# Application of REE in Resolving Nuclear Forensic Signatures For South African Mining And Processing

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LSC 2017
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# Overview

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- Aim of the Research
- Objectives
- Background
- Methodology
- Results & Discussions
- Conclusions

## Aim:

**To Determine REE patterns for Nuclear Forensic signatures for South African Uranium Mining and Processing.**

## Objectives are to:

- **Resolve the Lanthanide (REE) patterns for nuclear forensics signatures for the mine**
- **Use LSC 1220 to determine La-138, Ce-138, Eu-151, Nd-144, Nd-150, Gd-158, Pr-143, Tb- 158 and Lu-176, Dy-159 to develop a nuclear forensics Library from the REE of the mine**
- **Develop a nuclear forensic library for the Lanthanides and Pb isotopic ratios**

# Introduction: Nuclear Security

- Due to the development of nuclear security and safety by the IAEA, nuclear forensics has deterred and prevented nuclear terrorism as well as illicit trafficking of nuclear or radioactive material to an extent

- Nuclear forensics has thus provided answers to what;
  - is Identity of the radioactive material found,
  - the threat it poses,
  - the organization responsible for the loss, the origin of the material and
  - Are the national laws that have been broken.
- We can resolve these issues is by obtaining the characteristic parameters of the material, called nuclear forensic signatures
- These can be used as evidence for attribution of the seized nuclear or radioactive material.

# Introduction Cont…
## Nuclear forensics signatures

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- These include physical characterization, elemental, isotopic, chemical composition and REEs
- In this work we describe the
  - Application of Lanthanide patterns (REE) for developing Nuclear forensics (NF) signatures.
  - REE signature need to be combined with U-Pb signatures for a comprehensive NF library (IAEA, 2014).

# Introduction Cont…

## REE fingerprint signatures

- the fingerprint of the Lanthanide (REE) signatures in the uraninite ore is discussed.
- Interpretation of the results for possible tracing (attribution) of the origins of South African is provided

# MATERIALS AND METHODS



- **REE Concentrations).**

  **We have used the Perkin Elmer NexION 300Q ICP-MS to measure the REE Concentrations in the Gold/Uranium mine (Andersen 2002, Balcaen, Moens et al. 2010, Varga, Katona et al. 2010)**

- **Soil and water samples were digested using a Multiwave 3000, Anton Paar microwave oven**

- The EPA Method 3052 used in the sample digestion achieves total sample decomposition of the calcite samples (Mangum 2009)

- **The reagents used were of Suprapur analytical grade**

# MATERIALS AND METHODS

## ➢ Interference correction and digestion

- the oxides, hydrides, hydroxides and nitrides molecular ions are potential sources of interferences;

- Aqua Regia acid (3 ml of 55% $HNO_3$, 9 ml of 32% HCl)

- We flash with 2 ml of 2% $H_2O_2$ - which enhances the oxidation properties of nitric acid

- The aqua regia extraction is capable of complete recovery for La, Ce, …..Tb, Eu (our target elements)

# Study Area

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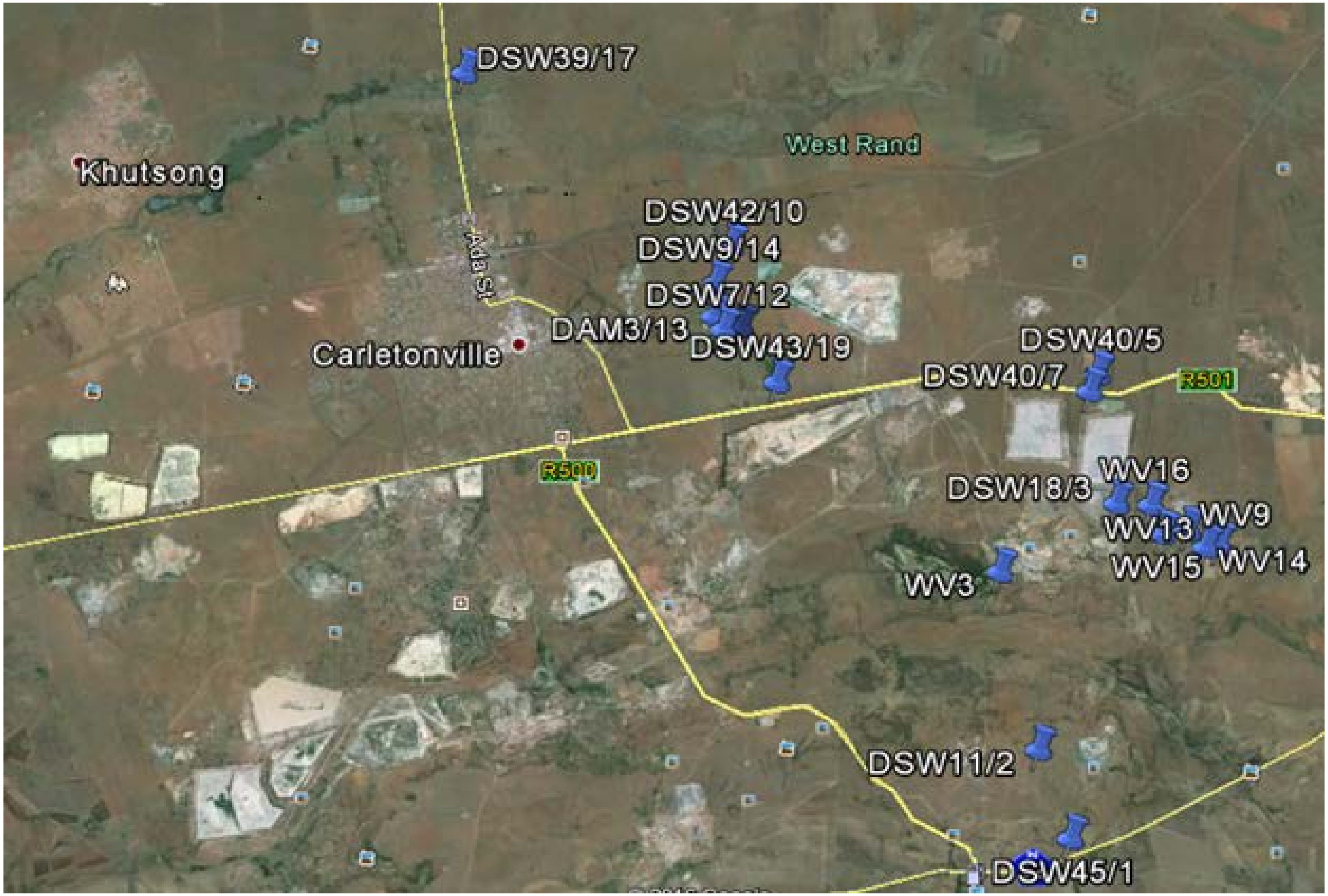


**Figure 1:** Study Area showing sampling points

## Results

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- During the processing of the ore, some nuclear forensic fingerprint may be lost.

- However, rare earth elements (REE) or Lanthanides retain their chemical properties (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.
- These were La, Ce, Pr and Nd. The REE concentrations for tailings dam 2 are slightly higher than that of tailing dam 1

- 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.
- RRUP contained REE mostly Ce and Nd.
- In this study, the samples contained mostly Ce and La.

# Table 1: Tailing Dam 1 REE Concentrations

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| 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 2: Tailing Dam 2 REE concentrations

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| 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 |

# Table 3: Tailing Dam  REE concentrations

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| Sample ID | REE | | | | | | | | | | | | | | ∑REE | ± ∑REE | GdN/YbN | LaN/YbN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | | | |
| **T1E1** | 0.058 | 0.114 | 0.012 | 0.036 | 0.007 | 0.001 | 0.006 | 0.002 | 0.004 | 0.001 | 0.002 | 0 | 0.002 | 0 | 0.245 | 0.032 | 2.480 | 20.07 |
| **T1E2** | 0.031 | 0.061 | 0.007 | 0.023 | 0.004 | 0.001 | 0.005 | 0.001 | 0.003 | 0.001 | 0.002 | 0 | 0.001 | 0 | 0.14 | 0.017 | 4.133 | 21.46 |
| **T1E3** | 0.048 | 0.094 | 0.01 | 0.032 | 0.005 | 0.001 | 0.006 | 0.001 | 0.004 | 0.001 | 0.001 | 0 | 0.002 | 0 | 0.205 | 0.026 | 2.479 | 16.61 |
| **T1E4** | 0.044 | 0.088 | 0.009 | 0.029 | 0.005 | 0.001 | 0.006 | 0.001 | 0.004 | 0.001 | 0.001 | 0 | 0.001 | 0 | 0.19 | 0.024 | 4.959 | 30.46 |
| **T1E5** | 0.061 | 0.124 | 0.013 | 0.041 | 0.007 | 0.002 | 0.008 | 0.001 | 0.004 | 0.001 | 0.002 | 0 | 0.002 | 0 | 0.266 | 0.035 | 3.306 | 21.11 |
| **T1E6** | 0.03 | 0.058 | 0.006 | 0.021 | 0.004 | 0.001 | 0.005 | 0.001 | 0.003 | 0.001 | 0.001 | 0 | 0.001 | 0 | 0.132 | 0.016 | 4.132 | 20.77 |
| **T1E7** | 0.038 | 0.081 | 0.009 | 0.027 | 0.005 | 0.001 | 0.007 | 0.001 | 0.004 | 0.001 | 0.002 | 0 | 0.002 | 0 | 0.178 | 0.022 | 2.89 | 13.15 |
| **T1E8** | 0.032 | 0.064 | 0.007 | 0.024 | 0.004 | 0.001 | 0.005 | 0.001 | 0.003 | 0 | 0.001 | 0 | 0.001 | 0 | 0.143 | 0.018 | 4.132 | 22.15 |
| **T1E9** | 0.05 | 0.102 | 0.011 | 0.035 | 0.006 | 0.001 | 0.007 | 0.001 | 0.005 | 0.001 | 0.002 | 0 | 0.002 | 0 | 0.223 | 0.028 | 2.892 | 17.30 |
| **T1E10** | 0.051 | 0.11 | 0.012 | 0.038 | 0.008 | 0.002 | 0.01 | 0.002 | 0.01 | 0.002 | 0.004 | 0 | 0.001 | 0.001 | 0.251 | 0.030 | 8.265 | 35.31 |
| **T1E11** | 0.061 | 0.124 | 0.014 | 0.045 | 0.008 | 0.002 | 0.01 | 0.001 | 0.007 | 0.001 | 0.003 | 0 | 0.003 | 0 | 0.279 | 0.035 | 2.755 | 14.07 |

# Discussions

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- **Tailings dam 1 has a slightly lower concentration of REE compared to 2. The ∑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. this values are lower than coarse and fine grained sediments which are found to have the ∑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 3 and 13.847 to 33.233 for tailing dam 5**

# Normalized REE/Chondrites

- 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.

# Discussions cont….

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- 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

# Discussions cont….

- Tailings dam 1 has a slightly lower concentration of REE compared to 2. The ∑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. this values are lower than coarse and fine grained sediments which are found to have the ∑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.

# REE signatures for Tailing Dam 3

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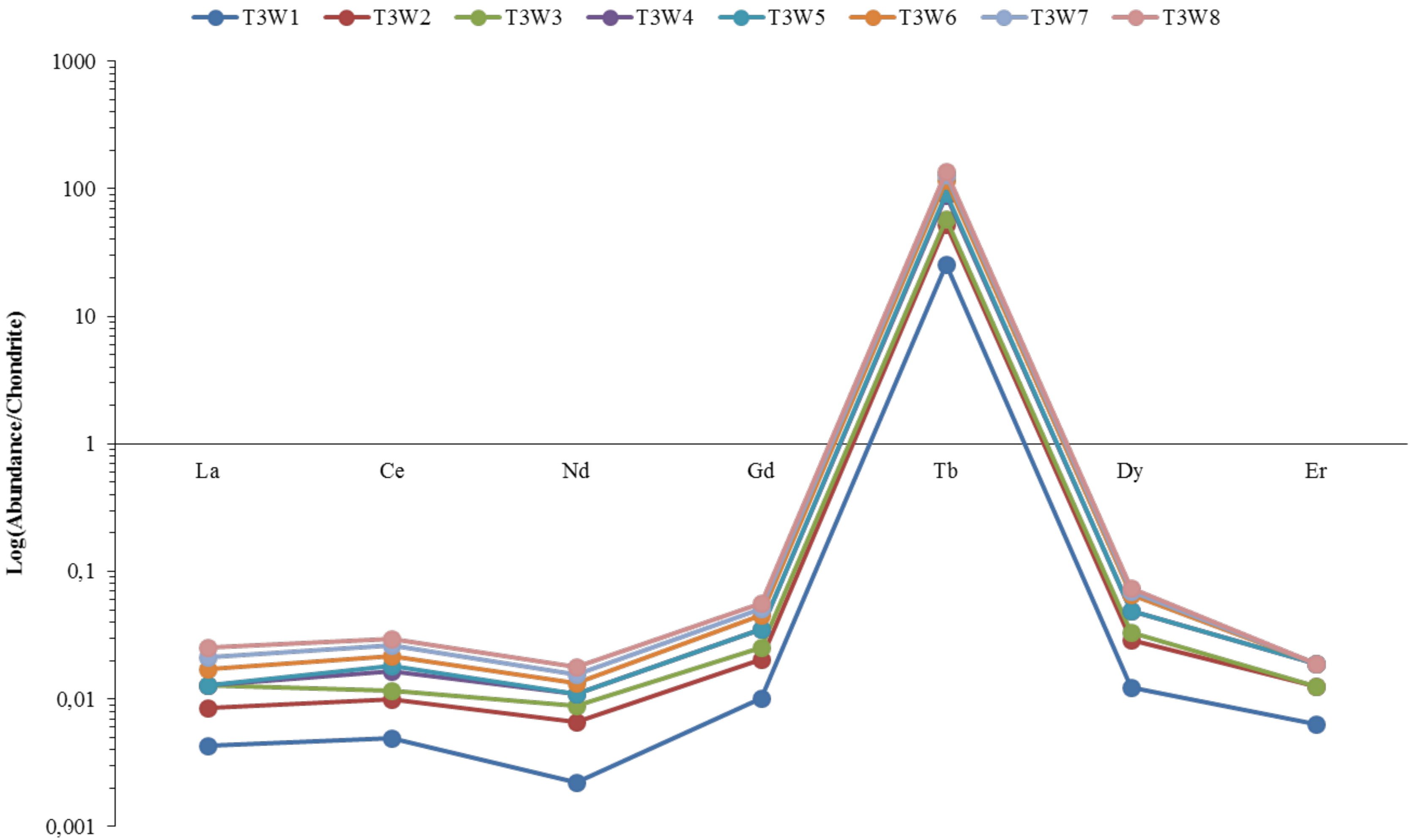
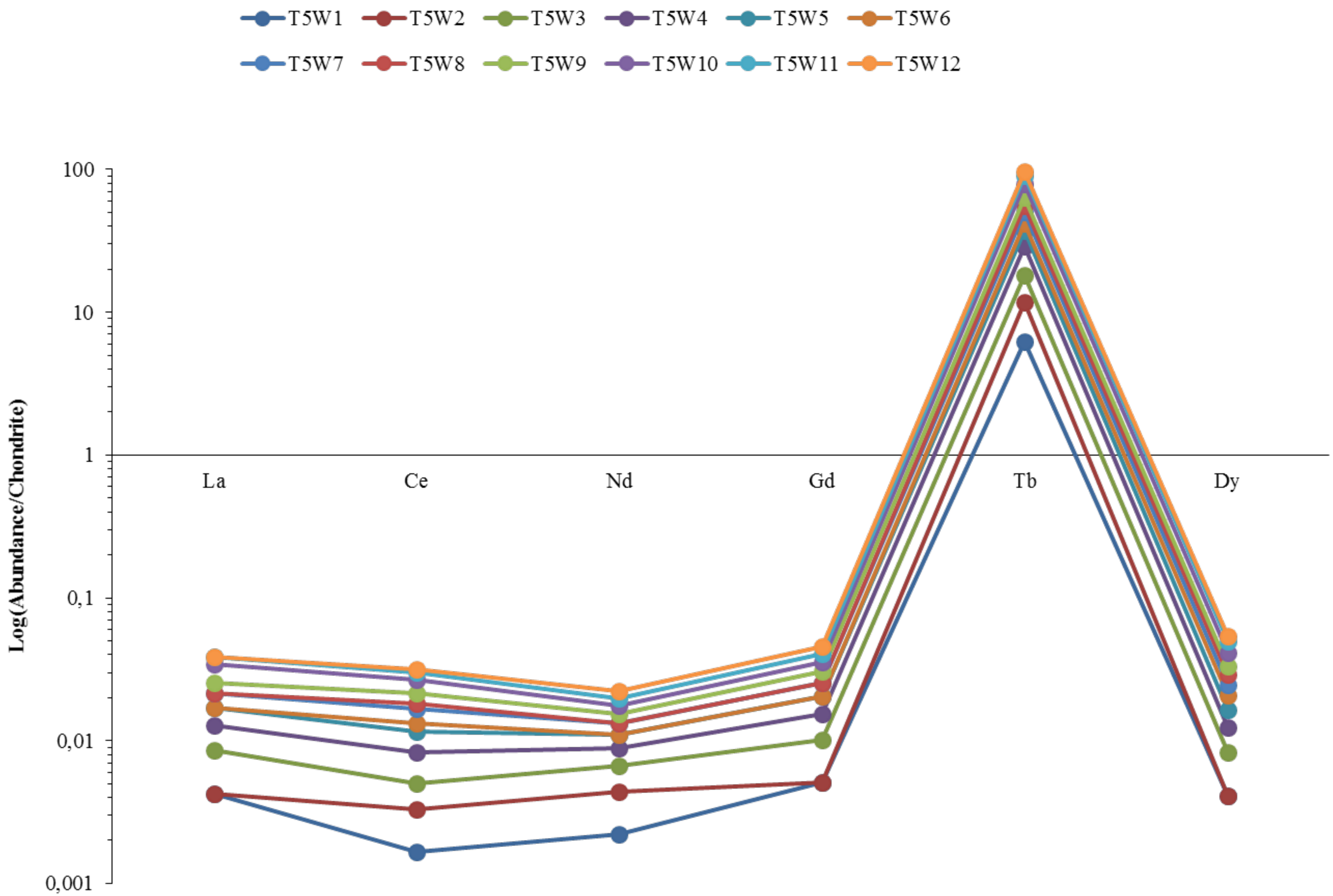



# Figure 2: REE signmatures for Tailing Dam 3

# REE signatures for Tailing Dam 5




## Figure 3: REE signatures for Tailing Dam 5

# Discussions conti…

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- 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.

# Further work: Instrument Comparison

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- Use Quantulus LSC 1220 to determine La-138, Ce-138, Eu-151, Nd-144, Nd-150, Gd-158, Pr-143, Tb- 158 and Lu-176, Dy-159 to determine the nuclear forensics signatures from the REE of the mine

- Compare with Perkin Elmer NexION 300Q ICP-MS Signatures

# CONCLUSIONS

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- REE found were mainly La, Ce, Pr, Nd and Tb.
- They can therefore be used as a distinct 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.

# ACKNOWLEDGEMETS

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- Authors would like to acknowledge the International Atomic Energy Authority for sponsoring this Project under CRP J2003.

- We also acknowledge the Faculty Research Committee for providing part of the sponsorship to this conference.

# Thank You...

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