

# **Application of ICP-MS and Isotopic Techniques in Resolving Nuclear Forensic Signatures in Uranium Mining and Processing**

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## **BSc (Hons) Medical Sciences (Microbiology)**

Dissertation submitted in *partial* fulfillment of the  
requirements for the degree of *Master of Science* in  
Applied Radiation Science and Technology at the  
Mafikeng Campus of the North-West University

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Graduation: October 2017

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## DECLARATION

I, **Ntokozo Khumalo**, declare herewith that the Dissertation entitled, "*Applications of ICP-MS and HPGe gamma ray detector in implementing Nuclear Forensic Signatures in Uranium Mining and Processing*", which I herewith submit to the North-West University as *partial fulfillment* of the requirements set for the Master of Science in Applied Radiation Science and Technology degree, is my own work and has not already been submitted to any other university.



Signed by student.....

...17 March 2017

**Ntokozo Khumalo**

**Date**

  
Signature

Singed by Supervisor .....

...17 March 2017

**Prof Manny Mathuthu**

**Date**

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## **ACKNOWLEDGEMENTS**

I would first like to thank my research supervisor Prof Manny Mathuthu of the Faculty of Agriculture Science and Technology at North West University (Mafikeng campus). The door to Prof. Mathuthu's office was always open whenever I experienced some difficulties or had a question about my research or writing. He consistently allowed this Dissertation to be my own work, but steered me in the right the direction whenever he thought I needed it.

I would also like to express my gratitude to the National Research Foundation (NRF) of South Africa for granting me the NRF-Internship for 2015. I cannot leave out the DST-NRF Scholarship for 2016/7 to do my Master's degree respectively.

I also acknowledge the Chief Technician Ms. Mpho Thseole who helped me with the ICP-MS sample analysis and CASRT students who helped me with the research.

Finally, I would like to thank my parents for the support and encouragement they gave me throughout my studies.



## **Abstract**

The nuclear and radioactive material is used in industries for academic purposes as well as for research and development. Cases of illicit trafficking of nuclear and radioactive material are being constantly reported. Nuclear forensics was introduced as a division in science to unanswered questions in support of law enforcement and intelligence. Nuclear forensic is the branch concerned with the analysis or characterization of seized nuclear or radioactive material based on chemical and isotopic composition, age dating and physical parameters in determining the origin of the interdicted radiological nuclear material. These parameters are called signatures and are stored in a nuclear forensic library as database or archives so each country can easily have access to them for attribution.

There are rising nuclear security concerns about the safety and proliferation of the nuclear materials used in these nuclear power plants (Molgaard et al., 2015a, Varga, 2008, Molgaard et al., 2015b) as well as possible diversion for illicit purposes by nuclear terrorists (Hutcheon et al., Kristo, 2012). This has necessitated the characterization of seized nuclear or radioactive material based on chemical and isotopic composition as well as physical parameters which can be used in determining the origin of the interdicted radiological nuclear material. The characteristic difference between lead isotopic composition from the earth's crust (e.g. uranium ore body) and that from industrial emissions enables the applications of this ratio in nuclear forensics investigations (Moody, 2015).

In South Africa there is a vast uranium ore (uraninite) deposits (Fuchs et al., 2016), with a lot of mining and processing activities. It is therefore imperative for the each country to properly collect and compile nuclear forensic signatures in databases and national libraries, that can be used as evidence for attribution of the seized nuclear or radioactive material.

Little information is available when it comes to developing a NNFL due to a lack of effort and finances (Davydov et al., 2014). A known nuclear material is required in order to identify the origin of the unknown intercepted material; hence there is a need for South Africa to develop a nuclear Forensics database and libraries. The aim of this study was to apply ICP-MS and HPGe gamma ray detector in implementing nuclear forensic signatures from a South African Uranium Mining and Processing plant.

In order to achieve this aim, soil, water and vegetation were sampled from a Gold mine in Carletonville, South Africa. The samples were analyzed to determine elemental concentration and isotopic ratio using ICP-MS and HPGe gamma spectrometry. Soil samples were digested using a Multiwave 3000, Anton Paar microwave oven. About 1 g of each sample was weighed into a microwave digester vial and then digested with the aqua regia acid (3 ml of 55% HNO<sub>3</sub>, 9 ml of 32% HCl) and 2 ml of 2% H<sub>2</sub>O<sub>2</sub>. The microwave rotor was transferred to a microwave reactor system for 20 - 45 minutes. Then an aliquot (10 ml) of each sample was transferred into a volumetric flask and topped up with ultra-pure distilled water up to 100 ml. Samples were stored at 4°C for another 24 hrs.

A whole set of 5 ml each of the water samples were mixed with 5 ml of nitric acid and 1 ml of hydrochloric acid and then left to digest in the Multiwave 3000, Anton Paar microwave oven for 24 hrs at room temperature. A 10 ml aliquot of each digested sample was then transferred into 100-ml flasks and topped up with Millipore Milli-Q system (resistivity 18 MΩ cm<sup>-1</sup>) distilled water up to 100 ml and left overnight for ICP-MS analysis.

About 1 g of the crop sample was weighed and the measured weight was recorded. The samples were dried in an oven furnace model (G132-002) for 16 hours at 800°C. A tong was used to remove them the following day and they were placed in a desiccator for 6 hours. The dry weight was recorded after aching and the samples were transferred into the rotor vessels. A volume of 1 ml nitric acid was added to the samples followed by 10 ml of hydrochloric acid and then placed into the microwave reactor for 20-45 minutes. The 10 ml aliquot of digested samples were transferred into volumetric flasks and topped up with water up to 100 ml and left to sediment overnight. The supernatant was then transferred into the centrifuge tubes for performing ICP-MS analysis.

About 2 kg of soil samples were carefully and systematically collected from the top of the uranium mine tailings. 800 g of each sample was measured into the Marinelli beaker. The beakers with the samples were sealed for 30 days so as to allow equilibrium between Radium-226 (<sup>226</sup>Ra) its daughters and also to prevent radon gas leakage. The samples were measured on the Canberra HPGe well type Detector (Model 747) for 24 hours.

The results obtained from tailing dam 1 show an average of Al (567.11 mg/L), Cr (4.42 mg/L), Cu (0.47 mg/L), Fe (1781.69 mg/L) and Zn (0.46 mg/L). Based on these elemental

concentrations, Al, Cr, Cu and Zn are at trace level whereas Fe is at a minor level specifically for this site. This family of elements is indicative of a carry-through from a precursor ore. La (0.046), Na (5.22), Sr (0.16) and Y (0.029) are low. This shows that open cast mining is not done in this mine. The concentration of uranium is below 10 ppm for both tailing dam 1 and 2 (Table 3 and 4). This mark or indicate an absence of a black shale deposit which generally occurs in carbonaceous marine shales. Trace elements and sulphur are predominant in our study indicating an acidic soil. The results from both ICP-MS and gamma spectrometry analysis were above the acceptable  $^{235}\text{U}/^{238}\text{U} = 2.38555 \times 10^{-3} \pm 4.7 \times 10^{-7}$  NIST ratio.

Four rare earth elements (REE) were found to be a fingerprint for this mine on both tailing dam 1 and 2. These include La, Ce, Pr and Nd. The REE concentrations for tailing dam 2 are higher than those of tailing dam 1.

The Lead Pb ratios are found to fall within the certified values or standard reference see Table 13 in appendix C. Also, Lead (Pb) isotope ratios for the studied gold mine have  $^{207}\text{Pb}/^{204}\text{Pb}$  values between 13 – 20 and  $^{206}\text{Pb}/^{204}\text{Pb}$  values ranging from 16 – 25, which confirm that the Carletonville gold fields are of uraninite detrital pyrite deposits. Trace elemental concentrations indicated a pyrite type of uranium deposit. Uranium in the deposit exhibits geochemical signatures of the radiogenic formations of the ore enhanced in  $^{206}\text{Pb}$ .

Signatures generated in this study will support and strengthen nuclear security towards combating theft of nuclear or radioactive material thereby minimizing illicit trafficking of nuclear material for perversion and proliferation purposes, and promoting peaceful use of such material.

*Keywords:* Nuclear forensic, lanthanides or REE; National nuclear forensic library (NNFL); Signatures; U-Pb Isochrons

## LIST OF ABBREVIATIONS AND ACRONYMS

|                |                                                |
|----------------|------------------------------------------------|
| AS             | Alpha Spectrometry                             |
| DOD            | Department of Defense                          |
| DOE            | Department of Energy                           |
| DA             | Destructive Analysis                           |
| NDA            | Non-Destructive Analysis                       |
| F <sub>6</sub> | Fluorine gas                                   |
| FAAS           | Flame Atomic Absorption Spectroscopy           |
| GDMS           | Glow Discharge Mass Spectrometry               |
| HEU            | Highly Enriched Uranium                        |
| HKED           | Hybrid K-edge Densitometry                     |
| HPGe           | High Purity Germanium                          |
| HRGS           | High-Resolution Gamma Spectrometry             |
| IAEA           | International Atomic Energy Agency             |
| ICP-MS         | Inductively Coupled Plasma - Mass Spectrometry |

|                               |                                                          |
|-------------------------------|----------------------------------------------------------|
| ICP-OES                       | Inductively Coupled Plasma-Optical Emission Spectrometry |
| IDMS                          | Isotope Dilution Mass Spectrometry                       |
| ITDB                          | Incident and Trafficking Database                        |
| ITU                           | Institute for Transuranium Elements                      |
| JRC                           | Joint Research Centre                                    |
| LEU                           | Low Enriched Uranium                                     |
| NECSA                         | South African Nuclear Energy Corporation                 |
| NNFL                          | National Nuclear Forensic Library                        |
| REE                           | Rare Earth Elements                                      |
| SEM                           | Scanning Electron Microscopy                             |
| SIMS                          | Secondary Ion Mass Spectrometry                          |
| TEM                           | Transmission Electron Microscopy                         |
| TIMS                          | Thermal Ionization Mass Spectrometry                     |
| UF <sub>6</sub>               | Uranium hexafluoride                                     |
| UOC                           | Uranium Ore Concentrate                                  |
| UO <sub>2</sub>               | Uranium dioxide                                          |
| U <sub>3</sub> O <sub>8</sub> | Triuranium octaoxide                                     |
| UO <sub>3</sub>               | Uranium trioxide                                         |
| U                             | Uranium                                                  |
| WGPU                          | Weapons-Grade Plutonium                                  |



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## CHAPTER 1: INTRODUCTION AND PROBLEM STATEMENT

### 1.1 Introduction

Trafficking of nuclear and radioactive material arose during the early 90s with the first case reported in Italy and Switzerland then later in the (Soviet Union) in 1991. Subsequent cases were reported in Germany, Czech Republic, Hungary and other central European countries (Mayer et al., 2007). Nevertheless, during those early 1990s nuclear forensics had not become a remarkable technique until the nuclear terrorist attack of New York City's Twin Towers and Washington in September 2011 (Kristo, 2012). Earlier in 1992, the IAEA's illicit trafficking database reported that there were about 11 cases of smuggled highly enriched uranium or plutonium specifically in Russia and Europe (Kristo, 2012). Consequently, questions concerning the origin, trafficking route and intended use of the nuclear or radioactive material were raised. Ultimately, nuclear forensics was introduced as a division in science to resolve these unanswered questions in aid of law enforcement and intelligence (Kristo, 2012).

Nuclear forensics is a branch of science which is associated with the analysis or characterization of seized nuclear or radioactive material based on chemical, physical, isotopic composition and age dating in determining the origin of the interdicted radiological nuclear material (Stanley, 2012). Adding to the development of nuclear security and safety by the IAEA, nuclear forensics has discouraged and prevented nuclear terrorism as well as illicit trafficking of nuclear or radioactive material (Hutcheon et al., 2013).

According to the IAEA website, nuclear forensics provides answers to these questions namely: the name of the radioactive material found, the threat it poses, the organization responsible for the loss, the origin of the material and the national laws that have been broken. The scientific pathway to resolve these issues is by obtaining the characteristic parameters of the material called nuclear forensic *signatures*. These *signatures* are the features of a given sample of nuclear or radioactive material that allows one to differentiate that material from other nuclear or radioactive material (IAEA, 2014). The signatures include physical characterization, elemental, isotopic and chemical composition. There are some specific techniques which are applied to determine *nuclear forensic signatures* (Table 1).

Parameters to focus on, regarding physical characterization of solid samples include texture, size as well as shape and particle distribution for powder samples. These parameters give information about the manufacturing process such as in the case of uranium oxide powder. Chemical composition includes finding the form that the element is in. Again, uranium has various forms at different points of the nuclear fuel cycle and these include  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$  or  $\text{UO}_3$ .

Elemental signatures include major, minor as well as trace elements in the material. Each of these has a contribution towards obtaining a signature; for instance, major elements define the identity of the nuclear material, minor elements help to define the function of the material lastly trace elements indicate a certain process used to manufacture the nuclear material. Isotopic signatures of the material also help identify the fission or neutron capture products, which designate that the material has been in a nuclear reactor and is a representative fingerprint for the type and operating conditions of a given reactor. Isotopic signatures also come from decay products from the parent material which can be used to date the age of the material (Kristo et al., 2004).

Table 1: Analytical tools used in nuclear forensic analysis

| Parameter                           | Information                             | Analytical technique     |
|-------------------------------------|-----------------------------------------|--------------------------|
| Appearance                          | Material type (e.g. powder, pellet)     | Optical microscopy       |
| Dimensions (pellet)                 | Reactor type                            | Database                 |
| U, Pu content                       | Chemical composition                    | Titration, HKED, IDMS    |
| Isotopic composition                | Enrichment → intended use; reactor type | HRGS, TIMS, ICP-MS, SIMS |
| Impurities                          | Production process; geo-location        | ICP-MS, GDMS             |
| Age                                 | Production date                         | AS, TIMS, ICP-MS         |
| $^{18}\text{O}/^{16}\text{O}$ ratio | Geo-location                            | TIMS, SIMS               |
| Surface roughness                   | Production plant                        | Profilometry             |
| Microstructure                      | Production process                      | SEM, TEM                 |

### 1.1.1 Nuclear fuel cycle

Uranium is a heavy radioactive silver colored element naturally occurring in soil, sea water, rocks, plants, animals, and all human beings. It occurs in three isotopes namely  $^{238}\text{U}$  (99%),  $^{235}\text{U}$  (0.7) and  $^{234}\text{U}$  (0.005%). However,  $^{235}\text{U}$  is the main isotope used for generating nuclear power and

nuclear weapons but is in low quantity (Index, 2016). As a result, uranium enrichment process is applied so as to obtain both low enriched uranium and highly enriched uranium. Hence the nuclear materials used in any stage of the nuclear fuel cycle are a target to nuclear terrorist. They can be used as radiological dispersal devices (dirty bombs), radiological explosives (dirty bombs), or full scale bomb (which requires much ingenuity and expensive equipment). These materials include Co-60 powder or pellets, uranium as well plutonium and they are easily smuggled if nuclear security is not ensured. For making a full scale nuclear bomb, these radioactive materials are used in different forms namely Highly Enriched Uranium (HEU), separated plutonium and the plutonium content in fresh mixed oxide fuel (Index, 2016).

Knowledge in nuclear energy cycle is needed in order to understand these processes as follows:

***Steps involved in nuclear energy fuel cycle***

Three methods are used to mine uranium, namely, open cast or open pit, underground mining, heap and *in-situ* leaching.

- a) Open pit mining-** involves removal of the topsoil and an uneconomic rock that covers uranium ore (Figure 1). This is used for deposits that are less than 100 m deep (U.S. EPA, 2016)



**Figure 1:** Open pit mining (U.S. EPA, 2016).

- b) Underground mining-** involves digging and removing rock through an underground passage and this is used for deposits which are more than 100 m deep (Figure 2). Both open-pit and underground mining are called conventional methods because they require physical mechanical work as opposed to non-conventional methods described below (U.S.EPA, 2016).



**Figure 2:** Underground mining (U.S. EPA, 2016).

- c) **Heap leaching** – was used frequently during 1970 and 1980s. The ore is turned into sand by grinding it in a huge mill. This is then heaped in a pad made up of clay, coated concrete or asphalt. A leach solution composed of a lixiviate is sprinkled on top of a heap by a sprinkler system (Figure 3). The lime content of the ore determines the type of leach solution to be applied, i.e. acidic solutions are used when the ore consists of less than 12 percent of lime content whereas alkaline solutions are used only when the lime content is above 12 percent. The dripping of the leach solution into the ore results in the migration of metal including uranium into the solution. Further processing and uranium extraction in a mill to obtain a yellow cake is done once the solution has been collected by a pipe at the base of a mound into a pregnant pond or pit (U.S.EPA 2016).

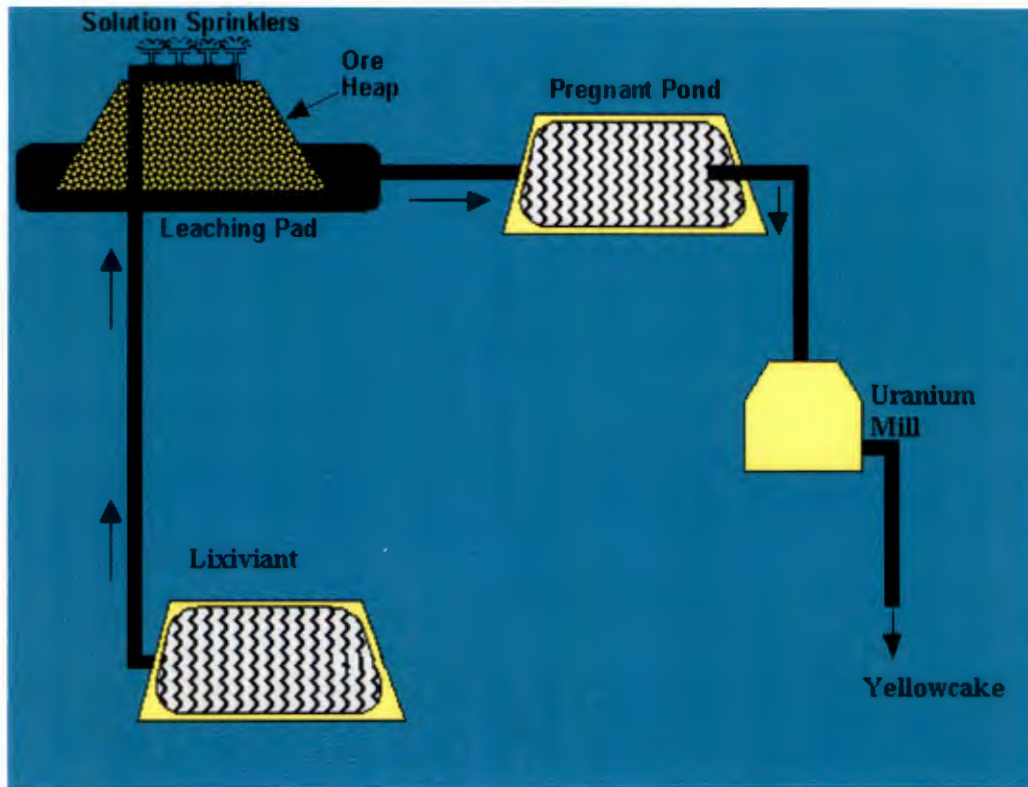


Figure 3: Heap leaching mine (U.S. EPA, 2016).

- d) ***In-Situ* leaching**- acids are used to dissolve uranium deep underground and the resulting suspension is pumped onto the surface (Figure 4) (U.S. EPA, 2016).

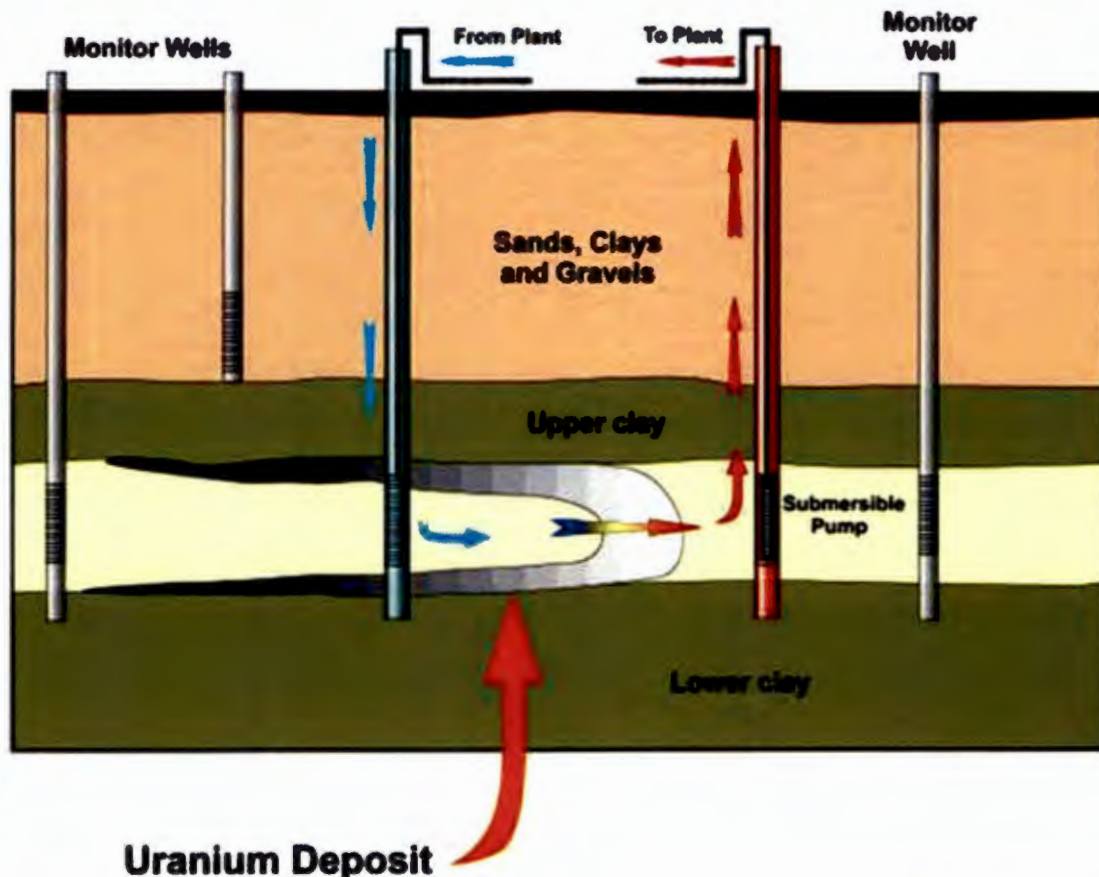


Figure 4: In-situ leaching mine (U.S. EPA, 2016).

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### 1.1.2 Milling process

Once uranium ore has been mined, it undergoes a milling process in milling plants near the mine site. The uranium ore is crushed and treated with chemicals to extract uranium. The product of the milling process is  $U_3O_8$  which is a yellow powder and is called *yellow cake*. The yellow cake is then transported to a conversion facility. What remains from the ore is called *tailings* which contain long-lived radioactive materials in low concentrations and toxic materials such as heavy metals (IAEA, 2009, IAEA, 2011).

### 1.1.3 Conversion

The uranium ore concentrate is converted into  $\text{UF}_6$  via a two-stage process. First stage involves conversion of uranium to uranium tetrafluoride ( $\text{UF}_4$ ) called *green salt*. During the second stage, uranium  $\text{UF}_4$  is converted to  $\text{UF}_6$  by a fluorination process. The conversion process can be done in two ways namely dry and wet process. The difference between the two processes is in the production of  $\text{UF}_6$ , with the dry process, the Uranium Ore Concentrate (UOC) is converted directly to  $\text{UF}_6$  to yield an impure form of  $\text{UF}_6$ . Purification follows later on, whereas with the wet process UOC is purified first before  $\text{F}_6$  or fluorine gas is added (Figure 5) (IAEA, 2009).

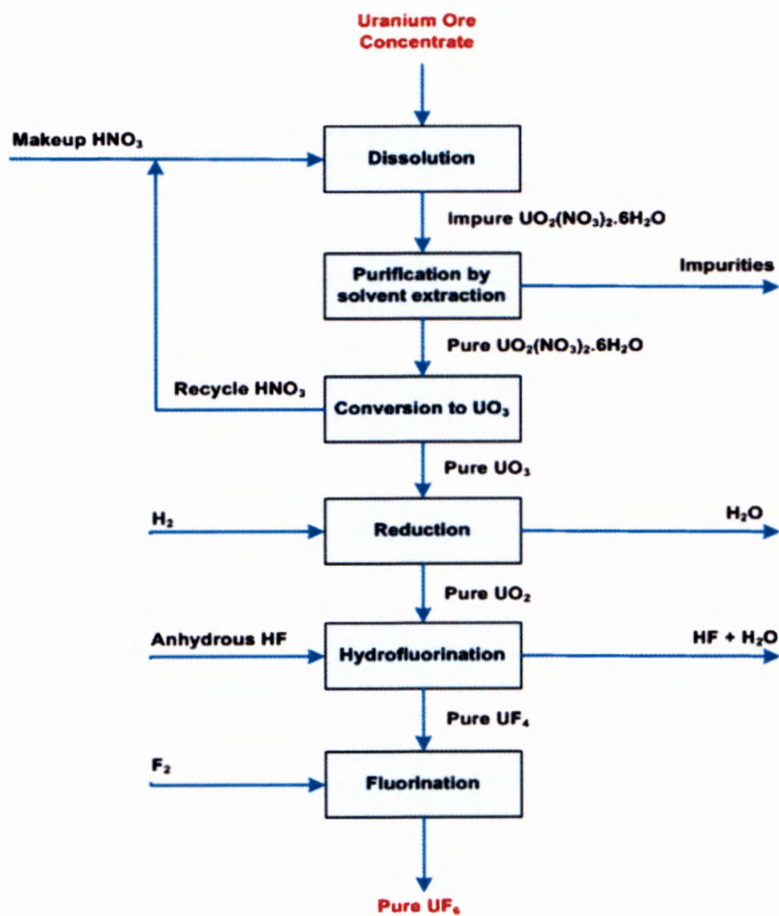


Figure 5: Stages involved in the wet process conversion (IAEA, 2009).

### ***Uranium enrichment***

Uranium enrichment is the process of increasing the concentration of  $^{235}\text{U}$  relative to the naturally occurring uranium (Index, 2016). This can be done by gaseous diffusion, laser enrichment and centrifugation. Only low enriched uranium (3-5%) is used for nuclear fuel and highly enriched uranium (>20%) is used in nuclear reactors as well as in the production of nuclear weapons.

### ***Uranium fabrication***

Once the anticipated level of enrichment is achieved, the uranium is fabricated into nuclear fuel, for the research reactors and the metal uranium for a nuclear bomb. HEU is also used to fuel submarines.

### ***Uranium waste management***

Waste is cooled by water in spent fuel ponds or stored in dry cask containers to be cooled by air. When it has cooled, the spent nuclear fuel is transported into the dump site in the ground for long-term storage (Index, 2016). Highly enriched uranium is mixed with natural uranium or blended down to get low enriched uranium which is used for nuclear fuel power (Figure 6).

## **1.2 Problem Statement**

There are rising nuclear security concerns about the safety and proliferation of the nuclear materials used in these nuclear power plants (Molgaard et al., 2015a, Varga, 2008, Molgaard et al., 2015b) as well as possible diversion for illicit purposes by nuclear terrorists (Hutcheon et al., Kristo, 2012). This has necessitated the characterization of seized nuclear or radioactive material based on chemical and isotopic composition as well as physical parameters which can be used in determining the origin of the interdicted radiological nuclear material.

In South Africa there is a vast uranium ore (uraninite) deposits (Fuchs et al., 2016), with a lot of mining and processing activities. It is therefore imperative for the country to properly collect and compile nuclear forensic signatures in databases and national libraries. Little information is available when it comes to developing a NNFL due to a lack of effort and finances (Davydov et al., 2014). A known nuclear material is required in order to identify the origin of the unknown intercepted material; hence there is a need for database and libraries (IAEA, 2002).



**Figure 6:** Nuclear fuel cycle (IAEA, 2011).

### **1.3 Research aims and objectives**

#### **1.3.1 Aim**

The aim of this research was to Apply ICP-MS and Isotopic Techniques (HPGe gamma detector) in implementing nuclear forensic signatures from South African Uranium Mining and Processing

#### **1.3.2 Objectives**

The specific objectives for the study were to:

- Apply the ICP-MS as well as HPGe Gamma ray detector to develop nuclear forensic signatures and libraries for Uranium.
- Contribute towards the development of a South African National Nuclear Forensic Library to improve Nuclear Security in the country. Verify the experimental data against Isoplot Code for Isochron plots from the Isotopic ratio data (as a quality control)
- Design a protocol for ICP-MS Isotopic Technique (DA) and Gamma spectrometry (NDA) for nuclear forensic analysis at the Centre for Applied Radiation Science and Technology (CARST).

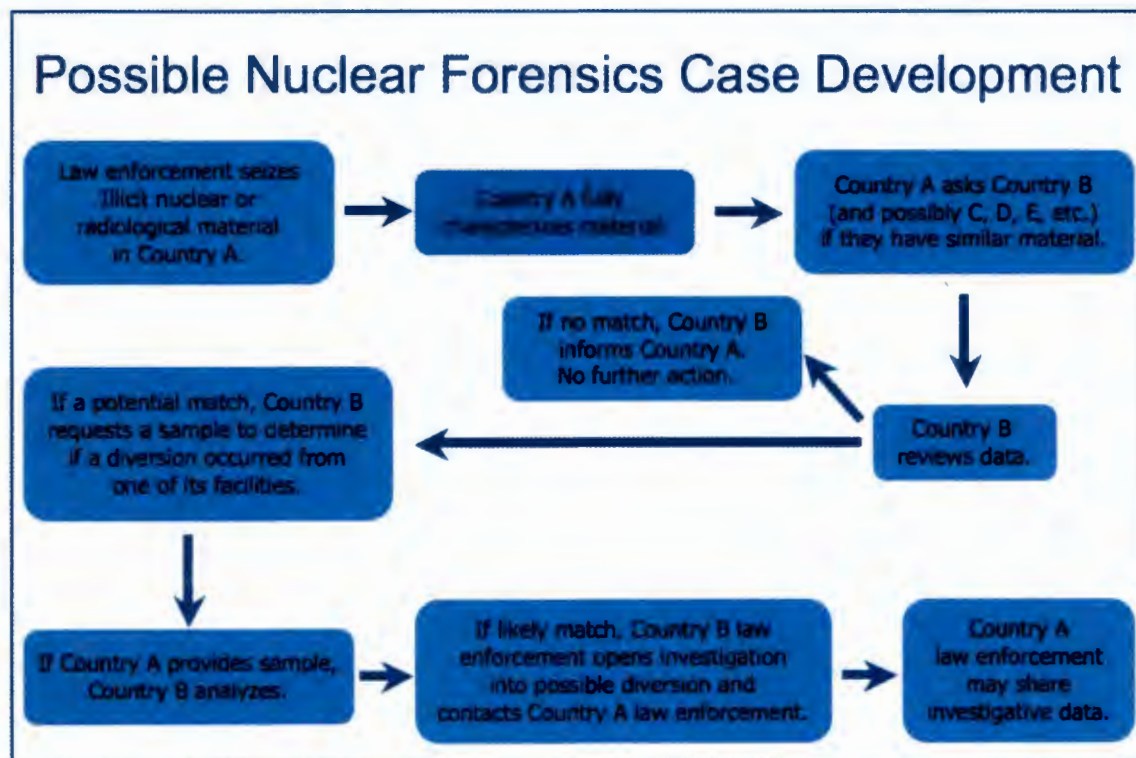


**Figure 7:** Ways of using national nuclear forensic library in supporting nuclear security

(Wacker and Curry, 2011)

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 Introduction**

Radioactive sources have been globally applied in various beneficial fields which include medicine, agriculture, industry, environment as well as in research (IAEA, 2002). Nevertheless, nuclear security and safeguards are still a cause for concern due to many orphaned radioactive sources. As a result, illicit nuclear trafficking subjects the society to nuclear terrorism which in its definition includes; the use of an explosive nuclear device by a terrorist organization, the stealing and detonation of an intact nuclear weapon, the seizure or purchase of highly enriched uranium (HEU) or plutonium, attacking nuclear facilities such as power plants for attaining radioactive material, the illegal acquisition of nuclear and radioactive materials used to construct a 'dirty bomb' or a radiation emission device (IAEA, 2015).

In the hands of terrorists, nuclear weapons still cause the most serious terrorist threat (Levy and Sidel, 2008) and are assured to cause an instantaneous huge destruction compared to biological, chemical and radiological weapons. As a result nuclear terrorism threat has increased to a great extent (Ferguson, 2006). The most popular events in history in which nuclear weapons were utilized was during the end of World War II in Hiroshima and Nagasaki. This resulted in 200 000 immediate deaths. The majority of people died afterwards due to cancer and other related chronic exposure conditions. Unlike nuclear weapons, radiological weapons do not result in a large number of people being killed; instead they cause everlasting huge disruptions even if the area has been decontaminated (Levy and Sidel, 2008). Despite the fact that decontamination can be done after detonation, this process requires several years as well as huge amounts of money which negatively affects the economy (Ferguson, 2006).

Nuclear terrorists acquire nuclear material or weapons in many ways, (for example, a nuclear weapon or bomb), they could steal, buy or create it up from scratch (Ferguson, 2006). Russia is the leading country which has missile material followed by Pakistan. Nations like Libya, Iran and North Korea have equipment used to manufacture HEU and have established techniques for making up atomic bombs (Medalia, 2005). These nations have the possibility of using these nuclear weapons themselves or they could sell or leak it to nuclear terrorists. The secure bomb states reported that more than 130 research reactors in more than 40 countries still use HEU as a

fuel with the premises having poor security. Lack of security simply provides easy access to HEU by nuclear terrorist (Medalia, 2005). There are basically two types of nuclear weapons targeted by nuclear terrorists namely gun-type (mass of HEU) which was used to detonate Hiroshima and secondly, weapons-grade plutonium (WGPU) (plutonium 239 isotope) which was used to detonate Nagasaki (Medalia, 2005).

Even though there are cases of nuclear terrorism, measures are being taken to counteract or prevent it. For instance, six countries namely Australia, Belgium, Czech Republic, Hungary, Italy and Poland took an oath to return HEU to the country of origin to be used for beneficial purposes after the end of a meeting in Seoul during 2013 (Davenport, 2012). During 1995, the IAEA established a database that does not only hold records of incidents of illicit trafficking of nuclear material and radioactive material, but can also be used to compare with and analyzes the material. This system is called Incident and Trafficking Database (ITDB) and is aimed at strengthening nuclear security. However, information stored in this database is only accessed by the IAEA as well as participating states (IAEA, 2014). As a result, other states are being encouraged to join and be members as well.

## **2.2 The Different analytical techniques**

According to Kristo et.al (2013), not only the U.S. is subject to nuclear terrorism. President Barrack Obama clearly stated that all countries need to contribute towards combating illicit trafficking of nuclear material (Parker, 2014). Consequently, Lawrence Livermore National Laboratories (LLNL) staff members are assisting countries which are affected by illicit nuclear trafficking to have their own nuclear forensic facilities and laboratories. Some of these countries include Russia, Ukraine, South Africa, Australia, Japan, China, Kazakhstan and Korea. At the South African Nuclear Energy Co-operation (NECSA), scientists are being routinely trained on how to operate nuclear forensic techniques including gamma spectrometer and inductively coupled plasma mass spectrometer (ICP-MS). *The Scientists from CARST will be therefore be working with their NECSA counterparts to develop the first national nuclear forensics library in the country.*

### 2.2.1 The ICP-MS isotopic ratio technique

The ICP-MS is considered as equipment with improved technique because it analyzes both isotopic and elemental composition (Table 1). However, owning a mass spectrometry system is costly because it requires a relatively large room, a skilled and trained Technician and is expensive (costs around \$200 000 to half million US dollars). In addition, the mass spectrometer techniques are destructive whereas gamma spectrometer is non- destructive and simple but enables the analysis of isotopic radio-activities from which isotopic composition can also be calculated (Nguyen and Zsigrai, 2006).

The ITU is one of nuclear research institute formed by JRC and situated in Karlsruhe, Germany. Ever since nuclear forensic science was established, this research institute has contributed much on this field and has played a major role to its development. The strategic plan usually applied by the Institute for Trans uranium Elements (ITU) to circumvent the disadvantage of mass spectrometer is that within 24 hours when the intercepted nuclear material is found, it is analyzed firstly non-destructively by gamma spectrometry (Wallenius et al., 2006). Further analysis is done by mass spectrometry because it enables the identification of accurate abundance of minor isotopes which is not possible with gamma spectrometry. NDA still takes the first preference around the world in the field of safeguards, nuclear security and safety compared to its comparative DA (Boshielo et al., 2014)



The seizure of illicit trafficking of nuclear material has spread to non-nuclear weapons states since the break-up of Soviet Union during 1990's. Consequently, these non-States have adequate nuclear material to make up improvised nuclear devices. One of the strategies to combat illicit trafficking of nuclear material is by the identification and characterization of nuclear material by each country. It is thus imperative for CARST laboratory to develop rapid analytical methodologies that can resolve the signatures of nuclear materials within hours of interdiction or recovery (Hall and Auxier, 2016, Auxier et al., 2016). These signatures are then compiled and stored in a nuclear forensic library (Davydov et al., 2014). A national nuclear forensic library for South Africa will enable the country to identify nuclear or radioactive material produced within its own borders, thereby keeping these materials under regulatory control (Davydov et al., 2016).

Also, in nuclear forensic investigations, isotopic composition of the radioisotopes is used to trace the origin of the unknown nuclear material (Davydov et al., 2016). However, studies conducted by Nelwamondo et al (2014) revealed that using isotopic signatures alone is not reliable to determine an unknown. Information like morphology, elemental impurity, trace element analysis as well as microscopic studies should be added to support isotopic analysis prior to nuclear security examination (Nelwamondo et al., 2014).

The most common isotopic ratios used for nuclear forensic signatures are those of the natural U-Pb systems. However, the ore bodies hardly behave as closed systems after they have either gained or lost Pb or U caused by weathering and chemical fractionation. This then causes higher variability of lead isotopic ratio thereby resulting in overlaps between the samples. Also, the chemical purification steps alters the radiogenic lead content of the ore which prevents matching the measured values of the ore concentrate to the initial ore (Varga et al., 2009). This then necessitates that the use of the isotopic technique for lead (Pb) isotopic signatures be checked against another method like using the lanthanides patterns or gamma spectroscopy.

### **2.2.2 Gamma spectrometry**

Gamma spectrometry is widely used for detecting estimate isotopic composition of the material. It is used for detecting activation products such as  $^{241}\text{Am}$ . However destructive methods are preferred over gamma spectrometry because  $^{241}\text{Am}$  is a low-energy gamma emitter and has a high background (Varga and Surányi, 2009). Apart from plutonium ( $^{239}\text{Pu}$ ) and uranium ( $^{235}\text{U}$ ),  $^{241}\text{Am}$  is also a fissile nuclear material (Vesterlund et al., 2015). It is used in ionizing smoke detectors, industrial gauging applications as well as a neutron source when combined with low Z elements such as beryllium or lithium.

Due to this property,  $^{241}\text{Am}$  is vulnerable to nuclear terrorists. Therefore, there is a need for it to be characterized and its signatures stored in a national nuclear forensic library (Vesterlund et al., 2015). From Varga and Surányi (2009) studies, it is clear that gamma spectrometry is not a reliable technique to perform  $^{241}\text{Am}$  analysis. Therefore, Vesterlund et al., (2015) suggested the use of advanced analytical methods than gamma spectrometry. Nevertheless, gamma spectroscopy

remains the main technique for rapid analysis of nuclear materials in the field after a detonation or nuclear accident. Gamma spectrometers are so far the safest equipment to safeguard investigators.

### **2.2.3 The ORIGEN AND DELFIC Codes**

Better analytical methods are helpful during characterization of nuclear material. This will help to produce good distinguishing features that make it possible to differentiate between nuclear materials of different origin (Nelwamondo et al., 2014). Prior to the application of the analytical methods for the analysis of debris soon after nuclear explosion, Jodoin et al., (2011) have come up with a software package to predict the best sample locations and determining dose exposure for the collectors. Nuclear forensics requires the collection of debris from possibly dangerous radiation areas. So far, two software tools have been implemented namely, Oak Ridge Isotope Generation (ORIGEN) Fallout Analysis Tool and the Defense Land Fallout Interpretive Code (DELFIC) Fallout Planning Tool.

Both these tools can describe the chemical, physical and radiological attributes of the debris. The majority of studies conducted by different researchers in the field of nuclear forensics have not used any of these tools. These include Wallenius et al., (2006), (2015); Keegan et al., (2014) etc. Keegan et al., (2008) utilized samples collected directly from the mines for characterization. Even so, it was imperative for them to first determine the radiological risks associated with a particular sample of interests. ORIGEN was used to determine the generation and decay of fission products, actinides, and activation products while DELFIC determined the dose rates, integrated doses, times of arrival, particle sizes and activity concentrations as a function of location and time (Jodoin et al., 2011).

### **2.2.4 The Principal Components Analysis (PCA)**

Another analysis tool important for determining the provenance of the seized nuclear material is principal components analysis (PCA) (Reading et al., 2016). This statistical tool is mostly preferred over other multivariate statistical tools because it focuses on variance only. This method groups related dependent variables into a series of components (Reading et al., 2016). PCA can be used to analyze data extracted from both NDA and DA. For instance, Keegan et al (2008) used

PCA for analyzing SIMS and ICP-MS data whereas Reading et al (2016) applied it in the analysis of gamma spectrometry as well as a destructive alpha spectrometry.

The drawback of PCA is that it lacks capability of considering the knowledge of sample classification (Keegan et al., 2012). Adding to that, the patterns of PCA can also sometimes masks real patterns of differences. However, having information about sample classification can provide a more meaningful interpretation of analytical data.

#### **2.2.5 The Canonical Analysis of Principal coordinates (CAP)**

The canonical analysis of the principal coordinates (CAP) circumvents the limitation of PCA. CAP is used to characterize the groups, visualize the groups and assess how these groups differ from one another in the multivariate space. It also produces a model prediction of the group membership for new chemical profiles (Keegan et al., 2012).

#### **2.5.6 Isoplot code**

The Isoplot code is another software which is an add-in program for Microsoft *Excel*, normally used for data analysis and graphical presentation of geochronology (age dating), and radiogenic isotope ratio data (Figure 8). It provides tools for the manipulation and plotting of radiogenic-isotope ratios, especially U-Pb,  $^{230}\text{Th}$ - $^{234}\text{U}$ - $^{238}\text{U}$  etc. (Poujol, 1999, Ludwig, 2012, Ludwig, 1998). The research chose this Isoplot program to check the results from the ICP-MS ratio technique following the procedure adopted by Schoene (2014) (Schoene, 2014).

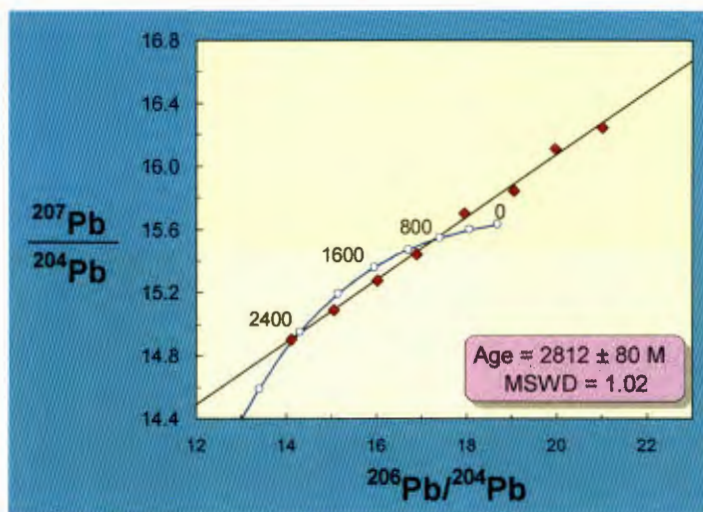


Figure 8: Example of a Lead-lead Isochron (Ludwig, 2012).

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### 2.3 Nuclear forensics databases

With regard to securing Uranium material from nuclear smuggling, there are uranium databases that have been developed which includes Discriminant Analysis and Verification Engine (DAVE/iDAVE) and ITU. The iDAVE consists of yellow cake chemical information, data for uranium ore and tetrafluoride of the nuclear energy cycle whereas that established at ITU stores data from nuclear fuel manufacturers of Western Europe and Russia (Parker, 2014). Here the data base stores dimensions of uranium pellets,  $^{235}\text{U}$  enrichment and typical impurities, information from research reactor fuels as well as from the open literature (Wallenius et al., 2006, Parker, 2014)

A fully ordered list of programs that has been done specifically in the U.S. to fight against nuclear terrorism include:

- a) Threat reduction programs in the former Soviet Union-The Soviet Nuclear Threat Reduction Act of 1991 (P.L. 102-226, Title II) accredited to the Department of Defense (DOD) program to facilitate in the eradication of Soviet nuclear and other nuclear weapons.
- b) Efforts to secure HEU worldwide
- c) Control of former Soviet and other borders- the DOE second line defense (SLD) as well as the State Department's Export Control and Related Border Security Assistance (EXBS)

Program facilitate Russia and other countries to prevent nuclear smuggling at border level by providing them with radiation detection monitors.

- d) Container security initiative- CSI implemented during 2002 scrutinizes containers in overseas ports before they are loaded onto U.S. bound ships.
- e) Proliferation security initiative.
- f) U.S. border security.
- g) Nuclear Forensics- this is the recent emerging branch of science which was established to strengthen nuclear security in preventing nuclear terrorism (Kristo and Tumey, 2013).

In this Research Project the researcher chose the ICP-MS Isotopic Ratio and Gamma spectrometry methods simply because:

- This is the first time in South Africa that such work is ever done
- There is a need to utilize the available resources to validate the principle of nuclear forensics as a nuclear security tool
- The aim was to demonstrate to South Africa that we can start from simple techniques and slowly develop a comprehensive National Nuclear Forensics Library from these two techniques.

## CHAPTER 3: MATERIALS AND METHODS

### 3.1 Study Area

The study area is indicated in Figure 9 and Figure 10, and the authors cannot give further details due to confidentiality agreements.

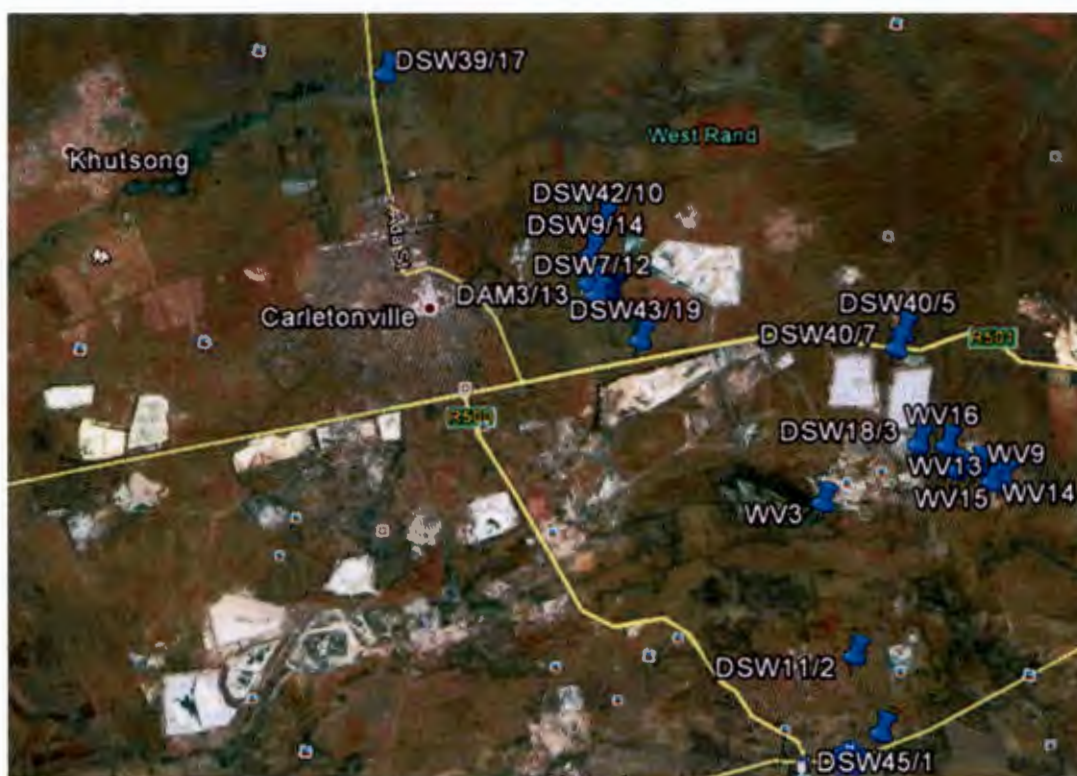


**Figure 9:** Water sampling points in the Carletonville goldfields Area of South Africa. From the top of this figure: DSW39/17- Water from DSW36/15 and DSW38/16; DSW36/15- Water from DSW9/14 and DSW42/10); DSW38/16- Discharge water from another mine; DSW42/10- Fissure water straight from underground; DSW9/14-Water from the settling point; DSW7/12-Water coming from the mine shaft and from process plants; DAM3/13-Water after (downstream of) the settling point; DSW43/19-Purified water; DSW40/5 & DSW40/7- Raw water from return water dam;

DSW18/3 & DSW112-Sewage water from mine shaft; DSW45/1- water from mine shaft; WV16, WV9, WV13, WV14, WV15 & WV3- Borehole water for public use from West village.

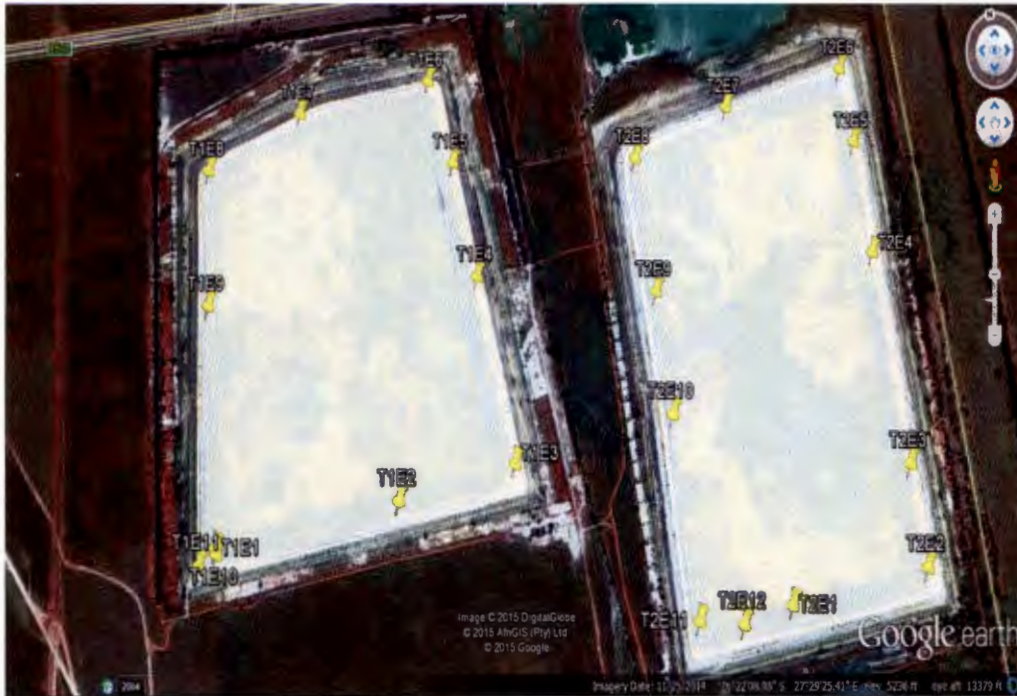


**Figure 10:** Soil (tailing, T1 & T2) sampling points in the Carletonville goldfields area of South Africa, LHS is T1 & RHS is T2.

### 3.2 Geology of the mining site

The sampling site falls within the Carletonville goldfields which is part of the so called B-Reef or Witwatersrand Super group of South Africa. The uraninite ( $\text{UO}_2$ ) (Balboni et al., 2016) deposits here are unconformity in nature lying on the sedimentary succession of the Witwatersrand super group, with an estimated age of about 2.59 Ga (Fuchs et al., 2016). Gold (and uranium) mining here uses the underground mining techniques as the mines are each estimated to be more than 2 km deep. These mines are now over 132 years old, (SAHO, 2016) and are still operational.

### 3.3 Sample collection

The Carletonville goldfields have a quartz-pebble conglomerate, intercalated with chert, jasper pebbles and minor shales, bound within siliceous to slightly argillaceous rocks, and were sampled from mining operations in the Welkom gold field (Fuchs et al., 2016)

The tailing dams in Figure 9 are located on the RHS of DSW7/12 (T3 no separate figure); below DSW43/19 (T3 no separate figure), between DSW40/7 & DSW18/3 (T1 in Figure 9) and above WV15 (T2 in Figure 9). Samples used in this study consisted of a total of 17 water samples (mixture of mine water- also called *fissure* water from underground at the ore deposits- used in cooling the drilling machines, waste water from the processing plant and 10 soil samples from the mine tailing dam, T1 & T2. It was observed that the slurry from the plant is deposited on the tailing dam in paddocks whose boundary contours are the edges of the different colors of the slurry, although some cross mixing could be seen. Figure 9 shows an example of a tailing with paddocks at different drying stages. These paddocks are filled from the outside inward and in a sequential manner following the perimeter of the Tailing dam. Hence they dry in that same sequence each paddock taking as long as more than a month to be reusable again (of course this depends on the size of the dam). The soil and some water samples were collected from the top of the tailing and the discharge canals respectively to represent uranium that has come from the milling and processing stage of the fuel cycle. Fissure water samples were also collected from the mine shafts outlets to represents uranium from the ore body.

During the manufacture of uranium fuel, impurities are released from the crushing of the uranium ore, leaching uranium from the ore, purifying, precipitating and calcination processes (Švedkauskaitė-LeGore` et al., 2008). The impurities indicate the production process as well as geolocation (Wallenius et al., 2006).

In this work, soil (2 kg), water (2 L) and vegetation (250 g) were collected from each of the sampling points shown in Figure 8 & 9 from a Gold mine in Carletonville, South Africa.

### **3.4 Sample analysis techniques**

#### **3.4.1 The ICP-MS isotopic technique**

Inductively coupled plasma- mass spectrometry (ICP-MS) is the most preferred method worldwide over ICP-OES and FAA. This is due to its capability of being applied in the analysis of assorted sample types ranging from environmental, geological, biomedical and nuclear samples. In contrast to other methods which are limited to the detection of higher concentrations, ICP-MS has the ability to carry out rapid multi-element determinations at the ultra-trace level (Thomas, 2013). This characteristic is achieved by the production and detection of huge amounts of these positively charged ions in the spray chamber (Figure 10).

#### **3.4.2 How ICP-MS isotopic technique operates**

One drawback of ICP-MS analysis is that the samples have to be in a liquid form. The sample is pumped into a nebulizer at 1ml/min where it is transformed into an aerosol with argon gas flowing at 1l/min. This gives out different sizes of fine and larger droplets by which the spray chamber filters out the larger ones. Fine droplets are transported into the plasma torch by a sample injector which generates positively charged ions. These ions are then transported into the mass spectrometer through the interface region which is composed of two metallic cones called the sampler and skimmer cones. These cones are specialized, with a small diameter to allow ions to pass through ion optics into the mass separation device. Ion detector transforms ion charges into an electrical signal which is processed by the data handling system and converted into an analyte concentration through ICP-MS calibration standards (Thomas, 2013).

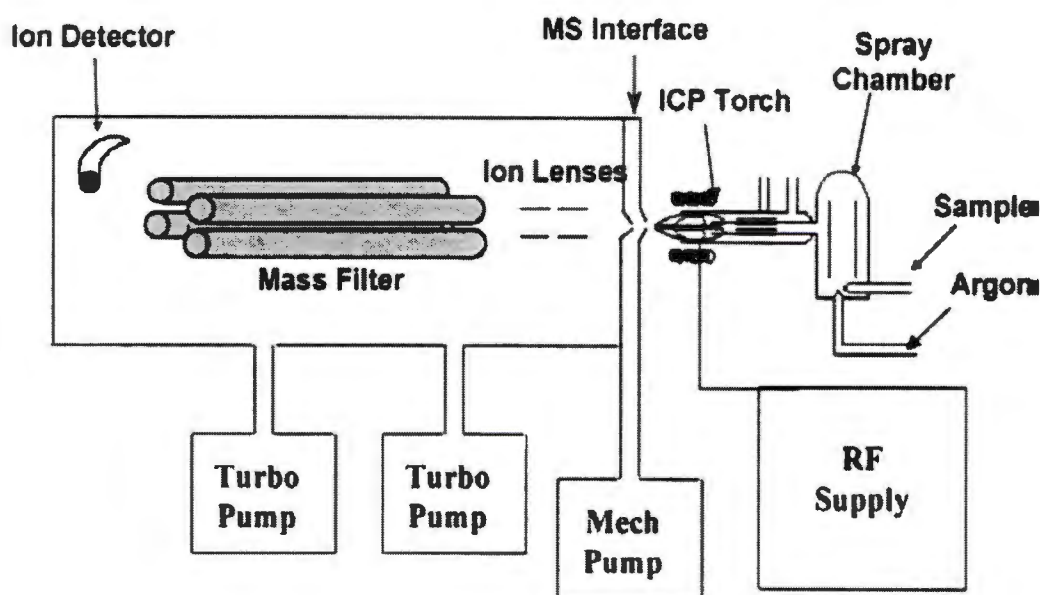


Figure 11: Basic components of the ICP-MS (Thomas, 2013).

### 3.4.3 ICP-MS isotopic technique methodology

#### *Soil sample digestion protocol by Multiwave 3000 Anton Paar Model*

Soil samples were digested using a Multiwave 3000, Anton Paar microwave oven. About 1 g of each sample was weighed into a microwave digester vial and then digested with the aqua regia acid (3 ml of 55%  $\text{HNO}_3$ , 9 ml of 32%  $\text{HCl}$ ) and 2 ml of 2%  $\text{H}_2\text{O}_2$  - which enhances the oxidation properties of nitric acid (Mangum, 2009)) following standard procedures. The aqua regia extraction is capable of complete recovery for Cd, Cu, Pb (our target elements) and Zn (Gaudino, Galas et al. 2007). That is, the microwave rotor was transferred to a microwave reactor system for 20 - 45 minutes. Then an aliquot (10 ml) of each sample was transferred into a volumetric flask and topped up with ultra-pure distilled water up to 100 ml. Samples were stored at 4°C for another 24 hrs. The reagents used were of Suprapur analytical grade (by Merck Laboratory Supplies Pvt. Ltd). The EPA Method 3052 used in the sample digestion achieves total sample decomposition (Mangum, 2009).

#### *Water sample digestion protocol*

A whole set of 5 ml each of the water samples were mixed with 5 ml of nitric acid and 1 ml of hydrochloric acid and then left to digest in the Multiwave 3000, Anton Paar microwave oven for

24 hrs at room temperature. A 10 ml aliquot of each digested sample was then transferred into 100-ml flasks and topped up with Millipore Milli-Q system (resistivity  $18 \text{ M}\Omega \text{ cm}^{-1}$ ) distilled water up to 100 ml and left overnight for ICP-MS analysis.

### *Digestion of vegetation samples*

Prior to the processing of samples, crucibles were cleaned i.e. they were soaked overnight in Analytical grade 12 M hydrochloric acid and then rinsed with Millipore Milli-Q system (resistivity  $18 \text{ M}\Omega \text{ cm}^{-1}$ ) distilled water. The crucibles were then dried at  $600^\circ\text{C}$  overnight in an oven and then placed in a desiccator for cooling for 6 hours. About 1 g of the crop sample was weighed and the measured weight was recorded. The samples were dried in an oven furnace model (G132-002) for 16 hours at  $800^\circ\text{C}$ . A tong was used to remove them the following day and they were placed in a desiccator for 6 hours. The dry weight was recorded after aching and the samples were transferred into the rotor vessels. A volume of 1 ml nitric acid was added to the samples followed by 10 ml of hydrochloric acid and then placed into the microwave reactor for 20-45 minutes. The 10 ml aliquot of digested samples were transferred into volumetric flasks and topped up with water up to 100 ml and left to sediment overnight. The supernatant was then transferred into the centrifuge tubes for performing ICP-MS analysis.

All digested samples were then preserved at  $4^\circ\text{C}$  before analysis in the Laboratory (Kamunda et al., 2016).

### **3.4.4 Instrumentation**



The Perkin Elmer, NeXION 300Q, Inductively Coupled Plasma Mass Spectrometer (ICP-MS), was used for all sample analysis in this work. It has a Quadrupole ion deflector that focuses the ion beam to the dual mode detector. The Isotope-ratio precision of this instrument is defined for the isotope ratio of  $^{107}\text{Ag}/^{109}\text{Ag}$  internal standard using a  $25 \mu\text{g/L}$  solution, which is achieved by single-point peak hopping with a relative standard deviation ( $= 100 \times \text{SD}/\text{AVERAGE}$ , ((0)) of  $< 0.2\%$  RSD (PerkinElmer 2010). The optimized operating parameters are summarized in Table 2.

Table 2: NexION 300q ICP-MS Instrumental Parameters (Bosnak and Pruszkowski, 2014)

| Parameter                               | Value                                                               |
|-----------------------------------------|---------------------------------------------------------------------|
| Nebulizer                               | Glass concentric                                                    |
| Cones (Sampler, Skimmer, super-skimmer) | nickel                                                              |
| Spray Chamber                           | glass cyclonic                                                      |
| Sample Uptake Rate                      | 300 $\mu$ L/min                                                     |
| Plasma gas flow                         | 18.0 L/min                                                          |
| Auxiliary gas flow                      | 1.2 L/min                                                           |
| Nebulizer Gas Flow                      | 0.98 L/min<br>(Optimized for 2% CeO <sup>+</sup> /Ce <sup>+</sup> ) |
| RF Power                                | 1600 W                                                              |
| Cell Gas                                | 99.99% Argon                                                        |
| Detector Type                           | Dual mode                                                           |
| Sweeps/Reading                          | 200                                                                 |
| Readings/Replicate                      | 10                                                                  |
| Replicates per sample                   | 3                                                                   |
| Mode / Universal Cell Technology™       | Isotope Ratio/Collision mode                                        |
| Total integration time                  | 0.5 s                                                               |

### 3.4.5 Interference reduction

It is well established that if the elements do not have two non-radiogenic isotopes (e.g., Pb) or two more isotope ratios, then the internal standard normalization method cannot be used to make mass correction (Horn et al., 2000, Lin et al., 2016, Thirlwall and Anczkiewicz, 2004). However, we can use *pseudo-internal* standard normalization to determine the mass fractionation normalization for one element by directly applying this normalization to another element of similar or neighboring mass in the periodic table (Thirlwall and Anczkiewicz, 2004, Lin et al., 2016). In addition, it has been argued that UV radiation causes the photo-oxidation of  $Tl^+$  to  $Tl^{+3}$ , which then exhibits a different chemical behavior than its single ionic state in the presence of Pb, resulting in higher values of Pb/Tl and  $^{205}Tl/^{203}Tl$  ratios (Yip et al., 2008b). On the other hand, UV oxidation of Ag is known to significantly enhance  $Ag^+$  release (Mittelman, 2015), and thus samples can be handled even in the open laboratory.

In the ICP-MS analysis of samples, the following molecular ions are potential sources of interferences; oxides, hydrides, hydroxides, nitrides (Horn, Rudnick et al. 2000, Thirlwall and Anczkiewicz 2004, Verni 2017). Their effect can however be reduced by using the Perkin Elmer NexION 300Q's desolvating nebulizer. Also, the instrument's quadrupole ion deflector focuses only the selected isotopes in the ion beam, to the dual mode detector. The other (interfering) ions are allowed to pass through to the waste (Bosnak and Pruszkowski 2014, Mangum 2015, Vilita 2016). Although the spectral resolution (0.7 amu) for this instrument is inadequate for discrete measurement of elements prone to sample-based spectral interferences, its collision-reaction cell technology render this problem as minor for the trace element determined in this work (UT, 2017). This capability of the NexION 300Q, combined with its Universal Cell Technology™, enables significant reduction in most or all the molecular ions in the sample (Woods 2014, Lin, Liu et al. 2016). Also instrument drift is automatically corrected by the Software (Schudel, Lai et al. 2015).

#### ***Sample Run***

The samples were loaded on to the auto sampler and initialized using the ICP-MS Instrument Control (Data Acquisition) Software. The instrument was set to Isotopic Ratio Method, operated in the Collision Mode for mass energy discrimination and filtration against interferences (Vilita, 2016).

#### **3.4.6 ICP-MS trace calibration for trace element analysis**

Quality control samples such as blanks, duplicates, spiked samples and certified reference material were included in the analyses (Keegan et al., 2008a)

For analysis of trace elements, the Perkin Elmer, NexION 300Q, (ICP-MS), calibration uses a Dual Detector Calibration Solution as the Atomic Spectrometric Standard, whose specifications are:

In the total quantitative method, the standards have 10 mg/L of Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U and Zn. For every measurement, the instrument was set to run a blank and a standard check at every ten samples.

#### **3.5 Gamma spectrometry**

Gamma spectrometry is an analytical tool that enables the detection and quantification of gamma emitting isotopes in different matrices. With little sample preparation, gamma spectrometry detects a variety of gamma emitting radio-nuclei in one single measurement of sample without destructing or manipulating the sample (Reguigui, 2006). Gamma ray spectrometry is applied in a wide variety of fields that includes monitoring in nuclear facilities, health physics, and nuclear medicine, research in materials, bioscience, environmental science, and industrial uses of radioisotopes, as well as even in the field after a nuclear incident like detonation (Auxier et al., 2016). The High Purity Germanium Detector (HPGe) used in this work is shown in Figure 11.

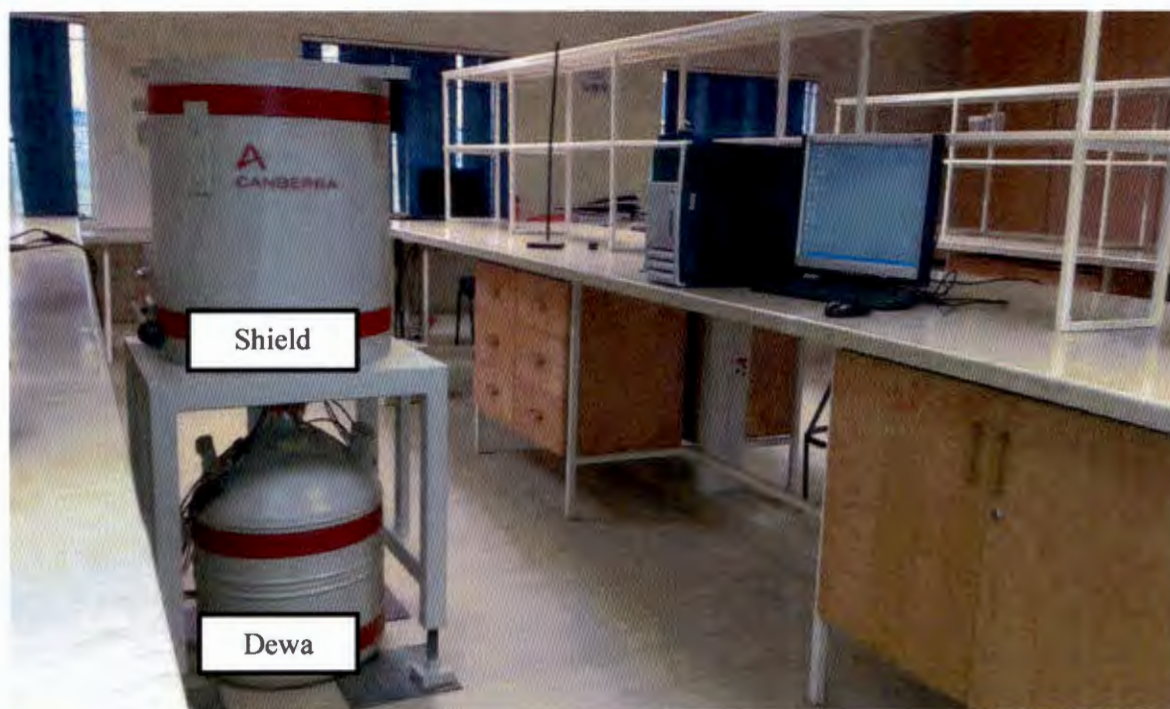


**Figure 12:** Gamma spectrometry HPGe detector set up at CARST.

### 3.5.1 Components of gamma spectrometry

A Gamma spectrometry consists of a High Purity Germanium (HPGe) detector, mechanical cooling system such as liquid nitrogen, preamplifier, detector bias supply, linear amplifier, analog-to-digital converter (ADC), multichannel storage of the spectrum, and data readout devices. The detector is shielded with 20 cm of a dense material, mainly lead, to prevent cosmic radiation. The lead itself is also shielded with a thin; two portion metal of copper and tin to absorb X-rays produced by the interaction of ambient photons with the lead.

The sample emits photons which interact with Ge crystals to generate a pulse. The energy of the photon absorbed by the Ge corresponds to the amplitude of the pulse which is shaped, amplified and sorted to produce a histogram of incident photons called a spectrum. The histogram represents counts per unit energy. These counts accumulate, thereby generating peaks that are identified by energy. If the detector has undergone calibration using a known standard sample for the sample matrix and geometry, then nuclide identities of the spectrum are easily identified (ORTEC, 2016).

### 3.5.2 Gamma spectrometry: principle and methodology

Natural uranium exists in three isotopes namely  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$ . However, all these three isotopes are hard to analyze directly using gamma spectrometry simply because  $^{234}\text{U}$  does not emit suitable energy photons for gamma spectrometry analysis,  $^{238}\text{U}$  does not emit low energy photons that can be detected by gamma spectrometry,  $^{235}\text{U}$  emits photons at a very low rate and has a longer half-life of  $7.04 \times 10^8$  years (Karangelos et al., 2004). One can measure  $^{238}\text{U}$  indirectly through its daughters in equilibrium ( $^{226}\text{Ra}$ ,  $^{234}\text{Th}$  and  $^{234\text{m}}\text{Pa}$ ).  $^{235}\text{U}$  in environmental samples can be analyzed by determining its photon with energy of 185.72 keV. A ratio of  $^{235}\text{U}/^{238}\text{U}$  can be used to represent  $^{234}\text{U}$  in determination of depleted uranium contamination (Karangelos et al., 2004). On the other hand uranium decay results in the lead isotopes. The so called common Pb is approximately 52%  $^{208}\text{Pb}$ , 24%  $^{206}\text{Pb}$ , 22%  $^{207}\text{Pb}$  and 1.4%  $^{204}\text{Pb}$ . The observed variations in the U and Th ratio from the original ore and the age of the deposit are reflected in these Pb isotopic ratios (Keegan et al., 2008b).

#### *Soil sample preparation and analysis*

To acquire data from the samples collected, we used the High Purity Germanium Detector [resolution (FWHM) at 122 keV ( $^{57}\text{Co}$ ) is 0.85 keV and at 1332.5 keV ( $^{60}\text{Co}$ ) is 1.86 keV and relative efficiency for energy 1.33 MeV relative to (NaI) Tl is 36%] (Dlamini et al., 2016).

About 2 kg of soil samples were carefully and systematically collected from the top of the uranium mine tailings. This ensured that only fine silt representative of all the mine shaft discharges was collected. All vegetation was removed before putting the samples in polyethylene plastic bags for analysis in the CARST laboratory. In the laboratory, 800 g of each sample was measured into the Marinelli beaker. The beakers with their samples were sealed for 30 days so as to allow for equilibrium between Radium-226 ( $^{226}\text{Ra}$ ) its daughters and also to prevent radon gas leakage. The samples were measured on the Canberra HPGe well type Detector (Model 747) for 24 hours. Calibration was done by using IAEA Standards (IAEA-35U, 35Th and 35K) with known amount of radioactive elements. Figure 12 shows the calibration energy and efficiency graphs.

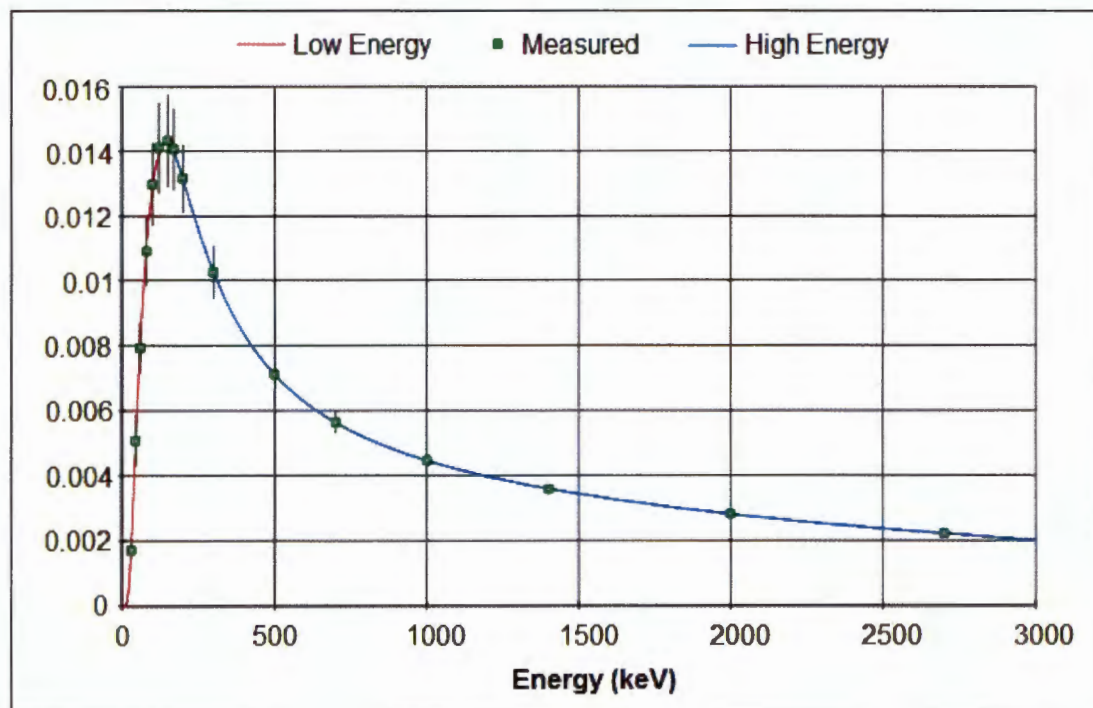


**Figure 13 a):** Efficiency calibration curve for the HPGe.

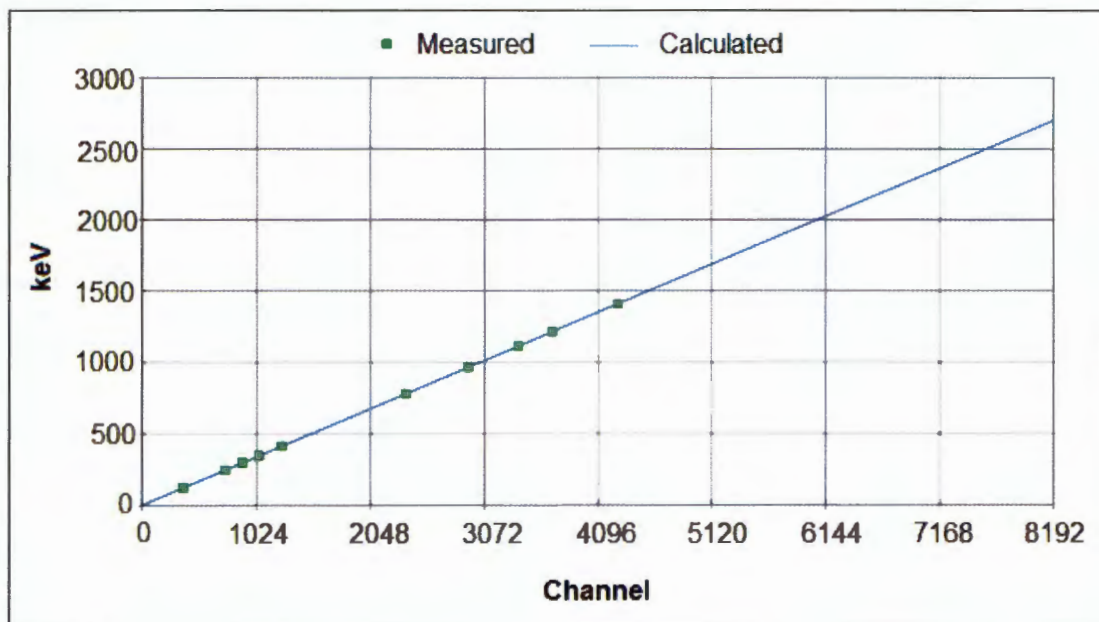


**Figure 13 b):** Energy calibration curve.

## CHAPTER 4: RESULTS AND DISCUSSIONS

### 4.1 Presentation of DATA

The aim of this study was to apply ICP-MS and HPGe gamma detector in implementing nuclear forensic signatures from a South African uranium mining and processing plant. The major objective was to develop the first ever data base of a national nuclear forensics library from these signatures. Such a library could be used to identify the origin of stolen nuclear material and the intended use and potential harm associated with such material. The library can only be comprehensive and complete if it contains all characteristic signatures of such material which include isotopic composition, elemental impurities, chemical composition, physical structure and trace-level radio nuclide content (Varga et al., 2015).

The results of this work are divided into four categories, viz.:

- REE and trace chemical elements concentrations
- REE -CI Chondrite normalized patterns
- Lead isotopic analysis with mass bias corrections
- Gamma spectrometric activities
- Isoplot isochron plots from the Isotopic ratio data (as a quality control)
- Protocol for ICP-MS Isotopic Technique (DA) and Gamma spectrometry (NDA) for nuclear forensic analysis at the Centre for Applied Radiation Science and Technology (CARST).

#### 4.2 REE and trace chemical elements concentrations

The results obtained from the tailing dam 1 show an average of Al (567.11), Cr (4.42), Cu (0.47), Fe (1781.69) and Zn (0.46) mg/L. Based on this elemental concentration, Al, Cr, Cu and Zn are at trace levels whereas Fe is at a minor level specifically for this site. This family of elements is indicative of a carry through from a precursor ore (Keatley et al., 2015). Boron (B) has an average of 0.00082 mg/L, which is a very low amount and this implies that there is no contamination from coal-fired power plant. The average for Ba is 0.049 mg/L representing a B-horizon or natural geogenic enrichments. La (0.046), Na (5.22), Sr (0.16) and Y (0.029) are low. As a result it shows that open cast mining is not done in this mine (de Caritat et al., 2001).

V (0.25), Ti (1.13) and Fe represent a type of leach solution obtainable from the in situ process (Morrell et. al., 2013). The value of Ni (1.59), Co (0.35) and Fe represents deterioration of the equipment or contamination introduced during U processing. High amounts of Fe are due to its abundance in the Earth's crust (Asai and Limbeck, 2015b). Ca (254.99), Mg (255.39) and sometimes Fe form oxides thereby giving ambiguity with the ratio of oxygen and metal in the fuel matrix.

The concentration of uranium is below 10 ppm for both tailings at dams 1 and 2 (Table 3 and 4). This marks an absence of a black shale deposit which generally occurs in carbonaceous marine shales. The sampling location in Carletonville is situated in an inland Gauteng Province of South Africa and the results of this work attest to that. The results show the presence of U, Ni, Co, As, Cu, Ag, and Au which represents polymetallic mineral assemblages followed by bitumen of a clay-bound proterozoic unconformity deposit. Although the values of Ag and Au were detectable but very low in concentration, their values were not recorded. Perigranitic vein deposits may contain pitchblende and gangue minerals or U, Co, Ni, As and Ag minerals. There is no intrusive deposit since uranium is below 20 ppm (IAEA, 2000). However, according to Varga *et al* (2012), the presence of P, Fe and REE is indicative of an intrusive deposit ore type with uraninite, uranothorite, allanite, cyrtolite, betafite and zircon as primary U minerals. The results of this work point to a uraninite mineralization for this mine.

Quartz, pyroxene, amphibole, biotite, muscovite, hematite, calcite, titanite, magnetite, zircon and pyrite are gangue minerals. The type of processing is an acid leach, ion exchange (IX), NaCl/H<sub>2</sub>SO<sub>4</sub> eluent, U precipitation is done using magnesia.

Mo, V, and Cr found in this study form volatile compounds. Li, B, Cd and certain lanthanides not recorded here cause neutron absorption. High concentrations of As, Ni and Mo are associated with unconformity-type ore deposits which are characterized by pitchblende, carnotite, uranophane, and coffinite primary U minerals. Gangue minerals are sulphides, arsenides, haematite, calcite, dolomite, quartz, and chlorite. Processing is done by making use of H<sub>2</sub>SO<sub>4</sub> leach and O<sub>2</sub> is used as an oxidant. Solvent extraction (SX) is done by using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> strip. NH<sub>3</sub> is used for the precipitation of U. The other alternative for processing is using an acid leach + NaClO<sub>3</sub>, SX and concentrated H<sub>2</sub>SO<sub>4</sub> strip. U is precipitated using H<sub>2</sub>O<sub>2</sub> or NH<sub>3</sub>.

High concentration of Cd is associated with a phosphorite deposit which has primary U minerals of apatite and fluorapatite. With regard to processing, U is recovered from phosphoric acid. Rb, Th, Cs, Pb, Ti and S represent a Quartz-pebble conglomerate deposit (Keegan et al., 2012). The primary U minerals found in this work are as follows: Uraninite, brannerite, gummite, brannerite, uraninite, monazite and thorium uraninite. These mineral signatures are in agreement with findings by Schoene (2014). The gangue or original deposits associated with these elements are quartz, feldspar, sericite, chlorite, and pyrite. The type of processing is H<sub>2</sub>SO<sub>4</sub> leach with NaClO<sub>3</sub> oxidant or no oxidant and solvent extraction (SX) done by the use of NO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> eluent. Impurity precipitation is performed by using CaO and NH<sub>3</sub> or CaCO<sub>3</sub> and MgO, U precipitation using NH<sub>3</sub> or magnesia. This was found in Lake Eliot mine in Canada. Al, Mg, Ca, Fe, K, Mn and are predominant in this Carletonville Mine. As a result, they are a distinctive characteristic of this mine. Data from the water and plant material samples collected from villages surrounding the mine are shown on Table 5 and 6(a) and (b).

The elemental concentrations depicted in the table 3-6 were also plotted in a graphical representation (Figure 14) as presented by some of the foremost authors including Keegan et al (2008). Tailings dam 1 and 2 show few elements in the following decreasing concentration arrangement: for tailings 1, Fe > Al > Mg > Ca; for tailings 2, Fe > Al > Mg > Ca > K > Si. According

to Rösner and Van Schalkwyk (2000) elevated Ca levels can be due to addition of lime to neutralize the acidic slime prior to its release to the tailings dam.

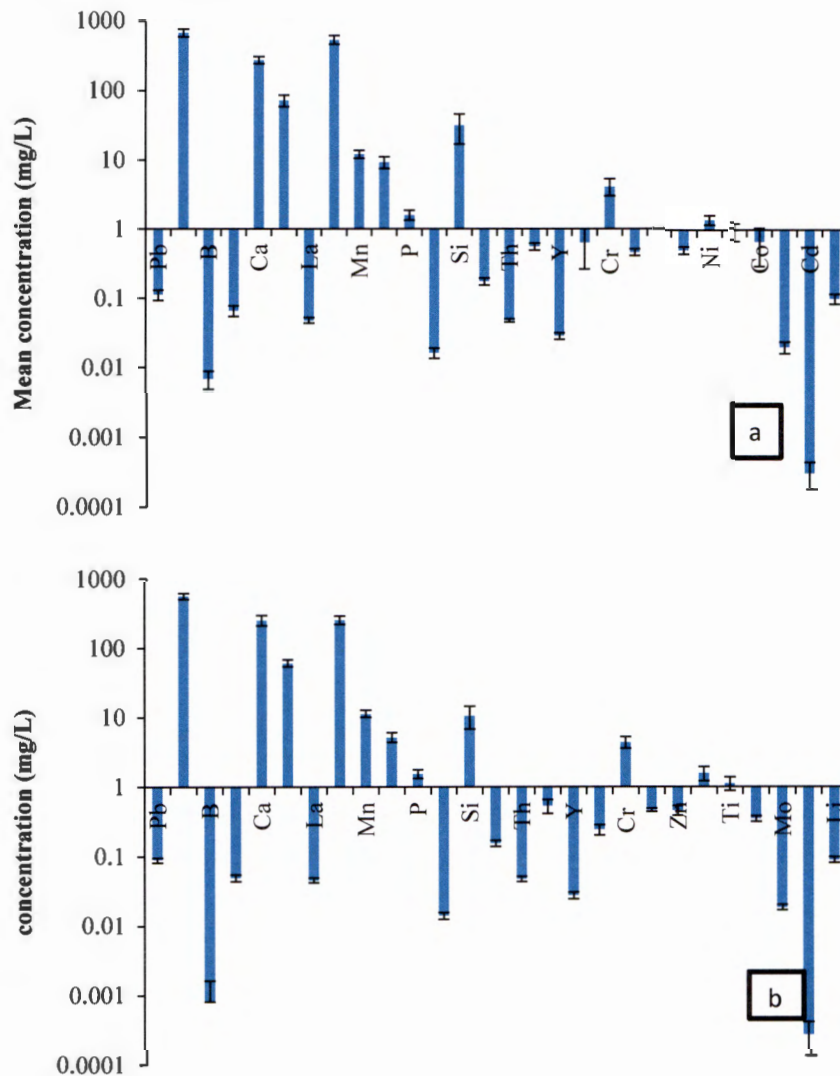
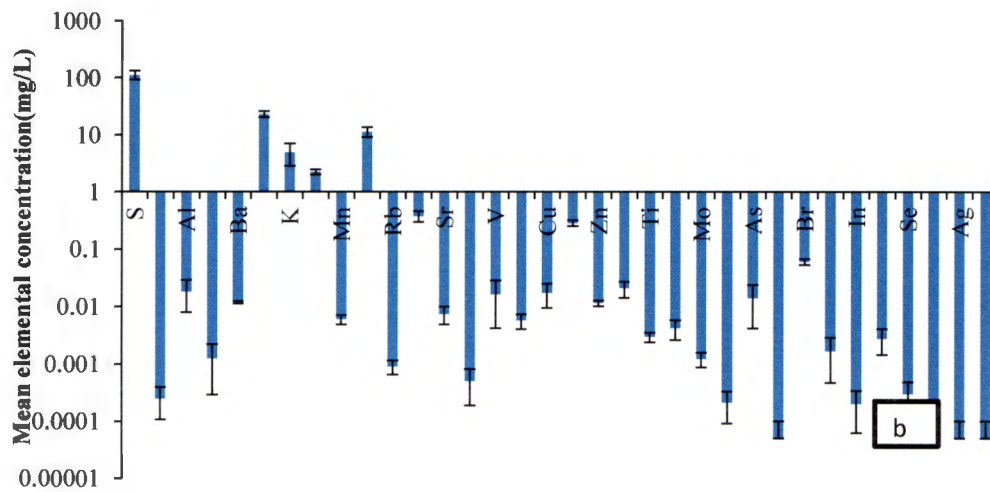
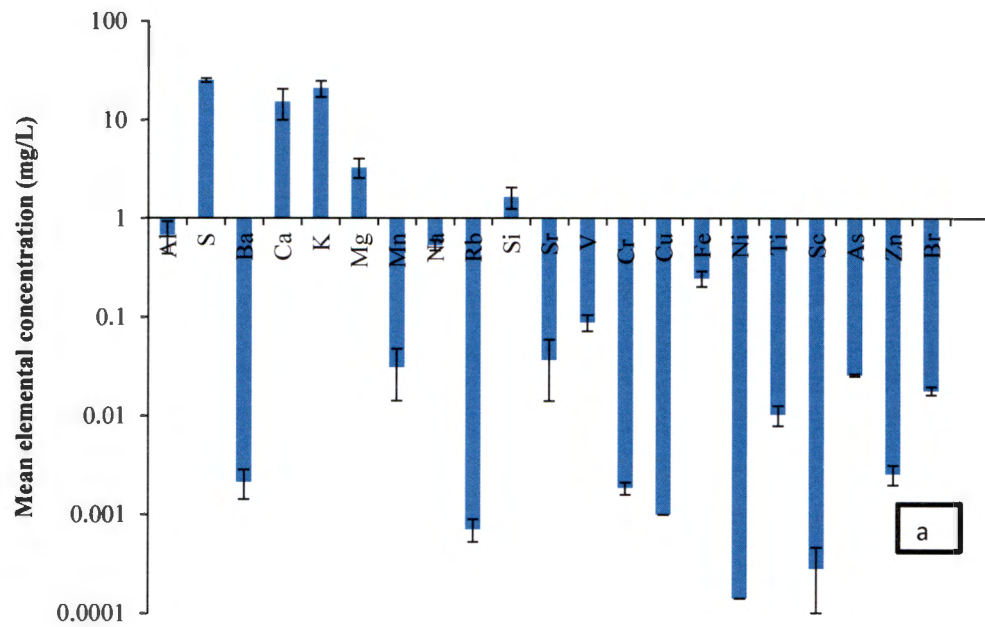


**Figure 14:** Elemental concentration of tailings a) tailing dam 1 and b) tailing dam 2.

From Figure 15 below, plant samples are dominated by Al, Si, Mg and K whereas water samples have Ca, Na and S. These elements can then be used as signatures for the mine studied. Table 3-6 show specific concentrations of all elements determined in the measured samples.



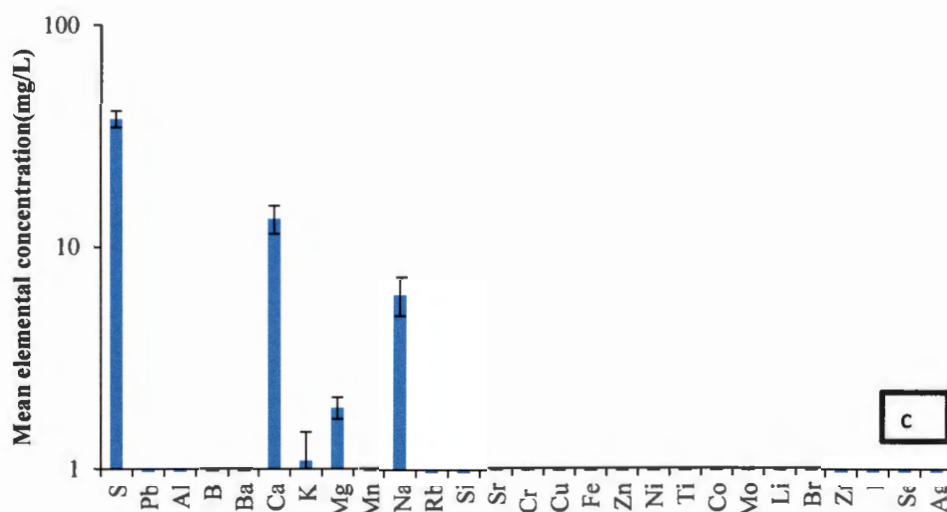


**Figure 15:** Mean concentration of a) vegetation samples taken around mine area Water (DSW) and c) VW.

Uranium impurities are not characterized to determine the origin only but also for assessing material quality and for regulating chemical processes (Peñkin et al., 2016). For instance, the presence of Co, Cr, Cu, Fe, Nb, Ni, Mn, Ta, Ti, V and Zn would indicate corrosion and erosion of the equipment utilized. High concentrations of Cl, F, Mg, Mn, N, Na, P, S; (which are organic elements) represent process related signatures. Trace levels of As, Au, Hf, Mo, Pb, Re, Th, W, Zr, rare earth and platinum group elements are useful or determining source-related signatures (Peñkin et al., 2016). Trace elements and sulphur were predominant in our study and this indicates an acidic soil (Rösner and Van Schalkwyk, 2000).

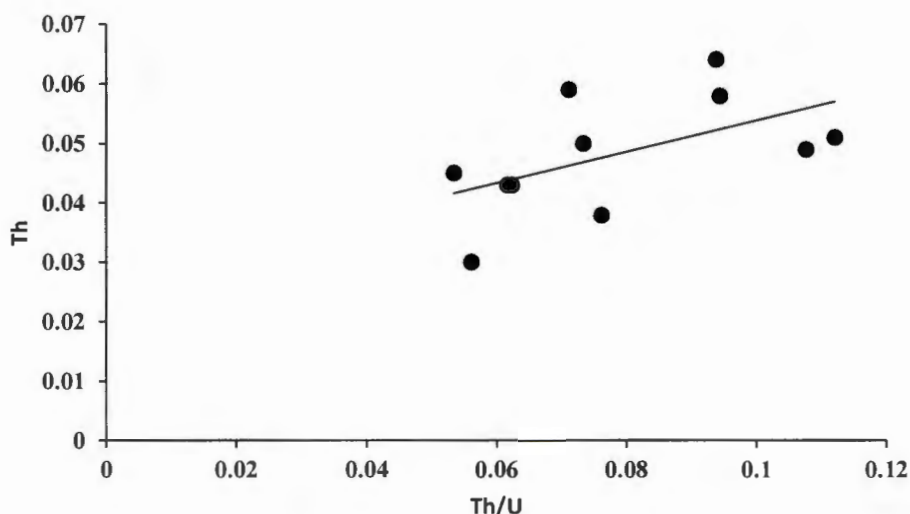


**Figure 16:** Plot of U/Th versus Th (mg/L).

Figure 16 above represents findings from samples collected from tailings dam 2. From the above it can be seen that the ratio of Th/U is very low. According to Silva et al (2016), the Th/U ratio reflects the degree of weathering: where Th is immobile and U is mobile in the ground. The low ratio implies that there is low chemical weathering (Silva et al., 2016). Particularly for this study, the  $^{235}\text{U}/^{234}\text{U}$  ratio was not determined because  $^{234}\text{U}$  was not detectable which might be due to little or no chemical weathering.  $^{234}\text{U}$  is generated from a leach during weathering of materials containing U (Brennecke et al., 2010). According to Tutu et al (2003) weathering of uraninite and brannerite precipitates a secondary chain of minerals such as U (VI) oxyhydroxides, silicates and sulphates.

### 4.3 REE chondrite normalized patterns

During the processing of the ore, some nuclear forensic fingerprint may be lost. However, rare earth elements (REE) or lanthanides retain their patterns (Hall et al 2015), and are thus used to determine the original deposit type after processing has been carried out. Differences in the concentrations of the REE create a fingerprint for a uranium ore deposit and varieties of uranium mines (Keatley et al., 2015).

The REE concentrations of the analyzed tailings dams are provided in Table 7 and 8. Tailing dam 1 has a slightly lower concentration of REE compared to 2. The  $\Sigma$ REE concentration for tailing 1 ranges from 0.132 to 0.279 mg/L whereas that of tailing 2 ranges from 0.134 to 0.33 mg/L. These values are lower than coarse and fine grained sediments which are found to have the  $\Sigma$ REE of 48.35 to 95.23 mg/Kg and 125.38 to 320.81 (Silva et al., 2016). The REE patterns are enriched with Light Rare Earth Elements (LREE) as the LaN/YbN ratio ranges from 13.155 to 35.311 for tailing dam 1 and 13.847 to 33.233 for tailing dam 2. The samples also show a negative europium anomaly. These results are consistent with the ones Silva et al. (2016) reported. The ratio of GdN/YbN varies from 2.4796 to 8.2655 for tailing dam 1 and 0.82655 to 4.9593 for tailing dam 2. As a result, tailing dam 1 has a higher fractionation of Heavy Rare Earth Elements (HREE) than tailing dam 2.

Table 7: REE Concentrations for tailing Dam 1

| Sample ID | REE   |       |        |       |        |        |        |        |        |        |         |        | $\Sigma$ REE | $\pm \Sigma$ REE | GdN/YbN | LaN/YbN |
|-----------|-------|-------|--------|-------|--------|--------|--------|--------|--------|--------|---------|--------|--------------|------------------|---------|---------|
|           | La    | Ce    | Pr     | Nd    | Sm     | Eu     | Gd     | Tb     | Dy     | Ho     | Er      | Yb     |              |                  |         |         |
| T1E1      | 0.058 | 0.11  | 0.012  | 0.036 | 0.0070 | 0.0010 | 0.0060 | 0.0020 | 0.0040 | 0.001  | 0.0020  | 0.0020 | 0.25         | 0.032            | 2.48    | 20.10   |
| T1E2      | 0.031 | 0.061 | 0.0070 | 0.023 | 0.0040 | 0.0010 | 0.0050 | 0.0010 | 0.0030 | 0.001  | 0.0020  | 0.0010 | 0.14         | 0.017            | 4.13    | 21.50   |
| T1E3      | 0.048 | 0.094 | 0.0100 | 0.032 | 0.0050 | 0.0010 | 0.0060 | 0.0010 | 0.0040 | 0.001  | 0.0010  | 0.0020 | 0.21         | 0.027            | 2.48    | 16.60   |
| T1E4      | 0.044 | 0.088 | 0.0090 | 0.029 | 0.0050 | 0.0010 | 0.0060 | 0.0010 | 0.0040 | 0.001  | 0.0010  | 0.0010 | 0.19         | 0.025            | 4.96    | 30.46   |
| T1E5      | 0.061 | 0.12  | 0.013  | 0.041 | 0.0070 | 0.0020 | 0.0080 | 0.0010 | 0.0040 | 0.001  | 0.0020  | 0.0020 | 0.27         | 0.035            | 3.31    | 21.12   |
| T1E6      | 0.030 | 0.058 | 0.0060 | 0.021 | 0.0040 | 0.0010 | 0.0050 | 0.0010 | 0.0030 | 0.001  | 0.0010  | 0.0010 | 0.13         | 0.017            | 4.13    | 20.80   |
| T1E7      | 0.038 | 0.081 | 0.0090 | 0.027 | 0.0050 | 0.0010 | 0.0070 | 0.0010 | 0.0040 | 0.001  | 0.0020  | 0.0020 | 0.18         | 0.023            | 2.89    | 13.20   |
| T1E8      | 0.032 | 0.064 | 0.0070 | 0.024 | 0.0040 | 0.0010 | 0.0050 | 0.0010 | 0.0030 | 0.00   | 0.0010  | 0.0010 | 0.14         | 0.019            | 4.13    | 22.20   |
| T1E9      | 0.050 | 0.10  | 0.011  | 0.035 | 0.0060 | 0.0010 | 0.0070 | 0.0010 | 0.005  | 0.0010 | 0.0020  | 0.0020 | 0.22         | 0.029            | 2.89    | 17.30   |
| T1E10     | 0.051 | 0.11  | 0.012  | 0.038 | 0.0080 | 0.0020 | 0.010  | 0.0020 | 0.01   | 0.0020 | 0.0040  | 0.0010 | 0.25         | 0.030            | 8.27    | 35.30   |
| T1E11     | 0.061 | 0.12  | 0.014  | 0.045 | 0.0080 | 0.0020 | 0.010  | 0.0010 | 0.007  | 0.0010 | 0.00300 | 0.0030 | 0.28         | 0.035            | 2.76    | 14.10   |

Table 8: REE Concentrations for Tailing Dam 2

| Sample ID | REE   |       |        |       |        |        |        |        |        |        |        |        | $\Sigma$ REE | $\pm\Sigma$ REE | GdN/YbN | LaN/YbN |
|-----------|-------|-------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------------|-----------------|---------|---------|
|           | La    | Ce    | Pr     | Nd    | Sm     | Eu     | Gd     | Tb     | Dy     | Ho     | Er     | Yb     |              |                 |         |         |
| T1E1      | 0.058 | 0.11  | 0.012  | 0.036 | 0.0070 | 0.0010 | 0.0060 | 0.0020 | 0.0040 | 0.0010 | 0.0020 | 0.0020 | 0.25         | 0.032           | 2.48    | 20.08   |
| T1E2      | 0.031 | 0.061 | 0.0070 | 0.023 | 0.0040 | 0.0010 | 0.0050 | 0.0010 | 0.0030 | 0.0010 | 0.0020 | 0.0010 | 0.14         | 0.017           | 4.13    | 21.46   |
| T1E3      | 0.048 | 0.094 | 0.010  | 0.032 | 0.0050 | 0.0010 | 0.0060 | 0.0010 | 0.0040 | 0.0010 | 0.0010 | 0.0020 | 0.21         | 0.027           | 2.48    | 16.62   |
| T1E4      | 0.044 | 0.088 | 0.0090 | 0.029 | 0.0050 | 0.0010 | 0.0060 | 0.0010 | 0.0040 | 0.0010 | 0.0010 | 0.0010 | 0.19         | 0.025           | 4.96    | 30.46   |
| T1E5      | 0.061 | 0.124 | 0.013  | 0.041 | 0.0070 | 0.0020 | 0.0080 | 0.0010 | 0.0040 | 0.0010 | 0.0020 | 0.0020 | 0.27         | 0.035           | 3.31    | 21.12   |
| T1E6      | 0.03  | 0.058 | 0.0060 | 0.021 | 0.0040 | 0.0010 | 0.0050 | 0.0010 | 0.0030 | 0.0010 | 0.0010 | 0.0010 | 0.13         | 0.017           | 4.13    | 20.77   |
| T1E7      | 0.038 | 0.081 | 0.0090 | 0.027 | 0.0050 | 0.0010 | 0.0070 | 0.0010 | 0.0040 | 0.0010 | 0.0020 | 0.0020 | 0.18         | 0.023           | 2.89    | 13.16   |
| T1E8      | 0.032 | 0.064 | 0.0070 | 0.024 | 0.0040 | 0.0010 | 0.0050 | 0.0010 | 0.0030 | 0.00   | 0.0010 | 0.0010 | 0.14         | 0.018           | 4.13    | 22.16   |
| T1E9      | 0.05  | 0.10  | 0.011  | 0.035 | 0.0060 | 0.0010 | 0.0070 | 0.0010 | 0.0050 | 0.0010 | 0.0020 | 0.0020 | 0.22         | 0.029           | 2.89    | 17.31   |
| T1E10     | 0.051 | 0.11  | 0.012  | 0.038 | 0.0080 | 0.0020 | 0.010  | 0.0020 | 0.010  | 0.0020 | 0.0040 | 0.0010 | 0.25         | 0.030           | 8.27    | 35.31   |
| T1E11     | 0.061 | 0.12  | 0.014  | 0.045 | 0.0080 | 0.0020 | 0.010  | 0.0010 | 0.0070 | 0.0010 | 0.0030 | 0.0030 | 0.28         | 0.035           | 2.76    | 14.08   |

There are four REE which were found to be a fingerprint for this mine on both tailings dam 1 and 2. These were La, Ce, Pr and Nd. These are the Light Rare Earth Elements and in this case they show that they are dominating in the study area. The REE concentrations for tailings dam 2 are slightly higher than that of tailing dam 1 (Table 9 and 10). A Kingswood mine in South West England had a vein-type uranium ore deposit with REE indicating a certain uranium mineral. The following are the minerals found in the Kingswood mine: Quartz, Pyrite, Mixed Quartz and pyrite, Chalcopyrite, Bukovskyite, Mixed Quartz and Bukovskyite, Quartz with iron impurity. Even though they found these minerals, most of samples contained sulphides and silicates more than the other samples. In the study conducted here, Ce has a slightly higher concentration compared to all the other REE found in both tailings dams. This indicated an enrichment of the Lighter REEs signifying a high uranium deposit.

From each sample, three mineral geological phases were detected namely, uraninite, metazeunerite as well as REE rich uranium phosphate (RRUP). Ca, Fe, W and Pb were impurities found in uraninite and this is normally the characteristic of vein type hydrothermal deposit. These elements were detected in most samples for this study. RRUP contained REE mostly Ce and Nd. In this study, the samples contained mostly Ce and La. The fingerprint of the Kingswood mine is non-measurable amount of Eu, Tb and other heavy REE which were measured in this mine but were very low in concentration. The uranium from Carletonville, South Africa can be said to have different REE signatures from that at Kingswood, UK.

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Figure 17 below is a graphical representation of the REE concentrations. The results show that in both tailings dams Ce was at the highest concentration followed by La, Nd and Pr which was at the least concentration. The tailings produced similar results and this is because the samples are from a single mine but different shafts. Therefore, these reported concentrations can be used as a signature for this mine. In studies done by Kegaan et al (2008), REE concentration was found to

be different in three mines namely Beverly, Ranger and Olympic Dam.

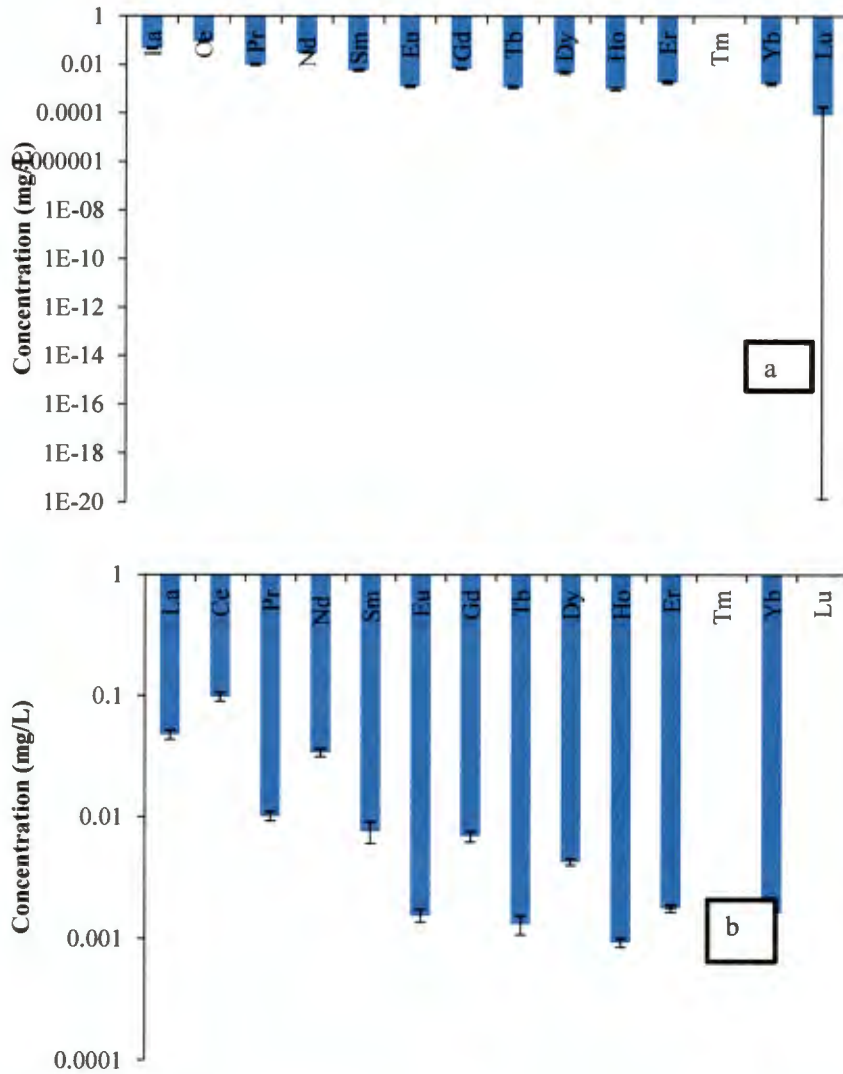
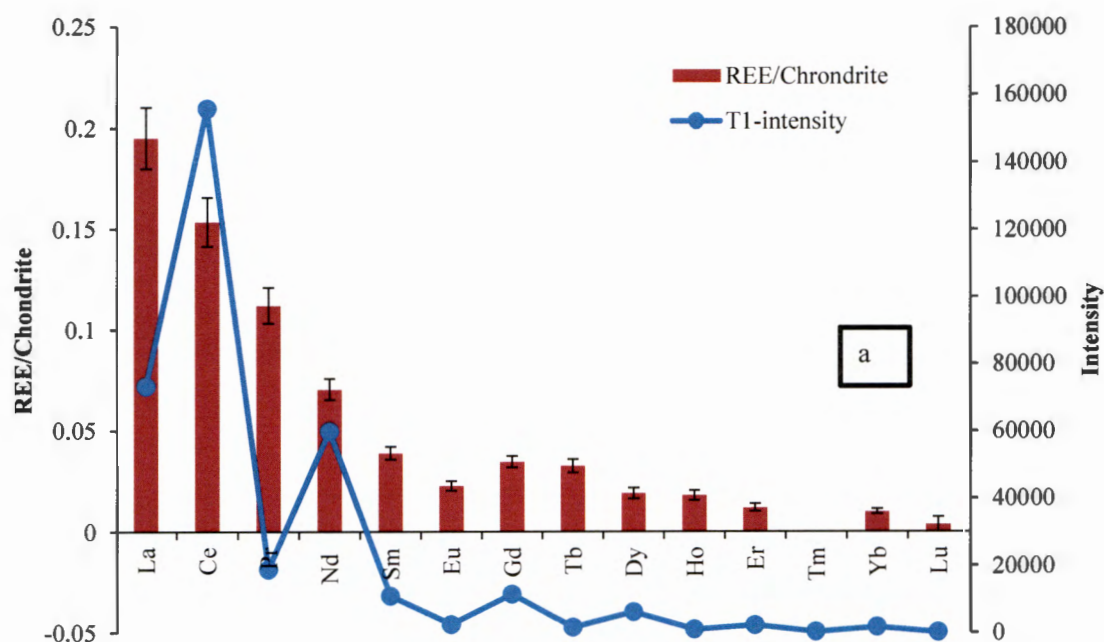


**Figure 17:** REE concentration for a) tailings dam 1 (n=11) and b) 2 (n=13).

Since the aim of the study was to generate signatures for NNFL, it is imperative that the fingerprint created differ for each mine so that they may represent a different deposit type. This was achieved by normalizing the REE data by using standard reference chondritic material of known composition (Keegan et al., 2008). As a result, the data for this study was also normalized to check for statistical variation in the REEs from different shafts of the same mine. Intensities of REE are shown in Figure 18 and along with the normalized REE/Chondrite.

The intensities of the REE decrease with the ascending order of atomic number for both tailings dams. Studies conducted by Asai and Limbeck (2015) reported a directly proportional relationship between REE atomic number and intensity or integrated counts which is the opposite of this work. This can be due to additional interference or elemental fractionation from the ICP-MS. Oxides and hydroxides of the light REE are the main causes of interference in REE measurement (Asai and Limbeck, 2015b). The intensity of tailings 1 is lower than that of tailings 2. However, the REE/chondrite ratios slightly differ from each other. The result of our study is dominated by LREE.



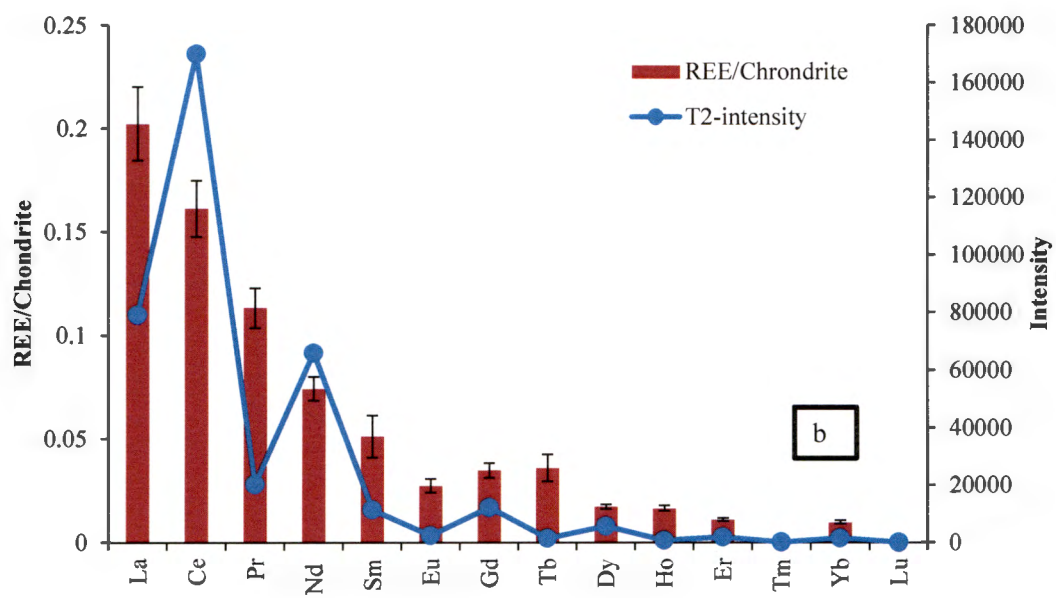


**Figure 18:** REE vs REE/Chondrite and intensities.

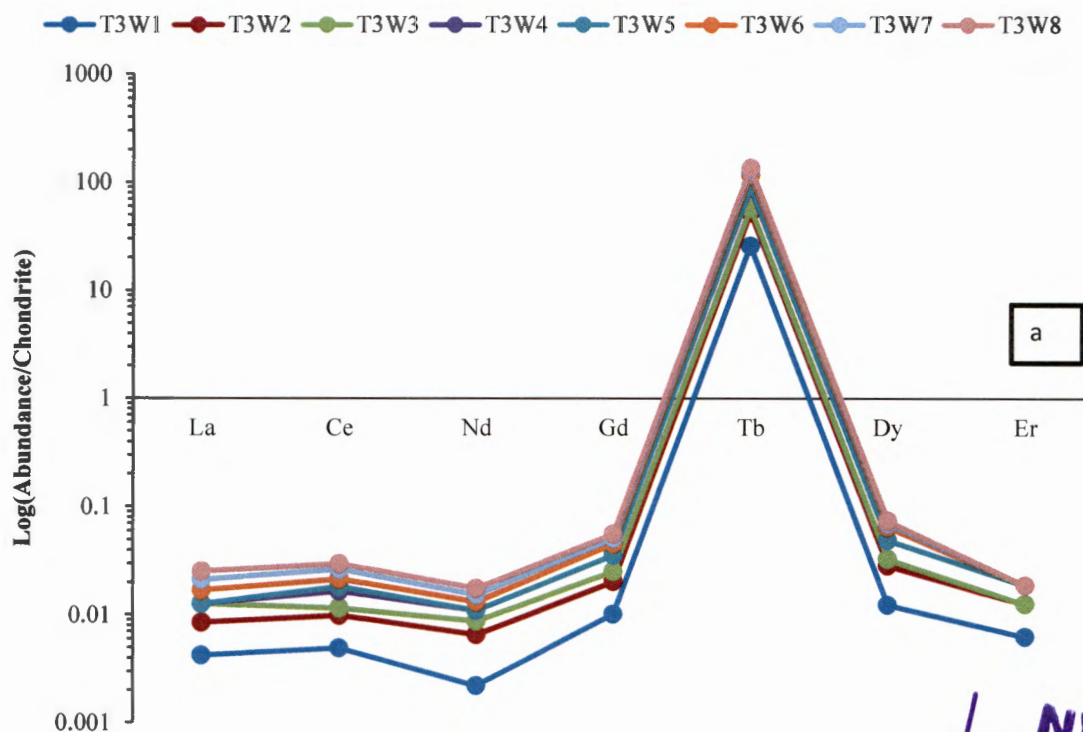


**Figure 19 (a):** Chondrite normalized lanthanide (REE) patterns for tailings dam 3.

All samples show a strong positive Tb anomaly indicating no fractionation of HREE (Tb– Lu). Probably this is due to geo-tectonic activity associated with the Witwatersrand area (Orkney earthquake of 2014). The seismic instability might be causing hydrothermal enrichment of Tb. The other HREE with atomic numbers greater than Er were all below the detection limit of our ICP-MS. LREE viz., La – Gd are relatively flat showing that they were not changed by uranium processing nor geological factors in the earth-quake prone mining area. However, the LREE do show small negative Nd anomaly and a very slight enrichment of Ce.

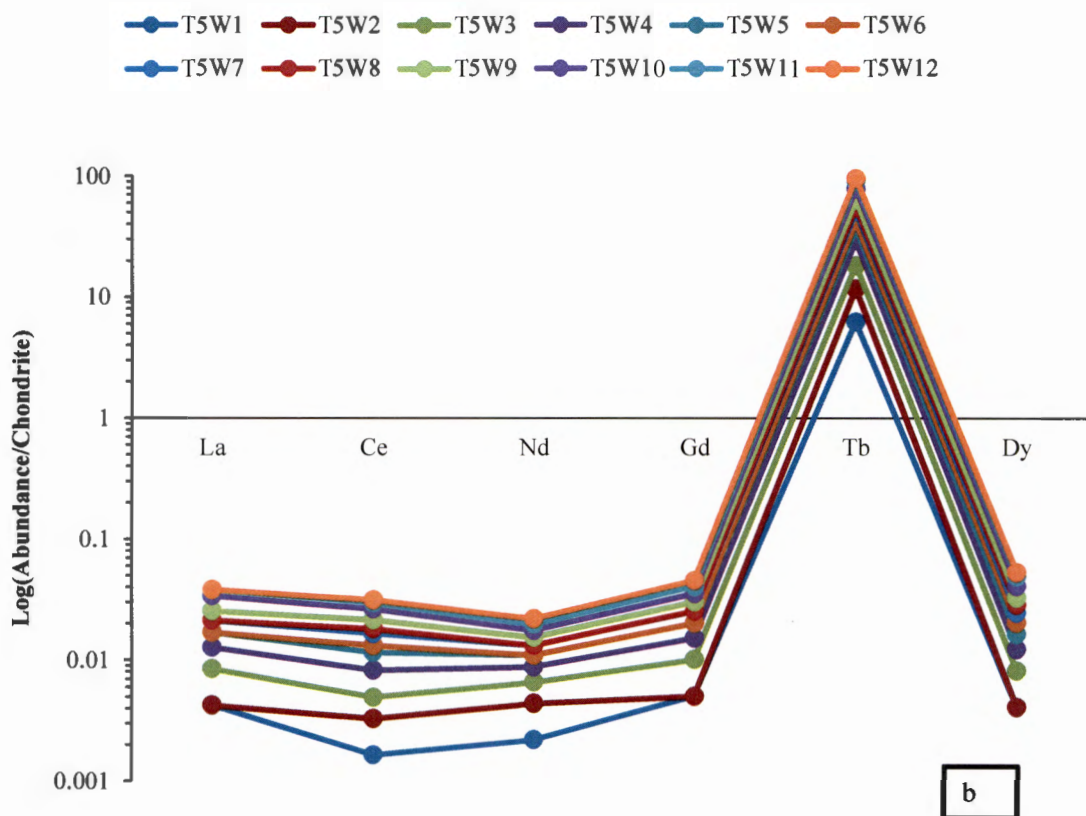


**Figure 19 (b):** Chondrite normalized lanthanide (REE) patterns for Tailings dam 5.

For both tailings, Sample ID T3W7 and T5W11 have lowest normalized ratios for all REE and Sample ID T3W and T5W12 have the highest ratios. Perhaps the sludge was from the same mine shaft. However in general the two tailing dams REE patterns are similar indicating the characteristic signature for this mine.

#### 4.4 Lead Isotopic technique

The use of isotopic ratio in nuclear forensics as fingerprints provide information about the following: enrichment value, age dating as well as actinide concentration (Bellucci et al., 2013a). Once isotopic signatures have been developed, they are then used to answer the questions in nuclear forensic investigations and hence facilitate law enforcement by the legal authorities (Marin et al., 2014). In the case of post-detonation three heavy elements are used, that is, uranium, lead

and plutonium. The isotopic composition of these elements is indicative of the type of fuel, ore and enrichment cycle. Thus, these elements are used to determine the origin of the nuclear material.

Natural lead has four stable isotopes namely  $^{204}\text{Pb}$  (1.4%),  $^{206}\text{Pb}$  (24.1%),  $^{207}\text{Pb}$  (22.1%) and  $^{208}\text{Pb}$  (52.4%) (Reimann et al., 2012). Amongst the three elements, lead is the preferred uranium impurity because of two reasons namely: the four lead stable isotopes are not altered in the geological environment and the radiogenic isotopes  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$  and  $^{206}\text{Pb}$  generated from uranium as well as thorium enable the determination of geological processes and hence the origin of the unknown sample.  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  are produced by the decay chain of  $\text{U}^{238}$  and  $\text{Th}^{232}$  whereas  $\text{Pb}^{207}$  is the end product of  $^{235}\text{U}$  decay chain (Table 11) (Cheng and Hu, 2010a, Švedkauskaitė-LeGore et al., 2008).  $^{204}\text{Pb}$  is a primordial lead isotope and can be used to measure the natural uranium content in the sample (Švedkauskaitė-LeGore et al., 2008, Varga et al., 2009).

Table 11: showing decay processes of  $^{232}\text{Th}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  to produce radiogenic lead isotopes (Cheng and Hu, 2010a)

| Reaction                                                                                      | Decay constant( $\text{year}^{-1}$ ) | Half-life (years)       |
|-----------------------------------------------------------------------------------------------|--------------------------------------|-------------------------|
| $^{238}_{92}\text{U} \rightarrow ^{206}_{82}\text{Pb} \rightarrow 8^4_2\text{He} + 6\beta^-$  | $1.55125 \times 10^{-10}$            | $4.468 \times 10^9$     |
| $^{235}_{92}\text{U} \rightarrow ^{207}_{82}\text{Pb} \rightarrow 7^4_2\text{He} + 4\beta^-$  | $9.8485 \times 10^{-10}$             | $7.038 \times 10^8$     |
| $^{232}_{90}\text{Th} \rightarrow ^{208}_{82}\text{Pb} \rightarrow 6^4_2\text{He} + 4\beta^-$ | $4.9475 \times 10^{-11}$             | $1.4008 \times 10^{10}$ |

The NexION 300Q ICP-MS has a sensitivity  $> 40 \text{ mg/L}$  and  $> 20 \text{ mg/L}$  (for  $^{24}\text{Mg}$ ) with a detection limit of  $< 0.2 \text{ ng/L}$  (for  $^{238}\text{U}$ ) (PerkinElmer, 2010). The instrument Short-term precision is defined as the relative standard deviation (% RSD) for a  $1 \text{ } \mu\text{g/L}$  multi-element solution, measuring  $^{24}\text{Mg}$ ,  $^{63}\text{Cu}$ ,  $^{114}\text{Cd}$  and  $^{208}\text{Pb}$ , without internal standardization. It is evaluated as  $< 3\%$  RSD. It has an Isotope-ratio precision which is defined for the isotope ratio of  $^{107}\text{Ag}/^{109}\text{Ag}$  using a  $25 \text{ } \mu\text{g/L}$  solution obtained using single-point peak hopping this value is  $< 0.2\%$  RSD.

The excellent sensitivity, precision and good accuracy of the ICP-MS operated under collision cell interface, has made it comparable to thermal ionization mass spectrometry (TIMS), for precise

isotope ratio measurements. The ICP-MS configuration now allows for the dissociation, thermalizing and neutralizing of the disturbing argon-based molecular ions. The application of the collision cell in ICP-QMS results in a higher ion transmission, improved sensitivity and better precision of isotope ratio (Becker and Dietze, 2000). These characteristics formed the basis for using our Perkin Elmer NexION 300Q ICP-MS in this work.

TIMS results shown in Fig 5b of Weis et al., 20 (Weis and Scoates, 2006), fall within the range shown in Fig 23 and Fig 24 of this work.

### **Sources of uncertainties**

The Pb-Pb ratios in these results are relatively lower than the true values. This could imply that instrument optimization alone is not sufficient to correct for mass fractionation although the NexION ICP-MS instrument used here does not use laser ablation (the most common source of mass fractionation (Lin et al., 2016) (Thirlwall, 2000)).

In this work the uncertainties were evaluated as follows:

- For trace elements- uncertainties are presented as STDEV of all the results in the Tables
- For Isotopic ratios - all results are average values of three replications by the instrument
- For all graphs- we calculated the STDEV ( $\sigma$ ) for each data set plotted and used that to plot the error bars as ( $\pm\sigma$ ) for each point on the graph.

#### 4.4.1 Lead isotopic ratio analysis

Lead (Pb) isotopic signatures are identified by isotope ratios based on the three combinations of  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ; for example,  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  (Yip et al., 2008a). The lead isotope ratios measured in this study for the gold mine are shown in Figures 21 and 22 below and the ratios are presented relative to the non-radiogenic  $^{204}\text{Pb}$ . Note that sample CW4 is a control sample collected 400 km away from any mining area. Attached in the appendix is an explanation of the sample names. The lead isotopic ratios are showing variation which are due to inhomogeneity of lead isotopic composition within the ore body as well as steady removal of the radiogenic lead by the chemical separation and continuous isotope dilution with natural lead caused by contaminating reagents during the milling process (Varga et al., 2009).

To minimize the isobaric interference described earlier, and for this geochronological study, we used the fingerprint of the two ratios,  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  (Cheng and Hu, 2010b, Lin et al., 2016). The instrument mass bias corrected isotopic ratios of lead normalized to  $^{208}\text{Pb}/^{206}\text{Pb}$  (Thirlwall, 2000) are shown in Table 13 below. The advantage of using  $^{206}\text{Pb}$  as the denominator isotope is that there is significantly less error magnification and much less error correlation between the measured ratios than for ratios to  $^{204}\text{Pb}$  (Thirlwall, 2000)

Table 12 shows the lead isotopic ratios before and after exponential law normalization for mass balance correction. The ratio of  $^{204}\text{Pb}/^{206}\text{Pb}$  falls within the National Institute of Standards and Technology (NIST) ratio of 0.059. None of the samples hit above this accepted lead isotopic ratio. The ratio of  $^{207}\text{Pb}/^{206}\text{Pb}$  is slightly lower than the one prescribed by NIST (0.91). However, these values are very close to the accepted standard. All samples measured for  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio are also closest to the standard value of 2.1681. In a study conducted by Bellucci et al (2013),  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio was employed as a basis to determine the instrumental mass bias factor. Below are the National Institute of Standards and Technology (NIST) values with errors based on 95% confidence limits (SRM NIST, 1991) and are given as:

- Atomic abundance Ratio,  $^{204}\text{Pb}/^{206}\text{Pb} = 0.059042 \pm 0.000037$
- Atomic abundance Ratio,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.91464 \pm 0.00033$
- Atomic abundance Ratio,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0008$

Adding to the above mentioned NIST values, Baker et al (2004) reported preferred working values for the Pb isotope composition other than NIST SRM (1991) (Table 13).

Table 14 shows isotopic ratio for  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{206}\text{Pb}/^{204}\text{Pb}$  per sample, respectively. According to Yuan et al (2016), the recommended reference values for lead isotopes are as follows:  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$   $16.9406 \pm 0.0003$  (2s, n 1135),  $15.4957 \pm 0.0002$  (2s, n 1128), and  $36.7184 \pm 0.0007$  (2s, n1128). These values are close to those obtained in this work. The sample DSW712  $^{207}\text{Pb}/^{204}\text{Pb}$  isotopic ratio of this study falls within the recommended ratio. The rest of  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios are either higher or lower than the recommended one. Same trend was observed with the other two remaining lead isotopic ratios. This observed phenomenon can be due to system errors or mass discrimination correction method (Yuan et al., 2016). A possible reason for the observed deviation of ratios could be due to the higher deposit age or presence of higher thorium or uranium content in the source rock (Varga et al., 2009). This is caused by higher content of radiogenic lead relative to the natural lead (Varga et al., 2009).

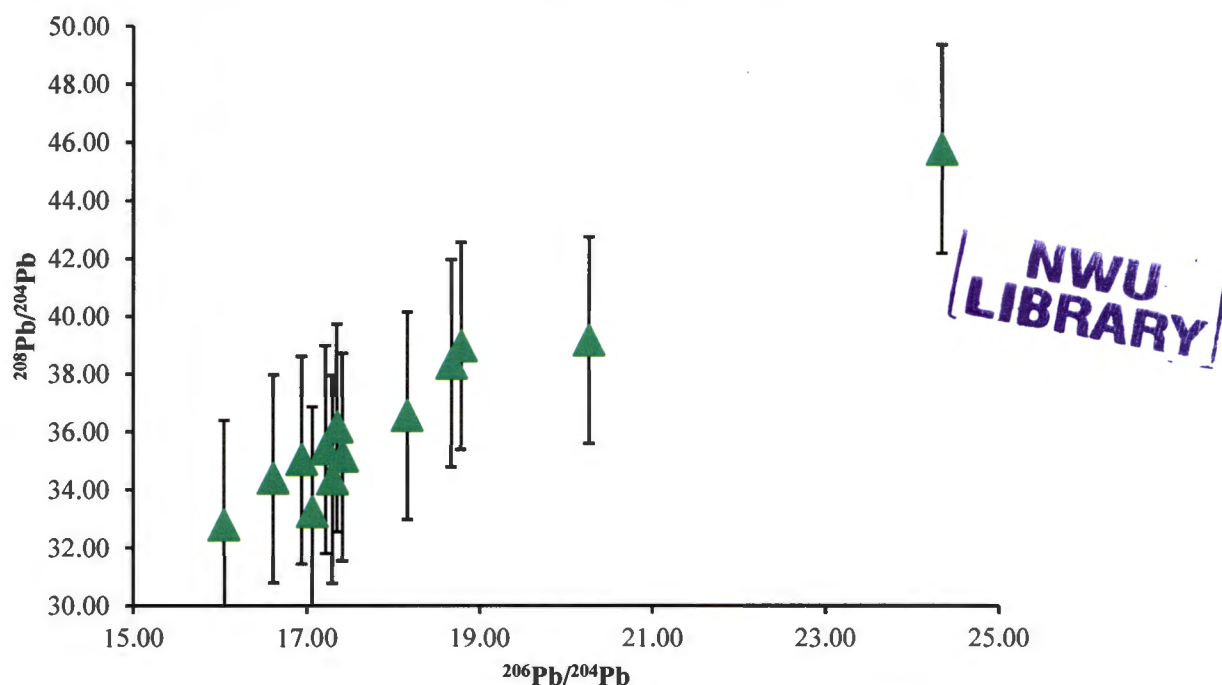


**Figure 20:** A plot of  $^{208}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  for water samples.

A close look at the isotopes in Figure 20 indicates that these two points are actually due to the observed much higher value of  $^{206}\text{Pb}$  (implying higher  $^{238}\text{U}$  concentration) and even lower value of  $^{204}\text{Pb}$  (implying these two deposits are of radiogenic origin (Fahey et al., 2010). The results in Figure 21 reflect the geological origin of the deposit (radiogenic in this case).

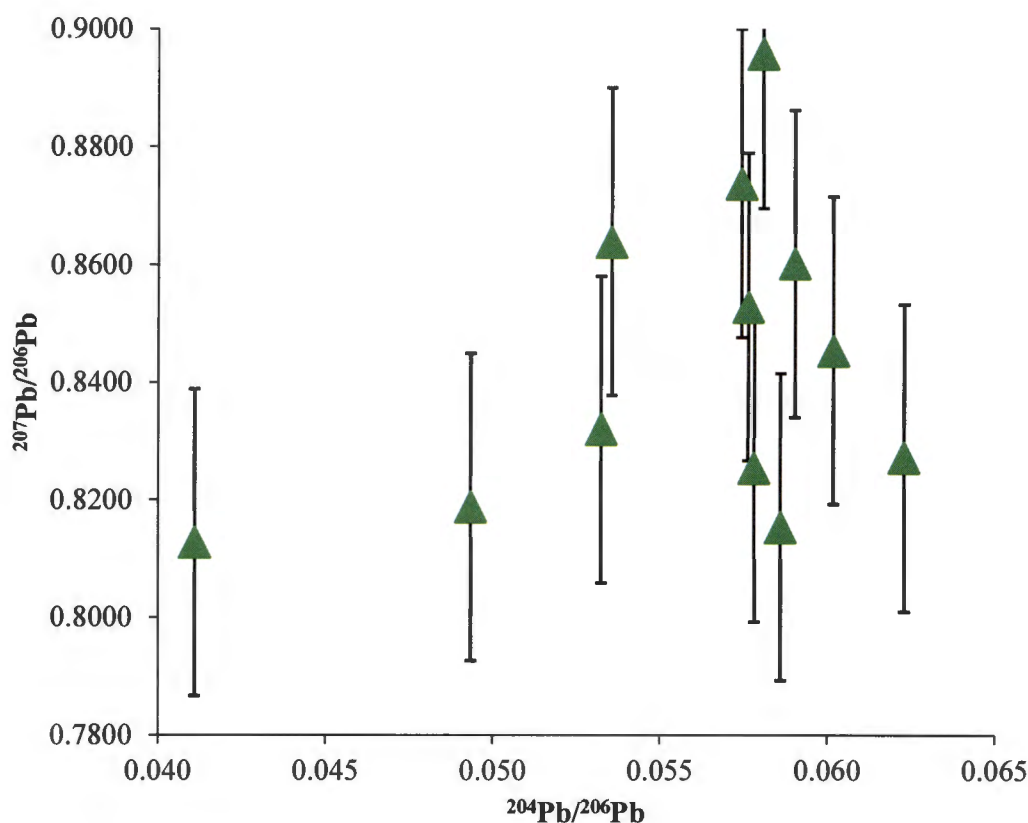
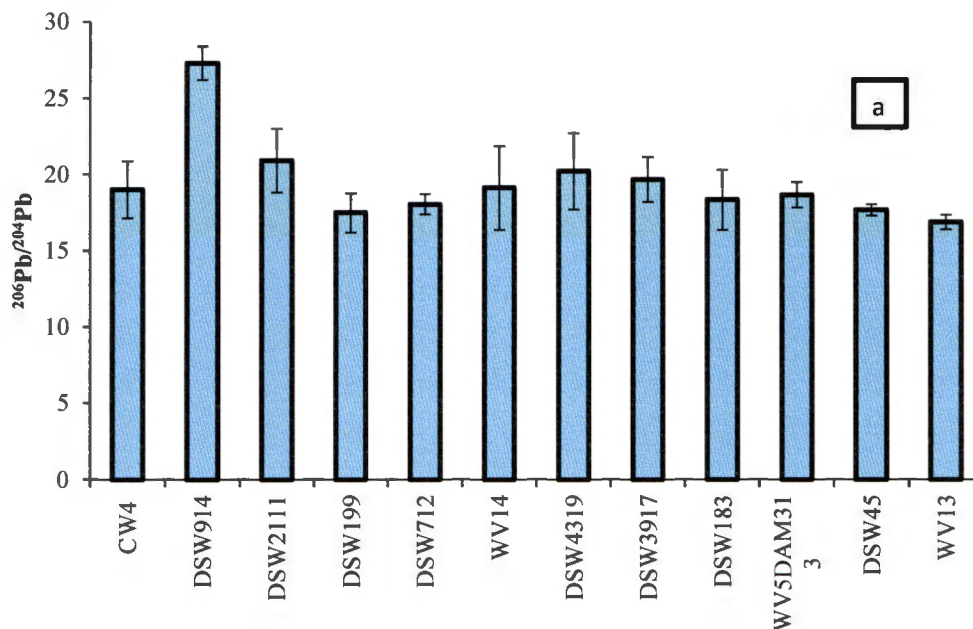


**Figure 21:** Isotopic composition of the mine water samples relative to  $^{206}\text{Pb}$ .

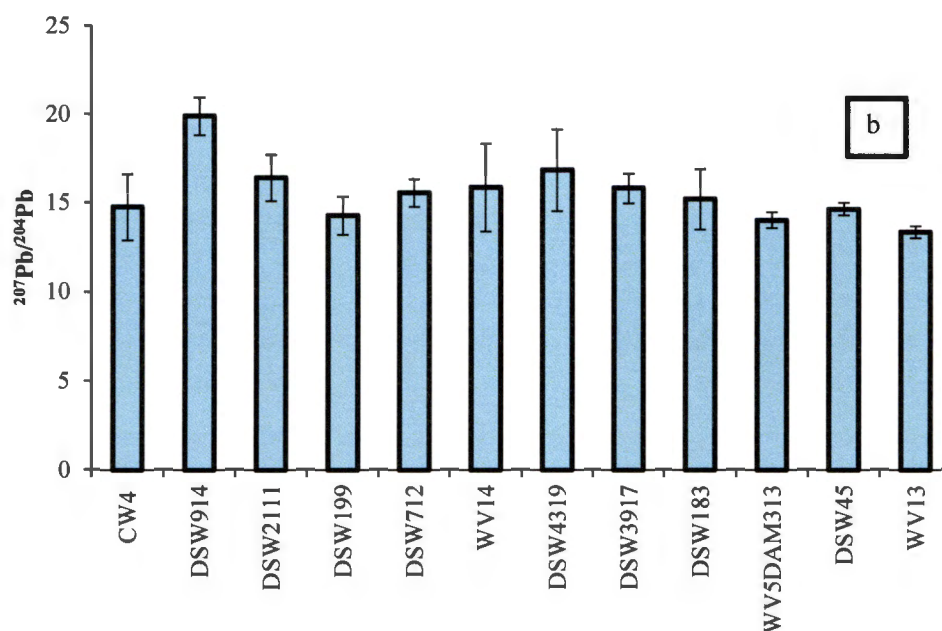
In Figure 21, the data scatter around values of  $^{204}\text{Pb}/^{206}\text{Pb} = 0.059$ , which is in good agreement with the NIST SRM 981 value of 0.59042.

Also the Pb-Pb plot for these results (Figure 20 & 21), confirms that the Carletonville gold fields are pyrite deposits, giving another signature for this mine. The similarity of these plots (data ranges) with those from (Poujol, 1999), suggest that the pyrites deposits are of detrital type.

Figure 22 below depicts Pb isotopic ratios relative to the  $^{204}\text{Pb}$  isotope which is a non-radiogenic lead.



The  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio shown in a) and Table 14 ranges from  $16.827 \pm 0.46553$  to  $27.263 \pm 1.0896$ . This ratio is similar to the one obtained by Lai et al (2016). However the range between samples is wide for both our study and Lai et al (2016) studies. According to Bellucci et al (2013), a  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio greater than 20 indicates that investigated Pb emanates from a uranium ore whereas a ratio less than 20 indicates a Pb- rich ore (Bellucci et al., 2013b). The U-bearing phases associated with the higher radiogenic Pb content are zircon, monazite and apatite (Bellucci et al., 2013b). This study had an extreme Pb  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio of 16.827-27.263 and it differs from that of 17.6-18.0 in Bellucci et al (2013) studies which represent a Pb-ore from Bunchas mine located in Newfoundland, Canada. As a result it can be used as a signature for the mine evaluated in this study compared to the mine in Canada.



The  $^{207}\text{Pb}/^{204}\text{Pb}$  ratio ranges from 13.290 to 19.815. Varga et al (2009) reported a value of  $15.8 \pm 1.1$  whereas Belluci et al (2013) reported a range of 15.5–15.6. In comparison with the work done for this study, some of the samples analyzed possess quite similar  $^{207}\text{Pb}/^{204}\text{Pb}$  ratio (Table 14). A list of all the acceptable working values for the Pb isotope composition adapted from NIST SRM 981, NIST SRM 610–612–614, NOD-A-1, JB-2, BCR-1 and AGV-1 is provided in Table 13. Some of our values here are quite consistent with these standards, for instance, the sample DSW 712  $^{207}\text{Pb}/^{204}\text{Pb}$  ratio is more or less the same as SMRR 981 value while W14 and DSW3917 are quite similar to NOD-A-1. In comparison to Keegan's (2014) results, our results are far better than those of that author since values of  $50.995 \pm 0.080$ ,  $38.158 \pm 0.019$  and 40 were reported for  $^{207}\text{Pb}/^{204}\text{Pb}$  isotopic ratio.

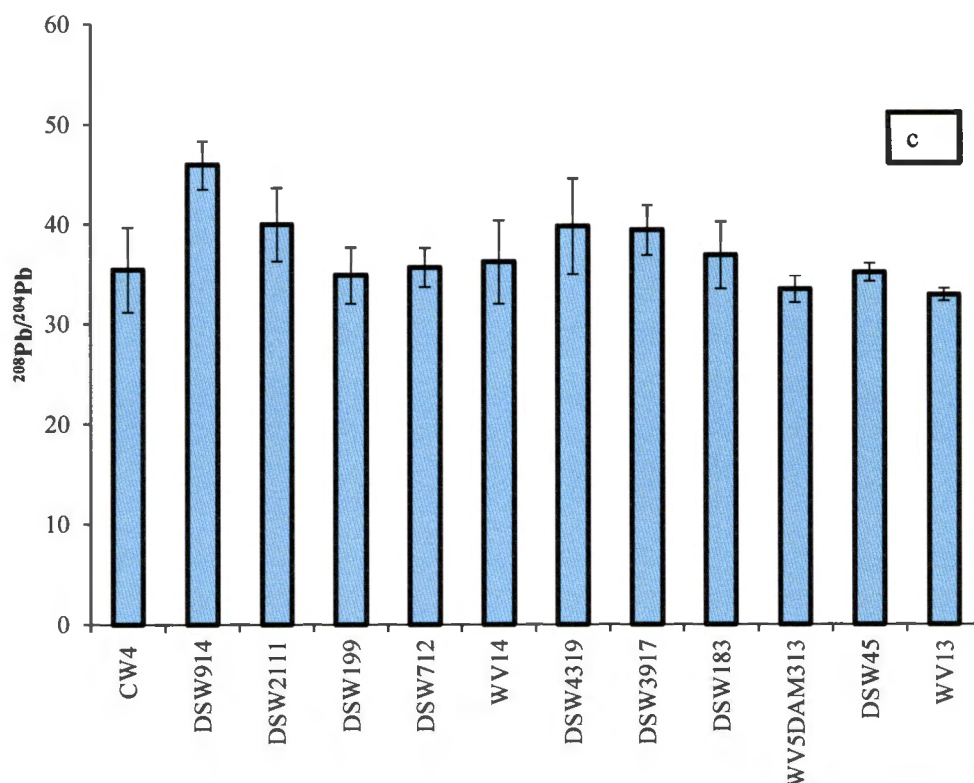


**Figure 22 a) – c):** Lead isotopic ratios for the gold mine combined with standard error around the mean  $n=3$  for all measured samples.

In nuclear forensic, the content of  $^{208}\text{Pb}$  plays a crucial part in determining the origin of the material because this isotope is the daughter of a  $^{232}\text{Th}$  decay series located in uranium ore (Varga et al., 2009). From the graph above  $^{208}\text{Pb}$  levels are high and this marks a quartz-pebble conglomerate deposit which is characterized by high thorium content. Samples from the Witwatersrand (South Africa) are expected to be characterized by this isotopic pattern (Varga et al., 2009). The results obtained in this study are similar to the ones of Varga et al (2009) for yellow cake samples from the Blind River-Elliot Lake district (Ontario, Canada) in Blind River, Stanrock, and Stanleigh (Varga et al., 2009). Figure 24 below illustrates lead isotope ratios plotted relative to  $^{206}\text{Pb}$ .

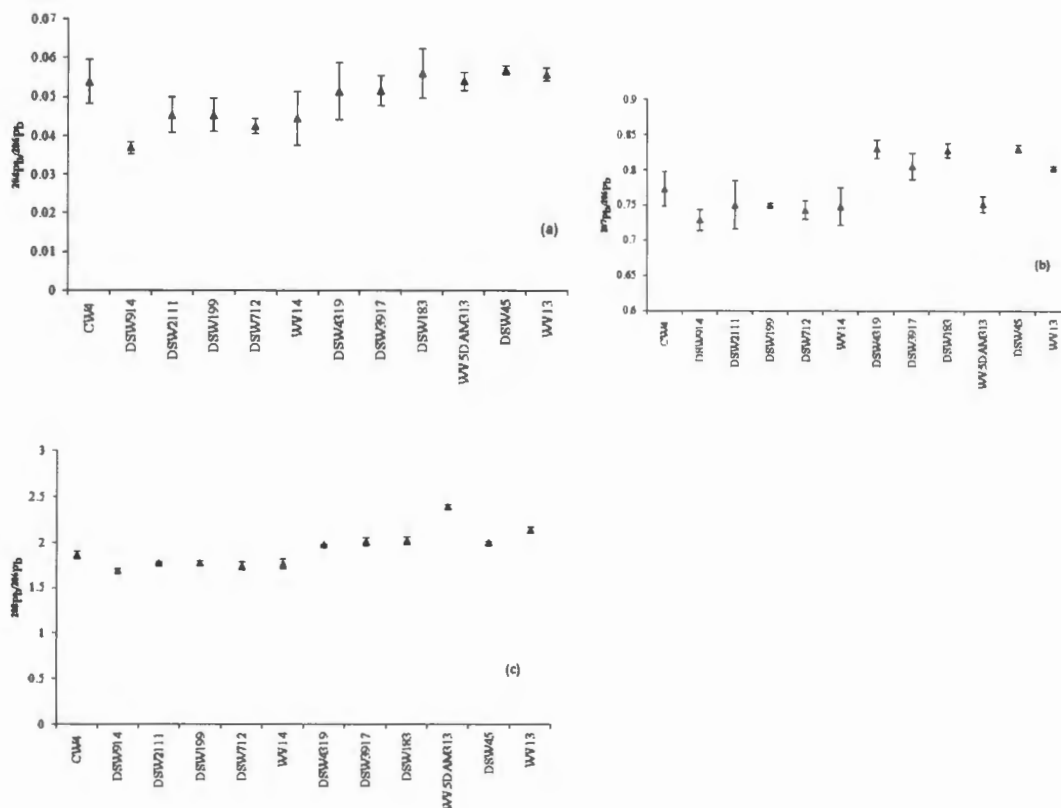


**Figure 23 a – c): Pb isotopic ratios (n=3) versus Sample ID.**

The figures have the same trend (Figure 23). However, the ratios are different and this is because of the differing percentages of the abundance of lead isotopes as it has been explained above.  $^{208}\text{Pb}$  (50.75%) occurs more abundantly than the other isotopes and that is why its ratio over  $^{206}\text{Pb}$  (26.62%) is higher compared to the other ratios. It could also be due to  $^{232}\text{Th}$  enrichment.  $^{204}\text{Pb}/^{206}\text{Pb}$  has the least ratio because  $^{204}\text{Pb}$  is only present in the Earth's crust at a small percentage of 1.4%.  $^{207}\text{Pb}$  (21.22%) is slightly lower than  $^{206}\text{Pb}$  and hence the ratio of  $^{207}\text{Pb}/^{206}\text{Pb}$  on the graph is moderate compared to other isotopic ratios (Reimann et al., 2012, Varga et al., 2009). The NIST Standard (NIST SRM, 1991), values for these four isotopes compare with results from our study in Table 14.

**Table 15:** Lead isotopic ratios from this study compared with the NIST SRM 981

| Isotopic Ratios for Lead Isotopes (NIST SRM 981)                          | Isotopic Ratios for Lead Isotopes (This work)                  |
|---------------------------------------------------------------------------|----------------------------------------------------------------|
| ➤ $^{204}\text{Pb}$ atom percent abundance<br>= $1.4255 \pm 0.0012$ %wt   | $^{204}\text{Pb}$ atom percent<br>abundance = $1.40 \pm 0.13$  |
| ➤ $^{206}\text{Pb}$ atom percent abundance<br>= $24.1442 \pm 0.0057$ % wt | $^{206}\text{Pb}$ atom percent<br>abundance = $26.62 \pm 1.12$ |
| ➤ $^{207}\text{Pb}$ atom percent abundance<br>= $22.0833 \pm 0.0027$ %wt  | $^{207}\text{Pb}$ atom percent<br>abundance = $21.22 \pm 0.41$ |
| ➤ $^{208}\text{Pb}$ atom percent abundance<br>= $52.3470 \pm 0.0086$ %wt  | $^{208}\text{Pb}$ atom percent<br>abundance = $50.75 \pm 0.96$ |

According to NIST (1991), the  $^{204}\text{Pb}$  atom abundance percent =  $1.4255 \pm 0.0012$  %wt (Table 15). Specifically for this study the  $^{204}\text{Pb}$  atom abundance =  $1.40 \pm 0.13\%$  and it lies within the NIST value. The  $^{206}\text{Pb}$  atom abundance =  $26.62 \pm 1.12\%$  is slightly above that of the standard and so is the error. However,  $^{207}\text{Pb}$  atom abundance =  $21.22 \pm 0.41\%$  and  $^{208}\text{Pb}$  atom abundance =  $50.75 \pm 0.96\%$  are slightly above the NIST values. The relative error of these values is high compared to the NIST and it might be due to the small number of samples collected for the study (Cicchetti, 2013). This explains the observed differences between NIST and this study.

From the above three graphs, it is deduced that  $^{206}\text{Pb}$  abundance is higher thereby giving a lower ratio of  $^{204}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ . It is observed that  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio is higher which implies that  $^{208}\text{Pb}$  is more abundant than the other lead isotopes. Studies done by Keegan et al (2008) showed that  $^{206}\text{Pb}$  abundance was higher for Ranger mine. As a result, this ratios can be used as a signature for this mine.

According to Reimann et al., (2012) cross-plots of  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $^{208}\text{Pb}/^{207}\text{Pb}$  or  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio can be used to indicate samples origin. In this study, cross-plots of  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio were developed (Figure 24). The ratio of  $^{206}\text{Pb}/^{207}\text{Pb}$  was found to be low in both tailings compared to other Pb ratios and this proves that samples contain Pb which emanates from the mine and not from the atmosphere (Cheng and Hu, 2010a).

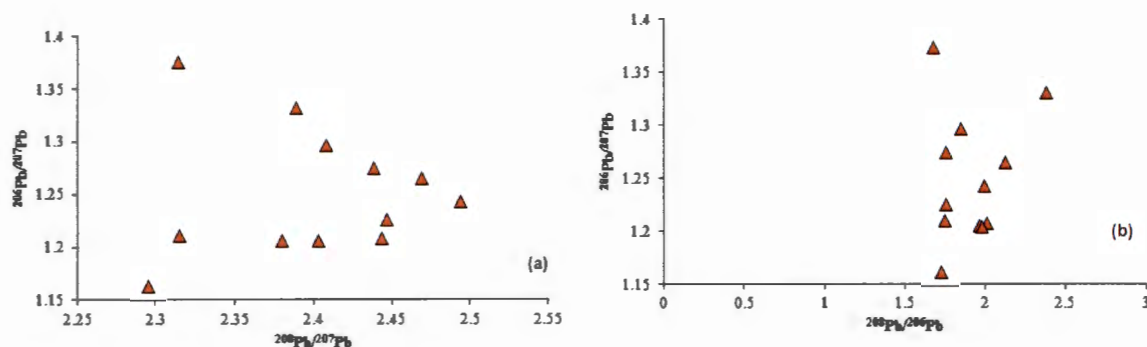


**Figure 24:** Cross plots of the Ratio of  $\text{Pb}^{206}/\text{Pb}^{207}$  vs a)  $\text{Pb}^{208}/^{207}\text{Pb}$  and b)  $^{208}\text{Pb}/^{206}\text{Pb}$ .

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Since there is an assurance that Pb in the samples comes from the mine, in order to determine the ore type, a ratio of  $^{208}\text{Pb}/^{207}\text{Pb}$  is used which marks or indicates whether the mine contains Pb-zinc ore or not (Reimann et al., 2012). Lower ratios indicate absence whereas higher ratios indicate the presence of Pb-Zn deposits. However, Precambrian igneous rocks of Finland are characterised by a low ratio of  $^{207}\text{Pb}/^{208}\text{Pb}$ . In Figure 25 below of this study, the ratio of  $^{207}\text{Pb}/^{208}\text{Pb}$  is low thereby marking an absence of Pb-Zn deposit and hence this is a signature for this mine.

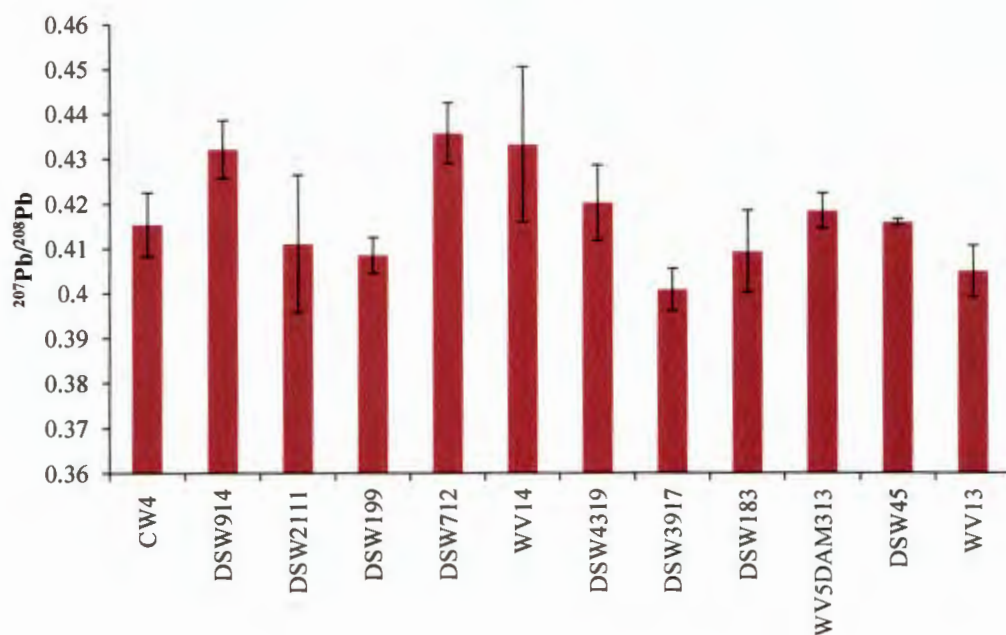


**Figure 25:**  $^{207}\text{Pb}/^{208}\text{Pb}$  ratio versus Sample ID ( $n=3$ ).

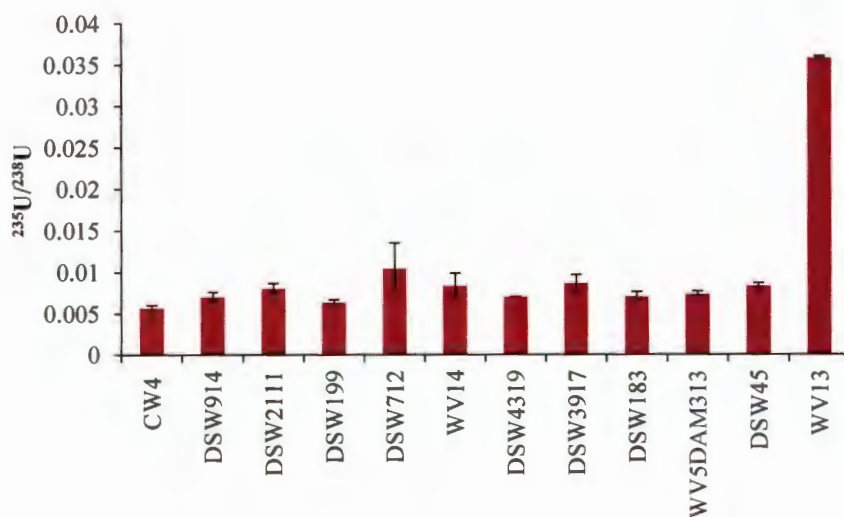


**Figure 26:**  $^{235}\text{U}/^{238}\text{U}$  Ratio versus Sample ID ( $n=3$ ).

This water contains natural uranium as all are above the natural uranium ratio. However sample WV13, in Figure 26, which was collected from west village shows very high  $^{235}\text{U}$  enrichment of about 3.75% which is reactor grade uranium. This can be explained by the fact that South Africa

did make nuclear bombs until the programme was closed in 1991. This ratio for sample WV13 is much above the certified NIST Ratio of  $2.38555 \times 10^{-3} \pm 4.7 \times 10^{-7}$  for natural uranium (Zimmer et al., 2014). The average from our data is  $10.0511 \times 10^{-3} \pm 7.8665 \times 10^{-3}$  ( $0.0100511 \pm 0.0078665$ ). High amounts of uranium can be due to the following reasons: a) the water sample was collected around a gold mine situated in Carletonville, Johannesburg. The tailing dams of mines are results of the distribution of uranium into the atmosphere (Tutu et al., 2003). b) Rain water oxidise pyrite to form sulphuric acid which penetrates through the tailing dam thereby dissolving heavy metals with uranium included. The heavy metals leach into the superficial layer of the slime and into the ground water. c) Reclamation of tailing dams which bares an economically usable gold (Rösner and Van Schalkwyk, 2000, Tutu et al., 2003).

#### 4.5 Gamma ray spectrometry analysis

As it has been mentioned in Chapter 3, gamma spectrometry is the most preferred radioanalytical technique simply because it is non-destructive, consumes less time and enables one to analyse several elements concurrently (Papachristodoulou et al., 2003, Yücel et al., 1998). This technique was applied in this study to determine isotopic signatures before the samples were run using ICP-MS technique. The results are shown in Tables 16 and Table 17 below. Uranium was the element of interest in this study and Figure 28 below shows a uranium, actinium and thorium decay series altogether with gamma ray energy lines emitted.

$^{234m}\text{Pa}$ - daughter of  $^{238}\text{U}$ - was used to determine the activity of  $^{238}\text{U}$  since it is impossible to measure its activity directly. This is because  $^{238}\text{U}$ - emits two weak gamma rays of 49.55keV (0.0697%) and 113.5keV (0.0174%) energy.  $^{234}\text{Pa}$ - (1001.1 KeV) was chosen for this study because it is a closest daughter and there is secular equilibrium with its parent.  $^{238}\text{U}$  daughters like  $^{210}\text{Pb}$ ,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  could also be used for this study. However disequilibrium caused by possible loss of radon gas cannot not be ignored (Huy et al., 2013, Papachristodoulou et al., 2003, Yücel et al., 1998). Therefore, this problem was overcome by sealing the samples for 30 days to create an equilibrium between  $^{222}\text{Rn}$  and  $^{226}\text{Ra}$  (Ebaid, 2010, Huy et al., 2013). However, there is still another geochemical disequilibrium that exists between  $^{226}\text{Ra}$  and  $^{238}\text{U}$ . This disequilibrium exist because in soil environment,  $^{238}\text{U}$  and  $^{226}\text{Ra}$ - possess different chemical properties and  $^{226}\text{Ra}$  has

a long lifetime of 1620 years. In order to measure  $^{238}\text{U}$  activity in accordance with  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ , one must neglect geochemical equilibrium (Huy et al., 2013).

The activity of  $^{235}\text{U}$  was assessed by taking 185.7 KeV energy line because studies done by Ebaid (2010) recommends it. Other peaks of  $^{235}\text{U}$  are avoided because of the summing-in effects due to the cascades of 19.6 with 143.76 and 185.7 keV. This is also in line with a study conducted by Smith et al (2010) (Smith et al., 2010).

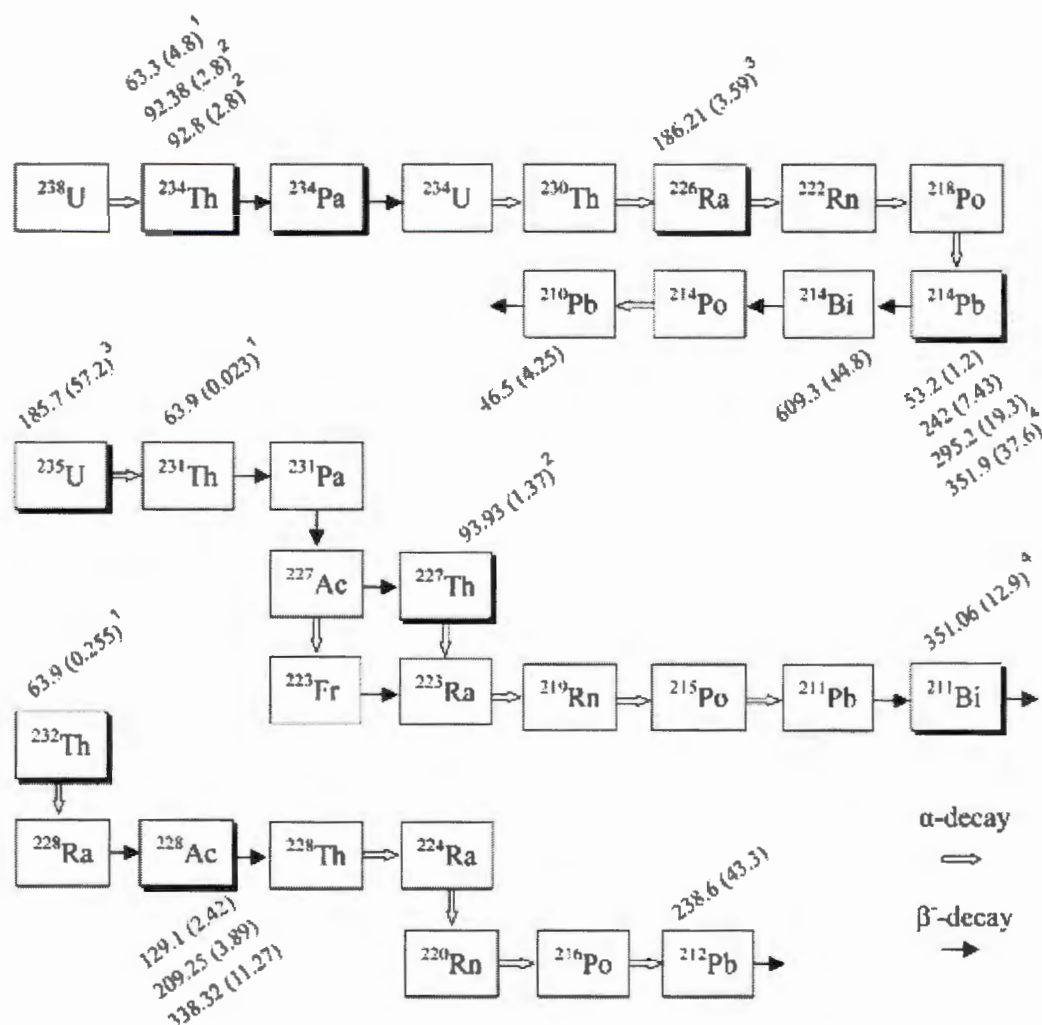


**Figure 27:** Decay series of uranium, actinium and thorium. The energy in keV units and percent emission probability of a respective radionuclide is also shown (Papachristodoulou et al., 2003).

As the objective of the study was to use HPGe gamma spectrometry to develop uranium isotopic signatures for nuclear forensic purpose, Table 16 and table 17 below depicts the results obtained.

Table 16: Tailing Dams Uranium 235 isotopic signature

| sample | Average $^{235}\text{U}/^{238}\text{U}$ | error    |
|--------|-----------------------------------------|----------|
| t1     | 0.111246                                | 0.003291 |
| t3     | 0.42067                                 | 0.087829 |
| t5     | 0.236646                                | 0.03241  |

The reference value for  $^{235}\text{U}/^{238}\text{U} = 2.38555 \times 10^{-3} \pm 4.7 \times 10^{-7}$ . The results obtained in this work shows that the samples possess a lot of  $^{235}\text{U}$ , since all the average values measured are above the reference value. ICP-MS analysis also verifies this observation in Figure 27 above. However, background radiation might also affect the results.

Table 17:  $^{238}\text{U}/^{235}\text{U}$  activity ratio

| tailing | average  | $\pm$ error |
|---------|----------|-------------|
| T1      | 9.023028 | 0.286961    |
| T5      | 4.517988 | 0.552567    |
| T3      | 3.049694 | 0.553795    |

$^{238}\text{U}$  is more abundant than  $^{235}\text{U}$ , with T1 having the highest ratio followed by T5 and T3 which has the least. This implies that T1 has smallest amount of  $^{235}\text{U}$ . However, T3 has an increased amount of  $^{235}\text{U}$  and hence the ratio of  $^{235}\text{U}/^{238}\text{U}$  is the lowest.. Tailing 3 has a lowest ratio compared to the other tailings. T1 has the least since  $^{238}\text{U}$  dominates the tailing. This is the signature for the mine studied. However, compared to NIST, all the tailings possess high amount of both  $^{235}\text{U}$  and  $^{238}\text{U}$  isotopes. The standard ratio for  $^{238}\text{U}/^{235}\text{U}$  are as follows: CRM 129A certified value 137.714 with a certified error (2SD) of 0.074, IRMM-184 certified value 137.697 with a certified error

(2SD) 0.042 (Brennecka et al., 2010). However, these values were determined using a mass spectrometer.

#### 4.6 Isoplot- isochron plots from the Pb-Pb isotopic ratios

The data in Table 18 is used to plot the Pb-Pb Concordia for our data (as a quality control test).

**Table 18:** Concordia data for this work

| <b>Pb206/Pb204</b> | <b>Pb207/Pb204</b> |
|--------------------|--------------------|
| 18.95              | 14.72              |
| 27.26              | 19.82              |
| 20.88              | 16.35              |
| 17.42              | 14.21              |
| 17.99              | 15.49              |
| 19.04              | 15.78              |
| 20.15              | 16.77              |
| 19.61              | 15.74              |
| 18.29              | 15.13              |
| 18.59              | 13.95              |
| 17.58              | 14.58              |
| 16.83              | 13.29              |
| STDEV 2.74         | 1.7                |
| STD ERR 0.826      | 0.511              |

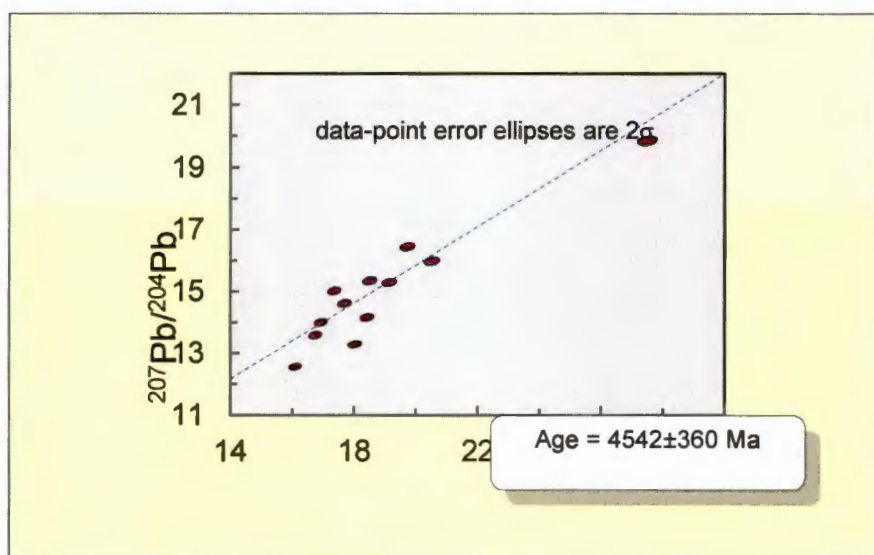


**Figure 28:** Pb-Pb isochron plot for results from this work.

From Figure 28, we deduce that the uranium mineralization from the samples used in this work has an age of  $4542 \pm 360$  Ma, with a Mean Square of Weighted Deviates (MSWD) = 137 (Ludwig, 1998), which is rather high.

These age result are in close agreement with those by Fuchs et al., (2016), which was given as  $2.588 \text{ Ga} \pm 7 \text{ Ma}$  to  $2.709 \text{ Ga} \pm 4 \text{ Ma}$  (Fuchs et al., 2016) .

From **Section 4.4**, Figure 21 and 22, we conclude that the Carletonville gold fields are pyrite deposits, suggesting that the pyrites deposits are of detrital type. However this conclusion is directly opposite to that of Ref (Fuchs et al., 2016), who said .....

*"The irregular to dendritic nature of the economic gold and uranium mineralisation shows clearly that it is not detrital in origin (because of the age of the deposit, 2.59 Ga, .....uraninite is unlikely to have been stable in the surficial environment"*

The samples collected from the top of the mine tailing and the mine water came from a 3 km depth of the mine. So the uraninite is not surficial.

Also results of this work agree with those from the REE and trace elements described in **Section 4.2** above. That is, there is no surficial mining of uranium.

In this preliminary work, the error margins for the ages of this mineralisation seem to be too large, probably, the decay constant errors of both U and Pb could have affected the errors of Concordia ages (Ludwig, 1998)

#### **4.7 Protocol for ICP-MS Isotopic Technique (DA) and Gamma spectrometry (NDA) for nuclear forensic analysis at the Centre for Applied Radiation Science and Technology (CARST).**

The summary of all the results described in this work is that, at the Centre for Applied Radiation Science and Technology (CARST), no nuclear forensics analysis technique is sufficient on its own. Results must be verified against other techniques.

For CARST, to minimize research costs in such an endeavor, it should use available resources, viz:

- Analysis with the Perkin Elmer ICP-MS 300Q Isotopic Ratio techniques
- Complimented by the HPGe Gamma spectroscopy
- The output of both checked against the Isoplot vs 3.75 Code sued for Geo-chronology.

This can be represented by a Protocol diagram as shown in Figure 29.

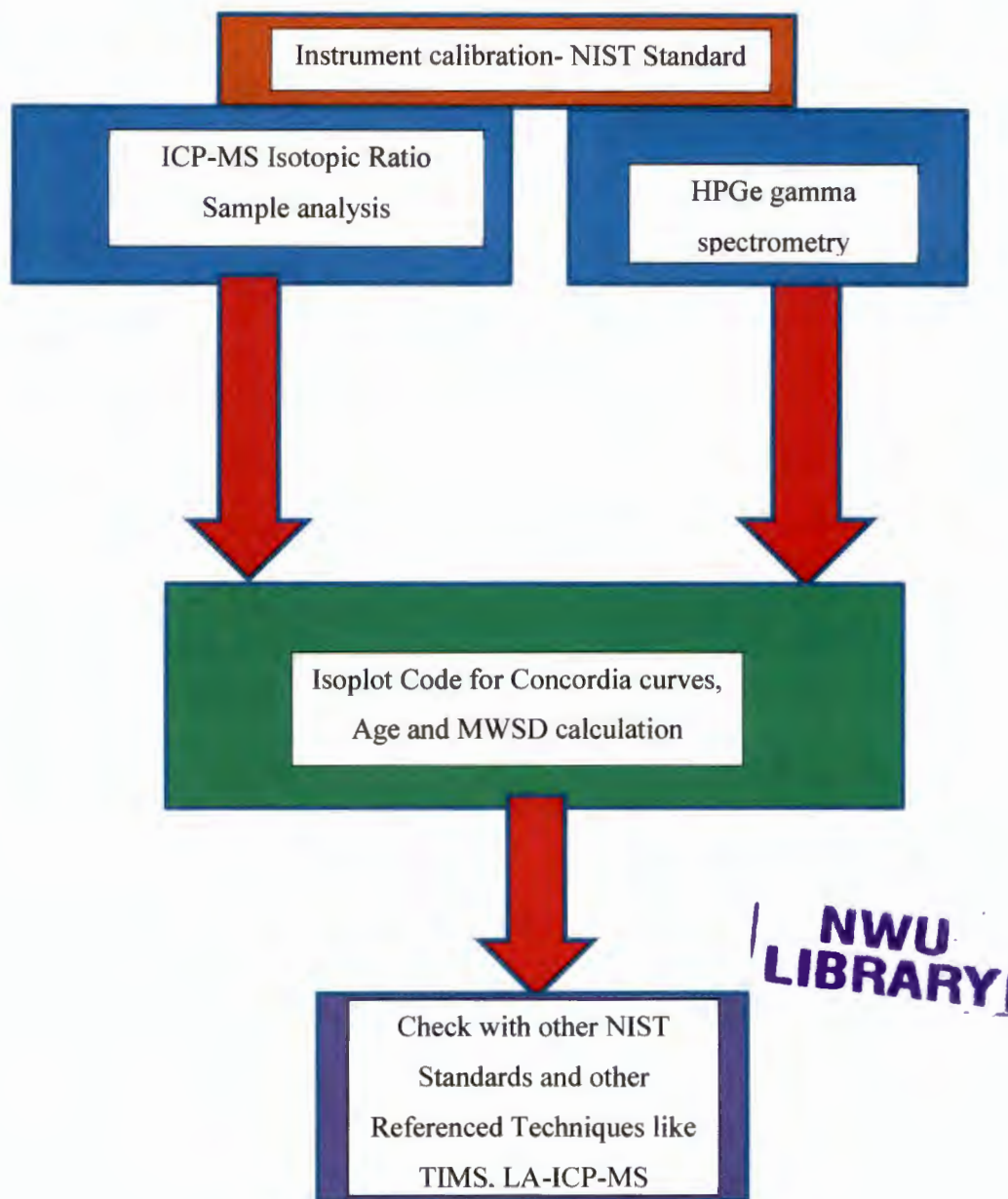


**Figure 29:** Proposed Nuclear Forensics Protocol for CARST.

## CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

### 5.1 Conclusions

In this study elemental and isotopic signatures for Sibanye gold mine were developed for the establishment of a national nuclear forensic library. This will support and strengthen nuclear security in preventing theft of nuclear material by nuclear terrorist for non-peaceful purposes around the world. In this study, lead isotopes were used to develop signatures for uranium since its an end product of uranium isotopes decay series.

Elemental signatures were developed using ICP-MS radioanalytical technique for the investigated mine. The mine was found to have trace elements and no major elements found. Trace elements mainly influence the pH of the soil. However, Fe was found to be a minor element since it is an abundant element in the Earth's crust. REE found were mainly La, Ce, Pr and Nd. They can therefore be used as a characteristic of the mine studied. Based on the  $(La/Yb)_N$  ratio, LREE were found to dominate the mine and there was a europium negative anomaly and a strong Tb positive anomaly in both analyzed tailings dams. The ratio of  $(Gd/Yb)_N$  indicated the presence of HREE in the mine.

The lead isotopic fingerprints plotted relative to  $^{206}\text{Pb}$  were relatively in good agreement with the NIST SRM 981 reference values which are as follows:  $^{204}\text{Pb}/^{206}\text{Pb} = 0.059042 \pm 0.000037$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.91464 \pm 0.00033$  and  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0008$  respectively. Pb values plotted against  $^{204}\text{Pb}$  were found to exceed those of the NIST values and that marks a U or Pb rich ore since  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  are radiogenic lead derived from  $^{232}\text{Th}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  series. The  $^{235}\text{U}/^{238}\text{U}$  ratio was high above the reference value specified by NIST SRM 981 of  $2.38555 \times 10^{-3} \pm 4.7 \times 10^{-7}$ . Due to illicit trafficking of nuclear material for perversion and proliferation purposes, signatures generated in this study will support and strengthen nuclear security towards combating theft of nuclear or radioactive material thereby promoting peaceful use of such material.

One challenge in using the ICP-MS isotopic ratio technique is the mass discrimination effect (mass bias). In this study the Perkin Elmer NexIon 300Q ICP-MS isotopic ratio is determined for the  $^{107}\text{Ag}/^{109}\text{Ag}$  ratio. Many researches use  $^{205}\text{Tl}/^{203}\text{Tl}$  for normalisation. However, Yip et al (2008), has also argued that Tl has been shown to produce  $\text{Tl}^{+3}$  under UV oxidation effect which does not

behave like Pb in solution. However Ag is stable under UV and does not oxidise to  $\text{Ag}^{+3}$  in solution if left under normal light in the laboratory. Hence we normalised our results against  $^{208}\text{Pb}/^{206}\text{Pb}$  as suggested by Keegan et al (2008) and mass discrimination effect were reduced. This added confidence to our lead ratios for use as forensic signatures. Finally a simple plot of Isochrons using our data produced concordia curves and ages that compare very well with those from (Ludwig, 1998) and (Fuchs et al., 2016) respectively, and with other techniques like TIMS & LA-ICP-MS (Burger and Riciputi, 2009), (Asai and Limbeck, 2015a)

Gamma spectroscopic results also confirmed the possibility of using a combination of ICP-MS, ICP-MS Isotopic Ratio, Gamma spectroscopy and Isoplot Isochronic Techniques for Developing Nuclear Forensics Signatures at the Centre for Applied Radiation Science and Technology (CARST). This could be a potential database for South Africa's NNFL. A proposed Nuclear Forensics Protocol for the Centre of Applied Radiation Science and Technology (CARST) is presented as the final product of this work.

This study clearly demonstrates that the nuclear forensics signatures (eg. isotopic ratios) from the gold/uranium mine shafts in Carletonville, South Africa can be distinguished using their elemental and isotopic profiles, especially when compared with other countries like the UK and Canada.

## 5.2 Recommendations

It is recommended that this work continue to cover other uranium samples from different mines in South Africa in order to produce a comprehensive and complete data base. That is all the 71 uranium mines in South Africa (<https://infcis.iaea.org/UDEPO/About.cshtml>) last opened 12 December 2016, (and all the mine shafts thereof) need to be examined and compared.

In future work, it is recommended that CARST will utilize the NIST isotopic standards for lead and uranium for better bench mark calibration. The development of novel sample specific references (e.g., for a geological location of a mine), is another option that needs to be looked at.

The radiochemical separation purity of each batch of samples can be tested by e.g. determining the ratio of  $^{230}\text{Th}/^{234}\text{U}$  at  $t = 0$  from the isochron (dating) graph (or  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio).

Comprehensive sampling to include the full cycle of any nuclear material (cradle to grave and mining to waste characterization).

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#### **Annexure A: Description of sample I.D's**

##### **Fruits and vegetables sampled from East village**

|       |                |
|-------|----------------|
| VV91  | Spinach        |
| VV92  | Turnip         |
| VV101 | Tomato         |
| VV102 | Turnip         |
| VV11  | Mulberry fruit |
| VV14  | Lime fruit     |
| VV15  | Mulberry fruit |
| VV17  | Mulberry fruit |

#### **Water samples**

|         |                                                                            |
|---------|----------------------------------------------------------------------------|
| WV2     | Borehole water for public use from West village.                           |
| WV3     | Borehole water for public use from West village.                           |
| WV4     | Borehole water for public use from West village.                           |
| WV5     | Borehole water for public use from West village.                           |
| WV9     | Borehole water for public use from East village.                           |
| WV13    | Borehole water for public use from East village.                           |
| WV14    | Borehole water for public use from East village.                           |
| WV15    | Borehole water for public use from East village.                           |
| WV16    | Borehole water for public use from East village.                           |
|         |                                                                            |
| DSW451  | Stream water from mine shaft that flows into a private dam for public use. |
| DSW112  | Sewage water from mine shaft that flows into a mine dam.                   |
| DSW183  | Sewage water from mine shaft                                               |
| DSW204  | Storm water from run-off around the mine which is reused.                  |
| DSW405  | Raw water of return water dam                                              |
| DSW406  | Raw water of return water dam                                              |
| DSW407  | Raw water of return water dam                                              |
| DSW358  | Sewage water from mine shaft.                                              |
| DSW179  | Sewage water from mine shaft.                                              |
| DSW4210 | Fissure water straight from underground                                    |
| DSW2111 | Process water from the water plant                                         |

|         |                                                          |
|---------|----------------------------------------------------------|
| DSW712  | Water coming from the mine shaft and from process plants |
| DAM313  | Water from the settling point                            |
| DSW914  | Water from the settling point                            |
| DSW3615 | Water from DSW914 and DSW4210                            |
| DSW3816 | Discharge water from another mine                        |
| DSW3917 | Water from DSW3615 and DSW3816                           |
| DSW1618 | Mine shaft and process plants water                      |
| DSW4319 | Purified water                                           |
| DSW2920 | Raw water from the return water dam of mine tailings     |

#### **Appendix B: List of Publications from this work**

1. **Manny Mathuthu**, Ntokozo Khumalo and Malayita M Baloyi: Determination of lead isotope ratios in uranium mine products in South Africa by means of Inductively Coupled Plasma Mass Spectrometry. *Journal of Radio-analytical and Nuclear Chemistry*. (**March 2017- under final revision**).
2. **Manny Mathuthu** and Ntokozo Khumalo. Determination of trace elements and lanthanide (REE) signatures in uranium mine products in South Africa by means of Inductively Coupled Plasma Mass Spectrometry. *Journal of Geochemical Exploration*. (**March 2017-under 1<sup>st</sup> revision**)
3. **Manny Mathuthu** and Ntokozo Khumalo: (03/2017), Developing Nuclear Forensics Signatures and National Nuclear Forensics Librariesfor the African Continent: A Case Review for South Africa. *International Journal of Applied Science - Research and Review*, Vol. 4 No. 1, pp: 1-3

#### **Appendix C: Tables**

Table 3: Tailings Dam 1 Average, Max and Min concentration (mg/L)

| Element | Average | Max     | Min     | STD.dev | STD.error |
|---------|---------|---------|---------|---------|-----------|
| Pb      | 0.089   | 0.13    | 0.053   | 0.024   | 0.0073    |
| Al      | 567.12  | 895.963 | 274.476 | 192.62  | 58.077    |
| B       | 0.00082 | 0.0090  | 0.00    | 0.0027  | 0.00082   |
| Ba      | 0.050   | 0.080   | 0.022   | 0.019   | 0.0056    |
| Ca      | 254.99  | 656.44  | 130.06  | 140.70  | 42.42     |
| K       | 61.18   | 94.87   | 22.82   | 24.06   | 7.26      |
| La      | 0.046   | 0.061   | 0.030   | 0.012   | 0.0035    |
| Mg      | 255.39  | 553.31  | 117.50  | 116.56  | 35.14     |
| Mn      | 11.44   | 23.19   | 5.89    | 4.44    | 1.34      |
| Na      | 5.22    | 11.99   | 2.22    | 2.80    | 0.84      |
| P       | 1.55    | 2.91    | 0.64    | 0.74    | 0.22      |
| Rb      | 0.014   | 0.025   | 0.0060  | 0.0054  | 0.0016    |
| Si      | 10.63   | 35.60   | 0.00    | 12.76   | 3.85      |
| Sr      | 0.16    | 0.28    | 0.097   | 0.053   | 0.016     |
| Th      | 0.048   | 0.088   | 0.038   | 0.014   | 0.0043    |
| U       | 0.53    | 1.37    | 0.00    | 0.41    | 0.12      |
| Y       | 0.028   | 0.051   | 0.015   | 0.010   | 0.0030    |
| V       | 0.23    | 0.55    | 0.093   | 0.14    | 0.042     |
| Cr      | 4.42    | 8.83    | 0.51    | 2.73    | 0.82      |
| Cu      | 0.47    | 0.63    | 0.34    | 0.080   | 0.024     |
| Fe      | 1781.68 | 2419.90 | 1127.09 | 428.59  | 129.22    |
| Zn      | 0.46    | 1.15    | 0.27    | 0.24    | 0.073     |
| Ni      | 1.59    | 4.96    | 0.79    | 1.191   | 0.36      |
| Ti      | 1.13    | 2.89    | 0.28    | 0.83    | 0.25      |
| Co      | 0.35    | 0.57    | 0.23    | 0.10    | 0.031     |
| Mo      | 0.018   | 0.026   | 0.011   | 0.0053  | 0.0016    |
| Cd      | 0.00027 | 0.0010  | 0.00    | 0.00047 | 0.00014   |
| Li      | 0.089   | 0.14    | 0.043   | 0.029   | 0.0088    |

Table 4: Tailings Dam 2 Average, Maximum and Minimum concentration (mg/L)

| Element | Average | Max     | Min    | STD.dev | STD.error |
|---------|---------|---------|--------|---------|-----------|
| Pb      | 0.11    | 0.28    | 0.041  | 0.068   | 0.019     |
| Al      | 684.70  | 1234.42 | 345.56 | 322.19  | 89.36     |
| B       | 0.0068  | 0.028   | 0.0010 | 0.0074  | 0.0020    |
| Ba      | 0.066   | 0.16    | 0.026  | 0.041   | 0.011     |
| Ca      | 277.10  | 566.60  | 138.43 | 118.72  | 32.93     |
| K       | 72.28   | 183.13  | 27.32  | 49.87   | 13.83     |
| La      | 0.047   | 0.077   | 0.025  | 0.015   | 0.0042    |
| Mg      | 541.23  | 1211.00 | 266.79 | 286.65  | 79.50     |
| Mn      | 12.14   | 25.80   | 4.59   | 5.81    | 1.61      |
| Na      | 9.30    | 27.94   | 4.50   | 6.45    | 1.79      |
| P       | 1.59    | 4.12    | 0.93   | 0.93    | 0.26      |
| Rb      | 0.016   | 0.039   | 0.0090 | 0.0099  | 0.0028    |
| Si      | 31.38   | 149.31  | 0.11   | 52.91   | 14.67     |
| Sr      | 0.17    | 0.35    | 0.093  | 0.074   | 0.020     |
| Th      | 0.0474  | 0.064   | 0.030  | 0.0094  | 0.0026    |
| U       | 0.55    | 0.84    | 0.00   | 0.24    | 0.066     |
| Y       | 0.028   | 0.051   | 0.012  | 0.011   | 0.0031    |
| V       | 0.63    | 5.02    | 0.12   | 1.33    | 0.37      |
| Cr      | 4.12    | 11.61   | 0.58   | 4.1     | 1.15      |
| Cu      | 0.46    | 0.98    | 0.27   | 0.20    | 0.054     |
| Fe      | 1925.71 | 3892.45 | 939.03 | 942.86  | 261.50    |
| Zn      | 0.52    | 1.15    | 0.27   | 0.22    | 0.062     |
| Ni      | 1.38    | 3.17    | 0.69   | 0.75    | 0.21      |
| Ti      | 0.96    | 3.31    | 0.14   | 0.99    | 0.28      |
| Co      | 0.67    | 5.19    | 0.18   | 1.36    | 0.38      |
| Mo      | 0.020   | 0.058   | 0.011  | 0.013   | 0.0037    |
| Cd      | 0.00031 | 0.0010  | 0.00   | 0.00048 | 0.00013   |
| Li      | 0.10    | 0.26    | 0.049  | 0.059   | 0.017     |

Table 5: Vegetation or crops elemental concentration

| Element | Average | STD.dev | STD.error | Max    | Min    |
|---------|---------|---------|-----------|--------|--------|
| Al      | 0.68    | 0.64    | 0.24      | 1.62   | 0.16   |
| S       | 25.06   | 2.9     | 1.1       | 28.896 | 20.63  |
| Ba      | 0.0021  | 0.0019  | 0.00071   | 0.005  | 0.00   |
| Ca      | 15.27   | 14      | 5.3       | 37.687 | 4.52   |
| K       | 20.89   | 10      | 3.88      | 33.19  | 3.50   |
| Mg      | 3.27    | 1.9     | 0.73      | 6.772  | 1.26   |
| Mn      | 0.031   | 0.044   | 0.017     | 0.096  | 0.0020 |
| Na      | 0.53    | 0.167   | 0.063     | 0.673  | 0.22   |
| Rb      | 0.00071 | 0.00049 | 0.00018   | 0.001  | 0.00   |
| Si      | 1.64    | 1.1     | 0.41      | 3.319  | 0.55   |
| Sr      | 0.0374  | 0.059   | 0.023     | 0.138  | 0.0010 |
| V       | 0.088   | 0.044   | 0.016     | 0.116  | 0.024  |
| Cr      | 0.0019  | 0.00069 | 0.00026   | 0.003  | 0.0010 |
| Cu      | 0.0010  | 0.00    | 0.00      | 0.001  | 0.0010 |
| Fe      | 0.25    | 0.11    | 0.043     | 0.37   | 0.10   |
| Ni      | 0.00014 | 0.00    | 0.00      | 0.001  | 0.00   |
| Ti      | 0.010   | 0.0062  | 0.0023    | 0.021  | 0.005  |
| Sc      | 0.00029 | 0.00049 | 0.00018   | 0.001  | 0.00   |
| As      | 0.026   | 0.0019  | 0.00071   | 0.027  | 0.022  |
| Zn      | 0.0026  | 0.0015  | 0.00057   | 0.005  | 0.0010 |
| Br      | 0.018   | 0.0045  | 0.0017    | 0.023  | 0.013  |

Table 6: Water samples from DSW and VW

a) DSW Samples

| Element | Average | STD.dev | STD.error | Max    | Min   |
|---------|---------|---------|-----------|--------|-------|
| S       | 112.00  | 89      | 19.91     | 422.88 | 0     |
| Pb      | 0.00025 | 0.00064 | 0.00014   | 0.002  | 0     |
| Al      | 0.019   | 0.047   | 0.010     | 0.19   | 0     |
| B       | 0.0013  | 0.0043  | 0.00096   | 0.019  | 0     |
| Ba      | 0.012   | 0.0026  | 0.00058   | 0.016  | 0.007 |
| Ca      | 22.97   | 13      | 2.9       | 67.82  | 8.688 |
| K       | 4.95    | 9.4     | 2.1       | 33.79  | 0.3   |
| Mg      | 2.22    | 1.0     | 0.23      | 4.13   | 0.392 |
| Mn      | 0.0061  | 0.00513 | 0.0011    | 0.02   | 0.002 |
| Na      | 11.25   | 9.9     | 2.2       | 42.27  | 0.89  |
| Rb      | 0.0009  | 0.0011  | 0.00025   | 0.005  | 0     |
| Si      | 0.37    | 0.35    | 0.078     | 1.14   | 0     |
| Sr      | 0.0074  | 0.011   | 0.0026    | 0.048  | 0     |
| U       | 0.0005  | 0.0014  | 0.00031   | 0.005  | 0     |
| V       | 0.016   | 0.054   | 0.012     | 0.24   | 0     |
| Cr      | 0.0057  | 0.0075  | 0.0017    | 0.02   | 0     |
| Cu      | 0.017   | 0.034   | 0.0077    | 0.12   | 0.001 |
| Fe      | 0.28    | 0.14    | 0.032     | 0.77   | 0.099 |
| Zn      | 0.011   | 0.0062  | 0.0014    | 0.024  | 0     |
| Ni      | 0.021   | 0.029   | 0.0066    | 0.13   | 0.006 |
| Ti      | 0.0029  | 0.0025  | 0.00056   | 0.01   | 0     |
| Co      | 0.0042  | 0.0071  | 0.0016    | 0.033  | 0.001 |
| Mo      | 0.0012  | 0.0015  | 0.00035   | 0.006  | 0     |
| Li      | 0.00021 | 0.00054 | 0.00012   | 0.002  | 0     |
| As      | 0.014   | 0.045   | 0.0097    | 0.17   | 0     |
| Sc      | 0.00005 | 0.00022 | 0.00005   | 0.001  | 0     |
| Br      | 0.06    | 0.031   | 0.0069    | 0.13   | 0.009 |
| Zr      | 0.00165 | 0.0053  | 0.0012    | 0.024  | 0     |

|    |         |         |         |       |   |
|----|---------|---------|---------|-------|---|
| In | 0.0002  | 0.00062 | 0.00014 | 0.002 | 0 |
| I  | 0.0027  | 0.0057  | 0.0013  | 0.024 | 0 |
| Se | 0.0003  | 0.00080 | 0.0001  | 0.003 | 0 |
| Au | 0.00015 | 0.00037 | 8.2E-05 | 0.001 | 0 |
| Ag | 0.00005 | 0.00022 | 0.00005 | 0.001 | 0 |
| Sb | 0.00005 | 0.00022 | 0.00005 | 0.001 | 0 |

b) VW samples

Table 9: Average REE concentration for tailings dam 1

| REE | average  | Std dev | Std error | min    | max    |
|-----|----------|---------|-----------|--------|--------|
| La  | 0.046    | 0.012   | 0.0035    | 0.030  | 0.061  |
| Ce  | 0.093    | 0.024   | 0.0074    | 0.058  | 0.12   |
| Pr  | 0.010    | 0.0026  | 0.00080   | 0.0060 | 0.014  |
| Nd  | 0.032    | 0.0078  | 0.0024    | 0.021  | 0.045  |
| Sm  | 0.0057   | 0.0016  | 0.00047   | 0.0040 | 0.0080 |
| Eu  | 0.0013   | 0.00047 | 0.00014   | 0.0010 | 0.0020 |
| Gd  | 0.0068   | 0.0018  | 0.00055   | 0.0050 | 0.010  |
| Tb  | 0.0012   | 0.00041 | 0.00012   | 0.0010 | 0.0020 |
| Dy  | 0.0046   | 0.0021  | 0.00064   | 0.0030 | 0.010  |
| Ho  | 0.0010   | 0.00045 | 0.00014   | 0.00   | 0.0020 |
| Er  | 0.0019   | 0.00094 | 0.00029   | 0.0010 | 0.004  |
| Tm  | 0.00     | 0.00    | 0.00      | 0.00   | 0.00   |
| Yb  | 0.0016   | 0.00067 | 0.00020   | 0.0010 | 0.0030 |
| Lu  | 9.09E-05 | 0.00030 | 9.09E-05  | 0      | 0.0010 |

Table 10:  
concentration

Average REE  
for tailings

dam 2

| REE | average | Std dev | Std Error | min    | max   |
|-----|---------|---------|-----------|--------|-------|
| La  | 0.047   | 0.015   | 0.0042    | 0.025  | 0.077 |
| Ce  | 0.097   | 0.029   | 0.0082    | 0.049  | 0.15  |
| Pr  | 0.010   | 0.0031  | 0.00086   | 0.0050 | 0.016 |

|    |         |         |          |        |        |
|----|---------|---------|----------|--------|--------|
| Nd | 0.034   | 0.0094  | 0.0026   | 0.018  | 0.051  |
| Sm | 0.0075  | 0.0054  | 0.0015   | 0.0040 | 0.025  |
| Eu | 0.0015  | 0.00066 | 0.00018  | 0.0010 | 0.0030 |
| Gd | 0.0068  | 0.0025  | 0.00069  | 0.0010 | 0.011  |
| Tb | 0.0013  | 0.00086 | 0.00024  | 0.0010 | 0.0040 |
| Dy | 0.0042  | 0.00093 | 0.00026  | 0.0020 | 0.0050 |
| Ho | 0.00092 | 0.00028 | 7.69E-05 | 0.00   | 0.0010 |
| Er | 0.0018  | 0.00044 | 0.00012  | 0.0010 | 0.0020 |
| Tm | 0.00    | 0.00    | 0.00     | 0.00   | 0.00   |
| Yb | 0.0016  | 0.00051 | 0.00014  | 0.0010 | 0.0020 |
| Lu | 0.00    | 0.00    | 0.00     | 0.00   | 0.00   |

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