

Original Research Article

Determination of Naturally Occurring Radionuclides and Heavy metals in Pegmatite Rock using Energy Dispersive X-ray Fluorescence (EDXRF)

ABSTRACT

Aims: To determine the concentration of naturally occurring radionuclides and heavy metals present in the samples.

Study design: The samples were analyzed using non-destructive Energy Dispersive X-ray fluorescence (EDXRF) spectrometer.

Place and Duration of Study: Centre for Energy and Research Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria between September 2016 and June 2017.

Methodology: In this study, the elemental composition of ten randomly selected rock samples was carried out. The elements detected were divided into three groups which include: radionuclides, major and minor elements which were related together using the Pearson correlation coefficient.

Results: The elemental analysis confirmed the presence of U (1.54 %), Th (0.40 %), and K (7.85 %) with concentrations higher than their permissible world values of 0.0002.8 %, 0.0007.4 %, and 1.3 %, respectively. The samples contain seven major elements (Fe, Mn, Pb, Ti, La, Ca, and Ta) and fourteen minor elements including some heavy metals (Zn, Sr, Zr, Cr, Nb, Mg, Ce, Re, Hf, V, Al, Nd, Sc, and Y). The results showed a large quantity of Fe with an average value of 37.67 %.

Conclusion: The presence of natural radionuclides and toxic metals like Cr, Pb, and Mn is of serious environmental and public concern were detected in significant quantity in some of the samples. There is an absolute possibility that the heavy metal and the radionuclides find their way into the natural ecosystem as a result of anthropogenic activities such as mining. This could pose miners, dwellers, and the general populace with a serious health risk.

Keywords: *elemental analysis, heavy metals, energy dispersive x-ray fluorescence, pegmatite.*

1. INTRODUCTION

Mining of minerals is of high interest including pegmatites rock because it is associated with rare metals, gemstones, and industrial minerals [1-3]. The characterization of pegmatites is mainly based on the differences in the size of their grains and these are mostly found in ordinary igneous rocks[4]. It demonstrates a strong diversity in the following ways; composition, mineralogy, shape, structure, distribution of rock types, depth, and temperature

of formation and age. They are associated with diverse rock types, including migmatites, metamorphic rocks ranging from granulites to greenschists, and igneous rocks, and exhibit chemical interactions with the wall rocks [4]. The earlier initiated and known classification was the one by Ferman [5]. In his research estimated temperature of solidification was used to classify pegmatites. According to Ginsburg and Rodionov [6], a depth layer was used and this has been a recent classification by Cern'y and Ercit [7].

In characteristic assemblages of minerals, the trace element content of major pegmatite-forming minerals, including feldspar, mica, and quartz, has potential for chemical classification, even though these minerals commonly show a strong chemical zonation within one pegmatite body. Other accessories and valuable minerals that can be found in pegmatites include beryl, tourmaline, spodumene, garnet, uranium, and topaz while rare minerals that can also be formed in them include columbite and tantalite. Pegmatite also serves as a host rock for many rare mineral deposits such as beryllium, bismuth, boron, cesium, lithium, molybdenum, niobium, tantalum, tin, titanium, tungsten, and other elements [8]. The research discoveries revealed that some pegmatites contain high-grade uranium resources that can perhaps, be profitably exploited [9-11].

In Nigeria, pegmatite rocks are generally mined by artisan miners who are only interested in their economic value and others from the communities around the mines use the tailings for domestic use such as landfilling and building construction without considering its elemental composition. Most times these rocks are composed of heavy metals that can endanger human lives. Heavy metals are regarded as metals or metal compounds that are toxic to the human body which could later harm human health. Due to an increase in urbanization and industrial activities, heavy metals found their way into the environment and this may affect human well-being [12-15]. According to recent research, it was revealed that nickel, zinc, and copper aid human well-being and also can be found everywhere [16]. The use of chromium element in commercial industries can be carcinogenic [17]. These elements contaminate the air, water bodies, and the food ingested by the people in such polluted environments [18-20].

Every rock is characterized by its chemical composition. To identify the contents in minerals such as rocks, a quantitative and qualitative analysis must be carried out [21,22]. The analysis of the rock samples in this study was carried out using x-ray fluorescence (XRF) techniques. This technique has been considered the most common and widely used in terms of its sensitivity, rapid detection of elements present in samples without a long process of preparation in ppm or %, and accuracy [23,24]. It can be used to analyze multi-elements. In Energy Dispersive X-ray Fluorescence spectrometry, the sample is bombarded with X-rays from the x-ray tube and generated characteristic X-rays and these are sent to the detector. The characteristics of X-rays interact with the detector and release pulses, proportional to the energy deposited. The total charge of the pulses is measured and the concentration of each element in the sample is determined. This research aims to ascertain the concentrations of radioactive elements and heavy metals present in the rock samples.

2. MATERIAL AND METHODS

2.1 Study Area

A total of ten pegmatite rock samples were randomly collected from the Wamba area of Nasarawa State, Nigeria, as shown in **Figure 1**. The study location falls within the Nigeria 400 km coverage 'pegmatite belt' between Longitudes 8° 30'E and 8° 40'E and Latitudes 9° 00'N and 9° 07' N which run between northwest to the central north of the country. According to research, it was revealed that Wamba pegmatite is the third largest pegmatite field after Jema'a and Egbe- Ijero pegmatite Matheis G. and Cean-Vachette M. [25]. The

area can be assessed through the Jos – Fadan Karshi and then enter into Wamba. This cut across the central pegmatite zone of Nigeria. Other minor roads connect (Gwon-Gwon) pegmatite at Wamba with settlements like Kuraga, Rimi, and Kejeri all within the study area. The area is majorly dominated by vegetation and thick forest and this made their main occupation to be farming.

2.2 Sampling

After the collection of the rock samples, they were transported and prepared for analysis. The samples collected were crushed and then ground in a ball milling machine. Each ground sample was packed in a drug dispensable nylon and transferred to the energy-dispersive x-ray fluorescence (EDXRF) laboratory for analysis. The samples were further pulverized manually to a very fine powder with an agate mortar and pestle. Pellets of 13 mm diameter were made from 0.4 g powder without binder with an 8- tons hydraulic press (CARVER INC. Model M, Serial no. 12000-270). The pellets were in new drug dispensable nylons to avoid contamination and kept in a polypropylene container until analysis. The EDXRF spectrometer at the Centre for Energy and Research and Development in Obafemi Awolowo University Ile-Ife was used to determine the elemental compositions in the pegmatite rock samples.

Comment [M1]: Add the detailed samples map

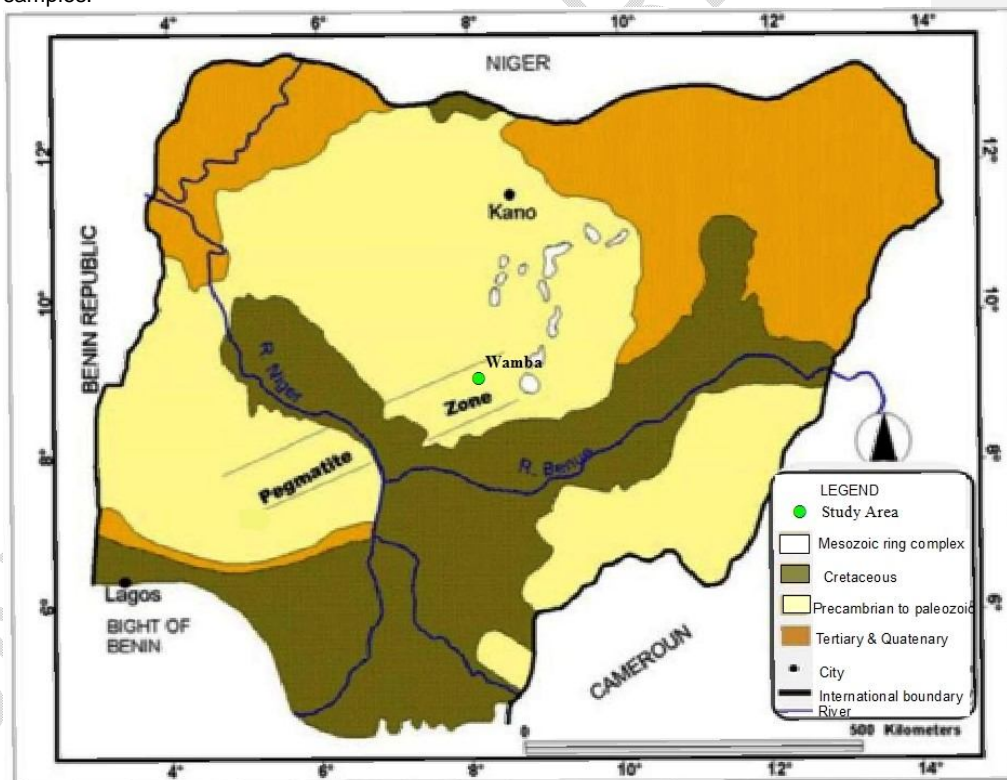


Figure 1: Map of Nigeria showing the study area [26,27].

2.3 Instrumentations

The spectrometer used in this study was an XR-100CR detector with its in-built preamplifier. The MINI-X consists of the X-ray tube which irradiates the sample before the rays were sent to the detector with voltage and current, 25 kV/50 μ A. The detector has a silicon thickness of 300 μ m and 500 μ m and a multilayer collimator. The setting used for the measurements in this study is the peak of the K-line of ^{55}Fe at 5.9 eV with a full width at half maximum (FWHM) of 186 eV for a shaping time constant of 20 μ s. The energy calibration for the spectrometer was carried out using the K-lines of five standard sources with their energies and channels. These standards are Ca, Fe, Zn, Zr, and Sr. The standards and samples were irradiated for the same duration of 1000 s. The settings of each of the units of the spectrometer remain constant. The spectra obtained were stored for qualitative and quantitative analysis.

Comment [M2]: insert photograph of spectrometer

In this work, the quantitative analysis of samples was carried out using the Fundamental Parameter (FP) method in the Quantitative Analysis Software package. The software identifies and measures the concentrations depending on the sample. Each of the peaks in the spectrum corresponding to an element can be identified using the element library on the personal computer (PC) thereby giving a qualitative analysis. Quantitative analysis was carried out by obtaining the concentrations of the elements from the area under the peaks.

2.4 Statistical Analysis

In this research, a correlation between the naturally occurring radionuclides, major and minor elements was done. This was carried out by Statistical Package for Social Sciences (SPSS) version 2.0. It helps to know the relationship between the elements present in samples under study.

3. RESULTS AND DISCUSSION

The concentrations of 24 elements were identified using the EDXRF technique from the ten rock samples from the aforementioned mining site. These elements are divided into three (3) groups which are radioactive, major, and minor elements.

Radioactive elements such as U, Th, and K are referred to as naturally occurring radioisotopes (radioelements). The concentrations of the radioactive elements are presented in **Table 1**.

The major elements whose concentrations are greater than 1% by weight were categorized in the second group. These elements are Fe, Ti, Ca, Pb, La, Ta, and Mn. The concentrations of each element are shown in **Table 2**.

The minor elements are the elements with concentrations less than 1% by weight. These were 14 elements in number and are presented in **Table 3**.

In the first group presented in **Table 1**, Uranium was observed to have the highest concentration in WB3 followed by WB6, with the lowest concentration in WB4. The concentrations ranged from 0.35 ± 0.02 to 4.27 ± 0.10 % with a mean concentration of 1.54 ± 0.10 %. Large quantities of thorium were obtained both in WB7 and WB1. It varies from 0.08 ± 0.03 to 1.36 ± 0.01 % with an average value of 0.40 ± 0.10 %. The proportion of uranium and thorium in this study needed to be taken as a serious concern for both occupational and public exposure to radiation. Due to the significance of these radioelements (thorium and uranium) most importantly uranium, the miner may not be aware

of the aftermath of overtime exposure to these two elements to their health. Uranium can be used to power nuclear reactors to generate electricity. Also, it is used for other purposes such as the production of isotopes which can be used in medical, industrial, agricultural purposes, and defense. Significant concentrations of Potassium were obtained in all the samples. It has the highest concentrations in sample 1. It ranges from 1.01 ± 0.05 to 21.13 ± 0.44 % with an average concentration of 7.85 ± 0.20 %.

In **Table 2**, Fe and other major elements obtained from the samples are presented. Fe had the highest concentration in the rock samples which varied from 16.59 ± 0.19 to 49.72 ± 0.12 % with a mean value of 37.66 ± 0.20 %. Fe has been the most abundant element on earth and the tenth position in the universe with a mass of 34.6 %. It is an essential element in plant nutrition. It has been useful in all sectors in particular construction of the building and other materials that are significant to human existence. Titanium concentration ranged from 0.88 ± 0.05 to 5.93 ± 0.10 % with an average mean of 4.15 ± 0.10 %. According to Olabanji [28], it was revealed that a large quantity of titanium in minerals may not expose people to severe health risks in the sense that its absorption by plants is poor. Lead was found to be high in WB7 with 1.87 ± 0.10 and the lowest values in WB4 and WB9 with a concentration of 0.24 ± 0.01 . The average value of Pb was obtained to be 0.89 ± 0.04 %. The lead element can be regarded as a harmful pollutant that is very hazardous to human body organs. Pb could be absorbed by the skin and also by the respiratory and digestive systems.

Table 1: Concentration of Radioelements in the Pegmatite Rock Samples [wt. (%)]

Samples	Elements		
	U	Th	K
WB1	0.99 ± 0.06	1.15 ± 0.01	21.13 ± 0.44
WB2	1.28 ± 0.07	0.54 ± 0.15	2.09 ± 0.12
WB3	4.27 ± 0.10	0.70 ± 0.01	3.06 ± 0.12
WB4	0.35 ± 0.02	0.09 ± 0.01	1.01 ± 0.05
WB5	0.82 ± 0.05	0.55 ± 0.14	12.56 ± 0.29
WB6	2.39 ± 0.07	0.18 ± 0.01	1.97 ± 0.09
WB7	0.88 ± 0.08	1.36 ± 0.01	21.28 ± 0.64
WB8	1.06 ± 0.05	0.22 ± 0.01	11.72 ± 0.22
WB9	1.27 ± 0.04	0.08 ± 0.03	1.49 ± 0.06
WB10	2.04 ± 0.06	0.14 ± 0.01	2.16 ± 0.09
Min.	0.35 ± 0.02	0.08 ± 0.03	1.01 ± 0.05

Max.	4.27±0.10	1.36±0.01	21.13±0.44
Mean value	1.54±0.10	0.40±0.10	7.85±0.20

Over time exposure to Pb can lead to cardiovascular disorders due to immune modulation, it can also disrupt the balance oxidant-antioxidant system and cause alteration in physiological functions of the body which is associated with many diseases [29-31]. It is used in the production of weapons, in battery cells, and in devices used in shielding X-rays to avoid direct contact with the human body. La was not detected in WB1 and it has a mean value of 1.20 ± 0.10 %. It can be found in modern television sets, energy-saving lamps, and fluorescent tubes. It is used as a catalyst in the petrochemical industries. It has its side effects, especially in the petroleum-producing industry when it is not well disposed of, it could cause severe damage to plants and animals which may later cause nervous system disorders in human beings. Ta concentration varied from 0.43 ± 0.02 to 4.04 ± 0.16 with an average value of 1.55 ± 0.10 %. Tantalum oxide is found to be insoluble which made it impossible to be detected in the waters and it is also poorly absorbed by plants. This metal can be of advantage in various commercial high-temperature applications e.g. aircraft engines, electrical devices such as capacitors, and surgical implants. It can be harmful when inhaled or ingested. Also when it is absorbed by the skin, it could cause eye or skin irritation. According to research, low adverse effects of tantalum were observed in industrially exposed workers. Ca and Mn ranged between 0.57 ± 0.04 to 4.58 ± 0.28 , and 0.64 ± 0.03 to 2.12 ± 0.05 with mean values of 1.30 ± 0.10 and 1.10 ± 0.03 %, respectively. Manganese is abundant in nature and about 0.1 % of the earth's crust. According to Calabrese [32], elements like Fe, Mn, Zn, and Ca are regarded as essential and beneficial elements to the human body but if they continue to mount up in the body, they could bring about the metabolism of harmful elements such as Cd and Pb. Therefore, the mining of minerals like iron ore can lead to pollution or contamination of the environment as dust with enhanced radioactivity [33]. This can be inhaled or ingested by the miners or people living in the environment which might pose health risks. Also unknowingly to the public these tailings are bought and used in the construction of buildings which could lead to indoor radiation exposure.

Table 2: Concentration of Major Elements in the Pegmatite Rock in wt. (%)

Elements	Fe	Ti	Pb	La	Ta	Ca	Mn
Samples							
WB1	23.57±0.16	0.88±0.05	1.48±0.06	ND	3.04±0.09	1.72±0.12	2.11±0.05
WB2	42.86±0.19	5.93±0.10	1.21±0.06	1.95±0.20	1.05±0.06	0.72±0.05	0.64±0.03
WB3	33.39±0.15	11.70±0.13	0.77±0.04	0.49±0.09	1.04±0.05	1.11±0.06	1.11±0.03

WB4	47.82±0.13	4.57±0.05	0.24±0.02	3.01±0.15	0.60±0.03	0.39±0.02	0.84±0.02
WB5	35.42±0.17	1.56±0.06	0.59±0.04	0.52±0.10	1.82±0.07	1.66±0.09	1.54±0.04
WB6	43.14±0.15	5.44±0.07	0.39±0.02	2.36±0.16	1.13±0.05	0.77±0.04	0.83±0.02
WB7	16.59±0.19	2.03±0.11	1.87±0.10	1.27±0.29	4.04±0.16	4.58±0.28	0.87±0.05
WB8	38.29±0.14	1.47±0.04	1.53±0.05	0.04±0.02	1.42±0.05	0.74±0.04	0.76±0.02
WB9	49.72±0.12	3.54±0.04	0.24±0.01	0.32±0.04	0.43±0.02	0.72±0.03	1.07±0.02
WB10	45.85±0.15	4.41±0.06	0.54±0.03	1.36±0.12	0.97±0.04	0.57±0.03	0.87±0.02
Min.	16.59±0.19	0.88±0.05	0.24±0.01	ND	0.43±0.02	0.39±0.02	0.64±0.03
Max.	49.72±0.12	5.93±0.10	1.87±0.10	3.01±0.15	4.04±0.16	4.58±0.28	2.11±0.05
Mean	37.67±0.20	4.15±0.10	0.89±0.00	1.20±0.10	1.55±0.10	1.30±0.10	1.10±0.03

The concentrations of minor elements present in the rock samples were shown in **Table 3**. Nb has its highest concentration in the WB3 with 0.12 %. It was not detected in WB1. A large concentration of Y was observed in WB7 with a value of 0.21 %. Zinc has the highest concentration in WB8 which ranged between 0.10±0.01 to 1.21±0.02 % with an average value of 0.54 ± 0.01 %. Zinc has been of various importance, especially in the body. Zn can be regarded as the oldest of all metals. The hazardous impact of Zinc on humans depends on the interaction and the quantity of exposure. The major sources of zinc are industrial activities like the smelting of iron and the mining of mineral resources. Zr varies from 0.07 to 0.13 % and its highest values were obtained in WB2, WB6, and WB10. Sr has the highest concentration in WB3 and ranged between 0.03 to 0.19%. Cr has its highest concentration in WB7 (0.36 %) followed by WB1 (0.21 %) with an average value of 0.09 ± 0.01 %. Chromium element is a naturally occurring heavy metal that can be found in the earth's crust, water bodies, and industrial environments but an increase in body load may result in allergic reactions [34,35]. According to International Agency for Research on Cancer (IARC) report [36], group 1 carcinogen diseases were traced to be associated with hexavalent chromium element (Loomis et al., 2018). The easiest way to expose the general populace to chromium is the intake of food, water containing chromium, and skin contact with products that contain the element [37,38]. Magnesium was not detected in WB1, WB3, WB4, WB6, WB7, WB8, and WB 10. The element was present in WB 2, WB 5, and WB 9 with a concentration value of 0.33 ± 0.00 %. Both Hf and Re were detected in all the samples with the values ranging between 0.04 to 0.75% and 0.40 to 2.10 % respectively. Vanadium was detected in WB5 and WB7. It is relatively a toxic element and a tiny quantity in the diet can lead to a pharmacological effect on the organism [39]. Al was detected in WB2, WB5, and WB9 with a value of 0.25 %. With the significant proportion of aluminum in the samples, this revealed that in the cause weathering process of the rock, aluminum can be replaced by strontium and then calcium. However, if plant absorbs strontium instead of calcium and animal ingest these plants, this may cause poor bone formation in an animal. Nd was observed in WB1, WB7, and WB10. Sc was obtained in WB2 only with a concentration value of 0.0001 %.The

results of the Pearson correlation coefficients between the naturally occurring radionuclides, major and minor elements are presented in **Table 4**. The elemental compositions obtained from the rocks samples include the radionuclides, major and minor elements from the area under study were related together to establish the relationship between them. In **Table 4**, U showed a weak negative correlation to all elements except Ti, Nb, and Sr. Both the Th and K have a strong positive correlation with the following elements Ta, Y, Re, Hf, and a strong negative correlation with Fe. Iron and Titanium have a strong negative linear relationship with some of the elements like Pb, Ta, Ca, and others. La has negative correlations with the major and minor elements present in the sample. Pb has a strong correlation with Ta, Zr, Y, Re, and Hf. Mn, Zn, and Nb showed a weak negative correlation with all the minor elements in the study. Ta correlates strongly with Ca, Y, and Re. Ca has a significant linear relationship with Zr, Y, and Re. Mn, Zn, and Nb have weak negatives with most minor elements in the sample. Y has a strong linear correlation with Re and Sr has a weak correlation with the three following minor elements; Y, Re, and Hf. All three radionuclides obtained in this study are poorly correlated especially with major elements in the sample. This showed that the rock samples have uncommon geochemical behavior which means they are derived from different origins and do not interact with each other.

Table 4: Pearson correlation coefficient between natural radionuclides, major and minor elements present in the rock samples

Variable	U	Th	K	Fe	Ti	Pb	La	Ta	Ca	Mn	Zn	Nb	Zr	Sr	Y	Re	Hf
U	1																
Th	-.031	1															
K	-.372	.822**	1														
Fe	.031	-.958**	-.900**	1													
Ti	.845**	-1.66	-6.33	.2.53	1												
Pb	-1.87	.764	.787**	-.801	-.348	1											
La	-.210	-.155	-.369	.254	.130	-.283	1										
Ta	-.265	.909**	.937**	-.951**	-.478	.794**	-.126	1									
Ca	-.186	.842	.775	-.867	-.314	.658	-.143	.909**	1								
Mn	-.097	.467	.566	-.451	-.336	.116	-.459	.406	.172	1							
Zn	.106	-3.55	-.178	.192	.140	.126	-.436	-.287	-.188	-.564	1						
Nb	.844**	.055	-.283	-.050	.710*	-.366	-.078	-.179	-.138	.448	-.264	1					
Zr	.147	.653*	.470	-.672	-.021	.663*	-.011	.707*	.777**	-.211	-.095	.008	1				
Sr	.688*	.515	.013	-.393	.697*	.308	-.098	.168	.211	.030	-.104	.568	.419	1			
Y	-.078	.905**	.823**	-.937**	-.270	.674*	-.121	.949**	.967**	.320	-.276	-.006	.763*	.280	1		
Re	-.156	.907**	.950**	-.957**	-.403	.755*	-.402	.917**	.792**	.604	-.213	.019	.505	.273	.851**	1	
Hf	-.266	.788**	.738*	-.724*	-.375	.728*	.179	.748*	.484	.536	-.453	-.249	.380	.281	.596	.718*	1

** Correlation is significant at the 0.01 level

*Correlation is significant at the 0.05 level

4. CONCLUSION

The EDXRF spectrometry techniques used in this study showed the presence of radioelements with the mean values of U, (1.54±0.10 %) Th, (0.40±0.10 %) and K (7.85±0.20 %) major (Fe, Mn, Pb, Ti, La, Ca, and Ta), and minor (Zn, Sr, Zr, Cr, Nb, Mg, Ce, Re, Hf, V, Al, Nd, Sc, and Y) elements (including heavy metals). The concentration of naturally occurring radionuclides were higher than the world-recommended values (% by wt) [40]. The presence of heavy metals like Mn, Cr, and Pb in the soil could contaminate the farm products from this area due to the weathering of the rock being washed down to the parent soil including toxic substances. However, these toxic substances will also be taken by plants and then ingested into human bodies and this could be hazardous to humans. This study will serve as a piece of baseline information to know the level of exposure to radiation and other harmful elements via water and food ingested into the body of the miners and the people around the area.

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