# DETERMINATION OF RARE EARTH ELEMENTS IN JOS MONAZITE USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

BY

ABUBAKAR, ABDULKADIR

DEPARTMENT OF PHYSICS,

FACULTY OF SCIENCE,

AHMADU BELLO UNIVERSITY,

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**A THESIS SUBMITTED TO THE SCHOOL OF POST GRADUATE STUDIES, AHMADU BELLO UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE DEGREE IN NUCLEAR PHYSICS**

**DEPARTMENT OF PHYSICS,**

**FACULTY OF SCIENCE,**

**AHMADU BELLO UNIVERSITY,**

**ZARIA, NIGERIA**

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# DECLARATION

I declare that the work in this thesis “Determination of Rare Earth Elements in Jos Monazite Using Instrumental Neutron Activation Analysis (INAA)” has been carried out by me in the Department of Physics. The information derived from the literature has been duly acknowledged in the text and a list of reference provided. No part of this thesis report was previously presented for another degree or diploma at this or any other institution.

**ABUBAKAR ABDULKADIR** Date

# CERTIFICATION

This thesis report entitled DETERMINATION OF RARE EARTH ELEMENTS IN JOS MONAZITE USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) by ABUBAKAR ABDULKADIR meets the regulations governing the award of the degree of Master of Science in Nuclear Physics of Ahmadu Bello University, and is approved for its contribution to knowledge and literacy presentation.

______________________________ ____________________

Prof. Rabiu Nasiru Date
(Chairman, Supervisory Committee)

______________________________ ____________________

Dr. N.N. Garba Date
(Member, Supervisory Committee)

______________________________ ____________________

Prof. Rabiu Nasiru Date
(Head of Department)

______________________________ ____________________

Prof. S.Z. Abubakar Date
(Dean, School of Post Graduate Studies)

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# ABSTRACT

Monazite is a unique mineral obtained from the heavy sand found in the area of Jos, Plateau State, Nigeria. The characteristic of monazite is that it contains considerable rare earth elements (REEs). REEs are considered very useful elements in the local industries and scientific researches such as*:* misch metals in metallurgy, cracking catalyst in oil refinery, fluorescent material in monitors, phosphor materials in household lamps, semi-conductor research, optics and laser research, glass industry, ceramics, electronic industry, and nuclear engineering industry. Therefore, as an effort to increase the knowledge about their abundance, and assessing the extent of their usefulness in technical fields, instrumental neutron activation analysis (INAA) was used as tool to determine the contents of REEs in Nigerian monazite obtained from five areas of Plateau state namely; Barikin ladi 1, Barikin ladi 2, Kuru 1, Kuru 2 and Rayfield. Seven elements La, Ce, Nd, Eu, Tb, Yb and Lu were analysed using two national institute of science and technology (NIST) standard reference materials (SRM); 1633b and 1633c. Quantitative results of these seven elements are; **La** (112300±1460), **Ce** (124500±11454), **Nd** (37400±4862), **Eu** (127±3), **Tb** (409±7), **Yb** (4160±79), **Lu** (125±6) for Kuru (1) monazite, **La** (3914±63), **Ce** (12140±1117), **Nd** (BDL), **Eu** (17.4±1.9), **Tb** (88.6±1.8), **Yb** (3884±78), **Lu** (354±14) for Kuru (2) monazite, **La** (5966±76), **Ce** (22950±2111), **Nd** (7664±1027), **Eu** (33.7±2.4), **Tb** (1310±34), **Yb** (1732±52), **Lu** (1732±11) for Rayfield monazite, **La** (6142±209), **Ce** (10990±1011), **Nd** (BDL), **Eu** (140±14), **Tb** (51.4±2.5), **Yb** (1010±25), **Lu** (46.4±2.7) for Barikin Ladi (1) monazite, **La** (43340±823), **Ce** (70480±6484), **Nd** (26060±3387), **Eu** (75.8±3.1), **Tb** (303±5), **Yb** (4250±85), **Lu** (245±10) for Barikin Ladi (2) monazite were found, together with comparison in abundance of the REEs obtained from other materials, shows that REEs are abundant in Monazite than what was observed in previous work for REEs abundance in other materials.

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# ABBREVIATIONS

| Symbol | Description |
|---|---|
| BDL | Below Detection Limit |
| CERT | Centre for Energy Research and Training |
| DGNAA | Delayed Gamma Neutron Activation Analysis |
| HEU | Highly Enriched Uranium |
| HREE | Heavy Rare Earth Element |
| INAA | Instrumental Neutron Activation Analysis |
| LREE | Light Rare Earth Element |
| MNSR | Miniature Neutron Source Reactor |
| NIST | National Institute of Science and Technology |
| NIRR-1 | Nigerian Research Reactor -1 |
| NAA | Neutron Activation Analysis |
| PGNAA | Prompt Gamma Neutron Activation Analysis |
| REE | Rare Earth Element |
| REO | Rare Earth Oxide |
| PPM | Part Per Million |
| SAR | Safety Analysis Report |
| SRM | Standard Reference Material |
| WINSPAN | Multi-Purpose Gamma-Ray Spectrum Analysis software |

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background of the Study

In accordance with the introduction of new technologies and improvements in the manufacturing methodology, For the uses in the domestic manufacturing and industrial research, the practical applications of rare earth elements (REEs) and their compounds were found in the following categories: misch metals in metallurgy, cracking catalyst in oil refinery, fluorescent material in monitors, phosphor materials in household lamps, semi-conductor research, optics and laser research, glass industry, ceramics, electronic industry, and nuclear engineering industry etc (Griffiths 1984) . Rare earth elements are also essential for the defence industry and are found in cruise missiles, precision guided munitions, radar systems and reactive armour. Among many REEs, seven kinds of REEs, i.e., La, Ce, Nd, Sm, Gd, Eu, Pr and their mixtures showed greater demands and especially their contents are higher in the monazite or other ores such as bastnastite, xenotime (Chao 1974). The rest of the REEs for which their atomic weights are much higher, their utilizations are usually rather limited. The occurrence of high atomic weight REEs in nature is also very rare.

Nigeria has quite abundant reserves of monazite remaining unexplored. These monazite are very rich in REEs and processed from the heavy-sand deposits which are plentifully distributed along the North-Central Zone of Nigeria. Investigations of (REEs) in the environment depend on sensitive analytical techniques, due to the low concentration values of these elements.

Neutron activation analysis (NAA) appears to be an attractive technique for determining heavy metals and REEs present in environmental samples; soil, sediments, plants, water, air particulates, etc, (El-Shershaby *et al.*, 1999). Undoubtedly the most significant contribution of early NAA to modern geo-and Cosmo chemistry was the work dealing with the distribution of the (REEs) in meteorites, rocks and sediments. NAA is frequently used to obtain data for geological materials. Usually this technique provides good results within a reasonable timescale. The accuracy and the limit of detection of the (REEs) data using INAA depends, however, strongly on the type of material analysed and on the content of several interfering elements which provide either a high background or overall activity and therefore may prohibit reliable (REEs) analysts. One major difficulty in the neutron activation analysis of rare earth concentrations lies in the high absorption cross section of several isotopes. In practice, one has to consider such factors as the nature of the matrix, interference from simultaneously present (REEs), problems of the pre-treatment and incidental chemical separations, time consumption, the achievable accuracy, the given conditions and the cost factors arising from all this. Nevertheless, activation analysis could be the most frequent choice for the solution of analytical problems, as it is the case for the (REEs).

## 1.2 Statement of Research Problem

Though generally unfamiliar, the REE are essential for many hundreds of applications. The versatility and specificity of the REE has given them a level of technological, environmental, and economic importance considerably greater than might be expected from their relative obscurity.

From a technological point of view, Nigeria still lags behind relative to the developed world. On the other hand, the country has quite abundant reserves of monazite remaining unexplored. These Monazites are very rich in REEs and processed from the heavy-sand deposits which are plentifully distributed along the North Central

Zone of Nigeria; with more deposits in Jos, Plateau State. Therefore, in order to improve on our technology and diversify our economic life line, this work seeks to conduct an investigation on the Nigerian monazite for rare earth elements, which when utilised, can bring about the following;

1. Narrowing the gap in technology between the developed world and Nigeria, which still lags behind in technological innovation or
2. Gain a “foothold” in the world arena; to strive to achieve breakthroughs in key technical fields that concern the national economic lifeline and national security and
3. To achieve ‘leapfrog’ development in key high-tech fields in which China enjoys.

### 1.3 Aim and Objectives

The aim of this work is to determine the rare earth elements (REEs) present in Nigerian Monazite.

The main objectives of the work are;

1. To evaluate the REEs content of Nigerian Monazite using instrumental neutron activation analysis (INAA) technique as a tool.
2. To compare the REEs concentration of Monazite to those obtained in other materials.

### 1.4 Justification

Rare earth elements (REEs), which are not widely known because they are so low on the production chain, are critical to hundreds of high-tech applications, many of which define our modern way of life. Without rare earth elements, much of the world's modern technology would be vastly different and many applications would not be possible. For one thing, we would not have the advantage of smaller sized technology, such as the cell phone and laptop computer, without the use of rare earth elements. Rare earth elements are also essential for the defence industry and are found in cruise missiles, precision guided munitions, radar systems and reactive armour. They are also key to the emergence of green technology such as the new generation of wind powered turbines and plug-in hybrid vehicles, as well as to oil refineries, where they act as a catalyst (Hurst, 2010). They are integrated into every part of modern life. Although used in small quantities, without them many technologies would not function as well. Additionally, their uses in environmentally-beneficial technology puts them at a high priority for ameliorating environmental concerns (Gordon *et al.*, 2005).

The middle class families (growth of which is correlated with development of a country) are becoming increasingly reliant on these products. Developing countries would not become fully developed if supply of these product dropped as they would not have access to technologies like more efficient refrigerators, computers or clean energies such as wind turbine. Even if the products are not necessary, the demand for production of REEs products can yet stimulate a developing economy as not only a raw material supplier but also as an end product producer.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 General Information on Rare Earth Elements

The Rare Earth Elements (REE), also simply called Rare Earths (RE) or Rare Earth Metals (REM), are a group of 17 elements—according to the International Union of Pure and Applied Chemistry (IUPAC) (Connelly, 2005) The 17 REE therefore consist of the elements scandium (Sc), yttrium (Y) and the 15 so called lanthanoids (Ln) which are the elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Th), ytterbium (Yb) and lutetium (Lu) (Connelly 2005). Mortimer and Müller (2001) in their chemistry and Meschede (2006) in the physics both group the lanthanoids and rare earths synonymously and count 14 elements from Cerium to lutetium, i.e. without lanthanum itself (Mortimer and Müller 2007). Often the name lanthanides is used instead of lanthanoids. The ending—id however indicates a certain chemical structure like a sulphide whereas the ending—oid means that something is similar, looks or behaves the like. So the word lanthanoids would be the correct one to use as the REE are not derivations

These Rare Earth Elements are also called rare earth metals (REM) because all of the above elements are basically metals in nature. On the basis of atomic weight, REEs can be further divided into two groups: the Light Rare Earth Elements (LREEs) and the Heavy Rare Earth Elements (HREEs). LREEs are the lower atomic weight elements (Lanthanum to Europium) while HREEs are Gadolinium to Lutetium and Yttrium. REEs are highly electropositive and are predominantly trivalent (Ln), with the exception of Cerium (Ce) and Europium (Eu) in some environments. Since most REEs possess similar atomic radii and oxidation states, they can substitute for each in various crystal lattices. This capability of substitution leads to multiple REE occurrences within a single mineral and has resulted in a wide distribution within the Earth's crust (Jordens *et al*., 2013).

### 2.1.1 Occurrence and Abundance

The term rare earth is actually a misnomer arising from the rarity of the minerals from which they were originally isolated. Most REEs are not as uncommon in nature as the name implies. Certainly, REEs are relatively plentiful in the earth crust having an overall crustal abundance of 9.2 ppm as shown in the work of Rudnick and Gao, (2003). The crustal abundance of individual REE varies widely, from Cerium, the most abundance at 43 ppm (exceeding other important metals including Copper – 27 ppm and Lead – 11 ppm) to 0.28 ppm for thulium as shown in the work of Taylor and Mc Lenen (1985); and Rudnick *et al.*, (2005). That is to say, Cerium, the most abundant REE, comprises more of the earth's crust than Copper or Lead. Many REEs are more common than tin and molybdenum, and all but promethium are more common than silver or mercury.

Rare earth elements can be found in a variety of minerals, but the most abundant rare earth elements are found primarily in Bastnaesite and Monazite (Hurst, 2010). Bastnaesite typically contains Light Rare Earths (LREE) and a small amount of the heavies, while Monazite also contains mostly the light, with the fraction of Heavy Rare Earths (HREE) being two to three times higher. Other examples of minerals known to contain rare earth elements include apatite, Cheralite, Eudialyte, Loparite, Phoshporites, rare-earth-bearing (ion absorption) clays, secondary monazite, spent uranium solutions, and xenotime as obtained from U.S. Geological Survey. (2011).

### 2.1.2 General Chemical and Geochemical Properties

The rare earth elements lanthanum to lutetium (members of group IIIA) have very similar chemical and physical properties. This uniformity arise from the nature of their electronic configurations, leading to a particularly stable 3+ oxidation state and a small but steady decrease in ionic radius with their increase in atomic number for a given coordination number. Despite the similarity in their chemical behaviour, these elements can be partially fractionated, one from another, by several petrological and mineralogical processes. The wide variety of types and sizes of the cation coordination polyhedral in rock forming minerals provides a means for this chemical fractionation: it is this phenomenon which has important consequences in geochemistry. Yttrium (Y, atomic number 39) is also a member of the group IIIA and show a similar chemistry to that of the REE, and is sometimes included with them in descriptive accounts. The term lanthanons (abbreviated Ln) is applied to the sixteen elements in the group La to Lu plus Y. The lightest element in group IIIA, Scandium, shows a sufficiently distinct chemistry, owing to the small radius of its 3+ ion, to warrant separate description. The term Lanthanides is sometimes used as a name for the fourteen elements following Lanthanum in the periodic table (i.e Ce to Lu) (Henderson (1984).

The chemical, metallurgical, and physical behaviours of the rare earth elements are governed by the electronic configuration of these elements. In general, these elements are trivalent, $R^{3+}$, but several of them have other valences. The electronic configuration of the REEs are given in Table 2.1 below**.** For the ground state and for the +3 oxidation states. Lanthanum has an outer electronic configuration in the ground state of $5d^{1}6s^{2}$, but the next element, Cerium, has an electron in the 4f subshell (see Table 2.1)**.** The subsequent elements have electrons entering the 4*f* sub-shell, uptil at Yttrium whose 4*f* sub-shell is filled. The 4f electrons are well shielded by the eight electrons in the $5s^2$ and $5p^6$ sub-shell, so that they are not significantly involved in chemical interactions. In other words, the 4*f* electrons have lower energies than and radially lie inside the outer three valence electrons (i.e, the 4*f* are localized in part of the ion core), and thus they do not directly participate in the bonding with other elements when a compound is formed. Hence, any difference in the number of electros in the 4*f* sub-shell does not lead to much difference in chemical behaviour, nor to significant ligand field effects. The REE, therefore, tends to occur in any natural occurrences as a group rather than singly or as a combination of a few of their number. They are lithophile, in that they concentrate predominantly in the silicate rather than in the metal or sulphide phases when they coexist. They also tend to be ‘‘dispersed’’ elements since they are present in trace quantities in many minerals, only rarely occurring at high concentrations.

**Table 2.1** Atomic weight and ground state electronic configurations

| Atomic No. | Symbol | Configuration 0 | +3 |
|---|---|---|---|
| 57 | La | [Xe] $5d^1\,6s^2$ | [Xe] $4f^0$ |
| 58 | Ce | [Xe] $4f^1 5d^1\,6s^2$ | [Xe] $4f^1$ |
| 59 | Pr | [Xe] $4f^3\,6s^2$ | [Xe] $4f^2$ |
| 60 | Nd | [Xe] $4f^4\,6s^2$ | [Xe] $4f^3$ |
| 61 | Pm | [Xe] $4f^5\,6s^2$ | [Xe] $4f^4$ |
| 62 | Sm | [Xe] $4f^6\,6s^2$ | [Xe] $4f^5$ |
| 63 | Eu | [Xe] $4f^7\,6s^2$ | [Xe] $4f^6$ |
| 64 | Gd | [Xe] $4f^7\,5d^1\,6s^2$ | [Xe] $4f^7$ |
| 65 | Tb | [Xe] $4f^9\,6s^2$ | [Xe] $4f^8$ |
| 66 | Dy | [Xe] $4f^{10}\,6s^2$ | [Xe] $4f^9$ |
| 67 | Ho | [Xe] $4f^{11}\,6s^2$ | [Xe] $4f^{10}$ |
| 68 | Er | [Xe] $4f^{12}\,6s^2$ | [Xe] $4f^{11}$ |
| 69 | Tm | [Xe] $4f^{13}\,6s^2$ | [Xe] $4f^{12}$ |
| 70 | Yb | [Xe] $4f^{14}\,6s^2$ | [Xe] $4f^{13}$ |
| 71 | Lu | [Xe] $4f^{14}\,5d^1\,6s^2$ | [Xe] $4f^{14}$ |

[Xe] = configuration of Xenon: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$.

### 2.1.3 Oxidation State and Ionic Radii

The REEs are strongly electropositive and so, most of their chemistry is characteristic of ionic bonding, with only a minimal covalent contribution. The general sequence for the ionization of the REE is considered to be the removal first of the two 6*s* electrons, then either a 5*d* or a 4*f* electron which is relatively close in energy to that of the 6*s* electron. A 4*f* electron would be the fourth to be removed but ionization energy is too high for the +4 state to be common. In fact all the REEs show remarkably constant valency of three in their chemistry and geochemistry. Oxidation state of +2 may be shown by Eu and Yb, and of +4 by Ce and Tb. The existence of these states can be explained partly on the basis of the enhanced stability of the half-filled ($Eu^{2+}$ and $Tb^{4+}$) and completely-filled ($Yb^{2+}$) 4*f* sub-shells, while Ce has the electronic configuration of the noble gas Xenon. Very occasionally, the other REE may exhibit 2+ and 4+ oxidation state in their chemistry but not, apparently, in their geochemistry. (Goldschmidt 1937) suggest that there was some evidence for the presence of $Sm^{2+}$ in mineral but this has not been substantiated and is unlikely. Evidence for the occurrence of 2+ and 4+ state in natural systems is substantial only for $Eu^{2+}$ and $Ce^{2+}$. $Tb^{4+}$ has not been recorded in any mineral or natural aqueous medium. The existence of $Yb^{2+}$ has been invoked as an explanation for the presence of Eu and Yb negative anomalies, and the coherence of Eu and Yb concentrations in some inclusions in a carbonaceous chondrite. However, the existence of $Yb^{2+}$ would require extremely reducing conditions (more so, for example, than during the genesis of lunar rocks) and so alternative explanations for the Yb anomalies need to be sought (Mason and Martins 1977). Under the usual conditions prevailing in the crust, Yb is trivalent.

The REE occupy a wide variety of coordination polyhedral in minerals, from six-fold to twelve-fold or even higher coordinations. The smaller REE ions can occupy six-fold coordination sites but do so only rarely in minerals. Normally the coordination is greater; most coordinations from seven to twelve being represented, e.g. 7-fold in sphene, 8-fold in Zircon, 9-fold in monazite, 11-fold in allinite, and 12-fold in perovskite. The diversity of sites occupied by REE ion undoubtedly leads to complexity in REE mineral chemistry, much of which still remains to be elucidated (Henderson (1984).

A correlation between coordination and ionic radius is to be expected; the larger ion will tends to occupy larger sites and vice versa. The REE exhibit a gradual and steady decrease in their atomic volumes with increase in atomic number as a result of imperfect shielding of one electron by another in the same sub-shell, so that the effective nuclear charge acting on each 4*f* electron increases with increasing atomic number**.** Ionic radius is also a function of charge and coordination number.

### 2.1.4 Rare Earth Element Rock Abundances

Chondrite meteorites are generally considered to be composed of igneous materials that have not had an extensive history of melting and recrystallization, thus the REEs composition is considered to be representative of magma prior to any fractionation processes. Historically, igneous petrologists have used chondrite REEs concentrations to index or "normalize" rock samples (REEs ratio of the sample/ chondrite) to estimate the type and extent of magmatic processes responsible for lithosphere evolution. Rock REEs concentrations vary markedly with rock type and source area. The REEs actually have moderate concentration ranges compared with many other trace elements. Rhyolites and granites typically have greater REEs concentrations than basalts and peridotites with the LREEs concentrations markedly greater than the HREEs concentrations. Rare earth element concentrations have been routinely determined using instrumental neutron activation analysis (Helmke 1996). Argillaceous sediments and shales typically have greater REEs concentrations than limestones and sandstones. As with igneous materials, sedimentary materials typically exhibit greater LREEs concentrations than HREEs concentrations. The Oddon-Harkins rule states that an element with an even atomic number has a greater abundance than the next element in the Periodic Table. The REEs frequently obey the Oddon-Harkin rule;

such that, Ce (atomic number = 58) typically has a greater concentration than Pr (59) and culminating with Yb (70) having a greater concentration than Lu (71). Observation of the Chondrite sediments and other parent material elemental compositions reflect the Oddon-Harkin rule (Henderson, (1984)**.**

The importance of the REEs rests with their “signature,” which may be defined as either the actual REE concentrations or their normalized concentrations displayed according to their atomic number. Analysis of the REE signatures typically involves the summation of the total concentrations of all of the REEs (ΣREE) and evidence of fractionation, that is, LREE and HREE ratios, La/Yb ratios, Nd/Sm ratios, and the presence of Ce or Eu anomalies (Henderson, (1984)**.**

### 2.1.5 Some Rare Earths Application in Clean Energy

Rare earths are vital to some fast growing businesses in clean energy. New generation wind-powered turbines use NdFeB/DyTb permanent magnets. This critical component gives greater magnetic field strength and higher coercivity (resistance to becoming demagnetized) than other magnets. The use of rare earths in permanent magnets considerably reduces the size and the mass of the generator. Similar magnets are also used in motors for hybrid vehicles, hard disk drivers and many other electronic applications. Electric car motors require up to 200g of Nd and 30g of Dy. Wind turbine generators can contain one tonne of Nd per megawatt installed capacity as obtained from U.S Geological Survey, Mineral Commodity Summaries (2011).

Rare earth permanent magnets are the largest consumer of REE accounting for 39% of the production. The next largest REE consumers are catalysts (19%) and metal alloys (18%). About 12% of LREE is used for polishing, TV and computer monitors, mirrors and microchips. A total of 10% of the LREE are used in the glass industry.

Lanthanum, for example, increases the refractive index of glass and is used in camera lenses Zaicheng *et al.*, (2012).

The phosphorescent properties of rare earths, including Y, are heavily exploited in the production of energy-efficient compact fluorescent lamps (CFL) and light emitting diodes (LED). The new generation of organic light emitting diodes (OLED) uses rare earths (Eu, Tb, Tm) to produce transparent or surface emitting flat panel displays. The colour of the emitted light can be tuned by changing rare earth ion concentration as obtained in the work of Zaicheng *et al*, (2012).

Rare earths are also added to ceramic glazes for colour control (Campbell *et al.* 2010). Barium Titanate powder alloyed with REE is used in electronic applications. Yttrium is used to make ferrites for high frequencies and to stabilize Zirconia in Oxygen sensors (Yoldjian *et al.*, 1985). In 2008, 7000 t of REOs was used in this category, of which Yttrium Oxide accounted for 53 % and the remainder being Oxides of La, Ce, Nd and Pr.

Rare earths are widely used in medical technology. For example, Gd-based compounds are used as contrast agents to image tumours with MRI (Magnetic Resonance Imaging) and the MRI uses REE magnets (British Geological Survey, 2011). Erbium yttrium aluminium garnet (Er:YAG) lasers are used in dermatology for skin resurfacing to remove wrinkles.

The unique magnetic properties of Gd may be used in future refrigeration technology. These refrigerators do not require ozone-depleting or hazardous substances and reduce electricity consumption by up to 15 per cent due to higher energy efficiency (Kennedy 2010). A Thulium-doped lutetium Yttrium Aluminum Garnet (Tm:LuYAG) laser is used in meteorology to measure wind speed and direction, pollution and moisture.

Promethium occurs naturally in minuscule amounts (Attrep and Kuroda, 1968), however, it can be produced by bombarding Neodymium-146 with neutrons. Promethium can be used in nuclear powered batteries which use beta particles, emitted by the decay of Promethium, to induce a phosphor to emit light. This light is then converted into electricity by a device similar to a solar cell. This type of battery could provide power for up to five years.

In many applications, REE are advantageous because of their relatively low toxicity. For example, the most common types of rechargeable batteries contain either cadmium (Cd) or lead. Rechargeable Lanthanum-Nickel-Hydride (La-Ni-H) batteries are gradually replacing Ni-Cd batteries in computer and communications applications and could eventually replace lead-acid batteries in automobiles. Although more expensive, La-Ni-H batteries offer greater energy density, better charge-discharge characteristics, and fewer environmental problems upon disposal or recycling (Gordon *et al*, 2005).

## 2.2 Neutron Activation Analysis (NAA)

### 2.2.1 Theory of NAA

Neutron activation analysis was discovered in 1936 when (Hevesy and Levi, 1936) found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons. From this observation, they quickly recognized the potential of employing nuclear reactions on samples followed by measurement of the induced radioactivity to facilitate both qualitative and quantitative identification of major, minor, and trace elements present in the samples. Neutron activation analysis (NAA) is very useful as sensitive analytical technique for performing both qualitative and quantitative multi elemental analysis of major, minor and traces components in variety of terrestrial samples and extra-terrestrial materials. In addition, because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice when new procedures are being developed or when other methods yield results that do not agree. It is usually employed as an important reference for other analysis methods. Worldwide application of NAA is so widespread it is estimated that approximately 100,000 samples undergo analysis each year (Hamidatou 2009). The most common reaction occurring in NAA is the $(n,\gamma)$ reaction, but also reactions such as $(n,p)$, $(n,\alpha)$, $(n,n')$ and $(n,2n)$ are important. The neutron cross section, σ, is a measure for the probability that a reaction will take place, and can be strongly different for different reaction types, elements and energy distributions of the bombarding neutrons. Some nuclei, like $^{235}U$ are fissionable by neutron capture and the reaction is denoted as $(n,f)$, yielding fission products and fast (highly energetic) neutrons. (Hamidatou, 2009)

### 2.2.2 Requirement for NAA

The basic essentials required to carry out an analysis of samples by NAA are:

i. A source of neutrons,

ii. Suitable instrumentation for detecting gamma rays,

iii. A detailed knowledge of the reactions that occur when neutrons interact with target nuclei.

iv. Weight moisture content, matrix, interactions, correction factors etc.

### 2.2.3 Neutrons

Although there are several types of neutron sources (reactors, accelerators, and radioisotopic neutron emitters) one can use for NAA, nuclear reactors with their high fluxes of neutrons from uranium fission, offer the highest available sensitivities for most elements. Different types of reactors and different positions within a reactor can vary considerably with regard to their neutron energy distributions and fluxes due to the materials used to moderate (or reduce the energies of) the primary fission neutrons. In our case, the NAA method is based on the use of neutron flux in several irradiation channels of Nigerian Research Reactor-1 (NIRR-1) at the Center for Energy Research and Training (CERT) Ahmadu Bello University Zaria (ABU), as will be described later.

### 2.2.4 Neutrons from Accelerators

Accelerators provide fast mono-energetic neutrons. Fast neutrons contribute very little to the (n,γ) reactions, but instead induced nuclear reactions where the ejection of one or more nuclear particles (n, p), (n, n'), and (n, 2n) - are prevalent (Ali 1999).

### 2.2.5 Neutrons from Reactors with their Energy Distribution

In NAA, as stated earlier, various types of neutron sources (reactors, accelerators, and radio isotopic neutron emitters) can be used, nuclear reactor with high flux provide the best sensitivity. The neutron energy distributions in a reactor (see Fig.2.1 and Fig 2.2), are quite broad and consist of three principal components (thermal, epithermal, and fast). The figure 2.1 above shows the distribution of kinetic energies of neutrons in the thermal reactor. The fission neutrons (fast flux) are immediately slowed down to the thermal energies via a process called neutron moderation.

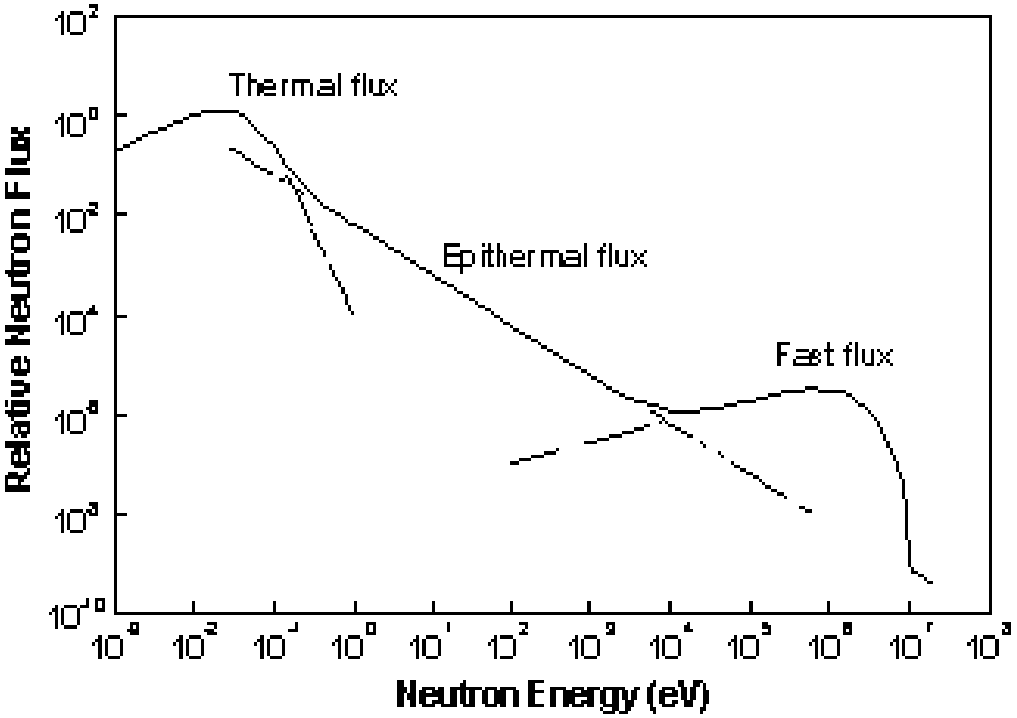

**Figure 2.1**: Relative Neutron Flux ϕ (E) vs. Neutron Energy (eV) (Glascock, D. M, 2010)

The thermal neutron component consists of low-energy neutrons (energies below 0.5eV) in thermal equilibrium with atoms in the reactor's moderator. At room temperature, the energy spectrum of thermal neutrons is best described by a Maxwell-Boltzmann distribution (as shown in figure 2.2) with a mean energy of 0.025 eV and a most probable velocity of 2200 m/s.

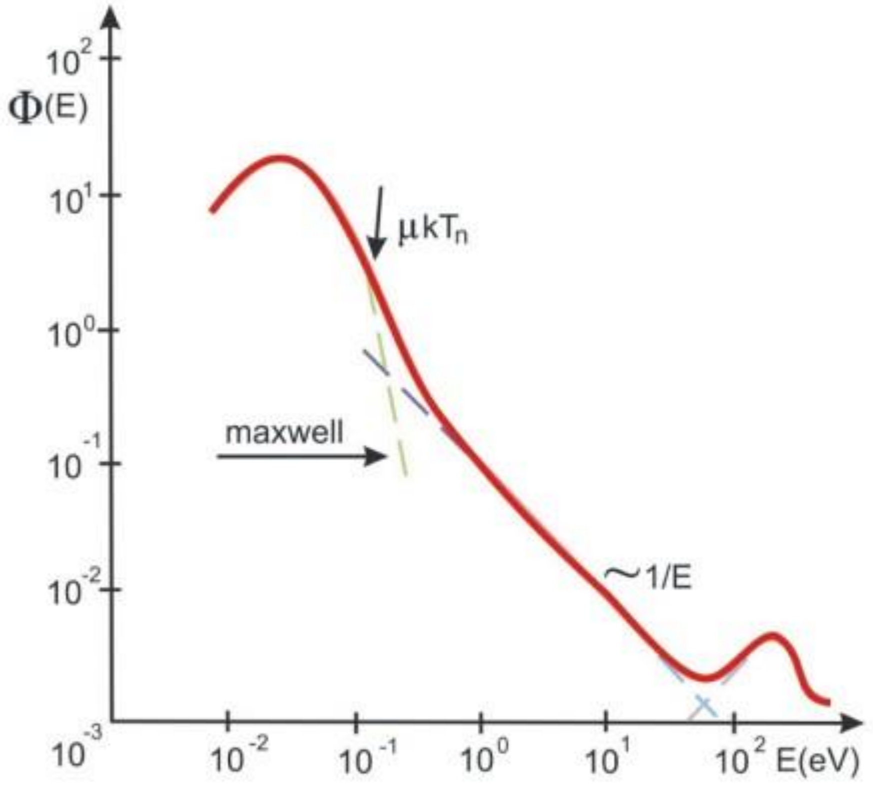

**Figure 2.2**: Distribution of neutron according to their energies in a nuclear reactor (http://www.naa-online.net/theory/equations/)

In most reactor irradiation positions, 90-95% of the neutrons that bombard a sample are thermal neutrons. In general, a one-megawatt reactor has a peak thermal neutron flux of approximately $1\times10^{13}$ neutrons per square centimeter per second.

The epithermal neutron component consists of neutrons (energies from 0.5 eV to about 0.5 MeV) which have been only partially moderated. A Cadmium foil 1 mm thick absorbs all thermal neutrons but will allow epithermal and fast neutrons above 0.5 eV in energy to pass through. In a typical unshielded reactor irradiation position, the epithermal neutron flux represents about 2% the total neutron flux. Both thermal and epithermal neutrons induce (n,γ) reactions on target nuclei. An NAA technique that employs only epithermal neutrons to induce (n,γ) reactions by irradiating the samples being analyzed inside either Cadmium or Boron shields is called epithermal neutron activation analysis (ENAA) Ali, (1999).

The fast neutron component of the neutron spectrum (energies above 0.5 MeV) consists of the primary fission neutrons which still have much of their original energy following fission. Fast neutrons contribute very little to the $(n,\gamma)$reaction, but instead induce nuclear reactions where the ejection of one or more nuclear particles - (n,p), (n,n'), and (n,2n) - are prevalent. In a typical reactor irradiation position, about 5% of the total flux consists of fast neutrons. An NAA technique that employs nuclear reactions induced by fast neutrons is called fast neutron activation analysis (FNAA) Ali, (1999).

### 2.2.6 Sensitivity Dependence.

The sensitivity of NAA depends on the irradiation parameters (neutron flux, irradiation time and decay time), counting conditions (measurement time, detector efficiency), and nuclear parameters (isotopic abundance, neutron absorption cross sections, half-life, and gamma-ray abundance. (Glascock 2010).

### 2.2.7 Description of the Nigerian Research Reactor (NIRR 1)

NIRR-1 is a Miniature Neutron Source Reactor (MNSR) designed by China Institute of Atomic Energy (CIAE) (Zhou 1986). First criticality was achieved on 03 February 2004 and has been operated safely (Jonah. *et al.,* 2011). It is specifically designed for use in neutron activation analysis (NAA) and limited radioisotope production. NIRR-1 has a tank-in-pool structural configuration and a nominal thermal power rating of 31 kW. The current core of the reactor is a 230 x 230 mm square cylinder and fuelled by U-Al4 enriched to 90% in Al-alloy cladding. It has a total number of 347 fuel pins and three Al dummies in the fuel lattice. The length of the fuel element is 248 mm, the active length being 230 mm with 9 mm Al-alloy plug at each end. The diameter of the fuel is 4.3 mm and the $^{235}$U loading in each fuel element is about 2.88 grams. The thickness of the Al-alloy cladding is 0.6 mm. There is only one Control Rod in NIRR-1 serving as shim rod, regulation rod as well as safety rod. The functions of reactor start-up, steady-state operation, and shutdown are accomplished by moving the control rod. The Control Rod (CR) is made up of a Cd absorber 266 mm long and 3.9 mm in diameter with stainless steel of 0.5 mm thickness as the cladding material. The overall length of the CR is 450 mm in length. A detailed description of the HEU core can be found in the final SAR (Jonah *et al.*, 2007). With a built-in clean cold core excess reactivity of 3.77mk measured during the on-site zero-power and criticality experiments, the reactor can operate for a maximum of 4.5 hours at full power, mainly due to the large negative temperature feedback effects. Under these conditions, with the same fuel loading, the reactor can run for over ten years with a burn-up of <1% An MCNP model of the reactor fuelled with HEU has been developed and benchmarked by measured data obtained during the on-site zero power and power rising experiments (SAR, 2005).

## 2.3 Neutron Activation Process

The initial step in neutron activation analysis is irradiating a sample with neutrons in a nuclear reactor or sometimes in other neutron sources (Siddappa *et al.*, 1996). The stable nucleus absorbs one neutron and becomes a radioactive nucleus. The concentration of the stable element of interest in the sample can be measured by detecting the decay of these nuclei (Nuclear Science Division and Contemporary Physics Education Project 2000).

The radioactive nuclei emit characteristic gamma rays. Detection of the specific gamma rays (of specific energy) indicates presence of a particular element. Suitable semiconductor radiation detectors may be used for quantitative measurement. The concentrations of various component elements in given samples are found by computer data reduction of gamma ray spectra. Sequential instrumental neutron activation analysis allows quantitative measurement of up to about 35 elements in small samples of 5 to 100 mg. The lower detection limit is in parts per million or parts per billion, depending on the element (Radiation Centre 2003) Brief descriptions of the NAA method, reactor neutron sources, and gamma-ray detection are given in the following section.

The sequence of events occurring during the most common type of nuclear reaction used for NAA, namely the neutron capture or (*n*, *γ*) reaction include the following;

(i) Creation of a compound nucleus forms in an excited state when a neutron interacts with the target nucleus via a non-elastic collision.

(ii) The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus.

(iii) The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays.

In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed gamma rays, but at a much lower rate according to the unique half-life of the radioactive nucleus. Depending upon the particular radioactive species, half-lives can range from fractions of a second to several years ((Hamidatou, 2009)

In principle, therefore, with respect to the time of measurement, NAA falls into two categories - the prompt gamma-ray neutron activation analysis (PGNAA), where measurements take place during irradiation, and the delayed gamma-ray neutron activation analysis (DGNAA), where the measurements follow radioactive decay. The latter operational mode is more common; thus, when one mentions NAA it is generally assumed that measurement of the delayed gamma rays is intended. About 70% of the elements have properties suitable for measurement by NAA (Hamidatou, 2009)

DGNAA (sometimes called conventional NAA) is useful for the vast majority of elements that produce radioactive nuclides. The technique is flexible with respect to time such that the sensitivity for a long-lived radionuclide that suffers from interference by a shorter-lived radionuclide can be improved by waiting for the short-lived radionuclide to decay or quite the contrary, the sensitivity for short-lived isotopes can be improved by reducing the time of irradiation to minimize the interference of long-lived isotopes. This selectivity is a key advantage of DGNAA over other analytical methods (Hamidatou, 2009).

In most cases, the radioactive isotopes decay and emit beta particles accompanied by gamma quanta of characteristic energies, and the radiation can be used both to identify and accurately quantify the elements of the sample. Subsequent to irradiation, the samples can be measured instrumentally by a high resolution semiconductor detector, or for better sensitivity, chemical separations can also be applied to reduce interferences. The qualitative characteristics are: the energy of the emitted gamma quanta ($E\gamma$) and the half-life of the nuclide ($T_{½}$). The quantitative characteristic is: the $I\gamma$ intensity, which is the number of gamma quanta of energy $E\gamma$ measured per unit time (Hamidatou, 2009).

### 2.3.1 Basic Principles

In typical NAA, stable nuclides ($^{A}Z$, the target nucleus) in the sample undergo neutron capture reactions in a flux of (incident) neutrons (Missouri University homepage 2003). The radioactive nuclides ($^{A+1}Z$, the compound nucleus) produced in this activation process usually decay by emission of a beta particle ($ß^{-}$) and gamma ray(s) with a unique half-life. A high-resolution gamma-ray spectrometer is used to detect these ‘delayed’ gamma rays in the presence of the artificially induced radioactivity in the sample for both qualitative and quantitative analysis.

The sequence of events that occur during the most common type of nuclear reaction used for activation analysis is shown in Figure 2.3. The incident neutron hits the target nucleus, which captures the neutron and is converted into a compound nucleus. The latter immediately emits radiation called prompt gamma radiation and forms the radionuclide, which then kicks out a beta particle and emits the delayed gamma radiation (since it is emitted after some time delay), forming the product nucleus.

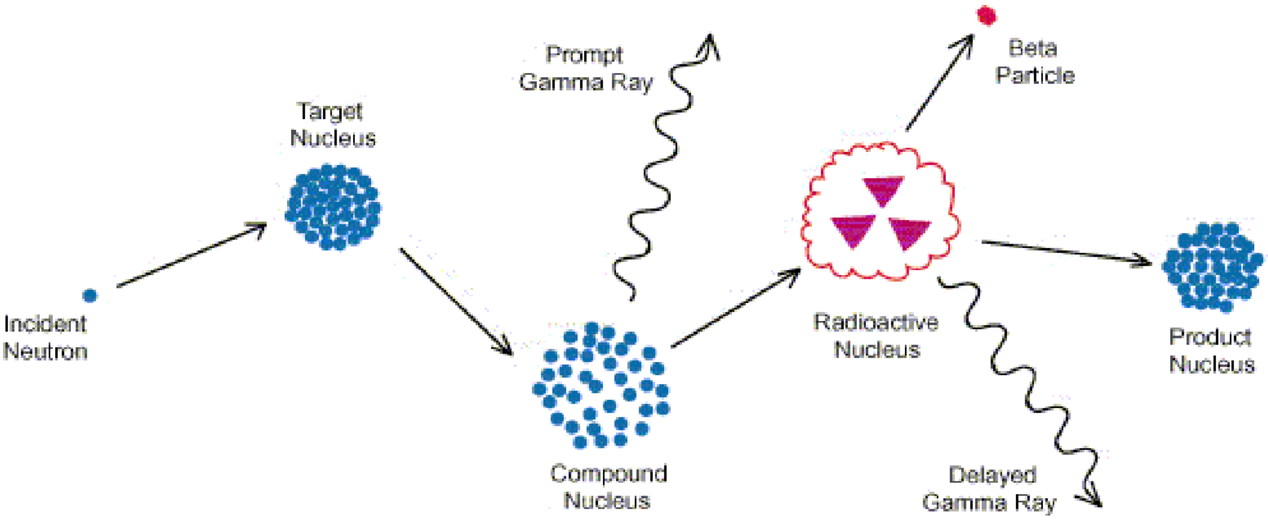

**Figure 2.3**: Sequence of events that occur during the most common type of nuclear reaction used for activation analysis.
(Nuclear Science Division and Contemporary Physics Education Project 2000).

Neutron activation analysis (NAA) stands at the forefront of techniques for the quantitative multi-element analysis of major, minor, trace and rare elements. The element is termed major if it is present in the sample in excess of 1.0%. It is said to be minor if its presence is between 0.01 and 1.0%. It is trace if its presence is less than 0.01%. NAA begins with neutron bombardment of a sample to convert stable isotopes to radioactive isotopes (e.g., natural sodium [$^{23}$Na] is converted to radioactive sodium [$^{24}$Na]). The usual procedure involves placing the samples to be analyzed plus a number of suitable standards into the neutron field produced by a neutron source. Radioisotopes created during the irradiation will decay with time. A portion of the energy released during decay is often in the form of gamma radiation, which is capable of travelling out of the sample. The gamma rays possess unique energies that are characteristic of the radioisotope undergoing decay. Gamma rays detected at a particular energy "are usually indicative of a specific radionuclides presence.

Using $^{24}$Na as an example, when it decays to stable $^{24}$Mg, gamma rays having energies of 1368.53 and 2754.09 kilo-electron Volts (keV) are released. If these gamma rays enter a suitable detector, their energy can be converted to an electrical signal that is processed as a count in an energy spectrum.

The accumulation of gamma counts at a particular energy will generate a curve, the area of which is proportional to the radioactivity of the characteristic radionuclide. By irradiating and counting standards containing known amounts of various elements, it is possible to establish a relationship between the radioactivity of the standard and the radioactivity of the sample, which in turn allows the researcher to determine the abundance of a particular element or elements.

The energies of the delayed gamma rays are used to identify component sample elements. The count of gamma rays of a specific energy indicates the amount of an element in the sample. For example, considering the equation 2.1 and 2.2, when a silver sample is irradiated, a fraction of the $^{109}$Ag atoms in the sample will capture a neutron and become $^{110}$Ag. The radioactive $^{110}$Ag atoms have a half-life of 24.6 seconds. Beta decay of $^{110}$Ag atoms to $^{110}$Cd occurs 4.5 % of the time with emission of a 658 keV gamma ray. The amount of silver in the original sample can be determined by measuring the count of 658 keV gamma-rays emitted from the sample in a given time interval after irradiating the sample.

$$^{109}\mathrm{Ag} + \mathrm{n} \rightarrow {}^{110}\mathrm{Ag} \qquad 2.1$$

$$^{110}\mathrm{Ag} \rightarrow \beta^{-} + {}^{110}\mathrm{Cd} + \gamma\ (658\ \mathrm{keV}) \qquad 2.2$$

The measured count rate ($R$) of the gamma rays from the decay of a specific isotope ($^{110}$Ag) in the irradiated sample can be related to the amount ($n$) of the original, stable isotope ($^{109}$Ag) in the sample through equation 2.3 (Nuclear Science Division and Contemporary Physics Education Project 2000).

$$R = \varepsilon\, I\gamma\, A = \varepsilon\, I\gamma\, n\, \varphi\, \sigma\, (1-e^{-\lambda t_i})\, e^{-\lambda t_d} \qquad 2.3$$

Where, $R$ = measured gamma-ray count rate (cps)

$A$ = absolute activity of isotope $^{A+1}Z$ in sample

$\varepsilon$ = absolute detector efficiency

$I\gamma$ = absolute gamma-ray abundance

$n$ = number of atoms of isotope $^{A}Z$ in sample

$\varphi$ = neutron flux (neutrons·cm$^{-2}$·sec$^{-1}$)

$\sigma$ = neutron capture cross section (cm$^{2}$) for isotope $^{A}Z$

$\lambda$ = radioactive decay constant (s$^{-1}$) for isotope $^{A+1}Z$

$t_i$ = irradiation time (s)

$t_d$= decay time (s)

If the neutron flux *φ*, neutron captures cross section *σ*, absolute detector efficiency *ε*, and absolute gamma-ray abundance *Iγ* are known, the number of atoms *n* of isotope $^{A}Z$ in the sample can be calculated directly. In most cases, however, a standard is irradiated and counted under similar conditions as the sample, and the mass of the element in the sample (*Wsam*) is found by comparing the measured count rates ($R$) for the sample and standard using equation 2.4.

$$W_{sam} = W_{std}\,\frac{R_{sam}}{R_{std}} \qquad 2.4$$

## 2.5 Previous Work

Ewa *et al.*, (1996), in their research developed an Instrumental Neutron Activation Analysis (INAA) method to investigate the pattern of ten rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Lu) in coal obtained from eight mines in Nigeria, namely Okaba, Enugu, Ogbete, Onyeama, Gombe, Lafia Asaba and Afikpo and were able to show in their result a fractionations with the highest index of 13.19 for Lafia coal, depletion in HREE, negative Eu anomaly for most of the coals, REE patterns that are consistent with chondritic trends; prominent $(Eu/Eu^{*})_{cn}$ for Okaba and Gombe coals. Variations in geochemical data observed could suggest strong departures from band metamorphism during the coalification events of the Benue Trough geosynclines, where the coal deposits are all located.

The mobilization of rare earth elements (REEs) in the environment requires monitoring of these elements in environmental matrices, in which they are mainly present at trace levels. The similarity in (REEs) chemical behaviour makes the separate determination of each element by chemical methods difficult; therefore based on nuclear properties of the elements to be determined, therefore, El-Tahir, (2007), in his research work, developed an Instrumental Neutron Activation Analysis(INAA), as a sensitive non- destructive analytical tool for the determination of rare earth element (REEs), to find out what information could be obtained about REEs of some Egyptian granite, collected from four locations in Aswan area in south Egypt. The locations are; wadi El-Allaqi, El-Shelal, Gabel Ibrahim Pacha and from Sehyel Island. The work also estimated the accuracy, reproducibility and detection limit of NAA method in case of the given samples. The result obtained indicates the viability of using the INAA for the determination of the elements La, Ce, Nd, Sm, Eu, Yb and Lu. The result shows that the concentration of the determined REEs in the old granite (wadi El-Allaqi and Gabel Ibrahim Pacha) are higher than the young granite (El-Shalal and Seyhel Island). The high concentrations in the old granite related to the following factors (a) The presence of radioactive accessory minerals such as uranothorite (b) The granitic rocks contain accessory minerals such as Zircon, Sphene and also Monazite and Appetite which readily accumulate in limited Uranium and Thorium. On this note they concluded that the INAA technique can be effectively used on routine basis for the analysis of a large number of samples in ore prospect and geochemical studies which the present work seek to adopt.

Peterman *et al.*, (2012), in their research developed a multi-step chemical abrasion thermal ionization mass spectrometry (CA-TIMS) methods for monazite using six samples that vary in composition and age — Amelia, Jefferson County, Burke, Elk Mountain, 554 and Madagascar to evaluate whether the multi-step CA-TIMS approach reveals complexities in either age or composition that might be masked by single-step analysis, this study presents a side-by-side comparison of monazite samples dated via multi-step TIMS (not annealed) and CA-TIMS (annealed), and measurement of rare earth element ratios for each dissolution step. The data demonstrated three important contributions. First, annealing reduces solubility—after one partial dissolution step, not-annealed fractions were 3.3 – 4.1 times more digested than the annealed fractions. The difference in solubility suggests that monazite does not fully self-anneal at low temperatures. Second, multi-step TIMS analyses yielded high-precision U–Pb plateau ages for the Burke and Amelia monazites; CA-TIMS analyses yielded high-precision U–Pb plateau ages for Madagascar and Amelia monazites. Jefferson County, Elk Mountain and 554 yielded more complex results and no U–Pb plateau ages. Third, chemical analysis of partial-dissolution steps reveals heterogeneous age and compositional data for annealed samples. Because not-annealed samples yielded more consistent age and compositional data, high-temperature annealing is not recommended for monazite. Instead, optimal TIMS results are provided by slow, partial dissolution of monazite in weak acid. Due to all of these, they concluded that the Burke and Amelia monazites may be suitable for use as reference materials.

Choudhury *et al*., 1989 in their research developed an Energy Dispersive X-ray Fluorescence (EDXRF) spectroscopy methods on some selected Indian monazite samples. They use three samples each obtained from Kerala (Chavara and Manavalakurichi), Orissa (Chattrapur) and Tamil Nadu (Tirunelveli) for the determination of their elemental composition using $^{109}$Cd (annular) and $^{241}$Am (disc) radioisotope sources. In their analysis, rare earth La, Ce, Pr, Nd, Sm, Gd, and Dy were analyzed using $^{241}$Am inside a source geometry, and elements Y, Zr, Mo, Pb, Th, and U were analyzed using $^{109}$Cd source. That is to say they also found five other elements in addition to the seven rare earth elements. Quantitative results on these 13 elements present in this ores were obtained by the EDXRF technique. Based on their conclusions, it was observed that despite the diverse geological setting, there is remarkable similarity in the elemental composition of these ores. Although some trace elements do show certain variations from sample to sample.

The present research however seeks to carry out a determination of rare-earth elements in Jos monazite using Instrumental Neutron Activation Analysis (INAA).

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Materials

The materials used in this work are as follows; Monazite sample, Polyethylene bags, Polyethylene vials, balance (metler 100), two National Institute of Science and Technology (NIST) Standard Reference Materials (SRM); NIST 1633b, and 1633c, NIRR-1, GEM HPGe detector, Computer, Maestro for spectral acquisition, WINSPAN (Chinese software).

## 3.2 Methodology

### 3.2.1 Study Area

Jos Plateau is in the North-central region of Nigeria and is located between longitudes $7^{0}30 – 10^{0}00^{1}$E and latitude $8^{0}00 – 11^{0}30^{1}$N, covering an area of about 22000km2. It is the twelfth largest state of Nigeria, and is located approximately in the centre of the country. It is geographically unique in Nigeria because its boundaries surround the Jos Plateau, having the entire plateau in its central and northern part (Opara *et al.*, (2015).

### 3.2.2 Geology, Climate, and Physiography of the Study Area

The Jos Plateau is thought to be an area of younger granite which was intruded through an area of older granite rock, making up the surrounding states. These "younger" granites are thought to be about 160 million years old. This creates the unusual scenery of the Jos Plateau. There are numerous hillocks with gentle slopes emerging from the ground like mushrooms scattered with huge boulders. Also volcanic activity 50 million years ago created numerous volcanoes and vast basaltic plateaus created from lava flows. This also produces regions of mainly narrow and deep valleys and pediments (surfaces made smooth by erosion) from the middle of rounded hills with sheer rock faces. The phases of volcanic activities involved in the formation of Plateau State have made it one of the mineral rich states in the country. Tin is still mined and processed on the plateau (Chiegeonu 2009).

### 3.2.3 Sample Collection

A total number of five representative Monazite samples (about 1kg each) were collected from five locations around Jos area of Plateau State namely; Barikin Ladi 1, Barikin Ladi 2, Kuru 1, Kuru 2, and Ray field, for investigation using instrumental neutron activation analysis (INAA) as a tool.

### 3.2.4 Sample Preparation

The samples were first ground into fine grains and thereafter, approximately 150mg-200mg of the sample measured using a balance (metler 100) was loaded into a high density polyethylene bag and heat- sealed. Simultaneously, two National Institute of Science and Technology (NIST) Standard Materials (SRM); NIST 1633b, and 1633c standards and flux monitors were also prepared by the same method as the sample. The sealed samples were then each arranged in polyethylene vials after which were sent to be irradiated under optimal conditions.

### 3.2.5 Sample Irradiation and Counting

After proper irradiation and cooling, the activated sample will then be placed over a detector; choosing the adequate counting time and geometry, the gamma spectrum which is produced by maestro for spectral inquisition will then be analysed and recorded by a computer program after which the concentration of the element of interest in the sample will be calculated from the analysis of acquired spectra using WINSPAN (Chinese software).

### 3.2.6 Sample Analysis

In this work, the standard reference material NIST 1633c was used to determine the calibration factors for the rare earth elements (REEs). The rare earth elements concentrations in our samples were quantitatively determined by comparison with the NIST (1633b, and 1633c) Standard Reference Materials (SRM) which were activated simultaneously. Table 3.1 shows the radioisotopes used to calculate the concentration of the analyzed elements as well as their nuclear data. The re-investigation of the Coal Fly Ash 1633c which was used as quality control to validate the analytical method is shown in Table 3.2.

The Standards and samples were irradiated at the Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria using NIRR-1 at a thermal neutron flux of $5 \times 10^{11}\mathrm{ncm}^{-2}\mathrm{s}^{-1}$ for long lived nuclides. Interference-free analytical $\gamma$ - energy lines, as shown in Table **3.1**, were used for peak integration for the rare earth elements.

**Table 3.1:** Nuclear data used for the determination of REEs

| Elements | Radio Nuclide | $\gamma$-Energy | Half-life |
|---|---|---|---|
| La | $^{140}$La | 1596 | 40.27h |
| Ce | $^{141}$Ce | 145 | 32.5d |
| Nd | $^{147}$Nd | 531 | 10.98d |
| Eu | $^{152}$Eu | 1408 | 13.33y |
| Tb | $^{165}$Tb | 879 | 72.3d |
| Yb | $^{169}$Yb | 198 | 32d |
| Lu | $^{177}$Lu | 208 | 6.71d |

With the introduction of high-resolution Ge (Li) $\gamma$-ray detectors, many trace elements, including the REE, could be determined simultaneously without any chemical separations in a wide variety of rocks and minerals by INAA. Irradiation, cooling and counting time were optimized depending on the half-lives of elements analyzed, in order to improve the ratio between the relative activity of each element and the bulk activity of the matrix. The irradiation time for all samples was 6 hours. The selection of photopeaks for the analysis is briefly discussed below for each element. For Lanthanum, the high abundance photopeak of $^{140}$La at 1596 keV was used, which is free of interference. The other peak at 487 keV cannot be used due to interferences from $^{47}$Ca 489 keV and $^{192}$Ir 488 keV. For Cerium, the photopeak of $^{141}$Ce at 145 keV was used. For Neodymium, the photopeak of $^{147}$Nd at 531 keV which is free of interference was used. The high abundance peak at 91 keV is surrounded by other peaks, which cannot be resolved from the 153 peak of $^{177}$Lu 113 keV. As far as Europium is concerned, $^{152}$Eu has a number of photopeaks where the high abundance peaks at 1408 and 799 keV are free from interference. Both peaks were used for the determination of this element. Another peak at 122 keV cannot be resolved from the 124 keV line of $^{154}$Eu. However, the combined peaks can be used as these are obtained from two isotopes of the same element and have similar half-lives. Ytterbium can be determined using the 198 keV peak of $^{169}$Yb. For Lutetium, the high abundance peak at 208 keV of $^{177}$Lu was used.

**Table 3.2** Comparison of certified values with our results in ppm or as indicated in % for the certified reference materials NIST-1633c

| Elements | NIST-1633c | | |
|---|---|---|---|
| | This work | Certificate Value | Standard Deviation |
| La | 70.60 ± 16.7 | 87.0 ± 2.6 | 7.57[a], 11.60[b] |
| Ce | 171.00 ± 27 | 180.00 | 6.36 |
| Eu | 4.88 ± 0.73 | 4.67 ± 0.07 | 0.15 |
| Tb | 5.72 ± 1.43 | 3.12 ± 0.06 | 1.84 |
| Yb | 12.00 ± 3.8 | 7.70 | 3.04 |
| Lu | 3.81 ± 0.57 | 1.32 ± 0.03 | 1.76 |

a* Lower limit ignored based on the Chauvnet's criterion (statistical rejection of data)
b* All limits considered

For irradiation, two schemes were chosen based on the half-life of product nuclides (Jonah *et al.*, 2006). For the elements leading to short-lived activation products, the samples are each packed and sealed in 7 cm$^3$ rabbit capsules and sent for irradiation in turn in an outer irradiation channel B4, where the neutron spectrum is 'soft'. The choice of the outer irradiation channel is to eliminate corrections due to nuclear interferences caused by threshold reactions, notably Mg in the presence of Al; Al in the presence of Si; and Na in the presence of P. This is due to the proximity of the inner channels of MNSR reactors to the core leading to relatively higher ratio of fast-to-thermal neutrons. For elements leading to long-lived activation products, samples wrapped in polyethylene films are packed in a stack inside the 7 cm$^3$ rabbit capsule and sealed for irradiation. Samples are irradiated for 6hrs in any of the small inner irradiation channels (i.e. A1, B1, B2 and B3) to take the advantage of the maximum value of thermal neutron flux in the inner channels. The neutron flux variability over irradiation volume was determined experimentally to be less than 2% through measured specific activities of irradiated Cu wires arranged axially and radially inside the vial. The stability of neutron flux throughout the period of irradiation, especially for long irradiation was checked by monitoring the neutron flux reading of a fission chamber connected to the micro-computer control system.

Analysis of the rare earth elements (REEs) measurement is performed by the PC-based gamma-ray spectrometry set-up. However, based on the half-life of product nuclide there used to be a first (4-5 days) and second count (10-15days). In this work, counting was made after 15-18 days of long irradiation which is as a result of a high detector's dead time of 40%. With respect to the long irradiation regime, the first round of counting is carried out for 60 min, following the long irradiation (i.e. L1) using the holder 'H2' after a waiting period of 15-18 days. Samples are counted using the plexi-glass holder ''H2''. The choice of cooling time and sample-detector geometry is such that detector's dead time is controlled to be less than 10%. A description of the irradiation and counting regimes adopted for NIRR-1 facilities in this work as well as the element of interest are given in Table 3.3. Identification of gamma-ray of product nuclides through their energies and quantitative analysis of their concentrations are achieved using the gamma-ray spectrum analysis software, WINSPAN 2004.

**Table 3.3** Irradiation and measuring regimes developed for NIRR-1 facilities

| Neutron flux/irradiation channel | Procedure | $T_{irr}$ | $T_d$ | $T_m$ | Activation products |
|---|---|---|---|---|---|
| $5 \times 10^{11}ncm^{-2}s^{-1}$ inner irradiation channels (B1, B2, B3, and A1) | L1 | 6 h | 4–5 d | 30 min | High detector dead time |
| | L2 | 6 h | 15-18 d | 60 min | **$^{140}$La, $^{141}$Ce, $^{152}$Eu, $^{175}$Yb, $^{177}$ Lu, $^{147}$ Nd**, **$^{160}$Tb** |

**L1**, and **L2** are first and second round of long irradiation counting

# CHAPTER FOUR

## RESULTS AND DISCUSSION

Seven REEs were found in the mineral (Monazite) collected from the study area namely; Four (La, Ce, Nd, Eu) of which were Light Rare Earth Elements (LREE), while three (Tb, Yb, Lu) were Heavy Rare Earth Elements (HREE) as classified in the work of (Henderson 1984).

Table 4.1 presents the average concentration in ppm of the rare earth elements (REEs) in the analysed samples obtained from the study area together with their coordinates.

**Table 4.1:** REE concentration of monazite from different regions investigated (in ppm)

| Sample Area | Latitude | Longitude | La | Ce | Nd | Eu | Tb | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|
| K(1) | N09$^0$57`43.8`` | E008$^0$52`59.2`` | 112300±1460 | 124500±11454 | 37400±4862 | 127±3 | 409±7 | 4160±79 | 125±6 |
| K(2) | N09$^0$57`46.9`` | E008$^0$53`56.3`` | 3914±63 | 12140±1117 | BDL | 17.4±1.9 | 88.6±1.8 | 3884±78 | 354±14 |
| R(1) | N09$^0$57`46.9`` | E008$^0$52`0.26`` | 5966±76 | 22950±2111 | 7664±1027 | 33.7±2.4 | 1310±34 | 1732±52 | 1732±11 |
| B(1) | N09$^0$09`0.65`` | E008$^0$43`57.3`` | 6142±209 | 10990±1011 | BDL | 140±14 | 51.4±2.5 | 1010±25 | 46.4±2.7 |
| B(2) | N09$^0$09`14.6`` | E008$^0$39`13.2`` | 43340±823 | 70480±6484 | 26060±3387 | 75.8±3.1 | 303±5 | 4250±85 | 245±10 |

**K** (kuru), **R** (Rayfield), **B** (Barikin Ladi)

When comparing the REE contents of different rocks or minerals, one generally normalizes the concentrations of the individual REEs to their abundance in chondrites (the meteorites that best represent the composition of the non-volatile fraction of solar system material). Table 4.2 shows the Normalized concentrations of the individual REE to their abundance in chondrites. The REE content (REE signature) which is defined as their normalized concentrations displayed according to their atomic number, typically involves the summation of the total concentrations of all the normalised REEs $(\Sigma REE)_{cn}$ and evidence of fractionation, that is, LREE and HREE ratios, La /Lu ratio, and the presence of Ce or Eu anomalies. This is illustrated in table 4.3. The Geochemical data obtained from the Monazite Rare Earth Elements Chondrites-Normalized $(REE)_{cn}$ values were determined for each sampling area. The chondritic values used for the normalization were those reported by Laul, (1979).

**Table 4.2:** Normalized concentrations of the individual REE to their abundance in chondrites (in ppm)

| Sample Area | REEs (chondritic value) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La(0.34) | Ce(0.87) | Nd(0.64) | Eu(0.037) | Tb(0.047) | Yb(0.22) | Lu(0.034) | La/Lu |
| K(1) | 330294.12 | 143103.45 | 58437.5 | 1739.72 | 8702.12 | 18909.09 | 3676.47 | 89.84 |
| K(2) | 11511.76 | 13954.02 | BDL | 238.36 | 1885.11 | 1765.55 | 10411.76 | 1.11 |
| R(1) | 17547.06 | 26379.31 | 11975 | 461.64 | 27872.34 | 7872.72 | 8176.47 | 2.12 |
| B(1) | 18064.71 | 13083.33 | BDL | 1917.81 | 1093.62 | 4590.91 | 1364.71 | 13.24 |
| B(2) | 127470.59 | 81011.49 | 40718.75 | 1038.36 | 6446.81 | 19318.18 | 7205.88 | 17.69 |

**Table 4.3:** Some geochemical data from the REEs in Nigerian Monazite

| Monazite Area | $(\sum REE)_{cn}$ | $(\sum LREE)_{cn}$ | $(\sum HREE)_{cn}$ | $(\sum LREE)_{cn} / (\sum HREE)_{cn}$ | $(La/Lu)_{cn}$ |
|---|---|---|---|---|---|
| K (1) | 279021 | 274327 | 4694 | 58.44 | 898.4 |
| K (2) | 20398 | 16071.4 | 4326.6 | 3.71 | 11.06 |
| R | 39933.7 | 36613.7 | 3320 | 11.03 | 3.44 |
| BL (1) | 18379.8 | 17272 | 1107.8 | 15.59 | 132.37 |
| BL (2) | 144753.8 | 139955.8 | 4798 | 29.17 | 17.69 |

**K** (Kuru)**, R** (Rayfield)**, BL** (Barikin Ladi)

From the summarized results of analysis of the monazite samples presented in Table 4.1 and Table 4.2, It was noticed that the REEs, La, Ce, Nd, Tb, Yb, and Lu, were rather abundant in all the sitse investigated with Ce being the most abundant as recorded for Kuru 1 Monazite. The amounts of Eu found was very small relative to others for all the study areas as seen in Figure1. Another observation is that the occurrence of LREE is more in abundance as compared to HREE which is the usual trend for all geological matrices. From the geometrical point of view, the REE are "dispersed" (not so rare) elements i.e., they are spread among all the mineral.

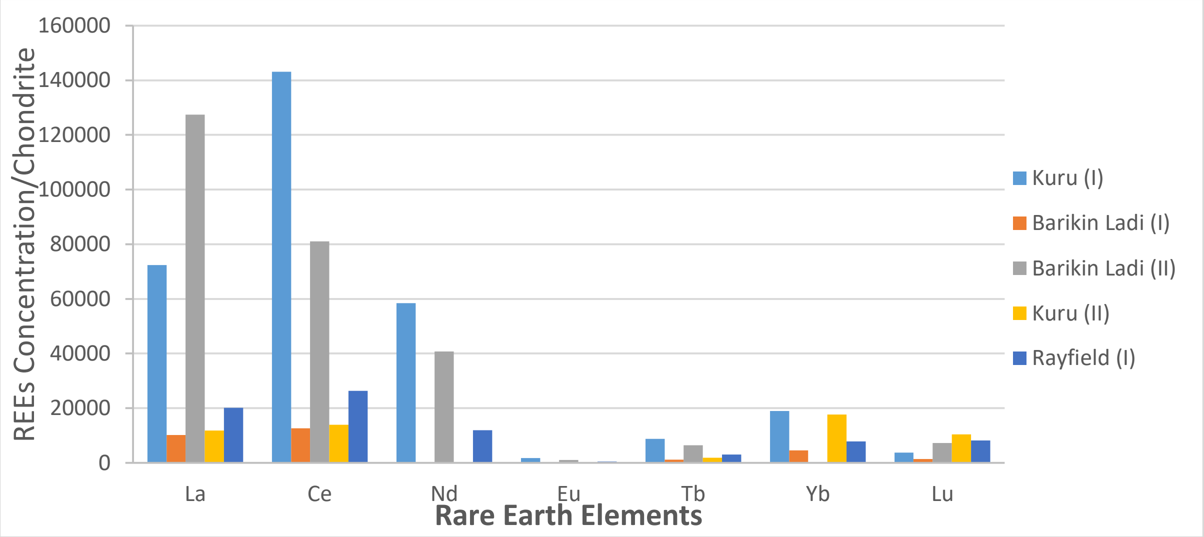

**Figure 4.1:** The concentration of the rare earth elements in the studied area

The REE pattern for some of these Monazites were identical, exhibiting coherent fractionations from LREE to HREE. This trend confirm the abundances of LREE in Monazite over HREE as evident in Chondrites which is a usual trend for all geological matrices (Ewa *et al*., 1996. The overall fractionation of REEs for each Monazite is depicted by the slope of the $(REE)_{cn}$ plot by the (La/Lu)cn ratio as presented in Table 4.3. Kuru 1 and Barikin Ladi 1 Monazite showed high ratio of 898.4 and 132.37 respectively, while others showed concentrations below 17.69 with the least been 3.44 for Rayfield Monazite.

Rare earth elements are found in a variety of minerals and soil but the most abundant REEs are primarily in Monazite and Bastnaesite. Table 4.4 presents a summary of results obtained from the analysis of some rare earth elements for different materials and also show comparison in the concentration of individual REEs.

**Table 4.4:** Comparison in abundance between REEs for monazite and other materials (in ppm)

| Sample Type | Rare Earth Elements (REEs) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | La | Ce | Nd | Eu | Tb | Yb | Lu | References |
| Monazite | 43340 | 70480 | 26060 | 75.8 | 303 | 4250 | 245 | This work |
| Granite | 95.6±2.1 | 138±3.4 | 73.4±5.2 | 3.2±0.1 | __ | 7.7±0.3 | 1.0±0.03 | El- Tahir, (2007) |
| Spessartine | 0.27±0.02 | <0.5 | <1.9 | 1.60±0.07 | 3.93±0.14 | 13.2±0.5 | 3.50±0.8 | Makreski, *et al*, (2011) |
| Almandine | 49.5±1.7 | 100±4 | 43.9±2.0 | 2.24±0.11 | 1.92±0.07 | 19.4±0.7 | 6.07±0.30 | Makreski, *et al*, (2011) |
| Soil | 112.6 | __ | __ | 9.45 | __ | 22.1 | 18.2 | Ladan, *et al*, (2012) |

From table 4.4, it is obvious that generally, concentrations of REEs in other materials are less compared to Monazite. Concentration in La, to Eu are very high while Tb to Lu are relatively high. From this observation, we can conclude that our work has proven that REEs are higher in concentration which agrees well with theory.

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The REEs content of the monazite from the five areas investigated namely; Kuru 1, Kuru 2, Rayfield, Barikin Ladi 1 and Barikin Ladi 2 was evaluated using the INAA method and a total of seven elements were obtained. These elements and their concentration (in ppm) for Kuru 1 are La (112300±1460), Ce (124500±11454), Eu (127±3), Nd (37400±4862), Tb (409±7), Yb (4160±79), and Lu (125±6). Concentration of Cerium (124500±11454) showed the highest as recorded for Kuru 1 monazite. Europium content recoded the least in all the samples.

In order to justify the abundance of the REEs in monazite as theory has shown, a comparison in REEs content in the Monazite used for this work to those obtained from other materials like granite, spessartine, almadine, soil was also carried out. The content of some of the REEs in granite in the work of El-Tahir (2007), showed La (95.6±2.1), Ce (138±3.4), Nd (73.4±5.2), Eu (3.2±0.1), Yb (7.7±0.3), and Lu (1.0±0.03), spessartine (Makreski *et al*, 2011) showed La (0.27±0.02), Ce (<0.5), Nd (<1.9), Eu (1.60±0.07), Tb (3.93±0.14), Yb (13.2±0.5), and Lu (3.50±0.8), almadine (Makreski *et al*, 2011) showed La (49.5±1.7), Ce (100±4), Nd (43.9±2.0), Eu (2.24±0.11), Tb (1.92±0.07), Yb (6.07±0.30), and Lu (3.50±0.8) and soil (Ladan *et al*, 2012) has La (112.6), Eu (9.45), Yb (22.1), and Lu (18.2). Concentration of all the REEs were observed to be higher in monazite which agree well with theory.

## 5.2 Recommendation

Based on the findings in this research work, the following were recommended:

1. Another technique other than NAA should for further studies be used so as to revalidate the present claims. For example, the inductive coupled plasma mass spectroscopy (ICP-MS).
2. Governmental agencies responsible for the control of illegal mining should impose restrictions on the areas where monazites are deposited.
3. A detailed study should be carried out on REEs concentration in order to come up with a potential reason(s) that makes it better utilized for our developing nation.

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