**143Nd/144Nd ratio – a powerful signature for origin assessment of natural uranium products**

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**Abstract.** Expanding the pattern of characteristic properties which helps to identify the origin of uranium-bearing sized material is one of the most important directions of nuclear forensic research and development. In this paper the usefulness of stable isotopic variations of Nd for provenance assessment in nuclear forensics has been evaluated. A novel procedure has been developed for the measurement of REE pattern, the 143Nd/144Nd isotope ratio and the Nd/Sm ratio in various uranium-bearing materials, such as uranium ores, and uranium ore concentrates (UOC). The method was validated by the measurement of standard reference materials (Morille, La Jolla, JB2 and BCR-2). The applicability of the method was demonstrated by the determination of 143Nd/144Nd isotope ratio in uranium samples originating from different uranium mines and milling facilities.

**1. Introduction**

Since the early 1990s illegal possession, transfer and other unauthorised acts involving nuclear materials have taken place. In order to identify the hazard, intended use and origin of the illicitly trafficked nuclear materials, new analytical methods using techniques such as radiometry, mass spectrometry and electron microscopy have been developed for nuclear forensics during the following years. Among the characteristic parameters that can be determined by the above-mentioned methods the concentration and the isotopic composition of some of the impurities of uranium materials have been found highly indicative to the feed material, production facility and its location as well as to the last chemical processing date of the nuclear material.

Up to now the isotopic patterns of Pb, Sr, and U have been investigated. Also the elemental pattern of the rare-earth elements (REE) has been studied and found characteristic to the geological formation of the uranium deposit [1-6]. Due to the similarity in chemical properties, their relative abundances remain mainly unaltered through the processing in the front-end of the nuclear fuel cycle. Among the REE, the 143Nd/144Nd isotope ratio is widely used in geology with *ε* notation and the 147Sm/143Nd isotope ratio for chronometry and provenance measurements. The 143Nd/144Nd ratio varies in nature due to the 147Sm decay to 143Nd (T1/2=1.06 \* 1011 a). As 144Nd is neither radioactive nor radiogenic, the number of 144Nd atoms does not change with time, which makes it suitable as a reference isotope [7, 8].Together with the other above-mentioned characteristic parameters in uranium, the Nd isotope ratio can be a promising signature for nuclear forensics. The measurement of 143Nd/144Nd isotope ratio in uranium samples is however analytically a challenging task as the concentration of Nd is very low (<ppb level) due to the effective production and purification process. Therefore pre-concentration of REE, before the measurement by ICP-MS, is often required.

The present work aims at evaluating the usefulness of stable isotopic variations of Nd for provenance assessment in nuclear forensics. For that purpose a novel procedure has been developed for the measurement of REE pattern, the 143Nd/144Nd isotope ratio and the Nd/Sm ratio in various uranium-bearing materials, such as uranium ores, and uranium ore concentrates (UOC). After the pre-concentration of REE from the uranium matrix, Nd and Sm were separated and further concentrated by extraction chromatography. REE were measured by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and the Nd isotope ratio was determined by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The method was validated by the measurement of standard reference materials (Morille, La Jolla, JB2 and BCR-2). When combining the REE pattern with the isotopic information of Nd, the deposit type where the uranium was mined from can be assessed with higher probability, therefore helping in the origin determination of unknown nuclear materials.

**2. Experimental**

***2.1. Reagents***

All labware was cleaned thoroughly with dilute ethanol, followed by dilute nitric acid, and finally rinsing with high purity water. For all the dilutions high-purity water was used (UHQ System, USF Elga, Germany). Hydrochloric and nitric acid was of Suprapur grade (Merck, Darmstadt, Germany), although the nitric acid was further purified by sub-boiling distillation.

Analytical grade Fe(NO3)3 salt was used as carrier for the co-precipitation (Alfa Aesar, Karlsruhe, Germany). Analytical grade sodium-hydroxide and ammonium-carbonate used for the precipitation were purchased from Sigma Aldrich (St Louis, MO, USA). Ammonium carbonate was further purified prior the use by Fe(OH)3 precipitation in order to remove the trace-level lanthanide impurities. TRUTM and LnTM extraction chromatographic resin (Triskem International, Bruz, France) was used for the lanthanide group separation and the forthcoming Nd separation. Respectively 1.6 mL and 0.4 mL of the resin was placed in plastic Bio-Rad holders and plugged with porous Teflon frit (Reichelt Chemietechnik Heidelberg, Germany) on the top of the resin to avoid mixing.

For the optimization of the chemical separation procedure and the measurements by ICP-MS, lanthanide standard solution and monoelemental Nd and Sm standard solutions (Alfa Aesar, Karlsruhe, Germany) were prepared by the dilution from 1000 μg mL-1, and 100 μg mL-1 standard solutions, respectively. The Morille (Cetama, France) U3O8 certified reference material, was used for the validation of the co-precipitation method. The relative background (signal to noise ratio) was less than 2% for all sample. All uncertainties quoted are given as expanded uncertainty using a coverage factor of *k*=2 with last significant digits in parenthesis.

***2.2. Instrumentation***

The analysis of REE fractions from the co-precipitation step was carried out using an ELEMENT2 (Thermo Electron Corp., Bremen, Germany) double-focusing magnetic sector inductively coupled plasma mass spectrometer (ICP-SFMS) in low resolution mode (*R* = 300). ). Instrument optimisation with respect to maximum sensitivity low UO+/U+ ratio was carried out using 1 ng g-1 multielement solution (Merck, Darmstadt, Germany.

Nd isotope ratio measurements were performed with a NuPlasma™ (NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) in low mass resolution mode. The sample introduction was done by a low-flow Teflon micro-concentric nebulizer in combination with a DSN-100 desolvation unit (NU Instruments, Oxford, United Kingdom). Instrument optimisation with respect to maximum sensitivity was carried out using a 100 ng g-1 Nd monoelemental solution (Alfa Aesar, Karlsruhe, Germany). The sensitivity was approximately 500mV for 143Nd+ in 100 ng g-1 Nd standard solution.

The distribution of U and Th during the co-precipitation was followed by gamma spectrometric measurements using a well-type HPGe detector (Canberra Industries Inc., USA). The measured spectra were evaluated using Genie 2000 v2.1 software. All gamma spectrometric measurements were performed as relative measurements to the original starting material before and after the separation at fixed geometry. Measurement time varied between 600 and 5400 s.

***2.3. Sample preparation***

Approximately 0.5 g of samples were weighed into a Teflon Erlenmeyer and dissolved in 6 mL 8 M ultra-pure nitric acid while heating to 90 °C on a hot-plate for 12 hours covered with a PE stopcock. Aliquot of this stock solution, corresponding to about 10 mg uranium of sample, was weighed into a polyethylene vial and diluted using ultra-pure water in order to adjust the required HNO3 concentration. The extraction chromatographic separation was performed in two stages.

(1) 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.

(2) In the second step, Ln resin was used in 0.05 M HCl medium for the Nd separation from Sm, which interferes otherwise with the ICP-MS analysis. A method blank was processed through the entire dissolution and separation procedure parallel to the samples. The final Nd fractions were analysed by MC-ICP-MS [9, 10].

In case of samples with low Nd concentration (<50 ng/g) pre-concentration of the samples was performed before the above mentioned two step chromatographic separation in the following way: About 3.0 mL of the stock solutions were transferred into a 50 mL polyethylene centrifuge vials corresponding to about 200 mg of uranium. Ln, Th and U were precipitated as hydroxides (pH 12-14) with 40 % sodium hydroxide in the presence of 2 mg Fe(III) carrier. The supernatant, containing most of the alkali-soluble matrix elements (e.g. alkali metals) were carefully discarded after thorough centrifugation. Subsequently the precipitate was rinsed with high-purity water. Selective (re-)dissolution of uranium from the precipitate was done with 10 mL 1% (NH4)2CO3 as uranium forms soluble di- and tri-carbonato complexes between pH 5-8 [11]. This step was repeated three to five times until clear solution was obtained; assuring that U was removed from the sample to the highest extent possible. The residual precipitate containing the Ln and Th was dissolved in 2 mL 3 M nitric acid to be in suitable form for further concentration by extraction chromatography.

**3. Results and discussion**

Representative aliquots of the supernatant of pre-concentration procedure were collected after each separation step in order to control uranium decontamination and Th recovery factors by gamma spectrometric measurements parallel to the separation. The achievable U decontamination factor was in the magnitude of 102 – 104, sufficiently high to use the extraction chromatography afterwards. From this final solution, containing the Ln and Th, 100 μL aliquots were taken for mass spectrometric measurements to evaluate recoveries and decontamination factors. The method was validated by the measurement of reference material (Morille, Cetama), the recovery for the certified rare earth elements (Sm, Eu, Gd, Dy) was better than 90% [12].

Three UOC sample (Rabbit Lake, Mary Kathleen and Nabarlek) were analysed to compare the REE pattern with and without pre-concentration step in order to verify that no interferences were introduced to the samples by the used reagents. As one can see from the Figure 1 the normalised REE patterns agree well.

REE_PRECONC_vs_TRU.wmf

*FIG 1 REE patterns of investigated uranium ore concentrate samples obtained from two separation type extraction chromatography (TRU) and co-precipitation (preconc)*

Table 1 Measured 143Nd/144Nd isotope ratios in the investigated uranium ore concentrate samples. All uncertainties quoted are given as expanded uncertainty using a coverage factor of *k*=2 with last significant digits. 143Nd/144NdTRU corresponds to the results obtained by using only TRU separation, while 143Nd/144Ndpreconc are the results of the present method with preconcentration.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **Country** | **Deposit type** | **cNd (ng/g) centration (ng/g)** | **143Nd/144NdTRU** | **143Nd/144Ndpreconc** |
| ESI | Canada | Phosphate | 90 | <DL | 0.51225(9) |
| Rössing | Namibia | Intrusive | 15 | 0.51363(230) | 0.51346(34) |
| Shirley Basin | USA | Sandstone | 8 | <DL | 0.51356(61) |

The 143Nd/144Nd isotope ratio of U-ore and UOC samples was measured and plotted against the Sm/Nd elemental ratio of the samples (Fig.2). The measured 143Nd/144Nd value of the BCR-2 standard was 0.512598(78). This value agrees with the certified value 0.512629(8) within uncertainty [13]. The Nd isotope ratio of Rössing sample had been measured previously using only EXC sequential separation and it resulted in a 143Nd/144Nd ratio of 0.51363(230). Comparing to our new result 0.51346(34), obtained with the improved sample pre-concentration procedure, one can see that the values are in good agreement. Moreover the uncertainty of the new result is almost an order of magnitude better. Shirley Basin (USA) and ESI (CAN) were previously under detection limit, but with the combined sample preparation procedure precise results were possible to obtain (Table 1).

 *FIG 2 Variation of the 143Nd/144Nd ratio as a function of Sm/Nd ratio in the investigated uranium ore and uranium ore concentrate samples. 'OD' – Olympic Dam; 'underlined labels' correspond to ore samples, 'label with asterisk' correspond to samples prepared by combined separation procedure [10].*

The obtained results show that the 143Nd/144Nd 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 *Nd* values, while for other deposit types we observe larger spread of the values. The 143Nd/144Nd 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, such as Pb and Sr. As the 143Nd/144Nd 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 (147Sm) and daughter (143Nd) 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 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. The results are discussed detailed elsewhere [10].

Investigation of correlation of Nd isotope ratio variations with Sr isotope ratio has been started, as previous geological studies showed that reservoirs with high 143Nd/144Nd tend to have low 87Sr/86Sr ratios (Fig 3.). This trend could be explained by the hypothesis that Nd and Sr isotopic variations in the earth mantle are the results of magmatic process induced Sm/Nd and Rb/Sr fractionations [14]. However, we can see that such correlation is not that obvious in case of uranium ore concentrates and further studies need to be done to understand properly the correlation between Nd and Sr isotopic variations and the deposit types.



*FIG 3 Distribution of 87Sr/86Sr isotope ratio as a function of 143Nd/144Nd ratio in the investigated uranium ore and uranium ore concentrate samples.*

4. **Conclusions**

Novel procedure has been developed for the measurement of REE pattern, the 143Nd/144Nd isotope ratio and the Nd/Sm ratio in various uranium-bearing materials, such as uranium ores, and ore concentrates (UOC). The obtained results show that the 143Nd/144Nd isotope ratio is highly variable in UOCs and ores; the value ranging between 0.510 and 0.515. This variation shows a relatively good correlation with the Sm/Nd ratio in the sample. The 143Nd/144Nd 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 143Nd/144Nd isotope ratio is still useful when complemented with other characteristics of the materials. The data evaluation and interpretation to find a correlation between the determined Nd ratio and other isotopic variation (e.g. Sr, and Sm) and the deposit type is on-going. The presented method, however, is not just useful for trace-level Nd isotope ratio analysis as demonstrated, but it is also a versatile and straightforward sample preparation procedure, which can be applied to pre-concentrate and separate other elements of interest, such as Th, Pu or Am from a single sample aliquot. These are just few examples of the promising potential of the new developed pre-concentration procedure.

**REFERENCES**

[1] IAEA Nuclear Security Series No. 2, Nuclear Forensic Support, Technical Guidance. STI/PUB/1241, ISBN 92-0-100306-4 (2006).

[2] PAYO, L., et al. Investigation of the oxygen isotopic composition in oxidic uranium compounds as a new property in nuclear forensic science. Fresenius’ J. Anal. Chem. **371** (2011) 348–352.

[3] Han, S.H., et al., Measurement of the sulphur isotope ratio (34S/32S) in uranium ore concentrates (yellow cakes) for origin assessment, J. Anal. At. Spectrom. **28** 12 (2013) 1919.

[4] VARGA, Z., et al., Application of lead and strontium isotope ratio measurements for the origin assessment of uranium ore concentrates. Anal. Chem. **81** (2009) 8327–34.

[5] SRNCIK, M., et al., Investigation of the 236 U/ 238 U isotope abundance ratio in uranium ores and yellow cake samples. Radiochim. Acta **99** (2011) 335–339.

[6] RICHTER, S., et al., Isotopic “fingerprints” for natural uranium ore samples. Int. J. Mass Spectrom. **193** (1999) 9–14.

[7] NIE, J., et al., Integrated provenance analysis of a convergent retroarc foreland system: U–Pb ages, heavy minerals, Nd isotopes, and sandstone compositions of the Middle Magdalena Valley basin, northern Andes, Colombia. Earth-Sci. Rev. **110** (2012) 111–126.

[8] MAAS, R., et al., Sm-Nd isotope systematics in uranium-rare earth element mineralization at the Mary Kathleen uranium mine, Queensland. Econ Geol **82** (1987) 1805–1826.

[9] VARGA, Z., et al., Determination of rare-earth elements in uranium-bearing materials by inductively coupled plasma mass spectrometry. Talanta **80** (2010) 1744–1749.

[10] KRAJKO, J., et al., Application of Neodymium Isotope Ratio Measurements for the Origin Assessment of Uranium Ore Concentrates. Talanta, (2014) DOI: 10.1016/j.talanta.2014.06.022.

[11] GOVINDAN, P., et al., Ammonium uranyl carbonate (AUC) based process of simultaneous partitioning and reconversion for uranium and plutonium in fast breeder reactors (FBRs) fuel reprocessing. J. Radioanal. Nucl. Chem. **295** (2013) 77–82.

[12] KRAJKO, J., et al., Determination of trace-levels of Lanthanides and Thorium samples. European Winter Conference on Plasma Spectrochemistry, Krakow, Poland, (2013).

[13] RACZEK, I., et al., Neodymium and Strontium Isotope Data for USGS Reference Materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, GSP-1, GSP-2 and Eight MPI-DING Reference Glasses. Geostand Geoanalytical Res. **27** (2003) 173.

[14] DEPAOLO, D. J., Neodymium Isotope Geochemistry: An Introduction. Minerals and Rocks Series no. 20. Springer-Verlag, ISBN 3 540 18648 4. (1988).