



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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



Judit Krajko^{a,b,*}, Zsolt Varga^a, Ezgi Yalcintas^c, Maria Wallenius^a, Klaus Mayer^a

^a European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany

^b Delft University of Technology, Faculty of Applied Sciences, Mekelweg 15, 2629 JB Delft, Netherlands

^c Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76128 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 26 March 2014

Received in revised form

5 June 2014

Accepted 11 June 2014

Available online 19 June 2014

Keywords:

Nuclear forensics

Neodymium isotope ratio

Origin assessment

Uranium ore concentrate

ABSTRACT

A novel procedure has been developed for the measurement of $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 worldwide origin. The investigated samples show distinct $^{143}\text{Nd}/^{144}\text{Nd}$ 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.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio varies in nature due to the presence of the long-lived parent nuclide ^{147}Sm ($T_{1/2} = 1.06 \times 10^{11}$ years), which decays to ^{143}Nd . The ratio depends on the type and

the age of minerals present. As the number of ^{144}Nd 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:

$$\epsilon_{\text{Nd}\cdot\text{CHUR}} = \left(\frac{n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{sample}}}{n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{CHUR}}} - 1 \right) 10^4, \quad (1)$$

where $n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{sample}}$ is the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in the sample, and $n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{CHUR}}$ is the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (0.512638(3)) in the Chondritic Uniform Reservoir (CHUR) [10].

The positive or negative ϵ_{Nd} values of $^{143}\text{Nd}/^{144}\text{Nd}$ in samples reflect the source and the history of a rock. A negative value of ϵ_{Nd} 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 ϵ_{Nd} value.

In natural uranium-based nuclear materials Nd is present at trace levels (below $\mu\text{g/gU}$) deriving from the ore [1]. The hydro-metallurgical processes are not expected to affect its isotopic composition significantly, therefore the $n(^{143}\text{Nd})/n(^{144}\text{Nd})_{\text{sample}}$ or ϵ_{Nd} 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 $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio is

* Corresponding author:

E-mail address: judit.krajko@ec.europa.eu (J. Krajko).

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 deposits there are a few available references mostly published by Maas et al. [19], and [20] and studies have been carried out on Namibian and Canadian deposits [21–24]. The results show distinct ϵ_{Nd} values for the different samples and when exploring its variation as the function of mineralisation age or the Sm/Nd ratio, valuable information about the history of the deposit can be obtained.

This work presents a novel method developed for the separation of neodymium and the subsequent measurement of the $^{143}\text{Nd}/^{144}\text{Nd}$ 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 (UOC) for precise $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio measurements by MC-ICP-MS.

2. Experimental

2.1. Instrumentation

A NuPlasmaTM (NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), equipped with 11 Faraday collectors and three discrete dynode electrode multipliers was used for the Nd isotope ratio measurements. The instrument was operated in low mass resolution mode. The samples were introduced into the plasma using a low-flow Teflon micro-concentric nebuliser operated in a self-aspirating mode in combination with a desolvation unit (DSN-100, NU Instruments, Oxford, United Kingdom). The instrument settings and the data acquisition parameters are summarised in Table 1.

Prior to the sample analysis the instrument was optimised using a 100 ng g^{-1} Nd mono-elemental solution (Alfa Aesar, Karlsruhe, Germany). The optimisation was carried out with respect to

Table 1

Optimised instrumental settings and data acquisition parameters.

MC-ICPMS instrument settings	
Forward power	1225 W
Cooling gas flow rate	14 L min ⁻¹
Auxiliary gas flow rate	0.75 L min ⁻¹
Sample introduction conditions (DSN-100)	
Nebuliser pressure	30.3 psi
Solution uptake rate	50 $\mu\text{L min}^{-1}$
Hot gas flow rate	0.15 L min ⁻¹
Membrane gas flow rate	3.28 L min ⁻¹
Spray chamber temperature	110 °C
Membrane temperature	110 °C
Data acquisition parameters	
Data acquisition time	50 s
Magnet delay between blocks	2 s
Mass resolution	300
Number of spectra acquired	3 × 10
Scan type	Static multicollection
Cup configuration of Faraday detectors	
L1 ^{142}Nd ; axial ^{143}Nd ; H1 ^{144}Nd ; H3 ^{146}Nd and H4 ^{147}Sm	

maximum sensitivity. The sensitivity was approximately 3.5 V for 100 ng g^{-1} total Nd, corresponding to about 420 mV for ^{143}Nd .

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). Mono-elemental Nd and Sm standard solutions (Alfa Aesar, Karlsruhe, Germany) used for the optimisation of the MC-ICP-MS instrument were prepared by the dilution of a $1000\text{ }\mu\text{g mL}^{-1}$ 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 TRUTM 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 Triskem (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 Triskem (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

Basalt, Geological Survey of Japan, Ibaraki, Japan) [26], as well as La Jolla Nd isotope standard [27] were used to validate the procedure.

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 TRU™ 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 2

Nd and Sm concentrations [31] and measured ¹⁴³Nd/¹⁴⁴Nd isotope ratios in the investigated uranium ore and ore concentrate samples. Uncertainties (*U*), given in parentheses with a coverage factor of 2, apply to the last significant digits of the value.

Deposit type	Mine/Mill	Country	Nd (ppm)	Sm (ppm)	Sm/Nd	Nd _{total} (µg)	¹⁴³ Nd/ ¹⁴⁴ Nd	<i>ε</i>
Uranium ore samples								
Sandstone								
	Arlit	Niger	2.89	0.80	0.28	0.03	0.51190 (21)	–14.4
Unconformity related								
	Rum Jungle	Australia	2.94	1.50	0.51	0.03	0.51106 (06)	–30.8
	Ranger	Australia	13.4	26.2	1.96	0.16	0.51442 (41)	34.8
Hematite Breccia complex								
	Olympic Dam1	Australia	234	66.8	0.28	2.74	0.51096 (05)	–32.8
	Olympic Dam2	Australia	201	61.1	0.30	2.35	0.51098 (04)	–32.3
Yellow cake samples								
Phosphorite								
	USA ESI	USA	1.53	0.47	0.31	0.02	0.51291 (68)	5.31
Vein								
	Rayrock	Canada	26.4	6.77	0.26	0.31	0.511320 (61)	–25.7
Intrusive								
	Madawasca	Canada	24.8	5.70	0.23	0.29	0.51243 (15)	–4.06
	Faraday	Canada	21.8	3.63	0.17	0.26	0.51216 (13)	–9.32
	Phalabora	S. Africa	2.13	0.47	0.22	0.02	0.51178 (26)	–16.7
	Nuclebras	Brasil	39.75	13.25	0.33	0.47	0.51255 (15)	–1.72
Quartz – pebble conglomerate								
	Denison	Canada	115	72.8	0.63	1.34	0.512978 (83)	6.63
	Stanrock	Canada	9.39	5.19	0.55	0.11	0.51215 (10)	–9.43
	Stanleigh	Canada	13.1	6.13	0.47	0.15	0.51253 (12)	–2.11
	Rio Algom	Canada	54.4	25.8	0.48	0.64	0.511951 (36)	–13.4
Sandstone								
	Beverley A1	Australia	48.6	17.8	0.37	0.57	0.51194 (12)	–13.6
	Beverley A2	Australia	69.9	24.0	0.34	0.82	0.511847 (11)	–15.4
	Beverley A3	Australia	49.3	18.1	0.37	0.58	0.511826 (65)	–15.8
	Beverley A4	Australia	69.7	23.9	0.34	0.82	0.511850 (50)	–15.4
	Yankee Yellow	USA	1.44	0.55	0.38	0.02	0.51209 (26)	–10.6
	Crow Butte	USA	1.20	0.29	0.24	0.01	0.51188 (10)	–14.9
	Mounana	Gabon	1.37	0.33	0.24	0.02	0.51169 (13)	–18.4
Metamorphite								
	Eldorado	Canada	23.0	14.1	0.61	0.27	0.51221 (15)	–8.35
Unconformity related								
	South Alligator	Australia	1.07	0.33	0.30	0.01	0.51284 (48)	3.94
	Key Lake	Australia	0.13	0.08	0.63	0.002	0.51306 (11)	8.23
	Rum Jungle	Australia	8.73	2.90	0.33	0.10	0.512344 (66)	–5.73
	Nabarlek	Australia	0.42	0.30	0.72	0.005	0.51470 (87)	40.2
Hematite Breccia complex								
	Olympic Dam	Australia	3.19	2.16	0.68	0.04	0.51141 (14)	–24.0
Metasomatite								
	Mary Kathleen	Australia	14.2	2.85	0.20	0.17	0.51068 (10)	–38.2

removing of the non-retaining matrix components with 800 μL of 0.2 M HCl, the Nd was stripped from the column into a Teflon beaker using 4.8 mL of 0.2 M HCl. After the addition of 100 μL ultra-pure HNO_3 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 ^{147}Sm , the contribution of Sm to the signal of ^{144}Nd was corrected for, assuming that the mass bias of Sm is the same as of Nd. For the mathematical correction of the ^{144}Sm the $^{144}\text{Sm}/^{147}\text{Sm}$ ratio of 0.20504 was used [29]. Finally, due to the instrumental mass discrimination, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio was normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ using the exponential law of Russel [30]. The calculations were done as follows:

$$^{143}\text{Nd}_{\text{calc}} = ^{143}\text{Nd}_{\text{meas}} - ^{143}\text{Nd}_{\text{blank}} \quad (2)$$

$$^{144}\text{Nd}_{\text{calc}} = (^{144}\text{Nd}_{\text{meas}} - ^{144}\text{Nd}_{\text{blank}}) - (0.20504(^{147}\text{Sm}_{\text{meas}} - ^{147}\text{Sm}_{\text{blank}})1.01392^\beta) \quad (3)$$

$$\beta = \ln\left(\frac{[(0.7219)/((^{146}\text{Nd}/^{144}\text{Nd})_{\text{meas}})]}{1.02392}\right) \quad (4)$$

where β corresponds to the mass bias coefficient for Nd and 1.01392 is the atomic mass ratio of the ^{146}Nd and ^{144}Nd 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 50–300 ppb. We can observe in

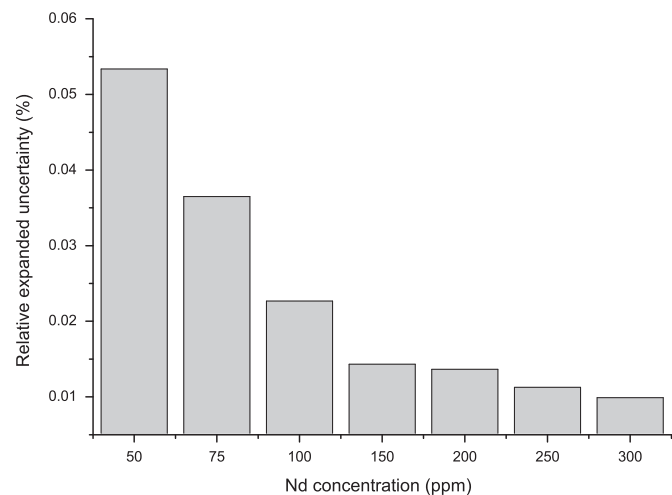


Fig. 1. Relative expanded uncertainty ($k=2$) of $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio measurement by MC-ICP-MS over the typical concentration range of Nd in the investigated samples.

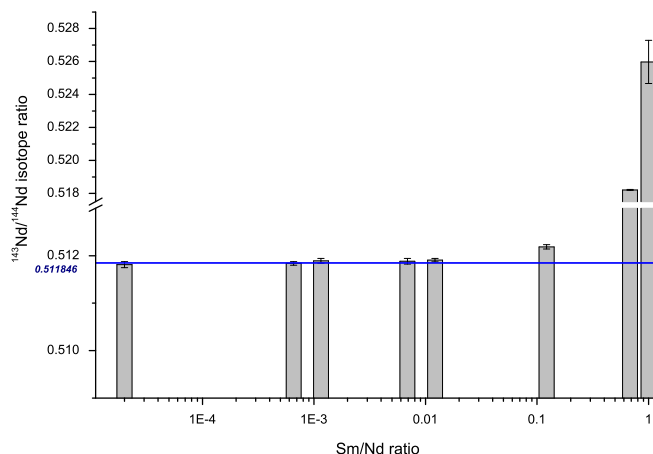


Fig. 2. Effect of increasing Sm amount on the Nd isotope ratio measurement of La Jolla Nd standard. The reference value of $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is 0.511846(3) [27].

Fig. 1 that the relative expanded uncertainty values expressed at $k=2$ level for these analyses range from 0.01% to 0.05%, which corresponds to 0.05 and 0.25 ϵ unit, respectively. As mentioned before, precise Nd isotope ratio measurement cannot be performed without eliminating the interfering Sm signal. Therefore, the effect of Sm isobaric interference was investigated by replicate analyses of La Jolla standard after adding increasing amounts of Sm to the Nd solution. It was observed that after Sm/Nd ratio became higher than 0.1, it altered the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio so significantly that even the mathematical correction could not compensate for it when comparing to the reference value (Fig. 2). Prior the Nd/Sm chemical separation, REE concentrations were measured by SF-ICP-MS (Element2, Thermo Scientific Inc., Bremen, Germany) and it showed that the investigated samples had in average Sm/Nd ratio higher than one [31]. After the Nd/Sm separation the elemental ratio was below 0.01 and therefore one could be confident that the Sm did not interfere significantly the isotope ratio measurements.

As no certified Nd isotope standard is available with uranium matrix, two basaltic rock geological reference materials were used to validate the developed method. The separation procedure described above was used for the preparation of the standards but with a modified digestion, which was necessary due to the more resistant geological matrix. Approximately 0.5 g of the powdered rocks was dissolved in 6 mL of concentrated ultrapure HNO_3 and 1 mL of concentrated HF in a Teflon beaker. The sample solutions were covered with a Teflon lid and heated on a hot plate for 15 h. Thereafter the samples were evaporated to dryness. The residue was taken up in 10 mL of 3 M HNO_3 and filtered through a 0.45 μm cellulose acetate membrane filter. The measured $^{143}\text{Nd}/^{144}\text{Nd}$ values of the BCR-2 and JB-2 standards were 0.512617(96) and 0.513098(84), which are in good agreement with the certified values 0.512629(8) and 0.513094(5), respectively [32], and [33].

Replicate analysis was done for an UOC sample to investigate the repeatability of the developed method including the sample preparation. For this purpose one of the Beverley sample (referred to as Beverley-3) was chosen and six subsamples were prepared. These were independently separated and measured resulting in an average $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio of 0.511827(39) (Fig. 3). The replicate results are in agreement with one another.

3.2. $^{143}\text{Nd}/^{144}\text{Nd}$ in uranium samples

The measured $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the uranium samples (ores and UOCs) show large variations between 0.510 and 0.515 (or ϵ_{Nd} –40 to +40). Most of the samples, however, show values in the range of ϵ_{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 ϵ_{Nd} value (Fig. 4). Certain samples belonging to specific deposit types, such as for intrusive deposits, show little variability of the ϵ_{Nd} values for the investigated samples and they also exhibit very similar Sm/Nd ratios. For sandstone type deposits the ϵ_{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 ϵ_{Nd} value.

As discussed before, the $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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 $^{143}\text{Nd}/^{144}\text{Nd}$ 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

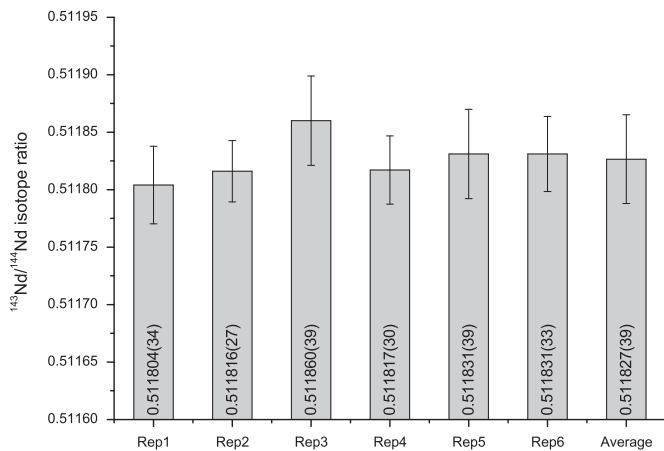


Fig. 3. Repeatability of the developed method for sample from Beverley Mine, Australia.

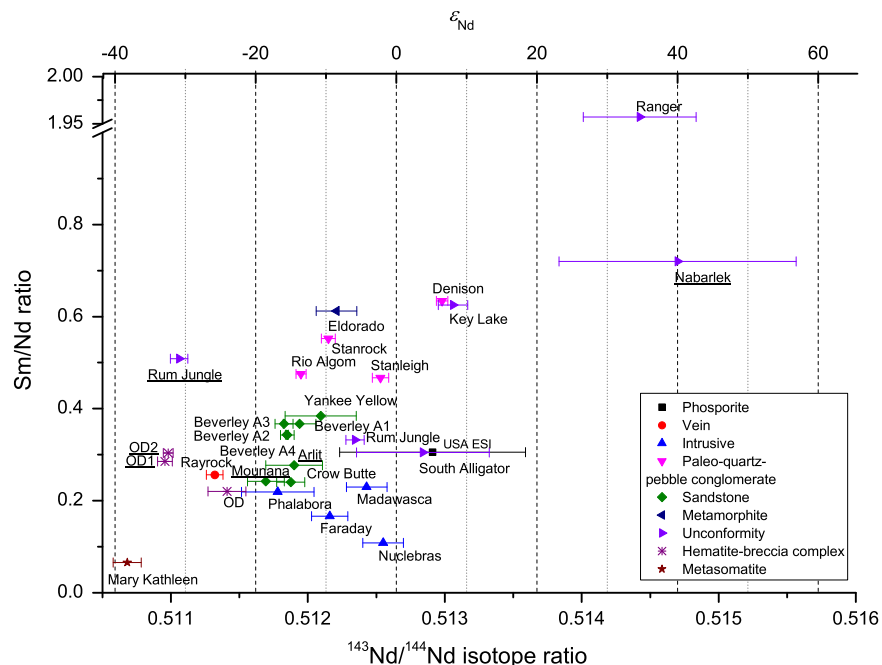


Fig. 4. Variation of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio as a function of Sm/Nd ratio in the investigated uranium ore and ore concentrate samples. OD – Olympic Dam; underlined labels correspond to ore samples.

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 isotopes, 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 $\text{ng}_{\text{Nd}}/\text{g}_{\text{sample}}$) 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 milling 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 ϵ_{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 ϵ_{Nd} values of the uranium ore concentrates, uranium ores and the deposit types.

References

- [1] K. Mayer, M. Wallenius, Z. Varga, *Chem. Rev.* 113 (2013) 884–900.
- [2] L. Pajo, K. Mayer, L. Koch, *Fresenius J. Anal. Chem.* 371 (2001) 348–352.
- [3] S.-H. Han, Z. Varga, J. Krajčó, M. Wallenius, K. Song, K. Mayer, *J. Anal. At. Spectrom.* 28 (2013) 1919–1925.
- [4] Z. Varga, M. Wallenius, K. Mayer, E. Keegan, S. Millet, *Anal. Chem.* 81 (2009) 8327–8334.
- [5] M. Srncik, K. Mayer, E. Hrnccek, M. Wallenius, Z. Varga, P. Steier, G. Wallner, *Radiochim. Acta* 99 (2011) 335–339.
- [6] S. Richter, A. Alonso, W. De Bolle, R. Wellum, P.D. Taylor, *Int. J. Mass Spectrom.* 193 (1999) 9–14.
- [7] G.A. Brennecke, L.E. Borg, I.D. Hutcheon, M.A. Sharp, A.D. Anbar, *Earth Planet. Sci. Lett.* 291 (2010) 228–233.
- [8] I. Temizel, M. Arslan, G. Ruffet, J.J. Peucat, *Lithos* 128–131 (2012) 126–147.
- [9] D.J. DePaolo, *Neodymium Isotope Geochemistry*, Springer, Berlin Heidelberg, Berlin, Heidelberg, 1988.
- [10] N. Olivier, M. Boyet, *Chem. Geol.* 230 (2006) 105–123.
- [11] D.J. DePaolo, G.J. Wasserburg, *Geophys. Res. Lett.* 3 (1976) 249–252.
- [12] M.F. Thirlwall, *Chem. Geol.* 35 (1982) 155–166.
- [13] J.S. Becker, *J. Anal. At. Spectrom.* 20 (2005) 1173–1184.
- [14] Y.-H. Yang, F.-Y. Wu, Z.-Y. Chu, L.-W. Xie, J.-H. Yang, *Spectrochim. Acta Part B: At. Spectrosc.* 79–80 (2013) 82–87.
- [15] P.J. Hooker, R.K. O’Nions, R.J. Pankhurst, *Chem. Geol.* 16 (1975) 189–196.
- [16] M.L.P. Reddy, T. Prasada Rao, A.D. Damodaran, *Miner. Process. Extr. Metall. Rev.* 12 (1993) 91–113.
- [17] E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond, D.M. Nelson, *Anal. Chim. Acta* 281 (1993) 361–372.
- [18] C. Pin, J. Zalduogui, *Anal. Chim. Acta* 339 (1997) 79–89.
- [19] R. Maas, M. McCulloch, *Chem. Geol.*, 88, 1990301–315.
- [20] R. Maas, M.T. McCulloch, I.H. Campbell, R.W. Page, *Econ. Geol.* 82 (1987) 1805–1826.
- [21] S. Jung, K. Mezger, S. Hoernes, *Precambrian Res.* 110 (2001) 325–355.
- [22] C. Carl, E. Pechmann, *Can. J. Earth Sci.* 29 (1992) 879–895.
- [23] Y. Jiang, H. Ling, S. Jiang, W. Shen, H. Fan, P. Ni, *Econ. Geol.* 101 (2006) 1613–1622.
- [24] R. Maas, M.T. McCulloch, I.H. Campbell, P.R. Goad, *Geology* 14 (1986) 585–588.
- [25] S.A. Wilson, The collection, preparation, and testing of USGS reference material BCR-2. Geological Survey Open-File Report 98, Columbia River, Basalt, U.S.
- [26] A. Ando, *Geochem. J.* 18 (1984) 215–216.
- [27] J. Nie, et al., *Earth-Sci. Rev.* 110 (2012) 111–126.
- [28] V. Badaut, M. Wallenius, K. Mayer, *J. Radioanal. Nucl. Chem.* 280 (2009) 57–61.
- [29] J.K. Böhlke, et al., *J. Phys. Chem. Ref. Data* 34 (2005) 57–67.
- [30] W.A. Russell, D.A. Papanastassiou, T.A. Tombrello, *Geochim. Cosmochim. Acta* 42 (1978) 1075–1090.
- [31] Z. Varga, M. Wallenius, K. Mayer, *Radiochim. Acta* 98 (2010) 771–778.
- [32] I. Raczek, K.P. Jochum, A.W. Hofmann, *Geostand. Geoanal. Res.* 27 (2003) 173–179.
- [33] B.M. Dreyer, J.D. Morris, J.B. Gill, *J. Petrol.* 51 (2010) 1761–1782.
- [34] J. Mercadier, et al., *Terra Nova* 23 (2011) 264–269.
- [35] R. Maas, *Econ. Geol.* 84 (1989) 64–90.