Rare earth elements in Uranium ore for nuclear forensic application

S.O.O. John¹, I.T. Usman², T.C. Akpa¹,³, U. Ibrahim¹

¹Department of Physics, Nasarawa State University, PMB 1022 Keffi, Nigeria
²Nuclear Structure Research Group (NSRG), School of Physics, University of the Witwatersrand, Johannesburg 2050, South Africa
³Radiological Safety Department, Nigerian Nuclear Regulatory Authority (NNRA) Abuja, Nigeria

Abstract. The contents of the Lanthanides, which are Rare Earth Elements (REE), that show consistent patterns under changing geochemical conditions in uranium ore have been studied. The objective is to determine the nuclear forensic parameters inherent to the various uranium ore samples collected from parts of northern Nigeria using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analytical technique for the purpose of baseline data generation and nuclear forensic application. The REE fingerprint obtained in this study suggests that the uranium is of uraninite/pitchblende granitic (vein-type) origin. The REE concentrations varied from 0.011 ± 0.000 ppm to 2.337 ± 0.082 ppm for Riruwai, 0.001 ± 0.000 ppm to 0.035 ± 0.002 ppm for Mika-I, 0.002 ± 0.000 ppm to 0.357 ± 0.007 ppm for Mika-II and 0.001 ± 0.001 ppm to 0.159 ± 0.005 ppm for Michika. A positive correlation between the REEs showed symmetrical chemical properties as well as their overall presence in the samples. The normalised REE/Cl-Chondrites pattern show Light Rare Earth Elements (LREE) enrichment, Heavy Rare Earth Elements (HREE) fractionation with a negative Europium (Eu) anomaly. The ΣLREE/ΣHREE ratio presented varied values for the samples while a negative value of ¹⁴⁴Nd/¹⁴⁴Nd ratio (0.512638) in the Chondritic Uniform Reservoir (CHUR) εNd(-0.64285) suggested LREE uniformity and radiogenic origin.

Keywords: Lanthanide patterns, Uranium ore, REE, Negative anomaly, Signature

1. Introduction

The information inherent to a nuclear material is revealed by the application of nuclear forensics and in nuclear security, it is an important component [1,2]. Nuclear forensics is the detailed investigation performed on a nuclear and other radioactive material in order to identify the possible origin, intended use and hazards related to the material, following its seizure from illicit trafficking or diversion [3-5]. Nuclear forensics considers the fact that
some measurable parameters or signatures are unique based on the geological source of the material under investigation [1,2]. A wide range of samples of nuclear and other radioactive materials from around the world have been successfully studied and characterised while signatures such as uranium isotopic compositions and ratios, elemental impurities, rare earth elements (REE) patterns, Neodymium (Nd), Strontium (Sr) and Lead (Pb) have been determined [5-10]. However, African region with abundant deposits of natural uranium still has a gap in data, which is yet to be filled [11].

Uranium ore concentrate (UOC) otherwise called yellowcake, which is produced from mined and milled uranium ore, is further processed to fabricate nuclear fuel for use in nuclear power plants [12,13]. The process has found a significant application in nuclear forensics, as the IAEA Illicit Trafficking Database [13] declared many incidents of trafficking in low-grade material with natural uranium (NU) inclusive. The mode of deposition of uranium ore mineral imparts greatly on the exhibited characteristics of the trace, REE, and isotopic signatures that relate to their chemical and other characteristics [14,15]. Therefore, characterising of various ores in order to obtain nuclear forensic signatures so as to trace their origin, is an imperative task.

Rare earth elements (REE) or lanthanides composition of uranium ores (uraninite and pitchblende) is a powerful tool to understand uranium deposits formation [15]. The fractionation of REEs in uranium ores presents a unique pattern [16], which is related directly to the variability of the process of mineralogy and geological settings between the deposit types of uranium, and its origin [17,18,19]. Therefore, they are an important signature to identify the ore-type and source used in uranium ore concentrate production [19,20].

Neodymium (Nd) isotope is a part of the lanthanide series or rare earth elements (REE). Nd is present at trace levels, (under μg/gU) in natural uranium-based nuclear material and it serves as a suitable reference isotope because it is not altered by radioactive decay [9]. Its ratios of $^{143}\text{Nd}/^{144}\text{Nd}$ have provided a reliable forensic signature since it is not prone to weathering, with potentials in identifying deposits of uranium from a given sample [21,22]. The Nd ratio in nature vary due to the presence of the long-lived parent nuclide of samarium ($^{147}\text{Sm}$, $T_{1/2}=1.06 \times 10^{11}$ years; $\lambda = 6.54$ E-12 y$^{-1}$) that decays to $^{143}\text{Nd}$, by alpha decay. The ratio $^{143}\text{Nd}/^{144}\text{Nd}$ is dependent on the type and age of the minerals and vary over range of 0.511 – 0.516 (1% only) with Sm/Nd amount ratios ranging from 0.05 to 0.8 in various uranium ores and ore concentrates samples [22]. However, it remains more consistent than other isotope ratios for a series of samples and that makes it the most promising signature for uranium bearing materials provenance emerging [7,23].

More so, variations in Nd isotopic ratio are also expressed as relative values by the use of a notation denoted by $\varepsilon$ determined using Eq. 1 as taken from Ref. [9,24].

$$\varepsilon_{\text{Nd.CHUR}} = \left( \frac{n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{sample}}}{n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{CHUR}}} - 1 \right) \times 10^4$$

where $n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{sample}}$ is the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in the sample, and $n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{CHUR}}$ is the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (0.512638) in the Chondritic Uniform Reservoir (CHUR).
The provenance of rock is shown by the positive or negative $\varepsilon_{\text{Nd}}$ values of the isotopic ratio $^{143}\text{Nd}/^{144}\text{Nd}$ in the sample. If a negative value of $\varepsilon_{\text{Nd}}$ is obtained, it means the rare-earth pattern of the rock or its precursors is enriched in light rare-earth elements (LREE) and vice versa[9,21].

The objective of this study is to determine the nuclear forensic parameters inherent to the various uranium ore samples collected from parts of northern Nigeria using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analytical technique for the purpose of baseline data generation and nuclear forensic application.

2. Study Location

The study area covers accessible locations in parts of northern Nigeria where mining activities of uranium ores are obtainable, which includes Adamawa (Michika) on N10° 39' 51"; E13° 29' 20", Kano (Riruwai) on N10° 43.340'; E008° 47.007' and Taraba (Mika) areas on N8° 58' 46"; E11° 36' 23" and N8° 58' 47"; E11° 36' 23", respectively. Global Positioning System-GPS navigator (eTrex 10 GARMIN USA) was used to register the coordinates of each sample locations. The map of sampling area of this study is shown in Figure 1.

Riruwai mine site is located at Kaffo, 10 km east of Riruwai, in Kano state, north-western Nigeria. The area was described as a ring complex, which composed of elliptical multiphase granitic massif bodies with related quartz veins that intruded into Pan-African basement. As Greisenized granite Precambrian (Age 541 - 4000 Ma) and part of Nigerian Younger granite provinces that comprises mainly of granitoids and volcanic rocks, it is endowed with 28 valid minerals, including gold, pyrochlore, coffinite, thorite and zircon. It is chemically different from the basement suites of per-alkaline and sub-alkaline [25, 26, 27]. Mika and Michika mine sites are however, located at Taraba and Adamawa states respectively, both in north-eastern Nigeria. Uranium mineralisation in the north-eastern Nigeria is of sandstone-hosted and vein-type mineralisation. Mika area are more of granites with fine-grained granite, medium-grained granite and porphyritic granite. Both primary and secondary uranium mineralisation is rhyolite and occurs at depth for pitchblende while near surface are mainly meta-autunite and coffinite [29]. Michika is made up of mostly granitic rocks associated with rhyolite veins and brecciated, silicified and mylonitized rocks. The area is underlain by crystalline basement rock of Precambrian age [30]. The Vein-type (Granite related U-deposit) mineralisation occurs in the granitoids, the major occurrences being deposits of Gubrunde, Kanawa, Ghumchi-Michika, Mika and Monkin-Maza.
Figure 1: Map of Nigeria showing Uranium Ore Sample Mine Sites (Riruwai, Mika-I, Mika-II and Michika) for this Study

3. Material and methods

3.1 Sample collection and counting

Based on the geological features and mineralisation of the sampling location, about 2.0 kg each of the uranium ore rock samples were collected at open pit-mining sites, and immediately transferred into a zip-lock plastic bag to avoid contamination. Figure 1 illustrate the study area. ICP-MS analytical technique require that sample be introduced in liquid or aerosol form. Hence, the rock samples were crushed and milled into powder texture, using Dickie and Stockler TS-250, Johannesburg, crushing and pressurised milling machines. Anton Paar Multiwave, PerkinElmer Germany, digital Microwave Digestive System was used to dissolve the samples. About 0.5 g of the sample weighed into Microwave digester vial and 2.0 mL of distilled water added, with 2.0 mL of concentrated HNO₃, 6.0 mL concentrated HCl and 0.5 mL H₂O₂. The vials containing the aliquot of sample are sealed into rotor, placed into the microwave reactor system then heated at 180 °C for a maximum period of 50 minutes. An aqueous solution in acidified matrix then obtained. The dissolved samples were then filtered using polyvinylidene fluoride (PVDF) 0.22 μm. A diluent, composed of 5 % (50 mL) HNO₃ and 1 % (10 mL) HCl acids, was added to the filtrate in two sets - by 10 % and 50 %. Both the prepared and blank samples, the calibration standards and quality control samples were
placed into the auto-sampler, for ICP-MS measurement and calibration, more details obtainable at [31,32]. Prior to the upload of the samples into the low flow sample introduction system, nitric acid was used to clean the tubing, to avoid washing of residual memory. The cleaning and rinsing of the tubing was repeated to avoid cross contamination per sample measurement. The samples are introduced into the nebuliser containing plasma at atmospheric pressure, with an extremely high temperature – 10,000 °C, which makes for easy transition of most elements from atoms to ions. Mostly, single charged positive ions are formed and because argon plasma is used, it becomes relatively simple for mass spectra to be generated and interpreted. The plasma ionises the samples and then through a vacuum interface, transfer to the mass analyser – A hyperbolic quadrupole mass analyser, which is sequential thereby measures elements in sequence. Due to ICP-MS abundant sensitivity, superior adjacent peak separation was achieved[31]. The separated ions are then detected by the ICP-MS detection system – a fast simultaneous dual mode detector (of 9 orders dynamic range), giving rise to data acquisition. Fifty elements were measured/identified including $^{238}$U, $^{232}$Th, trace elements and rare earth elements (REE), upon completion of measurement. The process is automatic and computerised. The control is performed on the computer system via an installed software - ICP-MS MassHunter Workstation software. The Agilent 7700 series, Agilent Technologies, Inc. USA, Inductively Coupled Plasma Mass Spectrometry was used for sample analysis with Rhodium Internal Standard, at Environmental Analytical Chemistry (EAC) Laboratory, University of the Witwatersrand, Johannesburg, South Africa.

4. Results and Discussion

4.1 Rare earth Elements (REE) Concentrations

REE which is the lanthanide series contains 15 elements of which promethium (Pm) is not captured in analysis because it is unstable. Table 1 presents the analytical data for REE concentration obtained in this study. The concentration range of the REE is 0.011 ± 0.000 ppm (Eu) to 2.337 ± 0.082 ppm (Ce) having a mean of 0.441 ppm and standard deviation of 0.615 for Riruwai. 0.0001 ± 0.0001 ppm (Lu) to 0.035 ± 0.002 ppm (Ce) with a mean of 0.008 ppm and standard deviation of 0.010 for Mika-I. 0.002 ± 0.000 ppm (Lu) to 0.357 ± 0.007 ppm (Ce) with a mean of 0.067 ppm and standard deviation of 0.099 for Mika-II and 0.001 ± 0.0003 ppm (Lu) to 0.159 ± 0.005 ppm (Ce) with a mean of 0.031 ppm and standard deviation of 0.046 for Michika. The lowest concentration value for the respective samples was presented by lutetium (Lu), except for Riruwai, which was from Europium (Eu) while the highest values were from Cerium (Ce). The ΣREE concentration for the investigated samples shown in Table 1, varied from 0.1028 ± 0.008 ppm to 6.179 ± 0.185 ppm, while that for Lu is 0.020 ppm and for Ce is 2.888 ppm. The concentration of REE tend to decrease with increase in atomic number, according to the Oddo-Harkins rule [33,34]: Ce > La > Pr > Sm > Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm > Lu. A similar order was presented by the ore samples in this study, with few exceptions in Dy enrichment and Eu depletion.

The ΣLREE concentrations ranged from 0.385 ppm to 4.992 ppm higher than that of ΣHREE concentrations, which varied from 0.014 ppm to 1.187 ppm. The ΣLREE/ΣHREE ratio presented varied values for the samples, indicative of LREE enrichment.
The REE bar graphs in Figure 2 showed similar pattern with varying concentration for the respective sample locations. Higher peaks (corresponding to higher concentrations) skewed to the left, at Cerium (Ce), Lanthanum (La) and Neodymium (Nd) but at varying concentrations an indication of light-REE property [34,35]. The statistical significance of these variations were determined by applying ANOVA or F-test on the dataset.

Table 1: Rare Earth Elements (REE) contents (ppm) from Uranium ore samples

| REE  | Riruwai     | Mika-I      | Mika-II     | Michika     |
|------|-------------|-------------|-------------|-------------|
| La   | 0.847 ± 0.024 | 0.019 ± 0.001 | 0.147 ± 0.004 | 0.087 ± 0.003 |
| Ce   | 2.337 ± 0.082 | 0.035 ± 0.002 | 0.357 ± 0.007 | 0.159 ± 0.005 |
| Pr   | 0.276 ± 0.006 | 0.005 ± 0.000 | 0.051 ± 0.009 | 0.020 ± 0.001 |
| Nd   | 0.906 ± 0.020 | 0.017 ± 0.001 | 0.184 ± 0.004 | 0.076 ± 0.002 |
| Sm   | 0.296 ± 0.010 | 0.005 ± 0.001 | 0.044 ± 0.002 | 0.017 ± 0.001 |
| Eu   | 0.011 ± 0.000 | 0.002 ± 0.001 | 0.011 ± 0.000 | 0.005 ± 0.000 |
| Gd   | 0.319 ± 0.007 | 0.006 ± 0.001 | 0.045 ± 0.002 | 0.021 ± 0.001 |
| Tb   | 0.079 ± 0.002 | 0.001 ± 0.000 | 0.008 ± 0.000 | 0.004 ± 0.001 |
| Dy   | 0.499 ± 0.015 | 0.006 ± 0.001 | 0.040 ± 0.002 | 0.021 ± 0.001 |
| Ho   | 0.105 ± 0.005 | 0.001 ± 0.000 | 0.007 ± 0.000 | 0.004 ± 0.002 |
| Er   | 0.287 ± 0.008 | 0.003 ± 0.000 | 0.019 ± 0.001 | 0.010 ± 0.001 |
| Tm   | 0.037 ± 0.001 | 0.001 ± 0.000 | 0.003 ± 0.000 | 0.002 ± 0.002 |
| Yb   | 0.163 ± 0.004 | 0.002 ± 0.000 | 0.013 ± 0.001 | 0.008 ± 0.003 |
| Lu   | 0.017 ± 0.001 | 0.000 ± 0.000 | 0.002 ± 0.000 | 0.001 ± 0.001 |
| ΣLREE| 4.992         | 0.089        | 0.839        | 0.385        |
| ΣHREE| 1.187         | 0.014        | 0.092        | 0.050        |
| ΣREEs| 6.179         | 0.1028       | 0.931        | 0.435        |
| ΣLREE/ΣHREE| 4.206 | 6.343 | 9.119 | 7.700 |

The analysis result for the REE data in Table 2 showed that, the F-values for the nuclide observed were greater than the F-critical. Implying that the differences in the measured values were not due to chance. In addition, P-values obtained were <0.05, indicating a very low probability that the differences were just a coincidence. A nuclide, Holmium (Ho) was undefined and no decision taken on it. Hence, it can be inferred that there was statistical significance in the differences in isotopic composition of the rare-earth elements (REE) in this study. They can be applied to nuclear forensic investigations as a viable signature.
**Figure 2:** Bar chart of Rare Earth Elements concentrations for the samples locations in this study.

**Table 2:** REE descriptive statistics for the uranium ore samples

| REE | F-Value | F-Critical | P-Value   |
|-----|---------|------------|-----------|
| La  | 7.016   | 3.49       | 0.006     |
| Ce  | 6.329   | 3.49       | 0.008     |
| Pr  | 6.979   | 3.49       | 0.006     |
| Nd  | 1.124   | 3.49       | 0.379     |
| Sm  | 6.361   | 3.49       | 0.007     |
| Eu  | 21.716  | 3.49       | 3.85E-05  |
| Gd  | 7.739   | 3.49       | 0.004     |
| Tb  | 7.851   | 3.49       | 0.003     |
| Dy  | 7.234   | 3.49       | 0.005     |
| Ho  | Undefined | 3.49   | Undefined |
| Er  | 6.841   | 3.49       | 0.006     |
| Tm  | 7.212   | 3.49       | 0.005     |
| Yb  | 7.298   | 3.49       | 0.005     |
| Lu  | 7.228   | 3.49       | 0.0078    |
The REE data were normalised by applying values of chondrite from Anders and Grevesse 1989[36], considered to consistently give the smoothest “REE patterns” for the wide variety of rock types [37]. From Figure 3a-d, the spectra and chondrite normalised REE pattern followed distinctive trend. Both showing a decrease in order of light REE to heavy REE with a Europium (Eu) anomaly, typical of granitic vein deposits. For Figure 3a, Riruwai sample had peak at Ce, with negative Eu anomaly. Figures 3b-dof Mika-I, Mika-II and Michika samples, both had peaks at La and lows at Lu, with negative Eu anomaly except for Mika-I sample. All peaks were at varying concentrations though. The REE characteristics show enriched Light-REE and depleted Heavy-REE, indicative to have fractionation with anomaly for Eu because of the distribution of REE in granitic mineralisation. Results in this study are comparable to the study by [17,19,20,23] and provide a unique signature for the respective samples.

Figure 3: Chondrites-normalised rare earth elements spectra of samples in this study
4.2 Neodymium (Nd) Isotope

Neodymium isotopes are part of REE and their ratios ($^{143}\text{Nd}/^{144}\text{Nd}$) offer a good forensic signature to determine uranium bearing material origin[7]. In this study, $^{146}\text{Nd}$ was measured by ICP-MS while other isotopes were determined from their abundance compositions obtained from Reference [38,39] of 17.20%, 23.80% and 12.20% for $^{146}\text{Nd}$, $^{144}\text{Nd}$ and $^{143}\text{Nd}$, respectively. Eq. 2 [40] was used and the isotopic concentration are presented in Table3.

\[
C_{^{143}\text{Nd}} = \frac{12.20}{17.20} \times C_{^{146}\text{Nd}}
\]  

(2)

where $C_{^{143}\text{Nd}}$ and $C_{^{146}\text{Nd}}$ are the concentrations of the $^{143}\text{Nd}$ and $^{146}\text{Nd}$ respectively. The value for the concentration of $^{144}\text{Nd}$ was also determined in similar way by replacing $^{143}\text{Nd}$ with $^{144}\text{Nd}$ together with the corresponding composition.

The range of isotopic concentrations for samples are 0.016 ± 0.001 ppm to 0.906 ± 0.039 ppm for $^{146}\text{Nd}$, 0.023 ± 0.001 ppm to 1.253 ± 0.055 ppm for $^{144}\text{Nd}$ and 0.012 ± 0.001 ppm to 0.642 ± 0.028 ppm. These values are comparable to those reported by [9,20], for vein type sample. The isotopic ratio $^{143}\text{Nd}/^{144}\text{Nd}$ has a variation range of 0.50967 to 0.51660[20]. Table 3 column 5 show that a common value of 0.512605 was obtained for all the samples in this study, which is within range. Significant variations might have not been observed, perhaps, because the isotopic composition was used in determining the concentrations.

As it can be observed from Table 3, column 6, a negative value of $\varepsilon_{\text{Nd}}(-0.64285)$ was obtained using Eq. 1. That implied that the rock sample in this study was enriched with LREE, which serve as a distinct signature for nuclear forensic attribution [41].

| Sample Location | Neodymium (Nd) isotopic concentrations (ppm) | $^{143}\text{Nd}/^{144}\text{Nd}$ | $\varepsilon_{\text{Nd, CHUR}}$ |
|-----------------|------------------------------------------|----------------------------------|--------------------------|
| Riruwai         | $0.906 \pm 0.039$ | $1.253 \pm 0.055$ | $0.642 \pm 0.028$ | $0.512605$ | -0.64285 |
| Mika-I          | $0.016 \pm 0.001$ | $0.023 \pm 0.001$ | $0.012 \pm 0.001$ | $0.512605$ | 0.64285 |
| Mika-II         | $0.184 \pm 0.008$ | $0.255 \pm 0.011$ | $0.131 \pm 0.006$ | $0.512605$ | -0.64285 |
| Michika         | $0.076 \pm 0.003$ | $0.105 \pm 0.004$ | $0.054 \pm 0.002$ | $0.512605$ | -0.64285 |
Figure 4: Neodymium (Nd) isotopic concentration and ratio from this study

Figure 4 show the bar graph for the Nd isotopic concentration. Riruwai samples from Figure 4a presented higher concentrations while Mika-I showed the lowest concentrations. The concentrations showed significant variations across and between mines. Nd isotope concentration in this study therefore provided a unique signature applicable in nuclear forensic investigation.

Figure 4b showed plot of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, with an invariant value of 0.512605 but within the natural Nd ratio range of 0.510 to 0.515 ± ~40 epsilon units [7] and comparable to the vein-type value of 0.51291 (68) for the USA ESI mine[20]. The similarity in the ratio reduces the possibility to differentiate the origin of the samples, however, it can still be used as supplementary information in order to characterise it. Further comparative analysis of the
ratio in terms of the Chondritic Uniform Reservoir (CHUR) yielded negative value of -0.64285. It implied that, comparing with chondritic value of rocks, the ratio of Sm/Nd was lower, based on Earth history. Meaning further, that the rare-earth pattern of the rock from this study was enriched in Light-REE.

5 Conclusion

The rare-earth elements concentration in uranium ore samples from parts of northern Nigeria have been determined. The Rare Earth Elements (REEs) were chondrite normalised and presented isotopic spectrum patterns that varied between mines. The dataset of REEs concentration were subjected to ANOVA test and yielded result that was unique enough to differentiate between the mines. Isotopic concentrations of Nd as part of REE analysed showed they are a distinct signature sufficient to differentiate between the various locations. The Nd relative ratios subjected to Chondritic Uniform Reservoir (CHUR), confirmed that the samples in this study do possess the REE pattern of the rock (or its precursors) that was enriched in light rare-earth elements (LREE). The REE signature results in this study suggests that uranium is of uraninite and pitchblende ore sources [19]. The following can therefore, be used to create nuclear signature for the respective mined samples - the concentrations and spectrum patterns of Rare-Earth Element (REE); the isotopic concentrations of Nd ($^{146}$Nd, $^{144}$Nd and $^{143}$Nd) and their corresponding ratios $^{143}$Nd/$^{144}$Nd. The implication of this research is that, these samples can be identified by their respective signatures that can be added up to National Nuclear Forensic Library (NNFL) for reference in support of investigation to curb illicit trafficking and smuggling of nuclear and other radioactive materials of this origin.

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