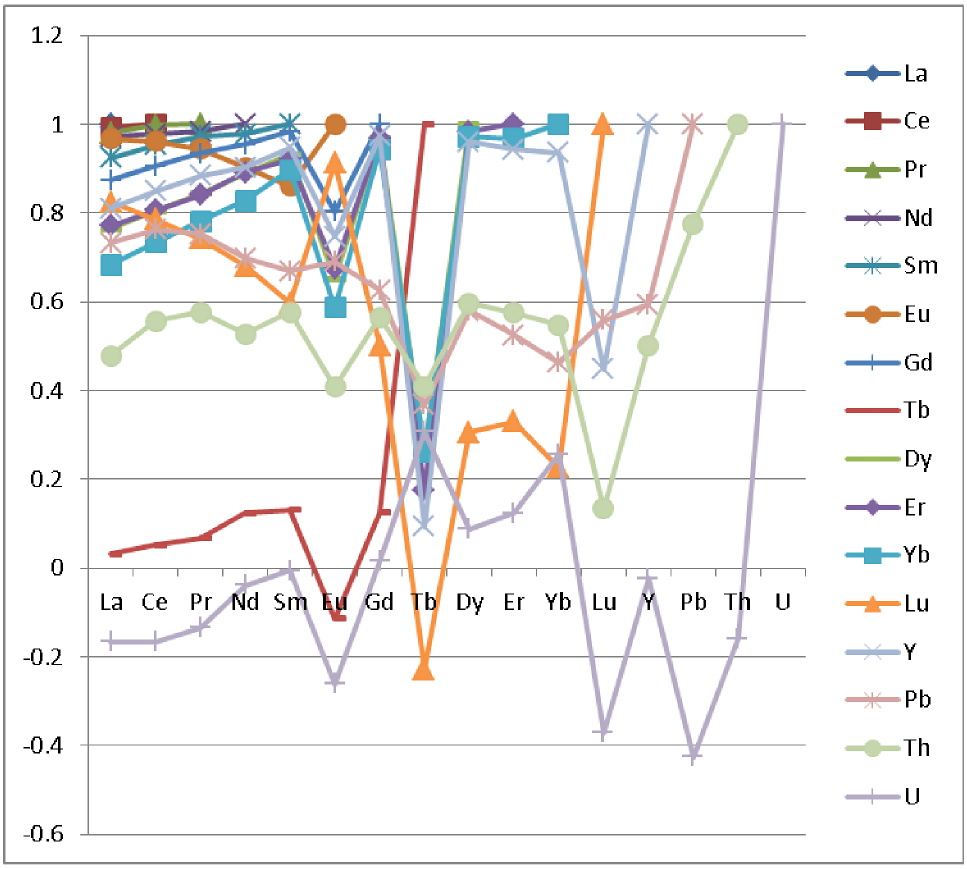


Fig 3. Correlation coefficient pattern for REE.(Tb has no plotted pattern)

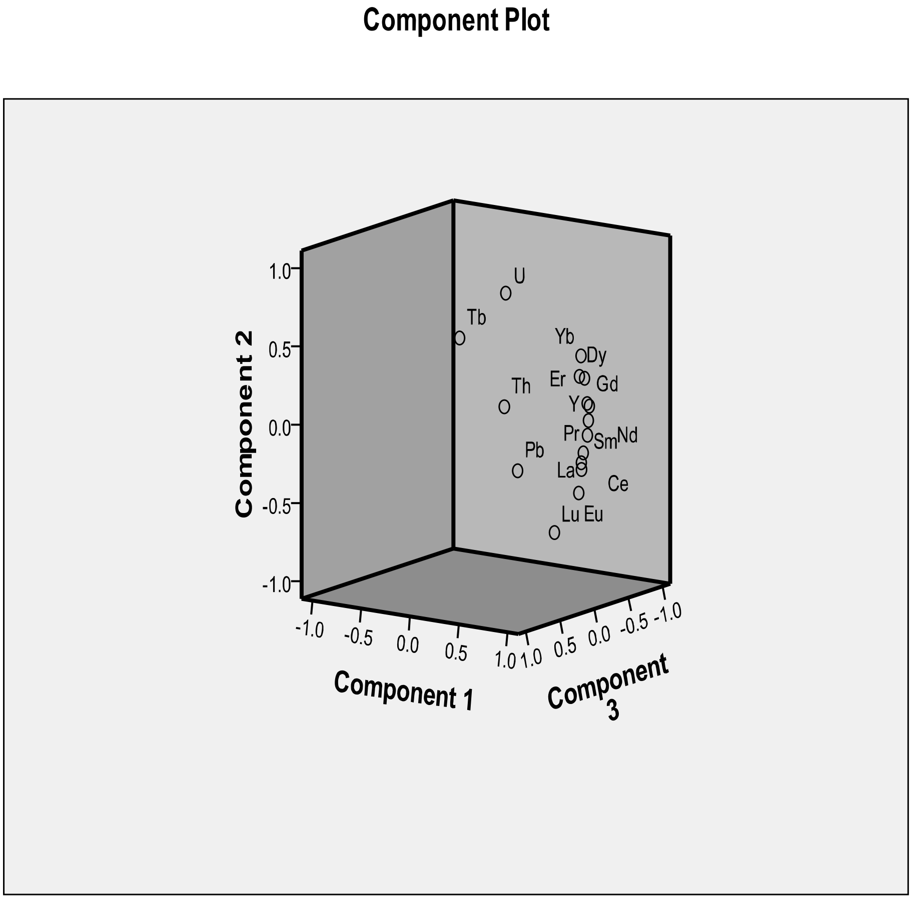


Fig 4. Three Principal component Plot of REE (PCP)