

APPLICATION OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR THE ELEMENTAL ANALYSIS OF VARIOUS ROCKS FROM AREAS AROUND DEBRE BIRHAN CITY, ETHIOPIA

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ABSTRACT

Instrumental neutron activation analysis (INAA) using high resolution γ -ray spectrometry was used to determine the elemental concentrations in rocks collected from areas around Debre Birhan City, Ethiopia. Corrections are made for neutron self shielding and for gamma photon mass absorption of the sample. For establishing the provenance (same or different origin) of the rock samples, Mn to Er concentration ratio as well as statistical cluster analysis was used using SPSS.20 statistical program. For the cluster analysis, concentration values of selected nine elements namely Mn, Na, Cd, Dy, Er, Ge, In, Se, and Sm were used. From these analyses, it was observed that the rock samples studied belong to three different groups.

Key words: INAA, Debre Birhan city, Elemental Analysis.

1. INTRODUCTION

The earth is composed of various kinds of elements. In the outer layer of the earth's crust about 98% of the total crust is composed of mainly eight elements by weight: Oxygen(47%), Silicon(28%), Aluminum (8%), Iron(5%), Calcium(4%), Potassium(3%), Magnesium(2%) and others form 1.41% only [1]. The elements in the earth's crust are rarely found exclusively, but are usually combined with other elements to make various substances known as minerals.

Debre Birhan is a city located to the north of Addis Ababa, the capital city of Ethiopia. The area surrounding the city has exceptionally various types of rocks. There are three commonly observed rocks in the area having black, white and gray colors.

The people in Debre Birhan city use these rocks for building their houses and road construction. The knowledge of the elemental content and the natural radioactivity of building materials is important for constructing durable houses and for the determination of population exposure to radiations. The presence of the radioisotopes in materials causes external exposure to the people who are living in the building. ^{226}Ra and ^{232}Th can increase the concentration of ^{222}Rn and ^{220}Rn and of its daughters in the building. The ^{40}K radionuclide causes external exposure while the inhalation of ^{222}Rn , ^{220}Rn and their short lived progeny leads to internal exposure of the respiratory tract to alpha particles [2]. Due to the health risks associated with the exposure to indoor radiation, many governmental and international bodies such as the International Commission on Radiological Protection (ICRP), the World Health Organization (WHO) etc. have adopted strong measures aimed at minimizing such exposures [3].

Because of the polishability of their surface and availability in a variety of attractive colors, many rocks are widely used as a building/construction material. They are mostly used as a lining on walls and floors in dwellings.

The question to be answered by this research is, what kind of elements do the rock minerals around Debre Birhan city made of? Do these rocks have similar or different origin?

The research tries to answer these questions by elemental analysis of selected representative samples by using Instrumental Neutron Activation technique.

Therefore the purpose of this research is to investigate the major and trace elements found in the rock samples. In addition the provenance of the rocks found in the area will be investigated.

Instrumental Neutron Activation Analysis (INAA) is a quantitative and qualitative method for the precise determination of a number of major, minor and trace elements in different types of samples. INAA, based on the nuclear reaction between neutrons and target nuclei, is a useful method for the simultaneous determination of more than 30 elements of geological, environmental, biological samples in ppb-ppm range without or with chemical separation [4].

In INAA, samples are activated by neutrons. During irradiation the naturally occurring stable isotopes of most elements are transformed into radioactive isotopes by neutron capture. Then the activated nucleus decays according to a characteristic half-life. Some nuclides emit β particles only, but most nuclides emit gamma- quanta, too, with specific energies.

The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma-ray lines in the spectra. As the irradiated samples contain radionuclide of different half-life different isotopes can be determined at various time intervals. INAA can be done in two ways, the absolute method and the standard method. In the standard method the intensity of the characteristic gamma-ray lines from the elements in the sample are compared with the intensity of the gamma-ray lines from the comparator or standard [5]. The thermal neutron flux (Φ_{th}) is given by an equation (1).

$$\phi_{th} = \frac{\left(\frac{dN}{dt}\right)}{\varepsilon_G I_\gamma K \sigma m N_A f (1 - e^{-\lambda T}) (1 - e^{-\lambda t_m})} A e^{\lambda t_d} \quad (1)$$

Were t_m -real time measurement, T -irradiation time, t_d - transporting time ε_G -geometry dependent efficiency of the detector, σ -thermal neutron capture cross-section,

λ - decay constant of product nuclei, A -the atomic weight of the element, m - mass of the bombarding element, $\frac{dN}{dt}$ -the activity of the emitted gamma, N_A - Avogadro number, f -the isotopic abundance of the target nuclei I_γ -the intensity of the gamma -ray line and K is the correction for the self absorption of gamma rays in the sample

The same expression eq. (1) is used for both elements in the comparator and unknown elements. The use of comparator method is usually selected to eliminate the geometry factors during irradiation and counting. In this work, the comparator method is selected. It compares the neutron induced activities in an unknown sample with activities induced in the comparator of known composition. The relationship is obtained by using equation (1) for both the sample and the standard [6]. Analysis of rock specimens by neutron activation analysis assists researchers to investigate the processes involved in the formation of different rocks through the provenance study of the samples [7].

2. EXPERIMENTAL

2.1 Materials and methods

The irradiation facility in our laboratory consists of 2 Ci cylindrical A m - B e source of 30 mm diameter and 40 mm height, surrounded by a cylindrical paraffin moderator of 750- mm diameter and 600 -m m height. Irradiation tubes of 30- mm diameter and 300- mm depth are located symmetrically on a circle of 80- mm radius around the axis of the source. The HPGe gamma spectrometer Canberra System is used for acquiring the gamma ray spectra, which consists of HPGe detector GX1520 with 0.5 mm Al window. The resolution and relative efficiency of the detector for 1332 keV (Co-60) are 2 keV and 50 %, respectively.

The ^{152}Eu gamma source with known activity was used to calibrate the spectrometer and photo peak detection efficiency of the detector. The absolute detector efficiencies (ε) were calculated by using the expression:

$$\varepsilon = \frac{n}{t \cdot P_\gamma(E) \cdot N_0 \cdot e^{-\lambda t_d}} \quad (2)$$

where n is the net area under the full-energy peak of gamma-ray energy E , t the counting time, $P_\gamma(E)$ gamma-ray emission probability at energy E , N_0 the activity of the source (Becquerel), λ the decay constant, $T_{1/2}$ the half-life of radio nuclide and t_d the decay time.

The detector and preamplifier are placed inside a low-background lead shield and cooled by liquid nitrogen from vertical dipstick cryostat (7500SL). The analysis was done using Canberra Modular MCA system and GENIE-2000 software.

The thermal neutron cross section and isotopic abundance values of the sought elements are taken from reference [8] and the gamma emission probability from reference [9].

2.2 Sample collection

Debre Birhan city is located 130km to the north of Addis Ababa, the capital city of Ethiopia. The city is located 2840m above sea level at $9^{\circ}41'39''$ 32'E. It is rocky area having different kinds of attractive rocks which can be observed when one walks around the city. The samples are collected from the five sites 3-5 km away from the center of the city. About 500g of each sample were collected from the sample sites shown in figure 1. The rock

samples were washed off to remove the sticking soil with water, wiped with soft cloth and sealed in a clean polyethene bag.



Figure 1: Hybrid Satellite map of Debre Berhan city which shows the study area (Adapted from Google earth, accessed on 2, April, 2011)

2.2. Sample preparation and irradiation.

The samples were dried by 110 °C temperature oven for 10 hours after grinded into fine size gravels to remove any moisture content. The fine size gravels were then powdered using agate pestle and mortar. Sample masses used were in the range of 3–7g. Disk shaped Polyethene sample holders having larger cross section were made. After the samples were weighted by a Sartorius standard balance they were sealed by a thin tape.

The standard used in the experiment is KI sample. The standard is also sealed in the same geometry sample holder to be irradiated at the same time with the samples. Two KI standards having equal mass were prepared. The sealed sample is again sealed in between the two standards. The Sample, together with the standards, was irradiated for 2 weeks in Am-Be neutron source for longer half-life isotopes and four days for medium half-life isotopes in the four thermal neutron irradiation position.

2.4 Gamma ray acquisition and calculation of concentration.

After appropriate cooling time, irradiated samples were mounted on very thin polyethene sheet for accusation of the gamma rays. The detector and preamplifier are placed inside a low-background lead shield. The signal processor has higher resolution spectroscopy amplifier with a pulse pile-up rejecter and a live time corrector, which allows the spectrum analysis. The information has been established from calibration measurements performed for disk shape sample holders and standards for calibration. The spectrum analysis is performed in the range up to about 2MeV. The full description of the set-up is described elsewhere in reference [10].

The irradiated samples, and comparator standard were counted in identical geometry with respect to the detector. Measurement times were 200–1800 s for short as well as medium-lived activation products and 1h–3 h for medium and long lived products. The measurement of the radioactivity of first group isotopes was made within 4 min cooling time after the end of irradiation, whereas for second and third groups of elements, measurements began after 12 hours of cooling.

3. RESULTS AND DISCUSSION

3.1. Sources of uncertainties

The uncertainty measurement is a critical issue in any experiment. The sources of uncertainty considered are the contribution from the sample and standard mass measurements, and the contribution from counting statistics.

Uncertainty contribution from neutron self-shielding during irradiation is minimized by taking the mean neutron flux falling on the sample. The mean neutron flux is obtained by taking the average of the flux falling on the standard in front of the sample (maximum Flux) and the flux falling on the standard at the back of the sample (minimum Flux). Gamma-ray self shielding is negligible in most cases of relatively small sample mass. The counting statistics components to uncertainty is available from the measurement results as the square root of the measured activity after the background is subtracted, as it follows the Poisson statistics [11].

3.2 Analysis results

The results of the elemental concentration of the activation analysis for the five rock samples are given according to their sample names. These results are given in Table 1. The bar graph plot of the elemental concentration of the samples is shown from Figure 2 to Figure 6.

The largest constituents of the rock minerals in the area are found to be Mn, Na, Ga, and Ge. Gd and In are also found in samples DBTR1 and DBTR2 as major elements. Cu is found only in DBTR4 and DBTR5, Dy in DBTR1 and DBTR5, Ti in DBTR2 and DBTR4 and Gd in rocks DBTR1 & DBTR4. On the other hand the element Y is found only in sample DBTR2. The elements Mn, Er and Ge are exceptionally found in all rock samples. As Mn is found to be the major element in all rocks, Ge is also found as major element in the three rocks DBTR1, DBTR4 and DBTR5. The other elements in the rock samples may be considered as minor elements and are found in many of the rock samples.

Table 1: Concentrations in mg/kg of elements in the rock samples

Element	Rock samples and their concentration in (ppm)				
	DBTR1	DBTR2	DBTR3	DBTR4	DBTR5
Mn-55	3.47±3.4*	2.90±0.81*	8.35±1.42*	4.21±1.72*	3.87±4.12*
Na-23	3.6±2.42*	986.96±6.02	8.37±1.46*	136±1.24	2.67±1.42*
Cd-116	132.23±3.21	330.08±6.23	234±1.28	123.43±7.30	142.04±1.40
Dy-164	122.41±7.06	86.32±1.04	248.36±3.46	76.32±1.03	156.20±2.52
Er-170	116.12±2.94	348.08±4.62	204.52±2.61	284.04±2.41	136.32±2.24
Ge-74	2.05±1.23*	645.02±8.05	134.12±2.60	2.25±2.10*	2.5±1.12*
In-115	164±2.14	426.82±3.86	114.82±1.12	2.77±2.40*	48.24±0.84
Se-82	134.12±4.31	236.03±3.42	342.08±4.56	34.72±0.62	174.36±2.36
Sm-154	112.68±1.14	332.26±2.84	246.02±1.68	64.68±1.14	168.42±3.80
Y-89	24.36±0.46	13.02±0.12	18.58±0.34	ND	ND
Ti-50	16.42±0.68	240.30±6.32	ND	286.42±2.43	ND
Ga-71	1.95±1.13*	ND	42.36±0.62	ND	1.55±3.13*
Gd-160	1.55±2.51*	ND	654.12±3.86	209.14±2.24	ND
Cu-63	ND	ND	ND	253.46±5.48	135.32±3.65
Te-130	ND	136.14±1.42	ND	ND	94.80±1.82
Kr-84	ND	132.65±2.68	142.68±6.42	ND	148.84±2.42
Xe-134	125.84±2.78	368.02±4.12	ND	262.84±6.34	ND

Key: ND-not detected, Concentration with symbol (*) is measured in mg/g

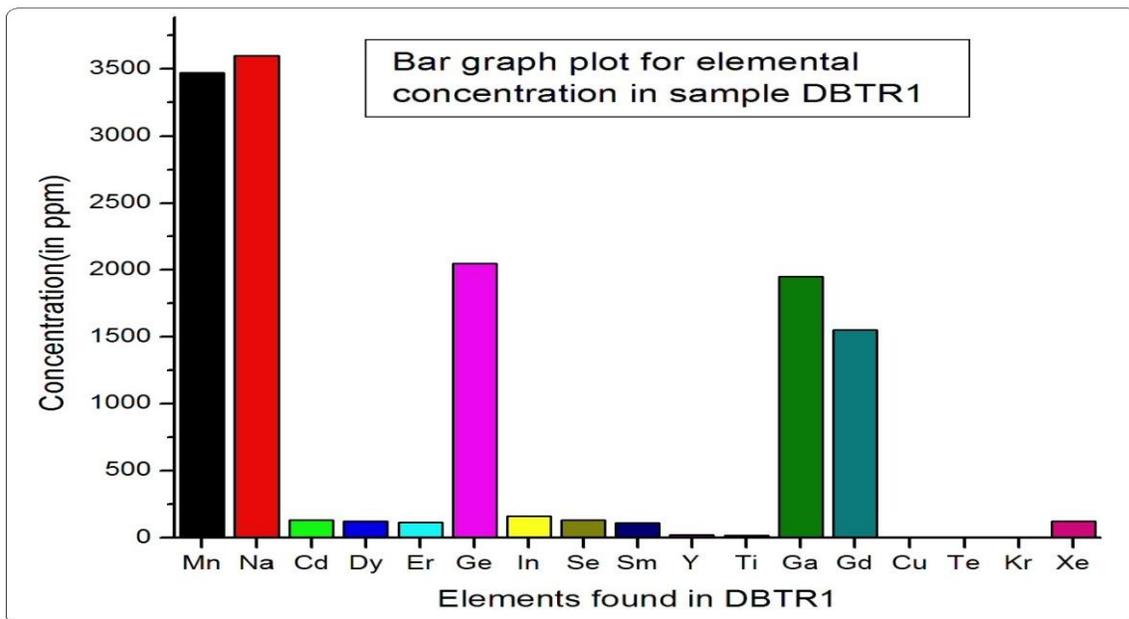


Figure 2. Elements and their concentration found in sample DBTR1

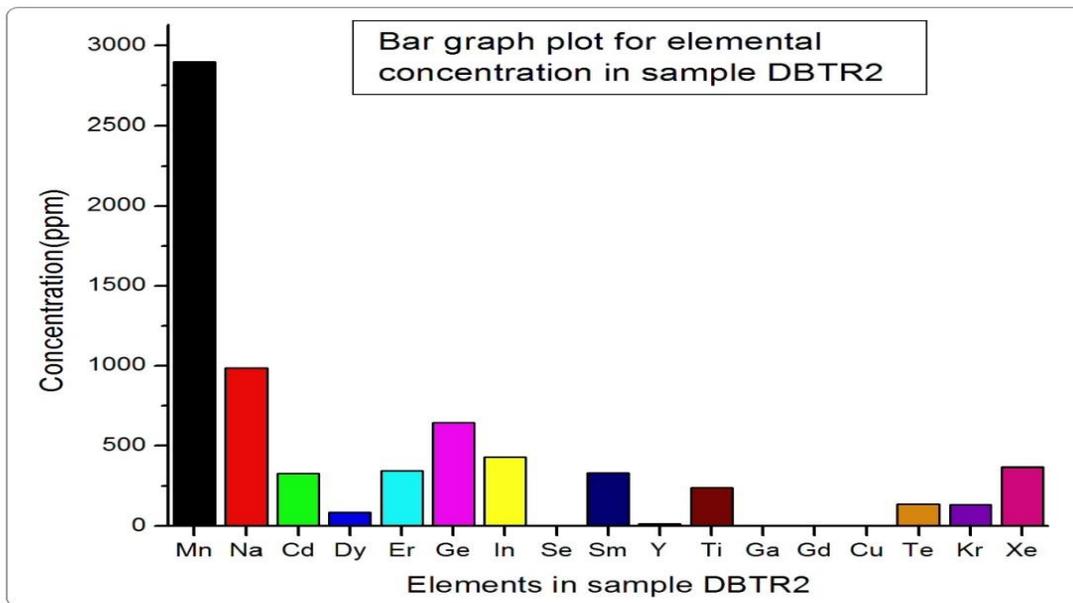


Figure 3. Elements and their concentration found in sample DBTR2

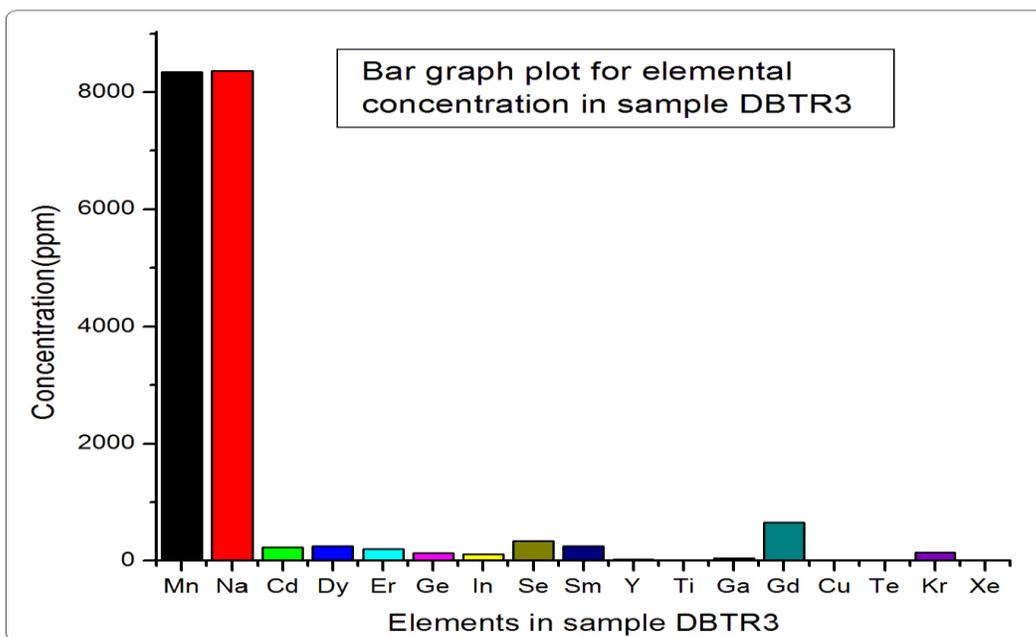


Figure 4. Elements and their concentration found in sample DBTR3

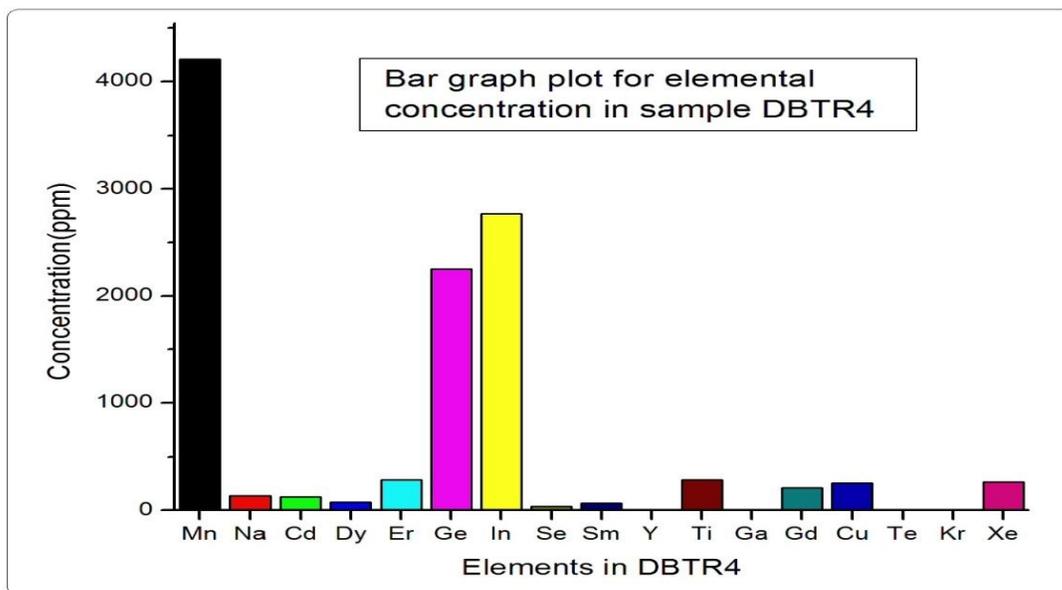


Figure 5. Elements and their concentration found in sample DBTR4

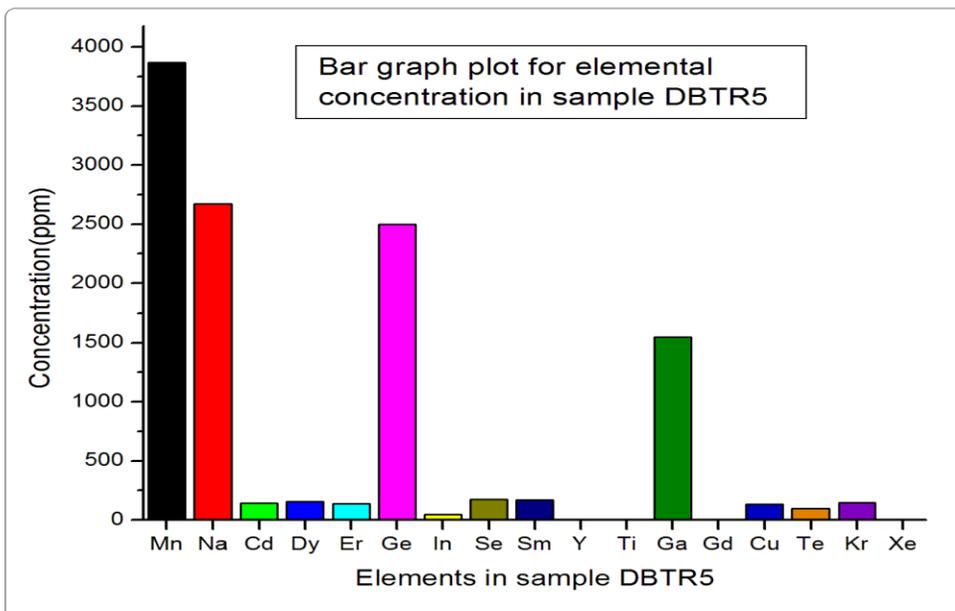


Figure 6.Elements and their concentration found in sample DBTR5

Table 2 : The natural abundance, capture cross section of the parent nuclei and the half life & the gamma intensity of the compound nucleus of the identified elements

Element	Target Elem (A)		The A+1 isotope		
	Natural abu.	σ (mb)	E(kev)	Half-life	PY(%)
Er-170	14.9	8.85	308.31	7.51 h	64.4
Gd-160	21.81	1.5	360.9	3.7 m	60.1
Cd-116	7.49	0.075	1303.3	2.49 h	18.4
In-115	95.7	73	1293.5	54 m	84.9
Mn-55	100	13.3	846	2.57 h	98.8
Na-23	100	0.53	1368.8	14.99 h	100
Dy-164	28.2	1000	94.7	2.33 h	3.58
Ge-74	35.94	0.28	246.6	83 m	11
Te-130	33.8	0.3	149.7	15.2 m	69
Ti-50	5.4	0.18	320	5.8m	93
Se-82	8.73	0.043	356.68	22.3 m	70
Y-89	100	1.28	1760.1	64 h	99.99
Ga-71	39.89	4.7	834	14.1 h	96
Xe-134	10.44	0.265	249.76	9.1 h	90
Cu-63	69.17	4.5	578.7	12.7 h	39
Kr-84	57	0.09	151	4.48 h	75
Sm-154	22.7	7.2	104	22.3 m	74.6

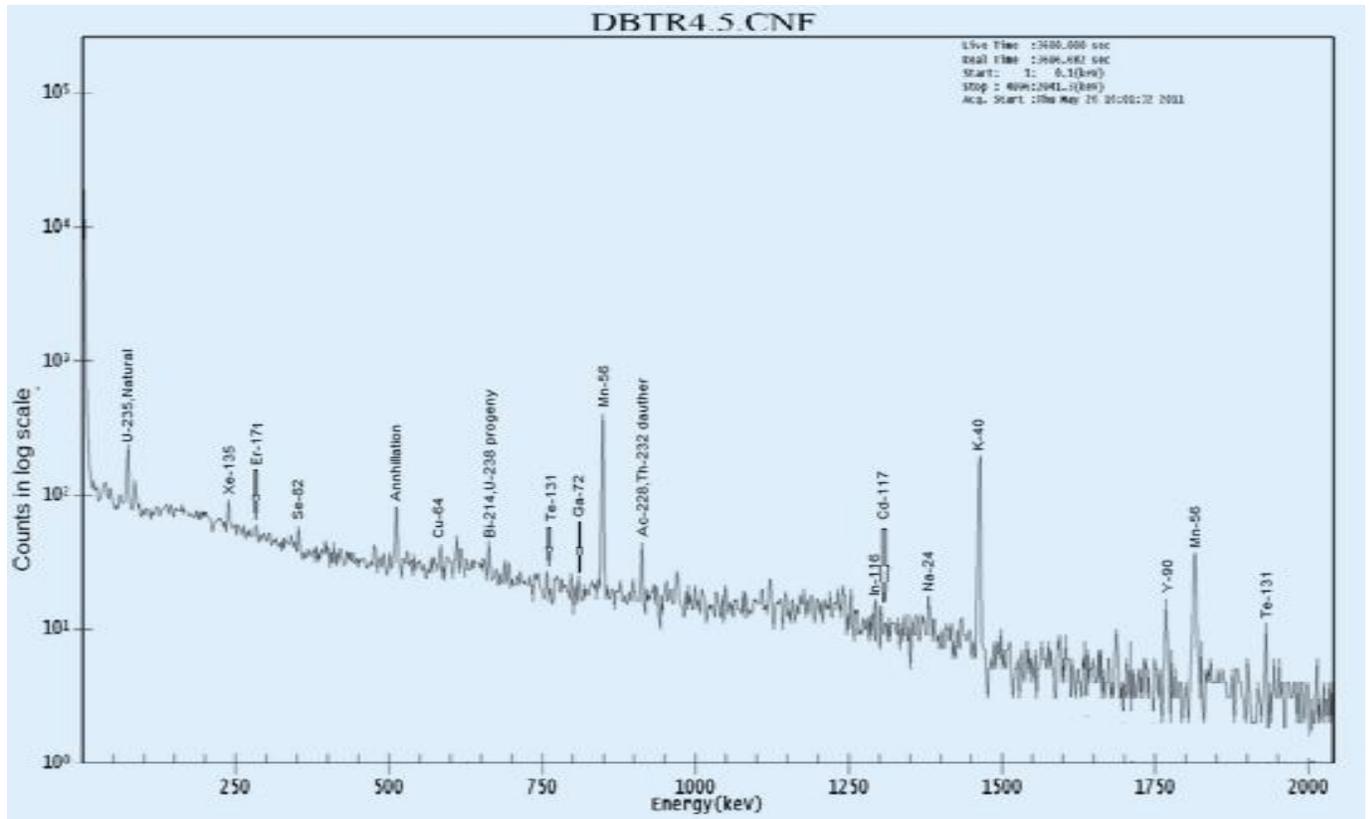


Figure 7: Spectrum of sample DBTR2 collected for 1h after a decay time of 2h.

For information on provenance study, the elemental concentration ratios of the two elements Mn and Er common to all rock types were evaluated. The ratios of Mn and Er values of the five rock samples are shown in Figure 8. From the bar graph concentration ratios, inter-site distance grouping of the rock samples along the principal axis was done and they fall into three groups: (a) DBTR1 and DBTR3, (b) DBTR2 and DBTR4 and (c) DBTR5

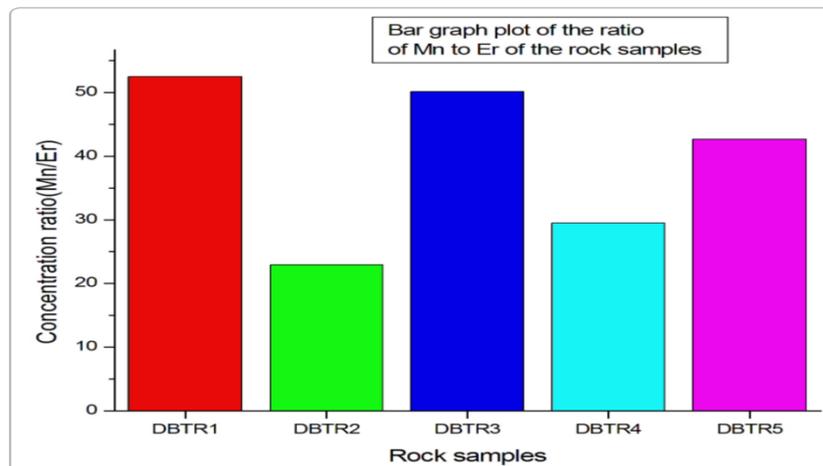


Figure 8. Bar graph concentration ratio of Mn to Er for the five rock samples

To validate the visual grouping, the results were subjected to cluster analysis using SPSS.20 statistical program. We have attempted to group these samples by considering some principal elements which are found in all rocks, namely Mn, Cd, Dy, Er, Ge, In, Se, and Sm. The other elements which are outliers to some samples and are not found in all rock samples are not considered in the cluster analysis.

The cluster analysis dendrogram of the five rock samples are shown in Figure 9.

Table 4. The ANOVA for clustered elements obtained by K-means clustering techniques

	Cluster		Error		F	Sig.
	Mean Square	df	Mean Square	df		
Manganese	8984175.000	2	469025.000	2	19.155	.050
Sodium	20327331.600	2	396850.000	2	51.222	.019
Cadmium	5084.462	2	10736.113	2	.474	.679
Dysprosium	9299.600	2	314.000	2	29.617	.033
Erbium	18165.600	2	1124.000	2	16.162	.058
Germanium	1535735.150	2	694631.250	2	2.211	.311
Indium	1330889.600	2	1376948.000	2	.967	.509
Selenium	15783.000	2	10601.000	2	1.489	.402
Samarium	4053.600	2	18740.000	2	.216	.822
Yttrium	45.750	2	186.250	2	.246	.803
Titanium	39856.600	2	593.000	2	67.212	.015
Gallium	1808805.600	2	40000.000	2	45.220	.022
Gadolinium	243146.350	2	611545.250	2	.398	.716
Copper	5504.100	2	20558.500	2	.268	.789
Tellurium	1543.000	2	6833.000	2	.226	.816
Krypton	2105.600	2	9832.000	2	.214	.824
Xenon	46128.750	2	6715.250	2	6.869	.127

The F tests should be used only for descriptive purposes because the clusters have been chosen to maximize the differences among cases in different clusters. The observed significance levels are not corrected for this and thus cannot be interpreted as tests of the hypothesis that the cluster means are equal.

The correlation among the nine principal elements which are found in all the rock samples is shown in Table 5. Correlation of Mn with Dy ($r=0.879, p<0.05$), Na with Dy ($r=0.961, p<0.01$), Cd with Sm ($r=0.958, p<0.05$) is significant. In addition the correlation between Mn with Na($r=0.867, p<0.05$), Se($r=0.635, p<0.05$), Na with Se($r=0.755, p<0.05$), Cd with Er($r=0.660, p<0.05$), Se($r=0.688, p<0.05$), Dy with Se($r=0.767, p<0.05$) and Se with Sm($r=0.810$) is also found to be positive and significant. The positive and significant association suggests that these elements can have the same provenance.

Table 5 : Correlation table for the nine principal elements concentration

Correlations ^c		Manganese	Sodium	Cadmium	Dysprosium	Erbium	Germanium	Indium	Selenium	Samarium
Manganese	Pearson Correlation	1	.867	.069	.879*	-.144	-.578	-.145	.635	.129
	Sig. (2-tailed)		.057	.912	.050	.818	.307	.816	.249	.837
Sodium	Pearson Correlation	.867	1	.109	.961**	-.441	-.572	-.578	.755	.246
	Sig. (2-tailed)	.057		.862	.009	.457	.314	.308	.140	.689
Cadmium	Pearson Correlation	.069	.109	1	.071	.660	-.825	-.335	.688	.958*
	Sig. (2-tailed)	.912	.862		.910	.225	.086	.582	.199	.010
Dysprosium	Pearson Correlation	.879*	.961**	.071	1	-.448	-.489	-.565	.767	.249
	Sig. (2-tailed)	.050	.009	.910		.450	.403	.321	.131	.686
Erbium	Pearson Correlation	-.144	-.441	.660	-.448	1	-.437	.478	.054	.457
	Sig. (2-tailed)	.818	.457	.225	.450		.462	.416	.931	.439
Germanium	Pearson correlation	-.578	-.572	-.825	-.489	-.437	1	.332	-.849	-.791
	Sig. (2-tailed)	.307	.314	.086	.403	.462		.585	.069	.111
Indium	Pearson Correlation	-.145	-.578	-.335	-.565	.478	.332	1	-.685	-.553
	Sig. (2-tailed)	.816	.308	.582	.321	.416	.585		.202	.333
Selenium	Pearson Correlation	.635	.755	.688	.767	.054	-.849	-.685	1	.810
	Sig. (2-tailed)	.249	.140	.199	.131	.931	.069	.202		.097
Samarium	Pearson correlation	.129	.246	.958*	.249	.457	-.791	-.553	.810	1
	Sig. (2-tailed)	.837	.689	.010	.686	.439	.111	.333	.097	

* Correlation is significant at the 0.05 level (2-tailed).
 ** Correlation is significant at the 0.01 level (2-tailed).
 c Listwise N=5

4. CONCLUSIONS

The largest constituent of the rock minerals in the area are found to be manganese, sodium gallium and germanium. Gadolinium and Indium is also found in samples DBTR1 and DBTR2 as major elements. Cuoper is found only in DBTR4 and DBTR5, Dysprosium in DBTR1 and DBTR5, Titanium in DBTR2 and DBTR4 and Gadolinium in rocks DBTR1 & DBTR4. On the other hand the element Yttrium is found only in sample DBTR2. Concerning the provenance of the rocks, as confirmed by this work, the rocks in the studied area fall into three groups. Although the number of samples considered in the study is limited it can show the of the provenance study of the rocks around the studied area.

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