Application of neodymium isotope ratio measurements for the origin assessment of uranium ore concentrates

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A B S T R A C T
A novel procedure has been developed for the measurement of 143Nd/144Nd isotope ratio in various uranium-bearing materials, such as uranium ores and ore concentrates (UOC) in order to evaluate the usefulness and applicability of variations of 143Nd/144Nd isotope ratio for provenance assessment in nuclear forensics.

Neodymium was separated and pre-concentrated by extraction chromatography and then the isotope ratios were measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The method was validated by the measurement of standard reference materials (La Jolla, JB-2 and BCR-2) and the applicability of the procedure was demonstrated by the analysis of uranium samples of world-wide origin. The investigated samples show distinct 143Nd/144Nd ratio depending on the ore type, deposit age and Sm/Nd ratio. Together with other characteristics of the material in question, the Nd isotope ratio is a promising signature for nuclear forensics and suggests being indicative of the source material, the uranium ore.

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1. Introduction

Nuclear forensics is a relatively young and dynamically progressing branch of science, including the characterisation of nuclear material (determination of sample physical and chemical characteristics) and the interpretation of data (providing hints on the intended use and origin of the material). There is a need for improving available methods, developing new methods and identifying new nuclear forensics signatures in order to support the investigations of unknown seized nuclear materials [1]. Up to now the isotopic patterns of O [2], S [3], Pb, Sr [4], and U [5–7] have been investigated and found to be valuable signatures. Besides these signatures the 143Nd/144Nd isotope ratio, which is widely used in geology for chronometry and provenance measurements, is another promising candidate as a new nuclear forensic signature, since its value is indicative of the age and origin of the minerals present [8] and [9].

The 143Nd/144Nd isotope ratio varies in nature due to the presence of the long-lived parent nuclide 144Sm (T1/2 = 1.06 × 1011 years), which decays to 143Nd. The ratio depends on the type and the age of minerals present. As the number of 144Nd atoms is not altered by the radioactive decay, it is a suitable reference isotope.

Nd isotopic ratio variations are commonly expressed as relative values using the so-called ε notation which is calculated relative to a given isotope standard:

\[ \epsilon_{\text{Nd}} = \left( \frac{n_{143\text{Nd}}}{n_{144\text{Nd}}} \right)_{\text{sample}} - 1 \times 10^4 \] (1)

where \( n_{143\text{Nd}}/n_{144\text{Nd}} \) is the measured 143Nd/144Nd ratio in the sample, and \( n_{143\text{Nd}}/n_{144\text{Nd}} \) is the 143Nd/144Nd ratio of the Chondritic Uniform Reservoir (CHUR) [10].

The positive or negative εNd values of 143Nd/144Nd in samples reflect the source and the history of a rock. A negative value of εNd implies that, on average over the history of the Earth, the Sm/Nd ratio of that rock (or its precursors) has been lower than the value of chondritic rocks. This in turn implies that the rare-earth pattern of the rock or its precursors was enriched in light rare-earth elements. The opposite conclusion can be drawn from a positive εNd value.

In natural uranium-based nuclear materials Nd is present at trace levels (below μg/g) deriving from the ore [1]. The hydro-metallurgical processes are not expected to affect its isotopic composition significantly, therefore the n(143Nd)/n(144Nd) sample or εNd is assumed to be indicative only of the ore the material was produced from. Due to the low concentration of Nd in nuclear materials the measurement of 143Nd/144Nd isotope ratio is...
analytically a challenging task. Nd isotope ratio measurements at this low concentration level require very high sensitivity and precision, and are therefore typically performed by thermal ionisation mass spectrometry (TIMS) [11,12] or by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [13,14]. Mass spectrometric measurements of Nd isotope ratios, however, may suffer from isobaric interferences of Ce and Sm isotopes [15]. While the similarity in chemical behaviour of the rare-earth elements (REEs) constitutes an advantageous prerequisite for a useful elemental pattern (thus a forensic signature), it poses a challenge for Nd isotope analysis, due to the difficulties to separate them from each other prior to the mass spectrometric measurements. The chemical separation needs to separate not only the REE from the U matrix, but also the interfering ones e.g. $^{144}$Nd from $^{144}$Sm. Traditionally, ion exchange [15] or liquid–liquid extraction [16] have been used for the group separation of REE from the sample matrix or from interfering analytes (e.g. Ba). Nowadays, a combination of these techniques or advanced techniques (such as extraction chromatography) is preferably applied due to the ease of use and the higher selectivity. As the Nd concentration in our natural uranium samples is very low, chemical reagent volumes were kept to a minimum for reducing the blank level and achieve subsequently lower limits of detection. Extraction chromatography is routinely applied for the separation of actinides [17] and lanthanides [18], therefore being also effective and straightforward solution for the separation of Nd from Sm with the application of consecutive columns containing different resins.

In contrast to the commonly investigated samples (e.g. sea water, geological samples), the Nd isotope variation particularly in uranium deposits is less frequently reported. For Australian water, geological samples), the Nd isotope variation particularly in resins.

The optimisation was carried out with respect to the value. This work presents a novel method developed for the separation of neodymium and the subsequent measurement of the $^{143}$Nd/$^{144}$Nd isotope ratio in uranium-bearing materials. The Nd/Sm chemical separation is based on the work of Pin and Zalduegui [18], and further developed for the separation and pre-concentration of trace-level Nd in various uranium ores and ore concentrates (UCO) for accurate rinsing with high purity water.

All uncertainties quoted are given as expanded uncertainty (U) using a coverage factor of $k=2$ and taking into account the uncertainty contributions from the method blanks, isotope masses, measured isotope ratios as well as mathematical corrections for instrumental mass discrimination (see Eqs. 2–4). They are given in parentheses and they apply to the last significant digits of the value.

### 2.2. Reagents and materials

As low blanks are of critical importance for Nd analyses, all labware were thoroughly cleaned before use with dilute ethanol and dilute nitric acid, and finally rinsed with high purity water (UHQ System, USF Elga, Germany). Monoelemental Nd and Sm standard solutions (Alfa Aesar, Karlsruhe, Germany) were used for the optimisation of the MC-ICP-MS instrument were prepared by the dilution of a 1000 μg mL⁻¹ standard solution.

For all the dilutions high-purity water was used (UHQ System, USF Elga, Germany). Hydrochloric and nitric acid used for the sample preparation was of Suprapur grade (Merck, Darmstadt, Germany). The Suprapur grade nitric acid was further purified by subboiling distillation.

For the lanthanide group separation, the TRU™ extraction chromatographic resin (100–150 μm particle size, active component: octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide dissolved in tri-n-butyl phosphate) was supplied by Skrism (Triskem International, Bruz, France). For the preparation of columns, 1.6 mL of the resin was placed in plastic Bio-Rad holders (diameter 8 mm) and plugged with porous Teflon frit (Reichelt Chemietechnik Heidelberg, Germany) on the top of the resin to avoid mixing. The free-column volume (FCV) of the column was approximately 1.0 mL.

For Nd separation, the Ln extraction chromatographic resin (100–150 μm particle size, extractant component: di(2-ethylhexyl) orthophosphoric acid) was supplied by Skrism (Triskem International, Bruz, France). For the preparation of columns, 400 μL of the resin was placed in plastic Bio-Rad holders and plugged with porous Teflon frit.

As no uranium-based reference material with certified Nd isotopes is available, geological standards BCR-2 (Columbia River Basalt, U.S. Geological Survey, Denver, USA) [25], and JB-2 (Volcano

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Optimised instrumental settings and data acquisition parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MC-ICPMS instrument settings</strong></td>
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<td>Forward powers</td>
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<tr>
<td>Cooling gas flow rate</td>
<td>14 L min⁻¹</td>
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<tr>
<td>Auxiliary gas flow rate</td>
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<tr>
<td><strong>Sample introduction conditions (DSN-100)</strong></td>
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<td>Solution uptake rate</td>
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<td>Hot gas flow rate</td>
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<td>Membrane gas flow rate</td>
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<td>Membrane temperature</td>
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<td><strong>Data acquisition parameters</strong></td>
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<td>Data acquisition time</td>
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<td>Magnet delay between blocks</td>
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<td>Number of spectra acquired</td>
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<td>Scan type</td>
<td>Static multicolonction</td>
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<tr>
<td><strong>Cup configuration of Faraday detectors</strong></td>
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<tr>
<td>L1 $^{142}$Nd; axial $^{143}$Nd; H1 $^{144}$Nd; H3 $^{146}$Nd and H4 $^{147}$Sm</td>
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</table>
2.3. Investigated samples

Uranium ore samples originating from four different mines and uranium ore concentrates originating from 20 different mills were included in this study. The investigated samples with the uranium deposit type are shown in Table 2. The used sample set contained multiple samples from two locations (Beverley and Olympic Dam), which were taken at different times. Replicate samples can be used to assess the robustness of the parameters investigated, i.e. how these parameters change over the course of time or over the different batches. For the latter purpose we chose four Beverley samples, taken at the beginning of the 2000 s, and obtained from two different batches produced within short time interval (Beverley-1,3 and Beverley-2,4, respectively) [28]. To validate the repeatability of the chemical separation replicate analysis of six aliquots of Beverley-3 were used.

2.4. Sample preparation

The Nd separation from the matrix and other interfering elements was performed in two steps: first, a lanthanide group separation, which was followed by the Nd separation. Approximately 300–500 mg of sample was weighed into a Teflon vial and dissolved in 9 mL 10 M ultra-pure nitric acid while heating to 90 °C on a hot-plate for 6 h. Approximately 300 μL of this stock solution was weighed into a polyethylene vial and diluted fourfold using ultra-pure water in order to adjust the required HNO₃ concentration. This aliquot was used for the lanthanide separation, corresponding to about 13 mg of sample (~10 mg of uranium in UOC samples). The lanthanide content of the sample aliquots was separated using extraction chromatography by the selective retention of trivalent lanthanides on the TRUTM resin in 3 M nitric acid medium. After conditioning of the resin with 10 mL 2 M HNO₃, the sample aliquot was loaded on the column. After washing the column and removing the non-retaining matrix components with 2 mL of 2 M HNO₃, the lanthanides were stripped from the column into a Teflon beaker using 1 mL concentrated HCl followed by 4 mL of 4 M HCl. The samples were evaporated twice to almost complete dryness on a hot-plate by addition of concentrated HCl. The residue was dissolved in 1 mL of 0.05 M HCl while heating slightly.

In the second step, Ln resin was used in 0.05 M HCl medium for the Nd separation. After conditioning of the resin with 8 mL 0.05 M HCl the sample aliquot from lanthanide group separation was loaded on the column. After washing the column and

<table>
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<tr>
<th>Deposit type</th>
<th>Mine/Mill</th>
<th>Country</th>
<th>Nd (ppm)</th>
<th>Sm (ppm)</th>
<th>Sm/Nd</th>
<th>Ndtotal (μg)</th>
<th>ε</th>
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<td>USA</td>
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<td>69.9</td>
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<td>49.3</td>
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<td>0.30</td>
<td>0.72</td>
<td>0.005</td>
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<td>Hematite Breccia complex</td>
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<td>Australia</td>
<td>3.19</td>
<td>2.16</td>
<td>0.68</td>
<td>0.04</td>
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<tr>
<td>Metasomatite</td>
<td>Mary Kathleen</td>
<td>Australia</td>
<td>14.2</td>
<td>2.85</td>
<td>0.20</td>
<td>0.17</td>
<td>0.51068 (10)</td>
</tr>
</tbody>
</table>

Basalt, Geological Survey of Japan, Ibaraki, Japan) [26], as well as La Jolla Nd isotope standard [27] were used to validate the procedure.
removing of the non-retaining matrix components with 800 μL of 0.2 M HCl, the Nd was striped from the column into a Teflon beaker using 4.8 mL of 0.2 M HCl. After the addition of 100 μL ultra-pure HNO₃ to the final fractions, the samples were evaporated to almost complete dryness on a hot-plate in order to destroy the organic resin residuals. The residue was dissolved in 1 mL of 0.1 M ultra-pure nitric acid while heating slightly. A method blank was run through the entire dissolution and separation procedure with each batch of samples. The final samples were analysed by MC-ICP-MS.

3. Results and discussion

3.1. Optimisation of the 143Nd/144Nd ratio measurements by MC-ICP-MS

Before every measurement, an on-peak-zero baseline measurement was done to eliminate the effects of the small, but persistent quantities of Nd accumulated in the instrument. Method blank was used for the background correction of the analysis. Although chemical separation was done to minimise interfering Sm signal, mathematical correction was also applied as follows: based on the signal intensity of interference-free 147Sm, the contribution of Sm to the signal of 144Nd was corrected for, assuming that the mass bias of Sm is the same as of Nd. For the mathematical correction of the 143Sm, the 144Sm/147Sm ratio of 0.20504 was used [29]. Finally, due to the instrumental mass discrimination, the 143Nd/144Nd ratio was normalised to 146Nd/144Nd = 0.7219 using the exponential law of Russel [30]. The calculations were done as follows:

\[
\begin{align*}
143\text{Nd}_{\text{calc}} & = 143\text{Nd}_{\text{meas}} - 143\text{Nd}_{\text{blank}} \\
144\text{Nd}_{\text{calc}} & = (144\text{Nd}_{\text{meas}} - 144\text{Nd}_{\text{blank}}) - (0.20504 \times 147\text{Sm}_{\text{meas}} - 147\text{Sm}_{\text{blank}}) \\
\beta & = \ln \left( \frac{(0.7219) / (146\text{Nd}_{\text{meas}})}{1.01392} \right)
\end{align*}
\]

where \( \beta \) corresponds to the mass bias coefficient for Nd and 1.01392 is the atomic mass ratio of the 149Nd and 144Nd isotopes.

For the optimisation of the measurement procedure, experiments with La Jolla isotope standard were performed. Measurement uncertainty was investigated with an external calibration in a concentration range between 50 ppm. The calculations were done as follows:

\[
\begin{align*}
143\text{Nd}_{\text{calc}} & = 143\text{Nd}_{\text{meas}} - 143\text{Nd}_{\text{blank}} \\
144\text{Nd}_{\text{calc}} & = (144\text{Nd}_{\text{meas}} - 144\text{Nd}_{\text{blank}}) - (0.20504 \times 147\text{Sm}_{\text{meas}} - 147\text{Sm}_{\text{blank}}) \\
\beta & = \ln \left( \frac{(0.7219) / (146\text{Nd}_{\text{meas}})}{1.02392} \right)
\end{align*}
\]

where \( \beta \) corresponds to the mass bias coefficient for Nd and 1.01392 is the atomic mass ratio of the 149Nd and 144Nd isotopes.

3.2. 143Nd/144Nd in uranium samples

The measured 143Nd/144Nd isotope abundance ratio plotted against the Sm/Nd elemental ratio in the investigated uranium
ores and ore concentrates is shown in Fig. 4. The corresponding results with additional information are seen in Table 2. It can be observed from Fig. 4 that the $^{143}$Nd/$^{144}$Nd ratios in the uranium samples (ores and UOCs) show large variations between 0.510 and 0.515 (or $\epsilon_{Nd}$ = -40 to +40). Most of the samples, however, show values in the range of $\epsilon_{Nd}$ = -30 to +10 with a few notable exceptions. The respective measurement uncertainties proved to be low enough to distinguish most of the samples from each other. The variation of Sm/Nd elemental ratio shows a relatively good linear correlation with the $\epsilon_{Nd}$ value (Fig. 4). Certain samples belonging to specific deposit types, such as for intrusive deposits, show little variability of the $\epsilon_{Nd}$ values for the investigated samples and they also exhibit very similar Sm/Nd ratios. For sandstone type deposits the $\epsilon_{Nd}$ values showed good agreement, while the Sm/Nd elemental ratio showed a larger variability. For other deposit types such grouping appears less obvious, using just these two parameters. In particular unconformity related deposits have shown a broad variety in their chemical composition. For instance, Varga et al. [31] and Mercadier et al. [34] found that rare earth element pattern of unconformity related deposits show high concentrations for the middle rare earth elements; centred on Tb or Dy. The light rare earth elements, however, shows distinct differences for different mines (e.g., Sm/Nd ratio for Ranger, Key Lake, Rabbit Lake and Nabarlek was 1.92, 1.06, 0.75 and 2.21, respectively). This could explain also the variations of the $\epsilon_{Nd}$ value.

As discussed before, the $^{143}$Nd/$^{144}$Nd isotope ratio in UOC samples is assumed to strongly correlate with that of uranium ores, i.e. the chemical processing should neither affect the Nd isotope ratios nor the REE pattern. The measured $^{143}$Nd/$^{144}$Nd ratio in Mary Kathleen (0.51068(10)), Nabarlek (0.51470(87)), and Key Lake (0.51306(11)) UOC samples is in a good agreement with the literature values of the corresponding uranium ores 0.50967–0.51105 [20], 0.51067–0.51485 [22] and 0.51289–0.51660 [35], respectively. We do have to recognise, however, that the given reference values vary over a wide range. The two uranium ore–ore concentrate pairs analysed in this study (Rum Jungle and Olympic Dam) showed small, but significant differences for both $^{143}$Nd/$^{144}$Nd ratio and Sm/Nd ratio (Fig. 4). The explanation for the inconsistency is likely that these pairs are not directly linked, i.e. the UOC sample has not been prepared from the respective ore sample as well as the inhomogeneity of the ore.

In order to investigate the variation of isotope ratios within one deposit and also between production batches (so called within-mine variations), we compared the $^{143}$Nd/$^{144}$Nd results of four different batches (1–4) of Beverley deposit with other stable isotope ratios, which have been previously studied for origin assessment purpose in nuclear forensics. The results suggest that the $^{143}$Nd/$^{144}$Nd isotope ratio in the investigated deposit has still lower spread than for Sr or Pb. The calculated relative standard deviation of Nd isotope values for the different batches (1–4) of Beverley samples is 0.01% (Table 2) while for Sr it is 0.06% and for Pb it is three orders of magnitude higher [4]. As the $^{143}$Nd/$^{144}$Nd ratio is related to the Sm/Nd ratio in the ores, we can assume that this smaller within-mine variation derives from the fact that both the parent ($^{147}$Sm) and daughter ($^{143}$Nd) nuclides are rare-earth elements and have similar chemical properties, which means that their ratio is less affected during the history of the rock, e.g. by fractionation due to weathering. In contrast to the Sm/Nd ratio, the pattern of unconformity related deposits show high concentrations for the middle rare earth elements; centred on Tb or Dy. The light rare earth elements, however, shows distinct differences for different mines (e.g., Sm/Nd ratio for Ranger, Key Lake, Rabbit Lake and Nabarlek was 1.92, 1.06, 0.75 and 2.21, respectively). This could explain also the variations of the $\epsilon_{Nd}$ value.

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Sr and Pb isotope variation is due to the presence of the chemically highly different parent/daughter pairs (Rb/Sr and U/Pb), which are more prone to fractionation. This finding suggests that within a uranium deposit smaller variation of the $^{143}\text{Nd}/^{144}\text{Nd}$ can be expected than the variation of the Sr and Pb isotopics, though this initial assumption has to be verified for more deposit types.

4. Conclusions

This work presents a novel method developed for trace-level analysis of $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio in uranium ores and ore concentrates (UOC) by multi-collector inductively coupled plasma mass spectrometry. The developed method comprises consecutive extraction chromatographic separations in order to, first separate REEs from U matrix and secondly, to separate Nd and Sm fractions from each other. With the developed method the measurement of Nd isotope ratio in most of the investigated samples (containing a few hundred $\text{ppm}$ of Nd) was possible with low uncertainty. For the validation of the Nd isotopic measurements La Jolla, JB-2 and BCR-2 geological reference materials were used. The applicability of the method was demonstrated by the determination of $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio in uranium ores and UOCs originating from different uranium mines and millling facilities.

The obtained results show that the $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio is highly variable in UOCs and ores; the value ranges between 0.510 and 0.515. This variation shows a relatively good correlation with the Sm/Nd ratio in the sample. This initial study suggests that certain deposit types (e.g. intrusive or quartz–pebble conglomerate) can have specific $\varepsilon_{\text{Nd}}$ values, while for other deposit types we observe larger spread of the values. The $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio in the investigated samples has also smaller within mine variation when comparing to other stable isotope ratios studied previously for nuclear forensic purposes. Although, the results show that certain deposit types have overlapping Nd isotope ratios and therefore it cannot be used as an exclusive signature, the $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio is still useful when complemented with other characteristics of the materials, such as Sr, Pb, or REE pattern.

Further studies will need to be undertaken in order to develop modified procedure including a further pre-concentration step for samples with very low Nd content and, in addition to that, to understand properly the correlation between the $\varepsilon_{\text{Nd}}$ values of the uranium ore concentrates, uranium ores and the deposit types.

References