Characterization of uranium in soil samples from a prospective uranium mining in Serule, Botswana for nuclear forensic application

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ABSTRACT
This study attempts a nuclear forensic characterization of uranium in soil samples from a prospective Serule mine in Botswana. The analysis involves the determination of forensic signatures found in uranium-bearing materials from the mine. These signatures include $^{232}$Th activity concentration, isotopic and activity ratios of $^{232}$Th/$^{238}$U and $^{235}$U/$^{238}$U, impurity concentration, rare earth elements (REE), as well as the mineralogy of the area, all of which were determined using both Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and X-ray Florescence (XRF) analytical techniques. Isotopic ratios determined reveal that there is a significant difference in the isotopic concentration, activity concentration of $^{232}$Th, $^{238}$U, and $^{235}$U, as well as the $^{232}$Th/$^{238}$U isotope ratio between the uranium ores from each mine. The REE/chondrite analysis indicates clear patterns, suggesting that it is possible to use this feature as a unique identifier for Serule uranium ore source.

1. Introduction
The growing interest in uranium mining in Africa has created a need for implementation of safety and security measures to prevent and respond to the illegal use of nuclear and other radioactive materials. The use of nuclear forensic techniques to create a national nuclear library is one such measure. similar to traditional forensics, nuclear forensics relies on the knowledge that there are measurable parameters that are characteristic of a particular material (Hutchison et al., 2013). These parameters are added into a database to enable comparison with analytical results of materials found out of regulatory control to facilitate the attribution process (Moody et al., 2014). In order to determine the origin of unattributed nuclear/radioactive material, a reference database containing signatures must be available (Keegan et al., 2017).

Although Lawrence Livermore group has created a large database, there are samples from African countries that are not part of the database. Very little research has been conducted pertaining to African countries that have uranium deposits (Mathuthu & Khumalo, 2017). Some countries such as South Africa, Namibia, Zambia, and Tanzania have been actively mining uranium as a primary or secondary product (Dasnois, 2012). South Africa has 71 uranium mines, Namibia has 42, Senegal, Tanzania, and Zambia have 10, Botswana has 9 and Nigeria has 2 (Mathuthu & Khumalo, 2017). These countries must observe the International Atomic Energy Agency (IAEA) Nonproliferation Treaty, which aims at safeguarding nuclear and other radioactive material to prevent illicit trafficking. Countries should therefore have National Nuclear Forensic Programs aimed at the characterization of nuclear and other radioactive material found in and out of regulatory control (Dunworth, 2013). This characterization involves the determination of chemical and isotopic concentration as well as physical parameters, which form signatures of the origin. Currently, there is no African country with a developed National Nuclear Forensic Library. Although South Africa has started, it does not possess a fully functional nuclear forensic laboratory (Mathuthu & Khumalo, 2017).

This study focuses on the Southern African region of Botswana, which has prospective uranium mining projects in the regions under investigation. The aim of this study is to analyze and characterize soil samples from Serule. The measured parameters will include the isotopic composition, concentration of the rare earth elements and the impurity spectrum. In addition to these parameters, the mineralogy of the samples will be determined. Thus, information and signatures found in this study can therefore be added to a National Nuclear Forensics Library and used as reference data to aid in source attribution of nuclear material found in and out of regulatory control.

2. Materials and methods
Thirty (30) slightly disturbed soil samples were randomly collected from five sampling areas S5-S9 from the Serule in Botswana where planned uranium mining

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projects are foresighted. Botswana lies between latitudes 17 and 27, longitudes 20 and 30 occupying 581,730 km² land area (Wikipedia contributors, 2019). Uranium deposits are primarily sandstone hosted roll-front/calcrete deposits, found in Gojwane, Serule, and Gorgon regions. The samples under investigation were sandstone collected from Serule region of Botswana shown in Figure 1.

2.1. Sample collection

In this study, the samples collected were in the soil matrix. Soil samples are easily collected, prepared, and stored, and they serve as proficient sorbents of actinides, lanthanides, and transition-metal analytes. Nuclear analytes sorb on soil by wet and dry atmospheric deposition processes, accidental release, and transport activities. Thirty (30) slightly disturbed soil samples were randomly collected from five sampling areas S5-S9 across the planned uranium mining area. At the sampling points, a bucket auger was used to drill into the ground and the samples were collected at a depth of 60 cm. Each sample was transferred into a polythene zip lock bag, weighed, and labeled accordingly. For detailed information on the sample collection procedures see Ref (Masok et al., 2018). The samples were then transported to the University of Witwatersrand (WITS) in the Republic of South Africa for subsequent measurements and analysis.

2.2. Sample preparation

Sample preparation is a significant part of the analytical process. For better precision and an accurate representation, samples need to be homogeneous prior to analyses. To guarantee homogeneity, all the samples collected were taken to the WITS University Geosciences Laboratory for crushing and pulverization. The milling media and grinding discs were washed with ethanol, and in addition, extra pure sand was grounded before milling of a new sample to avoid cross-contamination of samples. Once milled, the samples were then transferred into sealed bags, re-tagged, re-weighted, and transferred for storage awaiting measurement and analysis. Measurements and analysis of the samples were conducted at these two laboratories; WITS Analytical Chemistry Laboratory and WITS Earth Laboratory.

2.3. Instrumentation

The analysis required in the study was performed using ICP-MS and XRF analytical methods. Several techniques can be used for elemental analysis; of these techniques, ICP-MS offers a wider range of detection limits, multi-element analysis, and isotopic capabilities and time-efficient. Although highly accurate, ICP-MS cannot be directly used on solid samples but requires samples to be in liquid form. Samples in the soil matrix, such as those under investigation were therefore dissolved prior to measurements. In this study, Agilent Technology, 7700 Series ICP-MS was used for the measurement.

For the complete dissolution of the samples, a microwave system (Anton Paar Multiwave, PerkinElmer Germany) was used. 0.5 g of each sample was transferred into Teflon microwave vessels in preparation for acid digestion. The samples were diluted with deionized water, aqua rigia (a 1:3 mixture of HNO₃ and HCl respectively), and H₂O₂, then sealed and placed in a microwave. The system starts and slowly increases to a maximum of 190°C then drops back over a period of 30 minutes. An

![Figure 1. Map of Serule region in Botswana where samples were collected (Erdi-Krausz et al., 2003).](image-url)
aqueous was then obtained. Parameters used in the microwave digestion of milled soil samples into the liquid matrix are listed in Table 1.

For ICPMS measurements, the 0.5 g of each of the samples in the batch was taken, duplicated, and labeled. The samples were then diluted with 10 ml of HCl and 50 ml HNO₃. The digested samples batch together with the calibration standards (5 ppb, 20 ppb, 50 ppb, 100 ppb, 1000 ppb), blank samples, and quality control samples (20 ppb, 100 ppb) were loaded into the autosampler for measurements. The batch of samples was introduced to the nebulizer containing plasma (argon) at atmospheric pressure and a temperature of 10 000°C. The plasma ionizes the samples and transfers them through a vacuum interface to the hyperbolic quadrupole mass analyzer which measures elements in the sequence. The separated ions are then detected by the detection system, a fast simultaneous dual-mode detector (of nine orders dynamic range). The detection limits of the ICP-MS system in standard mode are shown in Figure 2.

Enhanced data analysis and reporting were performed using MassHunter software. A total of 40 nuclides were observed in the samples under investigation and results given in parts per billion (ppb). The isotopes measured include ²³²Th, ²³⁸U, REE, and impurity elements, which are of particular interest in nuclear forensic studies. The concentrations of the isotopes were provided in units of ppb for the different dilution factors.

For XRF, the samples were taken to the School of Geosciences Earth LAB where they were measured using Malvern Panalytical Axios WDXRF spectrometer. Once the experiment was done and measurements were concluded, the results were then provided for further analysis as discussed below.

2.4. Method of analysis

2.4.1. Determining the Isotopic concentration of ²³⁵U

The concentrations of ²³⁸U were not determined directly from the ICP-MS measurements. However, the isotopic abundance of uranium is constant in nature (99.27% ²³⁸U, 0.711% ²³⁵U) (Masok et al., 2018; Moody et al., 2014). Therefore, the concentration of ²³⁵U can thus be determined from the concentration of ²³⁸U by applying Eqn. 1.

\[
C_{U235} = \frac{0.0711}{99.27} C_{U238}
\]  

where \(C_{U235}\) and \(C_{U238}\) are the concentrations of ²³⁵U and ²³⁸U, respectively.

2.4.2. Determining the Activity concentration of ²³²Th, ²³⁸U, and ²³⁵U

The natural radioactivity of an environment is due to its geological and geographical conditions. These conditions are related to the activity concentrations of Th, U, and K of each rock type and have different levels in soil across the different regions of the globe (Bajoga et al., 2015). For the purpose of this study, the focus is primarily on Th and U. The elemental concentrations of these three radionuclides (²³²Th, ²³⁵U, and ²³⁸U) was converted into activity concentration in Bq.kg⁻¹ using Eqn. 2 (Bajoga et al., 2015):

![Figure 2. 7700 series ICP-MS detection limits (Garcia, 2020).](image-url)
where $A_E$ is the activity concentration of the nuclide E in the sample, $M_E$, $\lambda_E$ and $f_{AE}$ are the atomic masses (kg.mol$^{-1}$), decay constant (s$^{-1}$), and the measured elemental concentrations (ppm) of E, respectively. $N_A$ is Avogadro’s number (6.023 $\times$ 10$^{23}$ atoms.mol$^{-1}$) and C is a constant with the value 10$^6$.

The activity concentrations of $^{232}$Th, $^{235}$U and $^{238}$U can also be calculated from their measured elemental concentrations ($A = f_{AE}$) using the IAEA recommended conversion factors stated below (Spano et al., 2017; United Nations Scientific Committee on the effects of Atomic Radiation. Unsccear, 1998);

$$1.0^{(232)\text{Th}} = 4.06A^{(232)\text{Th}}$$

$$1.0^{(238)\text{U}} = 12.4A^{(238)\text{U}}$$

$$1.0^{(235)\text{U}} = 80.0A^{(235)\text{U}}$$

where $A^{(232)\text{Th}}$, $A^{(238)\text{U}}$, and $A^{(235)\text{U}}$ are the activity concentrations of $^{232}$Th, $^{238}$U, and $^{235}$U, respectively, in units of Bq.kg$^{-1}$. Determining the activity concentrations of Th and U using Eqn. 2 is consistent with the conversion factors shown in Eqn. 3, 4 and 5 given by the IAEA.

3. Results and discussion

This study was conducted to find the elemental composition of the uranium mined soil samples and determine the measured characteristic parameters that are relevant to nuclear forensics. In this section, the experimental results were analyzed and the characteristic signatures determined.

3.1. Characterization of uranium mined samples

ICP-MS was used to determine the elemental and isotopic concentrations of sample under investigation, while the XRF was applied on the samples to determine the major compounds in the samples. Table 2 shows the concentrations in parts per million (ppm) of $^{232}$Th, $^{235}$U, and $^{238}$U as measured by ICP-MS. The results from Table 2, illustrated in Figure 3, were used to calculate the activity concentrations in Bq.kg$^{-1}$ of $^{232}$Th, $^{235}$U, and $^{238}$U using Eqn 2 and the results are shown in Table 3 illustrated in Figure 4. Table 4 shows the activity ratios $^{232}$Th/$^{235}$U and $^{235}$U/$^{238}$U. These parameters, along with the rare earth elements (REE) profile and impurity spectrum are of interest in nuclear forensics investigations.

3.1.1. Uranium and Thorium composition in the samples

The results for the uranium and thorium isotopic concentrations in ppm for the individual sampling area are summarized in Table 2.

- $^{232}$Th

According to literature, the average crustal elemental concentration of $^{232}$Th is in the range 8–12 ppm (Erdi-Krausz et al., 2003). S9 has $^{232}$Th concentration of 6.797 $\pm$ 0.544 ppm. This range falls below the average crustal concentration. S5, S6, S7, and S8 range from 8.016 $\pm$ 0.641 ppm to 12.578 $\pm$ 1.006 ppm and fall within the average range. The mean isotopic concentration in

![Figure 3. Isotopic concentrations of $^{232}$Th, $^{235}$U, and $^{238}$U from the sampling areas as measured by ICP-MS.](image-url)
the world average range with a mean isotopic concentration of 3.40 ± 1.13 ppm, and mean isotopic concentration of 235U of 0.02 ± 0.01 ppm.

3.1.2. Activity concentration of uranium samples

The activity concentration serves as a valuable parameter in nuclear forensics. Table 3 shows the specific activity concentrations of 232Th, 238U, and 235U for the samples in Bq·kg⁻¹.

- **232Th**

The average activity concentrations of 232Th in the continental crust and in soil are 44 Bq·kg⁻¹ and 37 Bq·kg⁻¹ (Maxwell et al., 2013). S5, S8, and S9, had activity concentrations of 35.95 ± 1.80 Bq·kg⁻¹, 32.87 ± 1.64 Bq·kg⁻¹, and 31.52 ± 1.58 Bq·kg⁻¹, lower than the continental averages. S6 and S7 had activity concentrations of 37.30 ± 1.39 Bq·kg⁻¹ and 35.95 ± 1.39 Bq·kg⁻¹ with significantly higher values than the continental averages. The mean activity concentration of the area was therefore found to be 39.50 ± 10.53 Bq·kg⁻¹. The activity concentration graph in Figure 3(a) displayed slight variations, the activity concentrations obtained were therefore characteristic of the area.

- **238U and 235U**

From literature, average activity concentrations of 238U in the continental crust and soil are 36 Bq·kg⁻¹ and 22 Bq·kg⁻¹, respectively (Maxwell et al., 2013). The samples had concentrations ranging from 37.32 ± 1.87 to 65.77 ± 2.29 Bq·kg⁻¹ higher than the continental crust with the exception of S5 and S8 which were found to have activity concentration of 32.87 ± 1.64 Bq·kg⁻¹ and 31.52 ± 1.58 Bq·kg⁻¹. The mean activity concentration in the area was found to be 42.50 ± 13.98 Bq·kg⁻¹. The low activity concentrations of 235U compared to that of 238U were due to the natural abundance of the isotopes in the earth’s crust, i.e. 235U (0.75%) and 238U (99.8%). The activity concentration of 235U had a range of 1.47 ± 0.74 Bq·kg⁻¹ to

### Table 3. Activity concentrations of 232Th, 238U, and 235U from the sampling areas.

| Sample | 232Th (Bq·kg⁻¹) | 235U (Bq·kg⁻¹) | 238U (Bq·kg⁻¹) |
|--------|----------------|----------------|----------------|
| S5     | 35.95 ± 1.80   | 32.87 ± 1.64   | 31.52 ± 1.58   |
| S6     | 49.81 ± 2.49   | 65.77 ± 2.29   | 51.32 ± 2.57   |
| S7     | 51.32 ± 2.57   | 43.50 ± 2.18   | 32.71 ± 1.64   |
| S8     | 27.30 ± 1.39   | 37.32 ± 1.87   | 27.73 ± 1.39   |
| S9     | 27.73 ± 1.39   | 37.32 ± 1.87   | 27.73 ± 1.39   |
| Min    | 10.53          | 13.98          | 1.39           |
| Max    | 37.00          | 36.00          | 37.00          |

### Table 4. Activity concentration ratios 232Th/238U and 235U/238U from the sampling areas.

| Sample ID | 232Th/238U | 235U/238U |
|-----------|------------|-----------|
| S5        | 1.094      | 0.047     |
| S6        | 0.757      | 0.047     |
| S7        | 1.179      | 0.047     |
| S8        | 1.037      | 0.047     |
| S9        | 0.743      | 0.047     |
| Min       | 0.757      | 0.047     |
| Max       | 1.179      | 0.047     |
| SD        | 0.200      | 0.000     |
| Arithmetic mean | 0.960 | 0.047 |
| Continental average (Maxwell et al., 2013) | 1.200 | 0.047 |

The average crustal elemental concentration of 238U ranges from 2–3 ppm (Erdi-Krausz et al., 2003). S5, S7, S8, S9 had concentrations ranging from 2.38 to 3.01 ppm to 3.010 ± 0.241 ppm which falls within the world average range. The remaining sample, S6 had concentration of 5.304 ± 0.424 ppm which is greater than the world average. Figure 2(b,c), shows slight differences in the isotopic concentrations of 238U and 235U. This showed that the isotopic concentrations obtained were characteristic of that area and did not vary significantly at different points within the area. Overall, the samples can be characterized by 238U concentration that is within

![Figure 4](image-url)
3.08 ± 0.15 Bq kg⁻¹ and mean value of 1.97 ± 0.65 Bq kg⁻¹. The activity concentration shown in Figure 3(b, c) of S5, S6, S7, S8, and S9 had small variations. This showed that the activity concentrations obtained were characteristic of that region and can be added to a nuclear forensic library.

3.1.3. Activity ratio of Uranium samples

The activity ratio of ²³²Th/²³⁸U shown in column 2 of Table 4 where S9 was distinctly lower than the continental average of 1.2 (Maxwell et al., 2013). S5, S7, and S8 had values that were slightly lower than the continental average. Also, there were significant differences in the values obtained for most of the samples. The ²³²Th/²³⁸U activity ratio for all the samples ranged from 0.757 to 1.179 with a mean of 0.96 ± 0.20. The activity ratio for ²³⁵U/²³⁸U was equal to the continental average of 0.047 for all the samples, this was evident because the natural abundance of ²³⁵U was used to determine its isotopic concentration from the measured isotopic concentration of ²³⁸U. ²³²Th/²³⁸U activity ratio could be identified as a unique signature that is characteristic of the area. The relationship between uranium and thorium from Serule in Botswana can be considered in terms of the quotient of thorium and uranium. Figure 5 shows the correlation between thorium and uranium with a linear fitting relation type and a correlation coefficient of 0.87. The theoretical expected ratio of ²³²Th/²³⁸U is approximately 3.00 for normal continental crust (Tzortzis & Tsertos, 2004).

3.2. Rare earth elements

Samples from uranium mines were analyzed to determine the REE concentrations shown in Table 5. According to literature (Spano et al., 2017), the REE concentrations vary with origin, therefore form part of the fingerprint. The REE data in this study were normalized to examine the statistical variations and thus determine the CN-REE profile of the mine. Figure 6 illustrates these patterns.

The REE pattern shown in Figure 6 indicates a match between all the samples. The shapes of the CN-REE plot were all similar and formed peaks at the same elements (La, Ce, Nd). The REE profile obtained was therefore characteristic of the region that can be added to a nuclear forensic library.

3.3. Impurity Elements

Table 6 and Figure 7 present the concentration of the impurity which varies according to the sampling areas. However, the graphs in Figure 6 followed the same trend with the impurity elements displaying peaks at Zr, Ba, P, respectively. Zirconium had the highest abundance in S5, S6, and S7. For S8 and S9, Barium had the highest abundance. Therefore, the elemental concentration of impurities was not characteristic of this region but varies at different sampling points. The spectrum was found to be characteristic of the area and can thus form part of a fingerprint.

3.4. Mineral identification and quantification

The mean chemical composition of the samples was investigated and XRF measurements for quartz, aluminum oxide, and hematite were found. Table 7 shows the major minerals identified in the samples.

Quartz (SiO₂) was identified as the most dominant mineral ranging from 70.77% for S8 to 82.89% for S5. The abundance of Aluminum oxide (Al₂O₃) ranged from 7.2% for S5 to 14.91% for S6. Hematite (Fe₂O₃) ranged from 1.80% for S7 to 3.07% for S7 and S8. The mean chemical composition was as follows: 74.54% of SiO₂, 11.27% of Al₂O₃, and 3.96% of Fe₂O₃. Other minerals such as MnO, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, Cr₂O₃ were identified and were found to have abundances less than 1%. These results comply with the IAEA guideline (Keegan et al., 2017).

![Figure 5](image-url)  
**Figure 5.** Correlation between average concentrations of ²³⁸U and ²³²Th in all soil samples.
Table 5. REE concentration from the sampling areas as measured by ICP-MS.

| Nuclide | S5 | S6 | S7 | S8 | S9 | min | max  | \( \bar{x} \pm \sigma \) |
|---------|----|----|----|----|----|-----|------|--------------------------|
| La      | 19.43 | 23.84 | 11.32 | 18.59 | 15.63 | 11.32 | 23.84 | 17.764 ± 4.65 |
| Ce      | 40.14 | 53.79 | 42.46 | 46.94 | 45.79 | 40.14 | 53.79 | 45.82 ± 5.20 |
| Pr      | 3.86  | 5.49  | 2.43  | 4.54  | 3.953  | 3.86  | 5.49  | 4.05 ± 1.12 |
| Nd      | 15.03 | 22.17 | 9.22  | 18.45 | 16.19  | 9.22  | 22.17 | 16.214 ± 4.76 |
| Sm      | 2.76  | 4.41  | 1.82  | 3.80  | 3.42   | 1.82  | 4.41  | 3.24 ± 0.99 |
| Eu      | 0.62  | 0.96  | 0.43  | 0.89  | 0.79   | 0.43  | 0.96  | 0.73 ± 0.22 |
| Gd      | 2.77  | 4.46  | 1.97  | 3.70  | 3.37   | 1.97  | 4.46  | 3.25 ± 0.94 |
| Tb      | 0.35  | 0.59  | 0.23  | 0.51  | 0.47   | 0.23  | 0.59  | 0.43 ± 0.14 |
| Dy      | 1.96  | 3.47  | 1.44  | 3.04  | 2.79   | 1.44  | 3.47  | 2.54 ± 0.82 |
| Ho      | 0.39  | 0.69  | 0.29  | 0.61  | 0.55   | 0.29  | 0.69  | 0.51 ± 0.17 |
| Er      | 1.15  | 1.99  | 0.886 | 1.74  | 1.58   | 0.89  | 1.99  | 1.47 ± 0.45 |
| Tm      | 0.17  | 0.31  | 0.152 | 0.26  | 0.25   | 0.15  | 0.31  | 0.23 ± 0.06 |
| Yb      | 1.08  | 2.07  | 1.083 | 1.69  | 1.58   | 1.08  | 2.07  | 1.50 ± 0.43 |
| Lu      | 0.18  | 0.34  | 0.181 | 0.27  | 0.25   | 0.18  | 0.34  | 0.25 ± 0.07 |

Figure 6. CN-REE patterns for the mine samples.

Table 6. Impurity elements found from the sampling areas as measured using ICP-MS.

| Nuclide | S5  | S6  | S7  | S8  | S9  | Max  | Min  | \( \bar{x} \pm \sigma \) |
|---------|-----|-----|-----|-----|-----|------|------|--------------------------|
| Li      | 21.27 | 60.29 | 52.88 | 32.96 | 36.55 | 60.29 | 21.27 | 40.79 ± 15.71 |
| P       | 172.45 | 336.64 | 243.91 | 127.54 | 133.87 | 336.64 | 127.54 | 202.88 ± 87.94 |
| Sc      | 6.31  | 9.13  | 10.13 | 7.98  | 7.64  | 10.13 | 6.31  | 8.26 ± 1.44 |
| V       | 166.82 | 189.15 | 92.37 | 78.56 | 74.29 | 199.15 | 74.29 | 122.24 ± 57.01 |
| Cr      | 42.55 | 93.34 | 66.11 | 64.83 | 66.09 | 93.34 | 42.55 | 66.57 ± 18.01 |
| Co      | 10.12 | 11.14 | 6.51  | 10.59 | 10.25 | 11.14 | 6.51  | 9.72 ± 1.83 |
| Ni      | 20.13 | 39.51 | 20.42 | 26.62 | 27.59 | 39.51 | 20.13 | 26.86 ± 7.86 |
| Cu      | 14.78 | 29.17 | 12.44 | 27.79 | 26.10 | 29.17 | 14.78 | 22.05 ± 7.83 |
| Ga      | 9.47  | 21.54 | 18.03 | 12.53 | 13.14 | 21.54 | 9.47  | 14.94 ± 4.79 |
| Rb      | 26.02 | 27.63 | 34.92 | 69.09 | 56.88 | 69.09 | 26.02 | 42.91 ± 19.13 |
| Sr      | 29.28 | 74.82 | 56.30 | 141.78 | 129.40 | 141.78 | 29.28 | 86.32 ± 48.01 |
| Y       | 11.29 | 19.56 | 7.97  | 16.29 | 14.98 | 19.56 | 7.97  | 14.02 ± 4.49 |
| Zr      | 250.00 | 619.60 | 397.06 | 180.21 | 188.48 | 250.00 | 180.48 | 273.84 ± 69.04 |
| Nb      | 5.42  | 16.02 | 12.81 | 9.08  | 9.09  | 16.02 | 5.42  | 10.48 ± 4.05 |
| Ba      | 172.21 | 257.74 | 268.73 | 356.57 | 313.95 | 356.57 | 172.21 | 273.84 ± 69.04 |
| Hf      | 6.52  | 15.01 | 10.32 | 5.79  | 5.28  | 15.01 | 5.28  | 8.58 ± 4.10 |
| Pb      | 19.51 | 18.48 | 16.07 | 14.02 | 13.93 | 19.51 | 13.93 | 16.40 ± 2.54 |

3.5. Measured results using ICP-MS and XRF

Table 8 and Figure 8 are the results of the activity concentration of \( ^{232} \text{Th}, ^{235} \text{U}, \) and \( ^{238} \text{U} \); the rare earth elements (REE); major minerals and the impurity obtained from the soil samples using ICP-MS and XRF measurement techniques. The presence of impurities in soil samples collected in Serule, Botswana, is higher followed by the major mineral and thorium being the highest amongst NORM.
3.6. Correlation between rare earth elements (REE) and impurity material from Serule, Botswana

Figure 9 shows a correlation of 0.6576 between REE and impurities, similar observations were reported by other researchers (Keegan et al., 2017) and the results can be used for the forensic identity of NORM associated with the REE and minerals from Serule, Botswana.

3.7. Comparison between the current study and the world $^{238}$U and $^{232}$Th activity concentrations Bq. kg$^{-1}$

The activity concentrations of $^{238}$U for the current study are lower than most of the countries but, higher than the world results. While the activity concentration of $^{232}$Th for the current study is higher than Kubwa, Abuja, and Northern central Nigeria and lower than the rest of the countries as shown in Table 9.

4. Conclusion

The principal aim of this study was to characterize and identify signatures in uranium soil samples that could be added to a nuclear forensic database. To achieve this, an investigation on the prospective uranium mine 30 soil samples from five sampling points was collected and analyzed. The activity concentration from the current study was compared with the results from other parts of the world as presented in Table 10 (United Nations Scientific Committee on the effects of Atomic Radiation. Unsccear, 1998). Both $^{232}$Th and $^{238}$U concentrations from Botswana are much lower than the results obtained from other parts of the world. A nuclear fingerprint of the soil samples was created using the following parameters: Isotopic concentration and activity concentration of $^{232}$Th, $^{238}$U, and $^{235}$U; Activity ratio $^{232}$Th/$^{238}$U; CN-REE profile and Impurity pattern (Keegan et al., 2017) and are

Table 7. Major minerals found from the sampling areas as measured using XRF.

| Sample ID | SiO$_2$ (wt%) | Al$_2$O$_3$ (wt%) | Fe$_2$O$_3$ (wt%) |
|-----------|---------------|-------------------|-------------------|
| S5        | 82.89 ± 6.63  | 7.80 ± 0.62       | 3.07 ± 0.25       |
| S6        | 71.91 ± 5.75  | 14.91 ± 1.19      | 2.15 ± 0.17       |
| S7        | 74.65 ± 5.97  | 14.61 ± 1.16      | 1.80 ± 0.14       |
| S8        | 70.77 ± 5.66  | 9.35 ± 0.75       | 3.07 ± 0.25       |
| S9        | 72.46 ± 5.79  | 9.70 ± 0.78       | 2.94 ± 0.24       |
| Min       | 70.77 ± 5.66  | 7.80 ± 0.62       | 1.80 ± 0.14       |
| Max       | 82.89 ± 6.63  | 14.91 ± 1.19      | 3.07 ± 0.25       |
| $\bar{x}$±σ | 74.54 ± 4.88   | 11.27 ± 3.26      | 2.61 ± 0.53       |

Table 8. Comparison of the presence of naturally occurring radioactive material (NORM), thorium, uranium, major minerals, REE, and impurities in soil samples from Serule, Botswana.

| Sample ID | $^{232}$Th | $^{235}$U | Rare Earth Elements (REE-ICP-MS) | Major minerals (XRF wt%) | Impurity elements (ICP-MS) |
|-----------|-----------|-----------|----------------------------------|--------------------------|----------------------------|
|           | $^{232}$Th | $^{235}$U | (La; Ce; Nd; Gd ... )            | (SiO$_2$; Al$_2$O$_3$; Fe$_2$O$_3$) | (Zr; Ba; P; Sc; V; ... )  |
| S5        | 8.812     | 2.670     | 6.419                            | 31.253                   | 57.891                     |
| S6        | 12.298    | 5.342     | 8.898                            | 29.657                   | 114.202                    |
| S7        | 12.578    | 3.533     | 5.279                            | 30.333                   | 78.058                     |
| S8        | 8.016     | 2.560     | 7.503                            | 27.730                   | 69.543                     |
| S9        | 6.797     | 3.032     | 6.903                            | 30.620                   | 66.336                     |
Figure 8. Comparison between impurities, major elements, REE, Thorium and Uranium in soil samples from Serule, Botswana.

Figure 9. Correlation between REE and impurities in soil samples from Serule, Botswana.

Table 9. Summary of the concentration of radioisotopes in soil samples in Serule area of Botswana and other parts of the world (United Nations Scientific Committee on the effects of Atomic Radiation. Unsccear, 1998).

| Region/country                  | Range $^{232}$Th (Bq.kg$^{-1}$) | Range $^{238}$U (Bq.kg$^{-1}$) |
|---------------------------------|---------------------------------|---------------------------------|
| Botswana (current study)        | 26–52                           | 29–68                           |
| Dei-De 1, Abuja, North Central Nigeria | 45–98                           | 119–750                         |
| Kubwa, Abuja, North Central Nigeria | 32–84                           | 15–52                           |
| Ikogisi-Ekiti, South Western Nigeria | 1–108                           | 4–111                           |
| Malasia                         | 63–110                          | 49–86                           |
| China                           | 1–360                           | 2–690                           |
| India                           | 14–160                          | 7–81                            |
| Japan                           | 2–88                            | 2–59                            |
| United state                    | 4–130                           | 4–140                           |
| Egypt                           | 2–96                            | 6–120                           |
| Greece                          | 1–190                           | 1–240                           |
| Portugal                        | 22–100                          | 26–82                           |
| Russia                          | 2–79                            | 0–67                            |
| Spain                           | 2–210                           | -                               |
| World                           | 7–50                            | 16–116                          |
shown in Table 8. The unique results of the activity concentration of $^{232}$Th, $^{238}$U, and $^{235}$U; Activity ratio $^{232}$Th/$^{238}$U; CN-REE profile and Impurity pattern (Keegan et al., 2017) were obtained.

In terms of the mineralogy of uranium samples from Serule, it was established that even though there were slight variations in the concentrations of the minerals, Quartz was the dominant mineral in all the sites of the region. The data will be stored as sample information if the country approves this storage (Keegan et al., 2017) as sample required. If the data are sensitive and storage is prohibited, the results will be added externally only after obtaining results from comparison or it will automatically be deleted (Keegan et al., 2017). Therefore, approval from Botswana will be requested before the data can be added into a Nuclear Forensic Library and used as reference data.

Disclosure statement

No potential conflict of interest was reported by the authors.

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### Table 10. Characteristic parameters of Uranium mined ore from Serule.

| Parameter                  | Signature                      |
|---------------------------|--------------------------------|
| Isotopic concentration    | $^{232}$Th                     |
|                           | 9.68 ± 2.58 ppm                |
|                           | $^{238}$U                      |
|                           | 3.40 ± 1.13 ppm                |
|                           | $^{235}$U                      |
|                           | 0.02 ± 0.01 ppm                |
| Activity concentration    | $^{232}$Th                     |
|                           | 39.50 ± 10.53 Bq.kg$^{-1}$     |
|                           | $^{238}$U                      |
|                           | 42.50 ± 13.98 Bq.kg$^{-1}$     |
|                           | $^{235}$U                      |
|                           | 1.97 ± 0.65 Bq.kg$^{-1}$       |
| Activity ratio            | $^{232}$Th/$^{238}$U           |
|                           | 0.96 ± 0.20                    |
|                           | $^{235}$U/$^{238}$U            |
|                           | 0.047                          |

CN-REE profile

Impurity spectrum
radioelement mapping using gamma ray spectrometry data: Also as open access e-book. International Atomic Energy Agency (IAEA).
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