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ISOTOPIC SIGNATURES FOR ORIGIN ASSESSMENT OF NATURAL URANIUM SAMPLES

ISOTOPIC SIGNATURES FOR ORIGIN ASSESSMENT OF NATURAL URANIUM SAMPLES

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K. C. A. M. Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op maandag 13 juni 2016 om 10.00 uur.

door

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The doctoral research has been carried out within a cooperation of the Institute for Transuranium Elements (ITU) of the Joint Research Centre (JRC) of the European Commission and the Department of Radiation Science and Technology, Faculty of Applied Sciences, Delft University of Technology, The Netherlands.

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I dedicate this thesis:

To the loving memory of my mother.
Te voglio bene assai.

To Dani for his constant, unconditional love, patience and support.
Ma tanto ma tanto bene sai.

CONTENTS

1

INTRODUCTION

"Nuclear Security aims at the prevention and detection of and response to, theft, sabotage, unauthorized access, illegal transfer or other malicious acts involving nuclear material. Nuclear Forensics is a key element of nuclear security."

dr. Klaus Mayer

1.1. MOTIVATION FOR THIS WORK

THE need for a comprehensive science which could perform the analysis of intercepted illicit nuclear or other radioactive material and any associated material to provide evidence for nuclear attribution was first raised at the beginning of 1990s [1]. The first seizure (analysed at ITU) involving a number of low enriched uranium fuel pellets took place in Augsburg, Germany [2]. This first incident was followed by several others, whereas most of the involved material was seized in central and eastern european countries. However, materials were in most cases related to the former Soviet republics. In 1994, 560 g of weapons-usable Pu (87% ^{239}Pu) mixed with low enriched uranium was seized at Munich Airport together with 210 g Li-metal [3]. In Lithuania, uranium-oxide pellets were seized and found to be most probably a part of a stolen fresh fuel assembly from Ignalina Nuclear Power Plant. Between 1994-1995 seizures of highly enriched uranium powders were reported in the Czech Republic [4]. Afterwards incidents involving uranium and plutonium bearing material continued, but on a smaller scale [5]. These nuclear security related incidents are often connected to the end of the cold war and the fall of the former Soviet Union, leaving behind significant nuclear manufacturing and research facilities in the successor countries without adequate safeguards and security measures [6].

In response to the incidents, nuclear forensic science has progressed significantly in the past 20 years and applied analytical and interpretation methods have been developed. Over these years it was found that seized samples are always unique in terms of the circumstances of the incidents, the nature of the material and the objectives of the investigation [5].

1.2. LITERATURE REVIEW

1.2.1. NUCLEAR FORENSIC

The **aim** for nuclear forensic scientists is to identify indicators which represent relationships between measurable parameters of the material and its production history, origin and age. The **goals** of nuclear forensic investigations are therefore, (a) to identify those responsible for nuclear theft and the source (origin) of the sample; (b) to enhance protection, control, and accounting for nuclear materials; (c) to prevent and deter additional thefts or other unauthorised acts [6, 7]. The above mentioned nuclear forensic indicators, so-called **signatures**, can be various properties of the material in question, such as structure, morphology, major and minor elements, isotopes and impurities (Table 1.1).

Among these properties there are only a few predictive parameters, which would give straightforward information about an unknown sample without the need for a comparison sample or reference data. For example, the enrichment and concentration of uranium of an investigated sample could lead us easily to the intended use of the sample or to the stage of the nuclear fuel-cycle from which the sample originates. Furthermore, production date (age of the nuclear material), defined as the time elapsed since the last chemical processing of the material, belongs to self-explanatory data. However, the majority of the nuclear signatures belong to the so-called non-exclusive, comparative parameters. This means that the analytical results have to be compared with those of measured known material or reference data in databases in order to draw conclusions about the possible origin of the sample. For example, pellet dimensions and surface roughness can provide us with information about the reactor type and production plan, respectively. Furthermore, determination of age and intended use also support indirectly the origin determination. Knowing the date of the material production enables us to exclude those facilities which were not in production at that certain time. Also the intended use (e.g.: uranium enrichment) can narrow down the group of the facilities where the material could have been produced.

The assessment of the provenance of the seized material is a key point in nuclear forensic investigations. Signatures providing a hint of the origin of the material could be either material or process inherited. Rare-earth elements (REEs) occur with uranium mineralisation and their patterns (i.e. relative concentration of REE compared to each other) remain mainly unaltered during U production processes due to their similar chemical behaviour as U. Therefore at any step during the process, analysis of a sample, should reflect the characteristics of the geological environment the sample originates from [8–10]. To a lesser extent the Sr and Pb isotopic composition was also found to be a promising geological indicator [11], however, lead was found to be more prone to the chemical process applied during the course of uranium ore concentrate (UOC) production.

Table 1.1: Summary of nuclear forensic signatures developed during the last 20 years [7, 12–17]

Group of parameter	**Signature**		**Technique(s) used to determine analyte(s)**	**Information derived from analysis**	**Predictive / Comparative**
Physical appearance (Morphology)	Appearance		Optical microscopy	Material type (powder/pellet)	Comparative
	Dimension (pellet)		Comparison to data base	Reactor type	Comparative
	Surface Roughness		Profilometry, comparison to data base	Production Plant	Comparative
	Microstructure		SEM, TEM	Production Process	Comparative
Elemental content	Major elements	U, Pu	Titration, Hybrid K-Edge Densitometry, Isotope Dilution Mass Spectrometry	Chemical Concentration, nuclear fuel type,	Predictive / Comparative
	Impurities	Anionic (F^-, Cl^-, Br^-, $NO_3{}^-$, $SO_4{}^{2-}$, $PO_4{}^{3-}$)	FTIR combined with multivariate statistical analysis methods, IC	Composition of major and minor phases, identification of the type of uranium compound, production method of the material	Predictive (F^-) / Comparative
		Metallic (eg.: REE)	ICP-MS	Possible identification of the type of uranium deposit	Comparative
		Organic (Alamine® 336, decanol)	GC-MS	Possible indication of processing history based	Predictive / Comparative
Isotope ratios (IR)	Major Isotopic Composition	^{238}U, ^{235}U	Gamma Spectrometry, TIMS, ICP-MS, SIMS	Enrichment–intended use/reactor type, nuclear fuel type, weapon type, and device type	Predictive / Comparative
	Minor isotope ratio	$^{235}U/^{234}U$, $^{234}U/^{238}U$, $^{236}U/^{238}U$	MC-ICP-MS, TIMS, AMS	Possible identification of type of uranium deposit & type of depositional settings	Comparative

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Table 1.1: Summary of nuclear forensic signatures developed during the last 20 years [7, 12–14] (*continued*)

Group of parameter	**Signature**		**Technique(s) used to determine analyte(s)**	**Information derived from analysis**	**Predictive / Comparative**
Isotope ratios (IR)	Trace elements	$^{87}Sr/^{86}Sr$, $^{207}Pb/^{206}Pb$	MC-ICP-MS	Possible identification of origin of mine and the ore type	Predictive (Pb age) / Comparative
	Stable isotope	$^{18}O/^{16}O$	TIMS	Possible indication of processing history of UOC & location of the facility	Comparative
	Age	$^{230}Th/^{234}U$, $^{228}Th/^{232}Th$, $^{231}Pa/^{235}U$	Alpha spectrometry, TIMS, ICP-MS	Production Date	Predictive

Anionic impurities and isotopic abundance of oxygen are examples of primarily process - related signatures [11, 18, 19]. However, as no single signature provides a “silver bullet”, the development and validation of new signatures is still one of the most important tasks of nuclear forensics.

In 1995 IAEA established the Incident and Trafficking Database (ITDB) which serves as an information exchange system between 131 member states and several international organisations. The database differentiates the incidents in three big groups, (I) Illegal possession and related criminal activities (unauthorised possession, transaction, movement or use), (II) Thefts and Losses, and (III) Other unauthorised activities (e.g. discovery of orphan sources). Out of the approximately 2700 incidents confirmed by the member states between 1995 and 2014, 16% involved incidents from Group I and 26% and 56% from Group II and III, respectively [20]. Another noteworthy aspect of the data concerns the incidents involving nuclear material. According to the ITDB 68% of the incidents involve natural (e.g. uranium ore concentrates) and depleted uranium. Based on the ITDB, one can conclude that 90% of the involved nuclear material originates from the front end of the fuel cycle, while only 10% is coming from the processes of the back end of the fuel cycle. Therefore the majority of nuclear forensic signature development is currently focusing on natural uranium products. To have a better understanding of the term “natural uranium”, a brief introduction to the front end of the fuel cycle will be given.

1.2.2. NUCLEAR FUEL CYCLE

First of all, the definition of **"front-end"** involves the preparation of uranium for the use in a nuclear reactor. It includes the steps of mining and milling, conversion, enrichment and fuel fabrication (Fig. 1.1). Uranium occurs in different geological environments and these deposits have been grouped into 15 major categories by the IAEA [21], whose classification has also been used in this research (Table 1.2). The major primary ore mineral is uraninite (basically UO_2) or pitchblende (U_2O_5, UO_3 better known as U_3O_8) though a range of other uranium minerals can be found in particular deposits. These include carnotite (uranium potassium vanadate), the uranium titanates (davidite -brannerite - abesite), and niobates of uranium and rare earths. The concentration of uranium in the ore can range up to 20%.

Open pit and underground mining are the conventional methods for the extraction of uranium ore from the deposit [22, 23]. As a result of recent developments, alternative methods are gaining ground such as in-situ leaching (ISL) and heap leaching [24]. By traditional mining uranium ore is crushed, grinded and mixed with water to produce a wet slurry. In the case of ISL, chemical solutions are injected into underground deposits to dissolve uranium from the ore body through wells and bores. Dissolved uranium is then brought to the surface for purification. Heap leaching is a combination of these two methods, first uranium ore is mined with conventional mining, however grinded ore is then heaped on an impermeable plastic and/or clay lined leach pad where it can be irrigated with a leach solution to dissolve uranium on site.

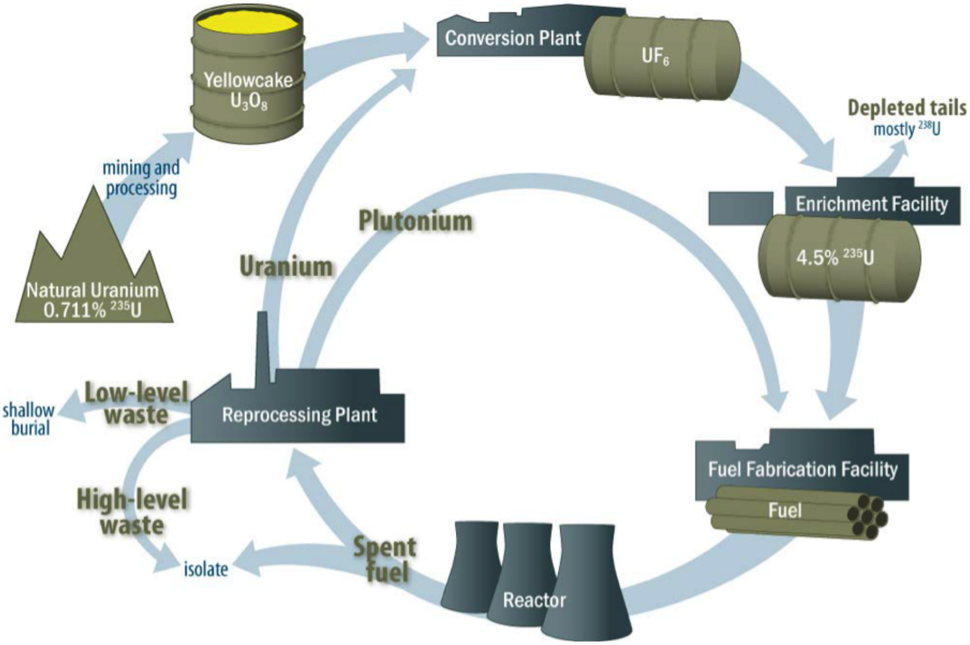

Figure 1.1: Simple flow sheet of the nuclear fuel cycle. *Source:* Congressional Research Service (2011) [25]

The mined ore or dissolved uranium slurry is transported to the uranium mills, normally built on the mine site or its vicinity. The crushed ore is further grinded according to the process needs. In the treatment of some ores (e.g.: with higher vanadium content) roasting may be necessary, to increase solubility and improve their physical characteristics for the subsequent leaching process. The applied milling process depends also on the type of deposit and mine, whether it originates from a mine specifically for uranium (e.g.: unconformity type deposit – McArthur River, Canada), or as a by-product from mines with a different main product such as copper, phosphate or gold (e.g. polymetallic-iron-breccia type deposit – Olympic Dam, Australia).

Chemical extraction of uranium is performed by alkaline or acidic leaching depending on the gangue constituents, especially on the amount of acid consuming carbonate minerals (e.g. limestone). Sulphuric acid and sodium carbonate are the commonly applied chemicals for the leaching. In general the leaching is followed by the separation of dissolved uranium from tailings. Uranium is purified and further concentrated by the application of ion exchange (IX) and/or solvent exchange (SX) circuits. Finally uranium is precipitated from the solution. In alkaline processing, carbonate-bicarbonate solutions are used to form sodium uranate (SDU), while in acid processing hydrogen peroxide, magnesia, ammonia or ammonium hydroxide can be used to precipitate uranium in various forms e.g.: ammonium-di-uranate (ADU), uranium-peroxide. At this stage uranium concentration is raised to more than 65 %, depending on the chemical form of the UOC [26]. UOC is also referred as 'yellow cake', due to its yellow colour (ADU), however it may vary in colour from yellow, orange to almost black depending on its exact chemical composition.

UOC is then transferred to the **conversion** plants. In general, conversion is a process in which the uranium is converted to a form suitable either for fuel fabrication or enrichment. For those power plants that do not require enriched uranium, the yellow cake is converted to uranium dioxide (UO_2). However, the majority of the power plants require enriched uranium. The yellow cake is converted into gaseous uranium hexafluoride (UF_6) by Tributyl Phosphate Purification or by Fluoride Volatility Process, also referred as wet and dry conversion process, respectively [27, 28].

Uranium ore samples investigated in this research are obtained from the collection of TU Bergakademie, Freiberg, Germany. Analysed uranium ore concentrates are part of the Springfield historic UOC samples collected by Springfield uranium processing facility, UK. Sample sets representing subsequent process steps through the course of uranium production (e.g.: Olympic Dam, Ranger, Nufcor) were provided by the IAEA.

Table 1.2: General description of uranium deposit types suggested by the IAEA and assigned on the basis of their geological setting (arranged according to their approximate economic significance) [14, 21]

	Deposit type	**Subtype**	**Ore Grade** (%U)	**Deposition temperature** (°C)	**Age** (Ma)	**Examples**
1	Unconformity related	Fracture controlled; Clay bounded	0.3 - 20	200-300	1500-1900	McArthur River (CAN); Ranger (AUS) Cigar Lake (CAN)
2	Sandstone	Roll front; Tabular; Basal Channel; Tectonic	0.05 - 0.5	25-100	540-66	Crow Butte (USA) Arlit (Niger), Colorado Plateau (USA) Beverley (AUS) Mikouloungou (Gabon)
3	Hematite breccia complex		0.02 - 0.05	200-500	1000-2500	Olympic Dam (AUS)
4	Quartz - pebble conglomerate	Monometallic;	0.05-0.12	50-300	2200-2700	Blind River/Elliot Lake (CAN)
		Polymetallic	0.01-0.03 (up to 0.15)			Witwatersrand district (S. Africa)
5	Vein (granit related)	Intragranitic; Perigranitic	0.01 - 2.0	200-500	2500-225	Massif Central (France) Shinkolobwe (Democratic Rep. of the Congo)
6	Intrusive	Alaskite; Pegmatite;	0.01 - 0.05	300-700	not related to age	Rössing, Trekkopje (Namibia); Campbell Island Mine (CAN)
		Peralkaline-syenite; Granite-monzonite; Carbonatite	0.01 (only as by-product)			Kvanjafeld (Greenland); Twin Buttes, Bingham Canyon (USA); Palabora (S. Africa),
7	Volcanic & Caldera related		0.03 - 0.3	200-500	not related to age	Xiangshan (China), McDermitt (USA)

continued on next page

Table 1.2: General description of uranium deposit types suggested by the IAEA and assigned on the basis of their geological setting (arranged according to their approximate economic significance) [14, 21] (*continued*)

	Deposit type	**Subtype**	**Ore Grade** (%U)	**Deposition temperature** (°C)	**Age** (Ma)	**Examples**
8	Metasomatite	Sodium (Albitites); Potassium (Elkonites)	0.05 - 0.2	300-700	2500-542	Lagoa Real (Brasil), Valhalla (AUS); Elkon Horst (Russian Federation)
9	Surficial		0.02 - 0.13	20-50	66 to recent	Yeelirrie (AUS), Langer Heinrich (Namibia)
10	Collapse breccia pipe		0.4-0.8	80-170	200-260	only in USA (e.g.: Orphan Lodge) and Peru (Turmalina)
11	Phosphorite	Bedded;	0.0025 - 0.03	20-50	541 - recent	Phosphoria Formation (USA);
		Nobular;	0.002-0.008			Land Pebble District (USA);
		Continental	0.18-0.24			Bakouma (Central African Rep.)
12	Other	Metamorphic	0.11	n.a.	1780-1100	Mary Kathleen (AUS)
		Limestone			Jurassic	Todilto, Grant district (USA)
		Uraniferous coal	0.002 -0.01		150-155	Serres Basin (Greece), Koldjat (Kazahstan)
13	Rock types with elevate U content	Black shale	0.02-0.03	2-20	n.a.	Ranstadt (Sweden), Chatanooga Shale (USA)
		Rare metal pegmatite	0.0006 - 0.002			Greenbushes and Wodgina pegmatite (AUS)

1.3. AIM OF THE WORK

The present work was intended to evaluate the usefulness of isotopic variations in selected light element (such as S) and Rare Earth Elements (REEs) to identify the origin of nuclear materials.

Abundance of Nd and S isotopes and their variation have been measured in natural uranium and its products. Nd is part of the group of REEs, whereas REEs have been widely studied in geochemistry and nuclear forensics as well. Its relative elemental pattern was found to be an extremely good indicator to the geological formation (deposit type). It was an obvious assumption that Nd isotope composition should have the same potential as a nuclear forensic fingerprint. On the other hand sulphur is assumed to be characteristic to the process as it is used in large amounts and different chemical forms during the course of uranium ore production. Both Nd and S seemed to be promising candidates as nuclear forensic signatures.

The ultimate goal of this research was the investigations of new possible nuclear forensic signatures and the evaluation of their usefulness to identify the origin of nuclear materials. In order to achieve this aim, several challenging tasks related to sample preparation, preconcentration and purification of elements of interest as well as accurate and precise measurement of the isotope ratios using mass spectrometric techniques, had to be solved.

1.4. OUTLINE OF THE THESIS

This section presents an outline of the thesis. All of the scientific challenges, explained in the previous paragraph, will be explained and solutions will be presented in the following chapters.

In **chapter 2**, a preconcentration method has been developed for the measurement of ultra-trace levels of REE in a high purity uranium matrix. The chondrite normalised pattern of REEs is one of the most straightforward signatures to trace back provenance of the material, as the relative concentrations remain mainly unaltered during the UOC production. As the typical concentration of REE is between 5 to 50 $\mathrm{ng\,g^{-1}}$ in high purity uranium samples, the standard methodologies are often not sensitive enough for the REE pattern measurement. Thus, an advanced chemical separation method is needed. Beside the method development, behaviour of REEs in U samples coming from the later stages of the refining process (e.g. UO_3 and UO_2) has been also studied.

In **chapter 3**, evaluation of the usefulness and applicability of variations of ^{143}Nd/^{144}Nd isotope ratio for provenance assessment in nuclear forensics has been performed. To achieve that, firstly an improved procedure has been developed for the determination of ^{143}Nd/^{144}Nd isotope ratio in various uranium-bearing materials, such as uranium ores and ore concentrates (UOC). Secondly, uranium ore samples originating from four different mines and uranium ore concentrates originating from 20 different mills has been measured and correlation with their origin has been investigated. Beside variations between different mines and mills, within mine variation has been also investigated by the measurement of multiple samples originating from one facility, but different production batches.

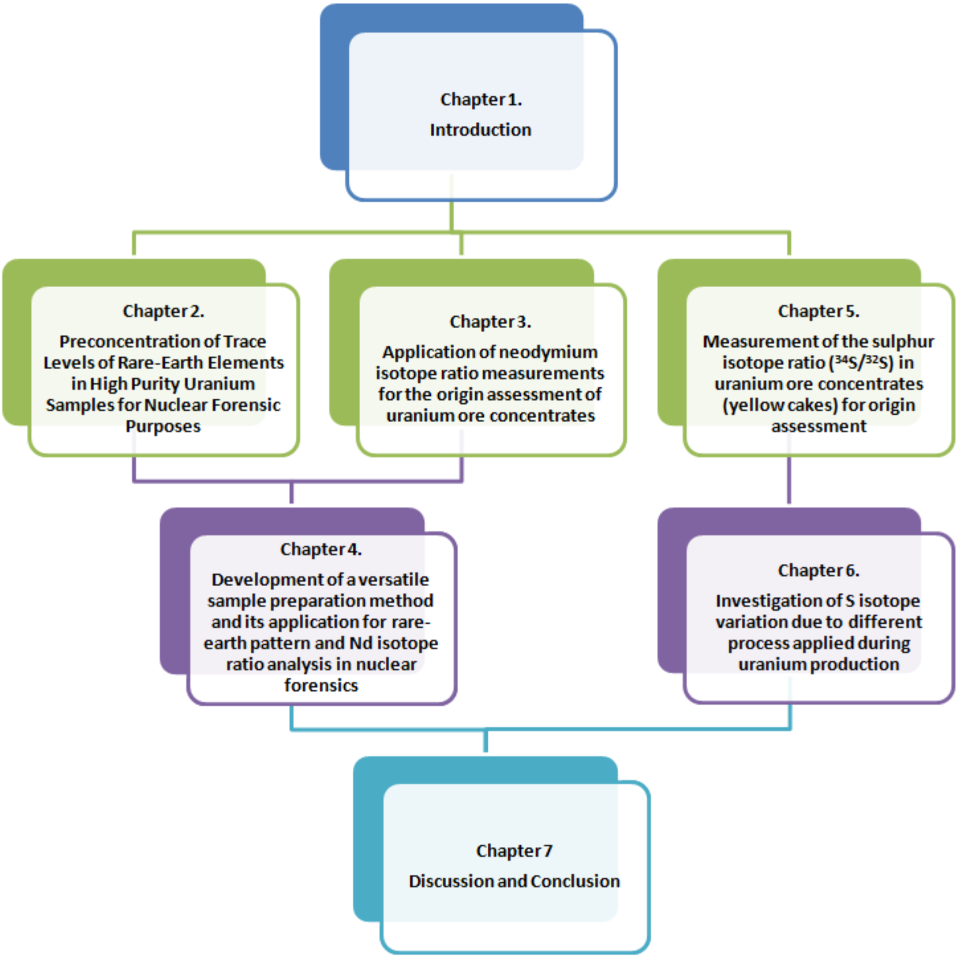

Figure 1.2: Schematic flowchart of the thesis

In **chapter 4**, further development of the separation methods described in chapter 2 and 3. The aim of the work was to enhance effectiveness of the chemical separation by a combination of pre-concentration and Nd separation. Furthermore, achieving lower limits of detection and sufficiently low uncertainty, to distinguish between samples were also the primary purpose of this study.

In **chapter 5**, evaluation of the usefulness and applicability of variations of the $^{34}S/^{32}S$ isotope ratio for provenance assessment in nuclear forensics has been performed. Similarly to Chapter 3, firstly a novel procedure has been developed for the chemical separation and measurement of the $^{34}S/^{32}S$ isotope ratio in uranium ore concentrates (UOC). Secondly, S isotope variations have been measured in uranium ore concentrates originating from 18 different mines. Correlation between the $^{34}S/^{32}S$ isotope and the geological origin, as well as process history has been evaluated.

In **chapter 6**, an extended study has been performed on the applicability and limitations of the sulphur isotope ratio as a nuclear forensic signature for origin assessment. The topic has been investigated from two aspects. (1) The effect of industrial leaching methods on the $^{34}S/^{32}S$ has been measured in order to investigate the dominant source of sulphur in the investigated samples. (2) The sulphur isotope ratio variation during UOC production, from ore to uranium ore concentrate product, has also been followed through two real sample sets in order to clarify whether the isotope ratio is indicative of the process or of the geological origin of the material.

Finally, **chapter 7** provides a conclusion and highlights the results of the thesis. It is intended to help understanding of where the new signatures fit into the nuclear forensic toolset, particularly into the previously investigated isotopic signatures. It also includes recommendations for future research.

As most of the following chapters are based on published or submitted papers, some of the information is repeated throughout the thesis. This enables easier reading of the chapters separately.

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2

PRE-CONCENTRATION OF TRACE LEVELS OF RARE-EARTH ELEMENTS IN HIGH PURITY URANIUM SAMPLES FOR NUCLEAR FORENSIC PURPOSES

Judit KRAJKO, Zsolt VARGA, Maria WALLENIUS, and Klaus MAYER

This paper describes the application of a method developed for the pre-concentration and analysis of trace-level amounts of rare-earth elements (REE) in high purity uranium (U) samples. The method comprises pre-concentration and subsequent group separation of REEs from the uranium matrix followed by their determination using inductively coupled plasma mass spectrometry. The achieved detection limit of the method (in the low pg/g range) with the high chemical recovery (around 90%) enabled the investigation of REE pattern in high purity refined uranium oxides. Applying this method one could follow the REE pattern along the front-end of the nuclear fuel cycle.

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2.1. INTRODUCTION

SINCE the early 1990´s 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, several analytical methods involving radioanalytical techniques, mass spectrometry and electron microscopy have been applied for nuclear forensics purposes, entailing complete characterization of the unknown nuclear materials. These methods can be grouped according to the measured characteristic parameters e.g., isotope abundances of the main elements, chemical composition, impurities and microstructure [2, 3].

Among these characteristic parameters the impurity content of natural uranium materials has been found to be indicative of its origin. However, when discussing the provenance of a material, one has to be aware that those signatures may be material inherited (i.e. due to geological environment, deposit) and process inherited (i.e. due to manufacturing process). As the concentration of chemical impurities will change due to the refining process it turned out to be advantageous in some cases to use the isotopic composition of these elements as nuclear forensic signatures, as previous studies have shown (e.g.: O, Pb, S) [4–6].

With regard to the rare-earth elements (REE), we note that their concentration (relative to uranium) will change during ore processing. However, the REE pattern (i.e. their relative concentration compared to each other) and isotopic composition of rare-earth elements are assumed to remain unaltered during uranium production processes due to their similar chemical behaviour with uranium. Therefore their relative amounts (i.e. REE pattern) and isotopic composition at any step during the process are expected to reflect the characteristics of the geological environment the sample originates from [7, 8]. In consequence, the REE are considered as one of the most useful nuclear forensic signature for origin assessment of natural uranium.

The REE concentration and chondrite normalised pattern has been studied extensively in uranium ores and uranium ore concentrate samples by several research groups [9–13], but experimental results cannot be found for uranium samples coming from the later stages of the refining process (e.g. UO_3 and UO_2) to support the earlier assumption.

The lack of experimental data can possibly be explained by the very low concentration level of the REEs in uranium product materials. Moreover, due to their very low concentration they may be more prone to influence of impurites present in the reagents or additives used in the industrial processes as well as possible mixing of uranium oxides of different origins at the conversion or at the pellet manufacturing step [14–16]. Additionally, for industrial application of uranium in several nuclear power plants, a part of the pellets present in the reactor are enriched with Gd, (sometimes Er) to adjust the initial reactivity and the power. In other cases REE are present in concentrations below a given maximum value, usually defined as Equivalent Boron Content (EBC) $< 4.0\ \mu g\,g^{-1}$ (B, Gd, Eu, Dy, Sm, Cd) [17]. Therefore it is very important to understand the propagation and robustness of REEs throughout the process. This work is an attempt to partially make up for this gap.

The most frequently applied techniques, such as mass spectrometry (e.g.: SIMS, ICP-MS), emission spectrometry (AES, OES), nuclear methods (e.g: NAA) to determine REE concentration from various sample matrices were reviewed by Zawisza et al. [18] and Verma et al. [19]. They found that mass spectrometric (MS) techniques provide the most precise REE data from geological samples compared to other techniques. Particularly REEs measurements from uranium matrices are usually performed by inductively coupled plasma mass spectrometry (ICP-MS). This technique produces analysis with the lowest achievable detection limit, however to perform a sensitive and precise measurement of the REE, it is important to remove the matrix, and eliminate molecular and direct isobaric interferences on the mass of the analytes of interest [20]. To reduce the interferences without chemical treatment of the sample, the use of a special sample introduction system (e.g. desolvation nebuliser), cones with different orifices or other instrumental modification, such as reaction cell have been applied [21, 22]. Mathematical correction (i.e. peak deconvolution) of the measurement data is also a possible way of elimination of some isobaric interference, thus improving accuracy [23].

Chemical separation of REEs from the matrix is another option to avoid spectral interferences and matrix-induced signal suppression in the first place as well as to preconcentrate the minute amount of REE in U-oxide samples. Most frequently precipitation (i.e. co-precipitation with carriers), solvent extraction, ion exchange or extraction chromatographic methods (EXC) are used to separate the REEs from other elements, i.e. the matrix [18, 24]. Among these methods co-precipitation was found to be the most appropriate method for our purpose. It is suitable to pre-concentrate trace and ultra trace levels of REEs from relatively large size of various samples matrices, such as sea water [25, 26], and geological samples [27, 28]. Co-precipitation was found to be suitable also to preconcentrate trace levels of REE from uranium matrices ($\sim 700\,\mathrm{mg}$) by Premadas and Strivastava [12]. They used a combination of oxalate precipitation with solvent extraction to preconcentrate REE in the filtrate from various uranium hydrometallurgical products. The achieved decontamination factor (DF) of uranium, however, was only around 10^2, which means that the uranium concentration after separation was still in mg level. They enhanced the separation factor by the application of an additional solvent extraction step, however they introduced to the procedure organic reagents. This shows that coupling co-precipitation with an additional separation step (e.g.: ion exchange, solvent extraction, extraction chromatography) is advantageous, not just in reducing interfering matrix elements but also to further pre-concentrate the analytes of interest.

Thus, the aim of this study was to develop a chemical separation method involving co-precipitation and extraction chromatography (EXC) for ultra-trace levels of REE in high purity uranium matrix. This was followed by ICP-MS analysis for the determination of REE concentrations to establish REE patterns.

2.2. EXPERIMENTAL

2.2.1. REAGENTS

THE Suprapur grade nitric acid (HNO_3) and hydrochloric acid (HCl) was purchased from Merck (Darmstadt, Germany). For the co-precipitation trace analysis grade 99.9995% (metal basis) sodium-hydroxide monohydrate (Fluka, Sigma Aldrich), and analytical grade (AG) ammonium-carbonate ($(NH_4)_2CO_3$) were used (Sigma Aldrich, St Louis, MO, USA). Fe(III)-nitrate salt (AG) was used as carrier (Alfa Aesar, Karlsruhe, Germany). Analytical grade linear non-ionic polyelectrolyte, Polyacrylamid (PAA) was purchased from Sigma-Aldrich (St Louis, MO, USA). Spiking solution used for the optimisation of the chemical separation procedure as well as the standard solutions used for the external calibration of the ICP-MS were prepared from a $100\,\mu g\,mL^{-1}$ lanthanide standard solution (Alfa Aesar, Karlsruhe, Germany) by step-wise gravimetric dilution. $1000\,\mu g\,mL^{-1}$ Rh standard solution (Alfa Aesar, Karlsruhe, Germany) was used as internal standard for mass spectrometric measurements. For dilutions ultra-pure water ($18.2\,m\Omega\,cm^{-1}$) was used (UHQ System, USF Elga, Germany).

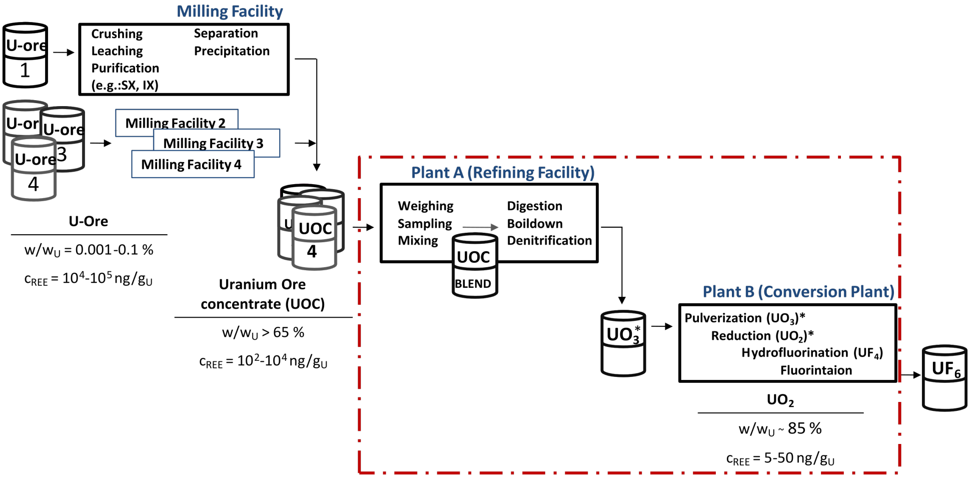

Figure 2.1: General overview of the uranium refining process and the uranium and REE concentration of the different uranium forms/products. $*$ denotes the samples have been investigated in this study.

For the purification of $(NH_4)_2CO_3$ solution surfactant-free cellulose acetate filters have been purchased from Nalgene^{TM} (Thermo Scientific, Australia). For purification of Fe carrier and the lanthanide group separation, the TRU^{TM} extraction chromatographic resin (100–150 µm particle size, active component: octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide dissolved in tri-n-butyl phosphate) was purchased from Triskem (Triskem International, Bruz, France). Resin was placed in plastic Bio-Rad holders (column diameter 8 mm) and plugged with porous Teflon frit (Reichelt Chemietechnik Heidelberg, Germany) on the top of the resin to avoid mixing.

As low blanks are of critical importance for ultra trace level REE analyses, all labware were thoroughly cleaned before use. First labware was leached in dilute ethanol then in dilute nitric acid, and finally rinsed with high purity water (UHQ System, USF Elga, Germany) and dried in laminar flow cupboard. For all the dilutions high-purity water was used.

2.2.2. SAMPLES AND STANDARDS

The UO_3 and UO_2 samples investigated in this study originate from a uranium refinery and a conversion plant (referred to as Plant A and Plant B, respectively). The samples represent one batch of material through the process shown in Fig. 2.1. U_3O_8 certified reference material (CRM), Morille (Cetama, France) was used for the validation of the method. This CRM is certified for selected impurities including four REEs (Dy, Gd, Eu and Sm).

2.3. SAMPLE PREPARATION

2.3.1. REAGENTS CLEANING PROCEDURE

Low background values (clean method blanks) are of vital importance to perform reliable measurements at sub-ppb levels. Therefore, suprapur grade nitric acid was further purified by subboiling distillation. Preliminary studies were performed using trace analysis grade sodium-hydroxide (NaOH) and Puratronic (99.999% metal basis) ammonium-carbonate $(NH_4)_2CO_3$ (Sigma Aldrich, St Louis, MO, USA). Results showed that using commercial high purity reagents does not always bring the expected benefits, as limits of detection (LOD) for REE (especially for Eu, Gd) were significantly limited by the method blank. HR-ICP-MS measurements were performed in order to clarify to what degree interfering elements (e.g., Ba as BaO) contribute to the count rates. To determine the yield of these oxide ions, multi-element solutions containing Ba and Eu in different concentrations were prepared. These solutions went through the preconcentration method and the final solutions obtained were then measured on the ICP-MS using high resolution mode. Results showed that Ba had effectively been removed by the chemical separation; therefore REE contamination should come from the reagents used. Impurity analysis of the reagents proved that the chosen trace analysis grade $(NH_4)_2CO_3$ and Fe carrier contained elevated amounts of REE compared to analytical grade ones. A similar phenomenon had also been reported by Shannon and Wood during the preparation of ferric iron reagent for the preconcentration of REE by ferric hydroxide co-precipitation [29, 30]. In order to achieve sufficient purity, an additional separation step was applied for $(NH_4)_2CO_3$ and Fe carrier as described hereafter.

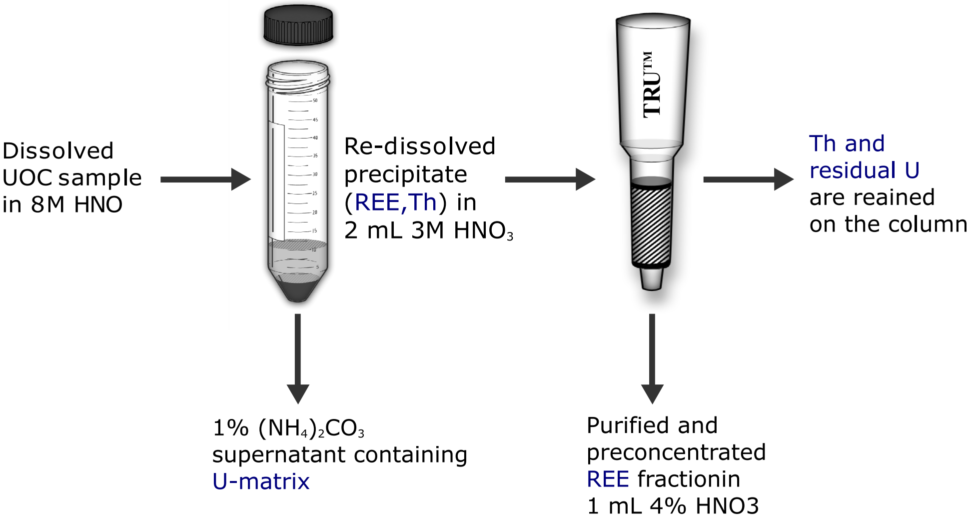

Figure 2.2: Schematic overview of the pre-concentration procedure consisting of a co-precipitation and an extraction chromatographic separation step.

Analytical grade ammonium carbonate was used to prepare a 10 wt% solution and it was mixed with 5 mg Fe in the form of dissolved iron-nitrate. After an equilibration period of three days, the solution was centrifuged and filtered through a 0.2 µm surfactant free cellulose acetate (SFCA) filter. After that the stock solution was diluted to the final 1% concentration and a second filtration using the same 0.2 µm SFCA filter was performed.

10 mg Fe(III)-nitrate was dissolved in 20 mL of 2 M HNO_3 and loaded on a column filled with 1.6 mL TRU resin. In 2 M HNO_3 media the REEs have high retention on the resin, while the iron is less retained. The effluent was collected in a Teflon beakers and evaporated to dryness. After adding 200 µL cc sub-boiled HNO_3, the solution was evaporated to dryness again. Finally, the residue containing the purified Fe was collected in 1 mL 4% HNO_3.

2.3.2. CO-PRECIPITATION

Approximately 0.5 g of uranium oxide samples (m_{sample}) were weighed into a Teflon Erlenmeyer and dissolved in 9 mL 8 M ultra-pure HNO_3 while heating to 90 °C on a hotplate for six hours covered with a PE stopper. After cooling down to room temperature, the weights of the solutions were taken (m_{stock}).

Around 3.0 mL of the stock solutions were weighed gravimetrically into a 50 mL polyethylene centrifuge vials (m_{load}) corresponding to about 200 mg of uranium. REEs, Th and U were precipitated as hydroxides (pH > 12) with 40% NaOH in the presence of 2 mg Fe(III) carrier and 0.5 mg linear PAA.

The supernatant, containing most of the matrix elements, was carefully separated and discarded after centrifugation. Subsequently the precipitate was rinsed twice with ultra-pure water. U was then re-dissolved in 2 mL 1% $(NH_4)_2CO_3$ and this step was repeated until a clear solution was obtained to make sure that most of the U was removed from the REEs.

The residue containing the REEs and Th was dissolved in 2 mL 3 M HNO_3, which is the suitable form for the forthcoming purification and separation by extraction chromatography. Chemical recoveries and decontamination factors were calculated for the REE and Th fractions collected after each step of the procedure. Schematic overview of the method developed can be seen on Fig. 2.

2.3.3. EXTRACTION CHROMATOGRAPHY

The REE content of the sample aliquots was further separated by extraction chromatography utilising the selective retention of trivalent lanthanides and actinides in the TRU^{TM} resin in 3 M HNO_3 medium.

First, the columns were pre-conditioned with 10 mL of 2 M HNO_3, followed by the load of the sample. Then, the columns were washed to remove the non-retained matrix components with 2 mL of 2 M HNO_3. The REE were stripped from the column using 1 mL concentrated HCl followed by 4 mL of 4 M HCl and they were collected in the Teflon beakers. The final fractions were evaporated to almost complete dryness on a hot-plate by addition of 200 µL concentrated ultra-pure HNO_3 in order to destroy the residuals of the organic resin. The residue was dissolved in 1 mL of 4% ultra-pure nitric acid while heating slightly. After the gravimetric weighing of the final fraction and the addition of Rh internal standard (m_{finfr}), the samples were analysed by ICP-SFMS. The REE concentrations were calculated using an external calibration curve established by analyses of uranium free lanthanide standards (described in section 2.1) (c_{finfr}). Detailed description of the development of EXC method for REEs in uranium bearing materials can be found elsewhere [13].

2.4. INSTRUMENTATION

2.4.1. ICP-MS

The mass spectrometric analyses of the REE fractions were carried out using a double-focusing magnetic sector inductively coupled plasma mass spectrometer (ICP-SFMS) equipped with a single electron multiplier (ELEMENT2, Thermo Electron Corp., Bremen, Germany). All measurements were carried out in low resolution mode (R = 300) using a low-flow microconcentric nebulizer operated in a self-aspirating mode (flow rate was about 100 µL min^{-1}). Prior to the sample analysis the instrument was tuned using a 1 ng g^{-1} multi-element solution (Merck, Darmstadt, Germany). The optimization was carried out with respect to maximum uranium sensitivity and low UO^+/U^+ ratio. The sensitivity was approximately 1×10^6 cps for 1 ng g^{-1} ^{238}U and the UO^+/U^+ ratio ~ 5×10^{-2}. Optimised instrumental settings and data acquisition parameters can be found in Table 2.1.

Table 2.1: Optimised instrumental setting and data acquisition parameters of Element2 ICP-MS

MC-ICP-MS instrumental settings	
Forward power (W)	1200
Cooling gas flow rate (L min^{-1})	16
Auxiliary gas flow rate (L min^{-1})	0.9
Solution uptake rate (µL min^{-1})	Approx. 100
Data acquisition	
Mass resolution	300
Runs and passes	5×5
Mass window (%)	125
Sampling time (s)	0.01
Samples per peak	20
Search window (%)	80
Integration window (%)	60
Integration type	Average
Scan type	Both
Internal standard	^{103}Rh
Measured isotopes	^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{232}Th, ^{235}U

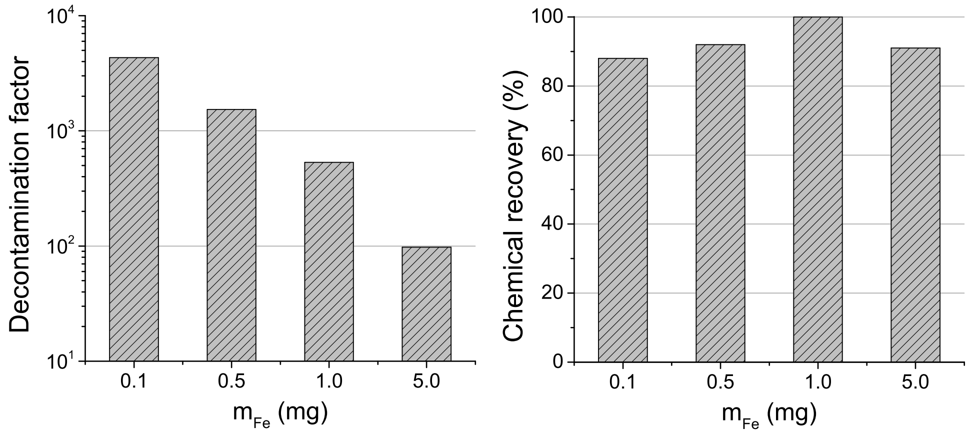

Figure 2.3: Calculated uranium decontamination factors [a] and thorium recoveries (%) [b] based on mass spectrometric results, are depicted as a function of increasing Fe(III) carrier amount applied during the optimisation of co-precipitation scheme.

2.4.2. GAMMA SPECTROMETRY

The gamma spectrometric measurements on the distribution of U and Th during the preconcentration were performed using a well-type HPGe detector (GCW 2022 model) with approximately 20% relative efficiency and a resolution of <1.7 keV at 185.6 keV (Canberra Industries Inc., USA). The gamma counting system consisted of a Canberra model 2022 amplifier and a Canberra model 8075 analog-to-digital converter. The measured spectra were evaluated using Genie 2000 v2.1 software. The measurement time varied between 600 and 5400 s. All gamma spectrometric measurements were performed at fixed geometries as relative measurements to the original starting material before the separation.

2.5. RESULTS AND DISCUSSION

2.5.1. OPTIMIZATION OF THE CO-PRECIPITATION SCHEME

The aim of the co-precipitation step is the quantitative recovery of REE (and Th), while the uranium matrix is eliminated by a combination of selective dissolution and complexation steps.

To achieve selective dissolution of uranium from the precipitate, carbonate can be used as a possible complexant, as UO_2^{2+} has a high affinity to this ion over a wide pH range [30, 31], yielding high uranium solubility. Na_2CO_3 and $(NH_4)_2CO_3$ were tested to verify firstly, if uranium remains in solution with the given carrier, and secondly, if the carrier forms a precipitate in the test solution. As a carrier Al, Fe, Pb, Sr and Zn were possible candidates to form precipitates at given pH, and thus co-precipitating the target analytes. A series of tests using Na_2CO_3 solutions as complexant and Zn, Pb, and Sr as possible carriers led to the conclusion that they were not suitable for our purpose as they were not forming precipitates and uranium was not selectively separated. Further analysis on the performance of Fe and Al as carriers showed that preconcentration in the presence of Fe is more robust and the reproducibility and the LOD were superior to using Al. Fe is also a good carrier because of its very low solubility constant (K_{sp}(FeOH$_3$)= 2.79×10^{-39}). The optimal ammonium carbonate (AC) concentration was determined to be 1%, since more concentrated solutions resulted in re-dissolution of the precipitate. PAA can also be added to the uranium solution before the precipitation, as it has been demonstrated in preliminary studies that the addition of non-ionic polyelectrolyte solution improves the precipitation by giving better stability, faster settlement and cleaner supernatant via coagulation even without centrifuging the solution. Our preliminary studies have shown that the optimum ratio of carrier to polyelectrolyte is 4:1, which is in good agreement with the findings of Amuda et al. [31].

Due to the limited solubility of the iron carrier in 3 M HNO$_3$ in the final step (redissolution of the co-precipitate) of the co-precipitation procedure and the fact that Fe(III) negatively affects the separation by decreasing the retention of Ln on the TRU resin, an optimal quantity of the carrier had to be first established. For the carrier quantity optimisation experiments, four parallel samples each containing approximately 100 mg of uranium, were prepared from the Morille CRM. The co-precipitation procedure was performed with increasing Fe carrier quantities of 0.1, 0.5, 1.0 and 5.0 mg, respectively. The distribution of U, Th and REE during the separation process was followed by gamma spectrometry and ICP-MS.

During the different washing steps, the separation of uranium was checked by gamma spectrometry while REE behaviour was followed by the measurement of Th, as it has similar low solubility behaviour in low carbonate concentrations [32]. Decontamination factor for uranium (defined as the ratio of amount of uranium contained in the sample before and after the chemical separation) was between 10^2 and 10^4 depending on the amount of Fe(III) carrier added (Fig.2.3a). Thus the U concentration after the co-precipitation is low enough (typically < $2\,\mu g\,g^{-1}$ to avoid the decrease in the sensitivity due to matrix effects during the ICP-MS measurement or to perform a subsequent extraction chromatographic (EXC) separation.

The recovery of Th (defined as the percentage of the ratio of thorium amount after and before the chemical separation) was better than 90 % (with 1.5% RSD) (Fig.2.3b), the average recovery of the REE was found to be 85-90%, hence at similar level. Based on the high chemical recovery and on the good uranium separation we decided to use 1 mg Fe carrier for each 100 mg uranium in the further experiments.

2.5.2. FIGURES OF MERIT AND VALIDATION OF THE METHOD

Concentration of the lanthanide elements (C_{Ln}) in the initial sample was calculated as follows:

$$C_{Ln} = \frac{m_{finfr} \times c_{finfr} \times M_{stock}}{M_{sample} \times M_{load} \times R} \tag{2.1}$$

where m_{finfr} is the weight of the final fraction, C_{finfr} is the concentration of the final fraction, M_{stock} is the weight of the sample after dissolution, M_{sample} is the weight of the uranium sample used for the preparation of stock solution, $M_{initial}$ is the weight

Table 2.2: Measured and reference values for Morille CRM with the achieved limits of detection (n=4).

Element	Developed pre-concentration method				C_{cert}		LOD_{STD}	$LOD_{preconc}$
	C_{det} ($\mu g g^{-1}$)		R (%)		($\mu g g^{-1} U$)		($ng g^{-1}$)	($ng g^{-1}$)
Sm	0.5	± 0.20	88.90%	±2.5%	0.5	± 0.12	3.5	0.01
Eu	0.52	± 0.05	87.30%	±2.3%	0.52	± 0.03	1.4	0.01
Gd	0.56	± 0.08	86.20%	±1.8%	0.56	± 0.06	1.3	0.04
Dy	0.51	± 0.11	96.00%	±3.5%	0.5	± 0.06	7.5	0.01

of the aliquot used for the pre-concenration method and *R* is the chemical recovery estimated by the measurement of spiked samples.

The procedure we developed was validated by applying it (including the preconcentration and measurement step) to the Morille CRM. The measured concentrations of the four REE which are certified in this CRM are shown in Table 2.2 as well as the respective reference values. The measured values agreed well with the certified reference values within the uncertainties ($k = 2$).

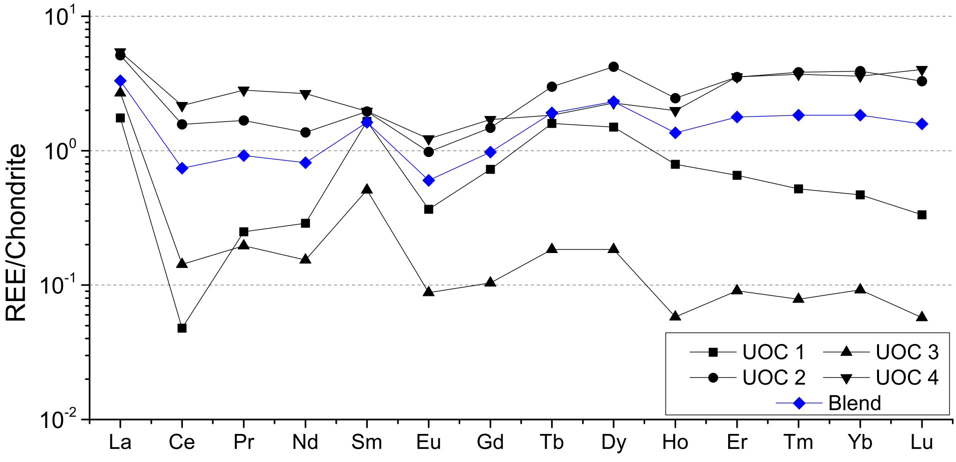

Figure 2.4: Comparison of the measured REE patterns in the four different feed UOC samples with the estimated blend.

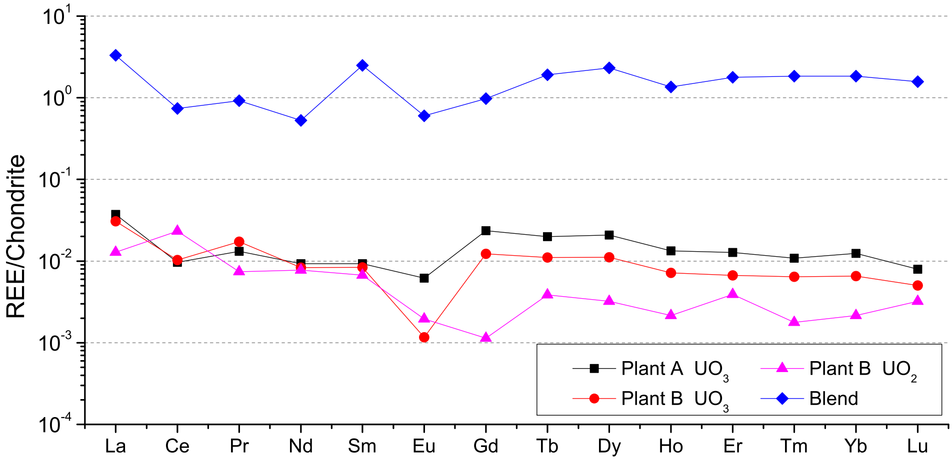

Figure 2.5: Comparison of the measured REE patterns in the three different feed UOC samples with the estimated blend.

2.5.3. APPLICATION OF THE METHOD

The applicability of the method was demonstrated by the measurement of the REE in high purity uranium oxide samples. First, samples containing 100 mg uranium were pre-concentrated by the co-precipitation technique. Uranium decontamination factor after this separation was in the range of 10^3 - 10^4, which means a uranium concentration at ppm level in the purified REE fraction. After additional TRU separation the achievable uranium decontamination factor is about five orders of magnitude higher (10^8 - 10^9).

The values were chondrite normalized [33] and the resulting REE patterns are shown in Fig. 2.4. In the interpretation of the data, however, the flow sheet of Plant A has to be taken into account. Specifically, the feed materials of Plant A consist of uranium oxide and peroxide UOCs, originating from four different facilities, each have different impurity (and REE) pattern. These feed materials are then mixed in order to obtain the necessary uranium concentration with a certain range of trace element content that will enable a steady operation of the purification process resulting in high quality UO_3. Hence, the relative amounts of the four UOC feeds may slightly vary from one lot to another during the continuous process. In this particular case we obtained information on the mixing amounts, therefore the estimated REE impurity pattern in the mixed feed (blend) could be calculated (Fig. 2.3).

2.6. CONCLUSION

Preconcentration and separation of REE and thorium from large size (100 - 200 mg) nuclear grade uranium-oxide samples and the subsequent measurement by inductively coupled plasma mass spectrometry are presented in this study. The developed method involves a simple precipitation of the analytes with an Fe(III) carrier under well-defined pH and an extraction chromatographic separation of REE. The distribution of uranium, thorium and REE was followed by gamma spectrometry and ICP-MS during the separation process. The typical uranium decontamination factor of first step (precipitation) is in the range of 10^3 - 10^4, while after additional TRU separation the achievable uranium decontamination factor is about five orders of magnitude higher (10^8 - 10^9). The limits of detection for different elements in question are in the pg/g range. The preconcentration procedure was validated by processing a certified reference material and the applicability of the method was demonstrated by the measurement of REEs in real-life high purity uranium samples. Hence, the method enables to follow the REE pattern during processing of natural uranium, even for well purified uranium products.

Besides the REE determination, the method can also be applied to the isotopic analysis of trace-level neodymium measured subsequently by MC ICP-MS [34]. In addition to that, the developed method preconcentrates also other elements of interest for nuclear forensics, such as thorium, plutonium and americium. Therefore its range of application could be extended to enriched uranium samples for preconcentration of Th in age determination when using the uranium/thorium chronometry [35] or for pre-concentration of Pu and Am to support detection of previous irradiation history of uranium [36].

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3

APPLICATION OF NEODYMIUM ISOTOPE RATIO MEASUREMENTS FOR THE ORIGIN ASSESSMENT OF URANIUM ORE CONCENTRATES

Judit KRAJKO, Zsolt VARGA, Ezgi YALCINTAS, Maria WALLENIUS, and Klaus MAYER

A novel procedure has been developed for the measurement of ^{143}Nd/^{144}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}Nd/^{144}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 world-wide origin. The investigated samples show distinct* ^{143}Nd/^{144}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.*

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3.1. 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 [2]. Up to now the isotopic patterns of O [3], S [4], Pb, Sr [5], and U [6–8] have been investigated and found to be valuable signatures. Besides these signatures the $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ 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 [9, 10].

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

$$\varepsilon_{Nd,CHUR} = \left[\frac{n\left(^{143}\mathrm{Nd}\right)/n\left(^{144}\mathrm{Nd}\right)_{sample}}{n\left(^{143}\mathrm{Nd}\right)/n\left(^{144}\mathrm{Nd}\right)_{CHUR}} - 1 \right] \times 10^4 \tag{3.1}$$

where $n\left(^{143}\mathrm{Nd}\right)/n\left(^{144}\mathrm{Nd}\right)_{sample}$ is the measured $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratio in the sample, and $n\left(^{143}\mathrm{Nd}\right)/n\left(^{144}\mathrm{Nd}\right)_{CHUR}$ is the $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ ratio (0.512638(3)) in the Chondritic Uniform Reservoir (CHUR) [11].

The positive or negative ε_{Nd} values of $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ 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 $\mu\mathrm{g\,g^{-1}U}$) deriving from the ore. The hydrometallurgical processes are not expected to affect its isotopic composition significantly, therefore the $n\left(^{143}\mathrm{Nd}\right)/n\left(^{144}\mathrm{Nd}\right)_{sample}$ 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 $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ 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) [10, 11] or by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [12, 13]. Mass spectrometric measurements of Nd isotope ratios, however, may suffer from isobaric interferences of Ce and Sm isotopes [14]. 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 [14] or liquid-liquid extraction [15] 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 [16] and lanthanides [17], 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. [18, 19] and studies have been carried out on Namibian and Canadian deposits [20–23]. 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}Nd/^{144}Nd isotope ratio in uranium-bearing materials. The Nd/Sm chemical separation is based on the work of Pin and Zalduegui [17], and further developed for the separation and pre-concentration of trace-level Nd in various uranium ores and ore concentrates (UOC) for precise ^{143}Nd/^{144}Nd isotope ratio measurements by MC-ICP-MS.

3.2. EXPERIMENTAL

3.2.1. INSTRUMENTATION

A NuPlasma™ (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 nebulizer 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 3.1.

Table 3.1: Optimised MC-ICP-MS instrumental setting and data acquisition parameters

MC-ICP-MS instrumental settings	
Forward power (W)	1225
Cooling gas flow rate ($\mathrm{L\,min^{-1}}$)	14
Auxiliary gas flow rate ($\mathrm{L\,min^{-1}}$)	0.75
Sample introduction conditions (DSN-100)	
Nebulizer pressure(psi)	30.5
Solution uptake rate ($\mathrm{\mu L\,min^{-1}}$)	50
Hot gas flow rate ($\mathrm{L\,min^{-1}}$)	0.15
Membrane gas flow rate ($\mathrm{L\,min^{-1}}$)	3.28
Spray chamber temperature (°C)	110
Membrane temperature (°C)	110
Data acquisition	
Data acquisition time (s)	50
Magnet delay between blocks (s)	2
Mass resolution	300
Number of spectra acquired	3 × 10
Scan type	static multi-collection
Cup configuration of Faraday detectors: ^{142}Nd: L1; ^{143}Nd: Axial; ^{144}Nd: H1; ^{146}Nd: H3 and ^{147}Sm: H4	

Prior to the sample analysis the instrument was optimised using a 100 $\mathrm{ng\,g^{-1}}$ Nd monoelemental solution (Alfa Aesar, Karlsruhe, Germany). The optimization was carried out with respect to maximum sensitivity. The sensitivity was approximately 3.5 V for 100 $\mathrm{ng\,g^{-1}}$ total Nd, corresponding to about 420 mV for ^{143}Nd. All uncertainties quoted are given as expanded uncertainty using a coverage factor of $k = 2$ taking into account the uncertainties of the method blanks, isotope masses, as well as mathematical corrections for instrumental mass discrimination (see Eq. 3.2-4). They are given in parentheses and apply to the last significant digits of the value.

3.2.2. 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) used for the optimization of the MC-ICP-MS instrument were prepared by the dilution of a 100 $\mu g\,g^{-1}$ 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^{TM} extraction chromatographic resin (100 to 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 to 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) [24], and JB-2 (Volcano Basalt, Geological Survey of Japan, Ibaraki, Japan) [25], as well as La Jolla Nd isotope standard [26] were used to validate the procedure.

3.2.3. 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 3.2. 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 2000s, and obtained from two different batches produced within short time interval (Beverley-1,3 and Beverley-2,4, respectively) [27]. To validate the repeatability of the chemical separation replicate analysis of six aliquots of Beverley-3 were used.

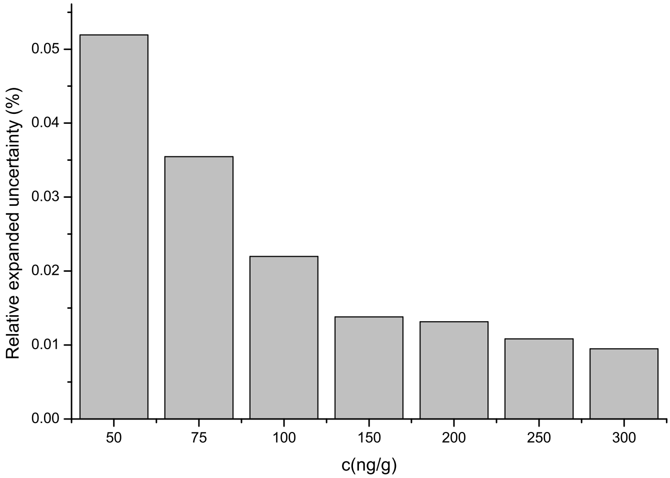

Figure 3.1: Relative expanded uncertainty ($k = 2$) of ^{143}Nd/^{144}Nd isotope ratio measurement by MC-ICP-MS over the typical concentration range of Nd in the investigated samples.

3.2.4. 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 to 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 six hours. 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 HNO_3 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^{TM} resin in 3 M nitric acid medium. After conditioning of the resin with 10 mL 2 M HNO_3 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 HNO_3, 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 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.

3.3. Results and discussion

3.3.1. Optimisation of the ^{143}Nd/^{144}Nd ratio measurements by MC-ICP-MS

Before every measurement, an on-peak-zeros 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 minimize 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}Sm/^{147}Sm ratio of 0.20504 was used [28]. Finally, due to the instrumental mass discrimination, the ^{143}Nd/^{144}Nd ratio was normalized to ^{146}Nd/^{144}Nd = 0.7219 using the exponential law of Russel [29]. The calculations were done as follows:

$$ {}^{143}\mathrm{Nd}_{calc} = {}^{143}\mathrm{Nd}_{meas} - {}^{143}\mathrm{Nd}_{blank} \tag{3.2} $$

$$ {}^{144}\mathrm{Nd}_{calc} = \left({}^{144}\mathrm{Nd}_{meas} - {}^{144}\mathrm{Nd}_{blank}\right) - \left(0.20504 \times \left({}^{147}\mathrm{Sm}_{meas} - {}^{147}\mathrm{Sm}_{blank}\right) \times 1.01392^{\beta}\right) \tag{3.3} $$

$$ \beta = ln\left(\frac{\left[\dfrac{0.7219}{({}^{146}\mathrm{Nd}/{}^{144}\mathrm{Nd})_{meas}}\right]}{1.02392}\right) \tag{3.4} $$

where β corresponds to the mass bias coefficient for Nd and 1.01392 is the atomic mass ratio of the measured ^{146}Nd and ^{144}Nd nuclides.

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 on Fig.3.1. 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}Nd/^{144}Nd ratio so significantly that even the mathematical correction could not compensate for it when comparing to the reference value (Fig. 3.2). 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 [30]. 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.

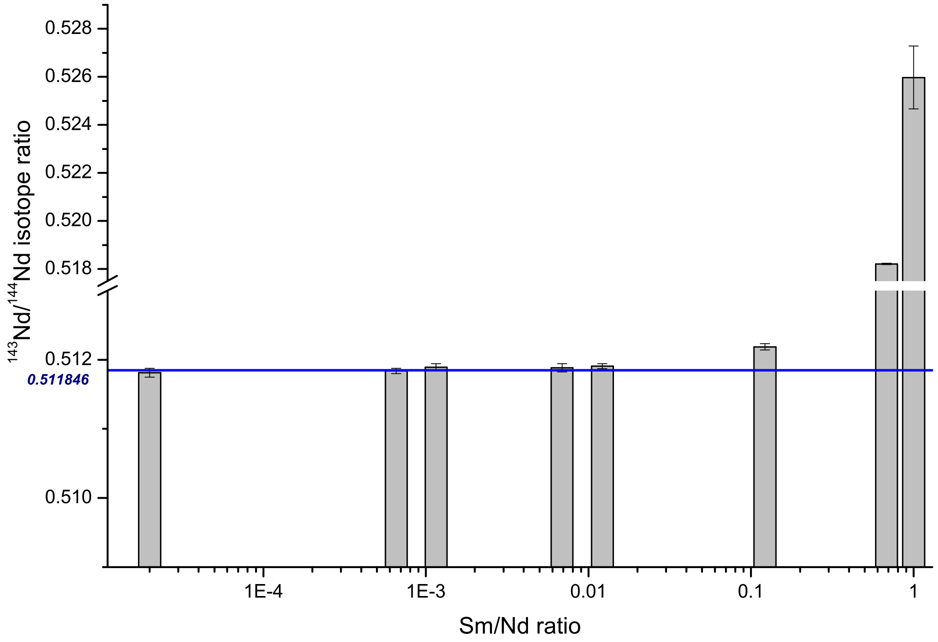

Figure 3.2: Effect of increasing Sm amount on the Nd isotope ratio measurement of La Jolla Nd standard. The reference value of ^{143}Nd/^{144}Nd ratio is 0.511846(3) [26].

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 hours. 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}Nd/^{144}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 [31], and [32].

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}Nd/^{144}Nd

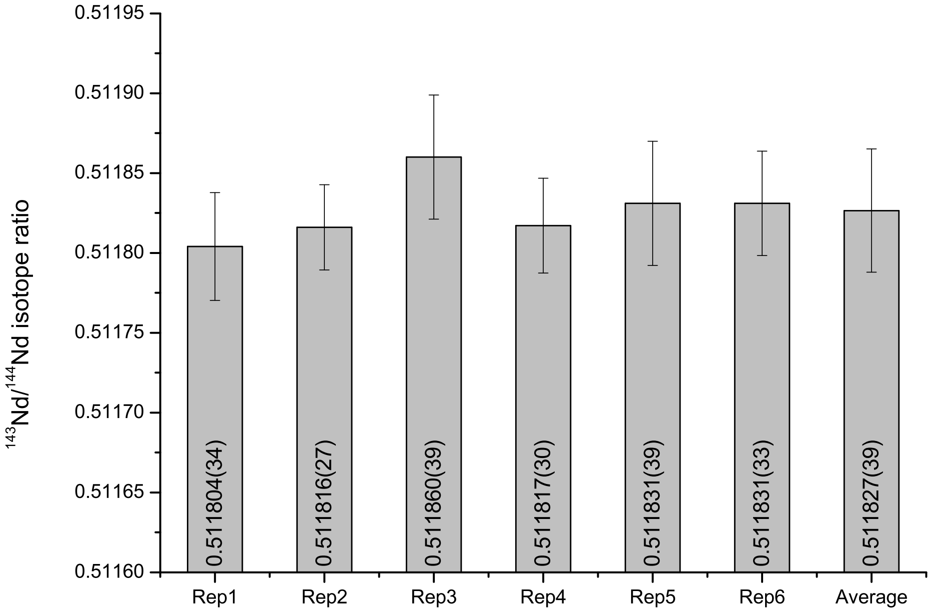

Figure 3.3: Repeatability of the developed method for sample from Beverley Mine, Australia.

isotope ratio of 0.511827(39) (Fig. 3.3). The replicate results are in agreement with one another.

3.3.2. $^{143}Nd/^{144}Nd$ IN URANIUM SAMPLES

The measured $^{143}Nd/^{144}Nd$ isotope abundance ratio plotted against the Sm/Nd elemental ratio in the investigated uranium ores and ore concentrates is shown in Fig. 3.4. The corresponding results with additional information are seen in Table 3.2. It can be observed from Fig. 3.4 that the $^{143}Nd/^{144}Nd$ ratios in the uranium samples (ores and UOCs) show large variations between 0.510 and 0.515 (or ε_{Nd} values in the range of −40 to 40). Most of the samples, however, show ε_{Nd} values in the range of −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. 3.4).

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 variation. For other deposit types such grouping appears less obvious, using just these two parameters. In particular unconformity related deposits have shows a broad variety in their chemical composition. For instance, Varga et al [30] and Mercadier et al [33] found that rare earth element

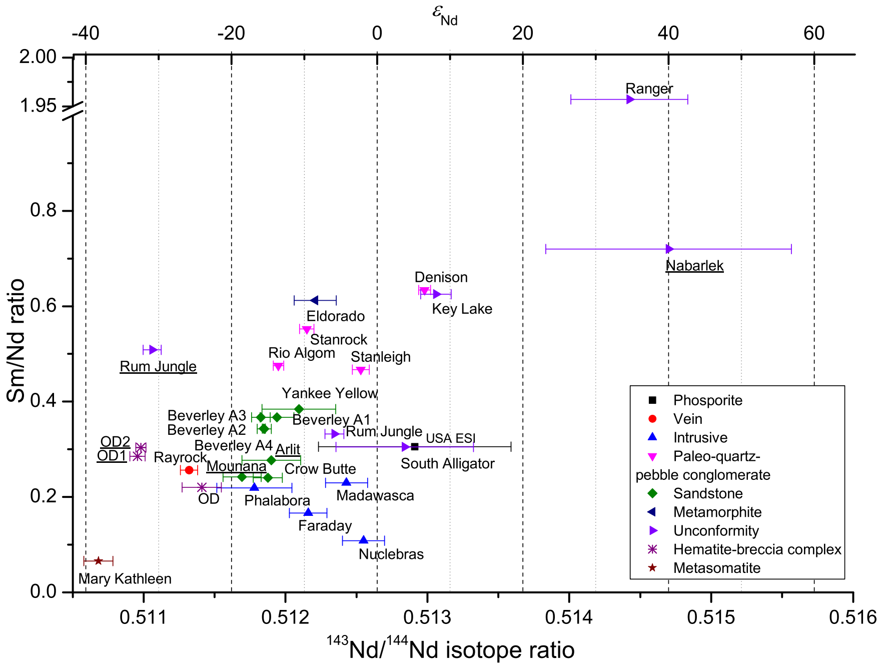

Figure 3.4: Variation of the ^{143}Nd/^{144}Nd ratio as a function of Sm/Nd ratio in the investigated uranium ore and ore concentrate samples. OD – Olympic Dam; underlined labels correspond to ore samples.

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 3.03, 1.92, 0.747 and 2.21, respectively). This could explain also the variations of the ε_{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 [19], 0.51067 - 0.51485 [21] and 0.51289 - 0.51660 [18], 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. 3.4). 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 3.2) while for Sr it is 0.06% and for Pb it is three orders of magnitude higher [5].

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 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 $^{143}Nd/^{144}Nd$ can be expected than the variation of the Sr and Pb isotopics, though this initial assumption has to be verified for more deposit types.

Table 3.2: Nd and Sm concentrations [31] and measured ^{143}Nd/^{144}Nd 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 (U)	ε
				Uranium Ore Samples				
Sandstone								
	Arlit	Niger	2.89	0.8	0.28	0.03	0.51190(21)	-14.4
Unconformity related								
	Rum Jungle	Australia	2.94	1.5	0.51	0.03	0.51106(6)	-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(5)	-32.8
	Olympic Dam2	Australia	201	61.1	0.3	2.35	0.51098(4)	-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	5.7	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

continued on next page

Table 3.2: Nd and Sm concentrations [31] and measured $^{143}Nd/^{144}Nd$ 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)	$^{143}Nd/^{144}Nd$ (U)	ε
Sandstone								
	Beverley A1	Australia	48.6	17.8	0.37	0.57	0.51194(12)	-13.6
	Beverley A2	Australia	69.9	24	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	1.2	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	14.1	0.61	0.27	0.51221(15)	-8.35
Unconformity related								
	South Alligator	Australia	1.07	0.33	0.3	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	2.9	0.33	0.1	0.512344(66)	-5.73
	Nabarlek	Australia	0.42	0.3	0.72	0.005	0.51470(87)	40.2
Hematite Breccia								
	Olympic Dam	Australia	3.19	2.16	0.68	0.04	0.51141(14)	-24
Metasomatite								
	Mary Kathleen	Australia	14.2	2.85	0.2	0.17	0.51068(10)	-38.2

3.4. CONCLUSION

This work presents a novel method developed for trace-level analysis of ^{143}Nd/^{144}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 $\mathrm{ng_{Nd}/g_{sample}}$) was possible with small 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}Nd/^{144}Nd isotope ratio in uranium ores and UOCs originating from different uranium mines and milling facilities.

The obtained results show that the ^{143}Nd/^{144}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}Nd/^{144}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}Nd/^{144}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 a 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.

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4

DETERMINATION OF THE ^{143}Nd/^{144}Nd ISOTOPE RATIO IN VARIOUS TYPES OF URANIUM SAMPLES WITH A VERSATILE SAMPLE PREPARATION PROCEDURE FOR NUCLEAR FORENSIC PURPOSES

Judit KRAJKO, Zsolt VARGA, Maria WALLENIUS, and Klaus MAYER

An improved sample preparation procedure for trace-levels of lanthanides (Ln) in uranium-bearing material samples was developed by inductively coupled plasma mass spectrometry. Our method involves a simple co-precipitation with Fe(III) carrier in ammonium carbonate medium to achieve the removal of uranium matrix. The procedure is an effective initial pre-concentration step for the subsequent extraction chromatographic separation. The applicability of the method was demonstrated by the measurement of Ln and ^{143}Nd/^{144}Nd *isotope ratio in uranium ore concentrate samples. Our procedure can be also a useful approach of sample preparation for Th and Pu/Am radiochronometry measurements.*

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4.1. INTRODUCTION

SINCE the beginning of the 1990s cases of illicit trafficking, and other unauthorised acts involving nuclear material from various stages of the nuclear fuel cycle have been taking place. Due to these incidents nuclear materials were started to be analysed in the context of criminal investigations, and a new branch of forensic science - nuclear forensics - was born. The IAEA defines the nuclear forensics as “the analysis of intercepted illicit nuclear or radioactive material and any associated material to provide evidence for nuclear attribution” [2]. The aim for nuclear scientists is therefore to identify indicators which represent relationships between measurable parameters of the material and the production history.

These nuclear forensic indicators, so-called signatures, can be various properties of the material in question, such as structure, morphology, major and minor elements, isotopes and impurities. Among these properties there are only a few exclusive parameters, which would give straightforward information about an unknown sample without the need for a comparison sample. For example, the enrichment and concentration of uranium of an investigated sample could lead us easily to the intended use of the sample or to the stage of the nuclear fuel-cycle from which the sample originates. However, the majority of the nuclear signatures belong to the so-called non-exclusive, comparative parameters. This means that the analytical results have to be compared with known samples or to data in databases in order to draw conclusions about the possible origin of the sample.

In order to support the investigations of unknown seized nuclear materials besides new method developments, the improvement of existing ones are important as well. Up to now the isotopic patterns of O, S, Pb, Sr, and U have been investigated and found to be valuable signatures [3–7]. Besides these signatures recently the ^{143}Nd/^{144}Nd isotope ratio was investigated, as is widely used in geology for chronometry and provenance measurements. It was founded a promising candidate as a new nuclear forensic signature, since its value is indicative of the age and origin of the minerals present [8, 9]. Although the ^{143}Nd/^{144}Nd isotope ratio in most of the UOC samples were possible to measure, there are still samples which contain so small amount of Nd that the measurement was not possible with the standard method (e.g. yellow cakes samples from the Canadian ESI facility or from the US Shirley Basin mill) or it could be performed only with too large uncertainty (e.g. sample from Rössing, Namibia).

This work presents an improved procedure developed for trace-level analysis of ^{143}Nd/^{144}Nd isotope ratio in uranium ore concentrates (UOC) by inductively coupled plasma mass spectrometry (ICP-MS). The aim of the study was to develop a more effective preconcentration prior to the chromatographic separation, which is capable of the measurement of Nd isotope ratio in uranium samples (below $\mathrm{ng\,g^{-1}}$ level). For high-purity uranium materials the major challenge is to achieve a high separation factor from uranium and the removal of uranium, as (even though the ICP-MS measurement is very sensitive) large amounts of sample (100 to 500 mg U) has to be used to yield measurable quantities of the analytes. For such large amounts of sample the standard methods (e.g. direct extraction chromatographic separation) cannot be applied, since the high amount of U precludes their use.

Applying co-precipitation for the preconcentration of traces of lanthanides (Ln) from larger amounts of environmental samples (e.g. sea water [10–12], geological samples [13, 14]) have been studied and it has been proved to be an effective method. Our procedure involves a co-precipitation of rare-earth elements as $Fe(OH)_3$ in the presence of Fe(III) carrier, followed by an extraction chromatographic group separation of the Ln and a sequential separation of Nd, Sm, and other HREE. Though the primary purpose of the study is the separation of lanthanides (Ln), the methodology can be extended for the pre-concentration of other important elements present at trace-level in nuclear materials, such as Th, Am or Pu.

4.2. EXPERIMENTAL

4.2.1. REAGENTS

Thorough cleaning of all labware is necessary before use for trace-level measurement of Nd isotope ratio. This was performed with dilute ethanol, followed by dilute nitric acid, and finally with high purity water rinsing. For all the dilutions high-purity water was used (UHQ System, USF Elga, Germany). Hydrochloric and nitric acids were of Suprapur grade (Merck, Darmstadt, Germany), whereas nitric acid was further purified by sub-boiling distillation.

Analytical grade $Fe(OH)_3$ 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 to use by adding about 10 mg of Fe(III) and precipitating $Fe(OH)_3$ to scavange the trace-level lanthanide impurities still present in the analytical grade ammonium carbonate solution.

For the lanthanide group separation, the TRU^{TM} extraction chromatographic resin supplied by Triskem (Triskem International, Bruz, France) was used. 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. For Nd separation, the Ln Resin^{TM} for the extraction chromatographic separation was purchased from 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.

For the optimization of the separation and the measurements, lanthanide standard solution and monoelemental Nd and Sm standard solutions (Alfa Aesar, Karlsruhe, Germany) were prepared by the dilution from 1000 $\mu g\,mL^{-1}$, and 100 $\mu g\,mL^{-1}$ standard solutions, respectively. The U_3O_8 certified reference material, Morille (Cetama, France) was used for the validation of the co-precipitation method is certified for four lanthanide content (Dy, Gd, Eu and Sm).

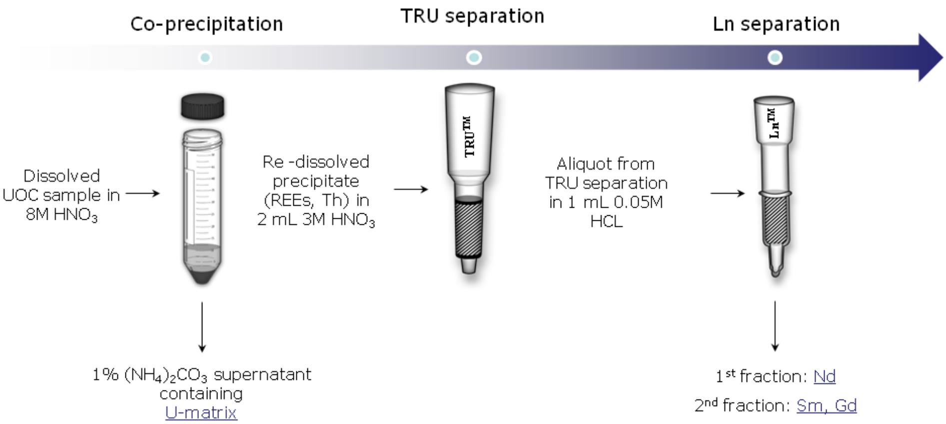

Figure 4.1: Simple scheme of procedure developed.

4.2.2. INSTRUMENTATION

The mass spectrometric analysis of aliquots 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) Measurements were carried out in low resolution mode (R = 300) using a low-flow microconcentric nebulizer (flow rate was about $100\,\mu\mathrm{L\,min^{-1}}$). Instrument was tuned using a $1\,\mathrm{ng\,g^{-1}}$ multielement solution (Merck, Darmstadt, Germany). The optimization was carried out with respect to maximum uranium sensitivity and low $\mathrm{UO^+/U^+}$ ratio.

For the Nd isotope ratio measurements NuPlasma$^{\mathrm{TM}}$(NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) was used. Low mass resolution mode was used for all measurements. 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 monoelemental solution (Alfa Aesar, Karlsruhe, Germany). The sensitivity was approximately 500 mV for $^{143}\mathrm{Nd}^+$ in $100\,\mathrm{ng\,g^{-1}}$ 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 (GCW 2022 model) with approximately 20% relative efficiency and a resolution of <1.7 keV at 185.6 keV (Canberra Industries Inc., USA). The measured spectra were evaluated using Genie 2000 v2.1 software. The measurement time varied between 600 and 5400 s. All gamma spectrometric measurements were performed as relative measurements to the original starting material before and after the separation at fixed geometries.

4.2.3. SAMPLE SEPARATION

Approximately 0.5 g of samples were weighed into a Teflon Erlenmeyer flask and dissolved in 6 mL of 8 mol L ultra-pure nitric acid while heating to 90 °C on a hot-plate for 12 hours covered with a PE stopcock. After cooling to room temperature, the solution weights were measured.

About 3 mL of the stock solution, corresponding to about 200 mg of uranium, was transferred into a 50 mL polyethylene centrifuge vial. 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 accurate centrifugation. Subsequently the precipitate was rinsed with high-purity water. Selective (re-)dissolution of uranium from the precipitate was performed with 10 mL 1% $(NH_4)_2CO_3$ (AC). 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 as possible. Representative aliquots of the supernatant were collected after each separation step in order to (i) control uranium decontamination and Th recovery factors by gamma spectrometric measurements parallel to the separation and (ii) use the achieved relatively pure uranium solution for other purposes (e.g. uranium isotope ratio measurement). The precipitate containing the Ln and Th was dissolved in 2 mL of 3 mol L nitric acid to be in suitable form for further concentration by extraction chromatography. From this final solution 100 µL aliquots were taken for each sample for mass spectrometric measurements to evaluate recoveries and decontamination factors.

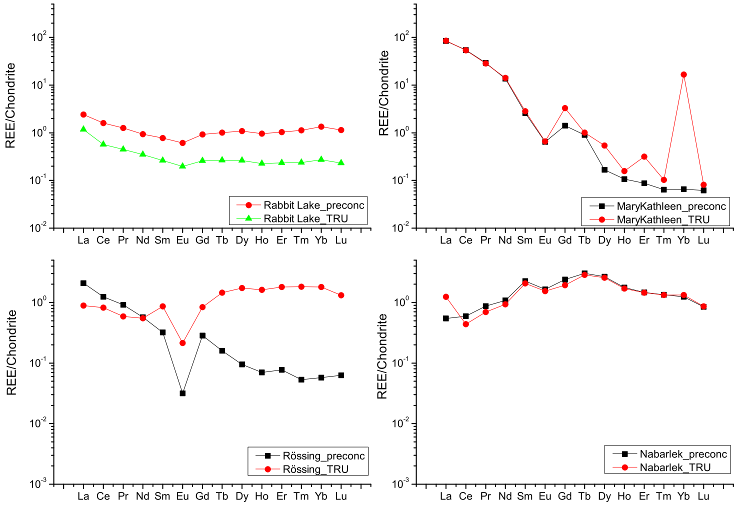

Figure 4.2: REE patterns of investigated uranium ore concentrate samples obtained from two separation type (I) extraction chromatography and (II) co-precipitation.

The Nd separation was performed in two steps: first a lanthanide group separation followed by the Nd separation. The second Nd purification is necessary for the removal of Sm, which interferes with the ICP-MS analysis. In the first step the lanthanide content of the sample aliquots was separated using extraction chromatography by the selective retention of trivalent lanthanides (Ln) on the TRU^{TM} resin in 3 mol L^{-1} nitric acid medium. In the second step, Ln^{TM} resin was used in 0.05 mol L^{-1} HCl medium for the Nd separation. After Nd was stripped from the column with 0.2 mol L^{-1} HCl, it was evaporated to almost complete dryness and dissolved in nitric-acid for mass spectrometric analysis. A method blank was processed through the entire dissolution and separation procedure parallel to the samples. The final samples were analysed by MC-ICP-MS. The simplified scheme of the entire separation procedure can be seen in Figure 4.1. The development of the preconcentration and extraction chromatographic separation procedure can be found in Chapter 2 and 3 [15, 16]. The method was validated by the measurement of reference material (Morille, Cetama), the recovery for the certified rare-earth elements (Sm, Eu, Gd, Dy) being better than 90 %.

4.3. RESULTS AND DISCUSSION

In our previous work it was found that samples containing a few hundred nanogram of Nd per gram sample can be measured with a sufficiently low uncertainty (~ 0.05 RSD%) allowing distinguishing between samples [16]. However, for samples with lower Nd concentration higher pre-concentration is necessary to understand properly the correlation between the Nd isotopic variation values of the uranium ore concentrates, uranium ores and the deposit types. Co-precipitation as the most effective pre-concentration method was selected to achieve the required limits of detection in the low pg g^{-1} range. Selective (re-)dissolution of uranium from the precipitate was done with 10 mL 1% $(NH_4)_2CO_3$ (AC) as uranium forms soluble di- and tri-carbonato complexes between pH 5-8 [17]. The achievable U decontamination factor is in the magnitude of 10^2 - 10^4. The method was validated by the measurement of reference material (Morille), the recovery for the certified rare earth elements (Sm, Eu, Gd, Dy) is better than 90%. Therefore, the procedure is an effective initial preconcentration step for the forthcoming extraction chromatographic separations.

Six uranium ore concentrate samples were chosen to evaluate the capabilities of the method developed. Although the effectiveness of co-precipitation were found very promising, for the sake of complexity the REE pattern of four UOC samples (Rabbit Lake, Mary Kathleen, Nabarlek, and Rössing) obtained from the co-precipitation were compared with the REE patterns resulted from previous TRU separation in order to verify that no interferences are introduced to the samples by used reagents (Figure 4.2).

We can see from the figures that normalised patterns of the samples in most cases agree well. In case of Rabbit Lake and Rössing samples two different batches which are also depicted in Fig. 4.2. Comparison of the different batch samples of Rössing shows different REE pattern which is possibly means an inhomogeneous sample. We can also observe that application of the pre-concentration method and the TRU separation does not agree completely. However, it can be conclude that Rössing sample separated by new method is from the second batch and it shows similarities with the corresponding TRU sample. By the application of the new method higher concentrations were measured

Table 4.1: Measured ^{143}Nd/^{144}Nd isotope ratios in the investigated uranium ore concentrate samples. All uncertainties quoted are given as expanded uncertainty using a coverage factor of $k = 2$.

U_{sample}	Country	Deposit type	^{143}Nd/^{144}Nd	ε	Sm/Nd ratio
ESI	Canada	Phosphate	0.51225(09)	-7.6(4)	0.263
Rössing	Namibia	Intrusive	0.51346(34)	16(2)	0.134
Shirley Basin	USA	Sandstone	0.51356(61)	18(3)	0.718

and smoother pattern was obtained. We can assume that the difference originates from the fact that with the TRU separation the total concentration of REE was in the vicinity of the detection limit which could explain the mismatches in the patterns. It can be also seen on Fig. 4.2. that high Yb level of Mary Kathleen sample is possibly related to isobaric interference if only TRU separation is applied. Our result of Mary Kathleen uranium ore concentrate sample is in good agreement with the recently published work of Keegan et al. [18]. Note that REE patterns of the investigated uranium ore concentrate samples are presented after chondrite normalisation and in logarithmic scale [19].

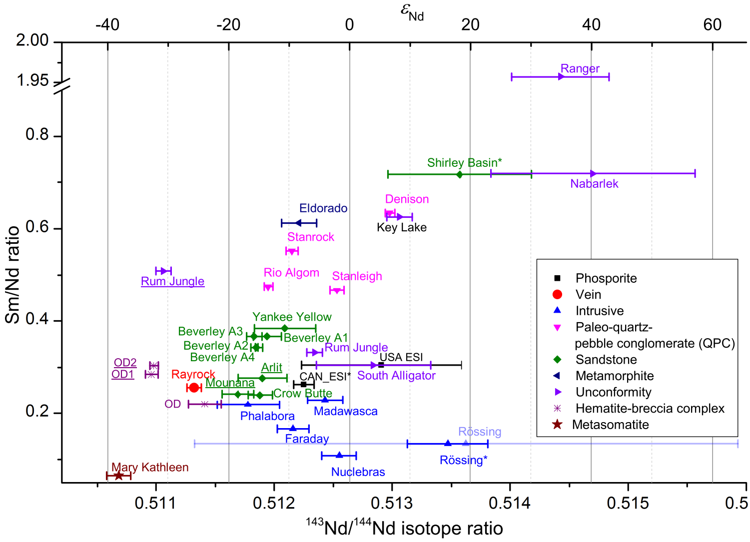

Figure 4.3: Summary on the variation of the ^{143}Nd/^{144}Nd ratio as a function of Sm/Nd ratio in the investigated uranium ore and ore concentrate samples with methods developed in Chapter 3. Underlined labels correspond to ore samples, while labels with $*$ stands for results achieved by preconcentration method.

Also the Nd isotope ratio of two samples (Rössing, Shirley Basin, CAN ESI) and BCR-2 geological standard were measured. The results and the description of the uranium ore concentrate samples can be found in Table 4.1 and Fig. 4.3. Nd isotope ratio of Rössing was measured previously after EXC sequential separation and it resulted in 0.51363(230). Comparing to our results now it can be seen that the Nd isotope ratios are in good agreement and the uncertainty of the new result is almost an order of magnitude better. The other three samples were previously under detection limit and with the new sample preparation scheme results were possible to obtain. This is a promising result, however, further studies are planned to be performed in order to validate the applicability for nuclear grade uranium samples.

4.4. CONCLUSION

The sample amount in nuclear forensic investigations is of crucial importance, not just because the available sample amount is often limited as an evidence specimen, but also due to the need of relatively high amount of sample for the high precision elemental or isotopic analysis. Therefore, careful planning and sequencing of the measurements are required to perform a comprehensive analysis. The proposed $Fe(OH)_3$ co-precipitation in 1% ammonium carbonate combines the effective pre-concentration of the trace-level constituents with the removal of the high amount of uranium matrix. The present method is not just a method useful for trace-level Nd isotope ratio analysis as demonstrated for the analysis of yellow cakes, but it is also a versatile and straightforward sample preparation procedure, which can be applied to pre-concentrate and separate several elements of interest, such as lanthanides, Th, Pu or Am, from a single sample aliquot. For instance, the purified Th can be obtained from the precipitate with high recovery and can be applied for age determination measurements. Similarly, Am and Pu are also co-precipitated under the given conditions, thus a forthcoming purification step can be used to obtain information about the use of reprocessed material as part of the starting material by the detection of activation products. According to our preliminary results these are just few examples of the promising potential of the newly developed pre-concentration procedure.

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5

MEASUREMENT OF SULPHUR ISOTOPE RATIO (^{34}S/^{32}S) IN URANIUM ORE CONCENTRATES (YELLOW CAKES) FOR ORIGIN ASSESSMENT

Han SUN-HO, Zsolt VARGA, Judit KRAJKO, Maria WALLENIUS, and Klaus MAYER

A novel method has been developed for the measurement of the ^{34}S/^{32}S *isotope ratio in uranium ore concentrate (yellow cake) samples for the origin assessment in nuclear forensics. The leachable sulphate is separated and pre-concentrated by anion exchange separation followed by the* ^{34}S/^{32}S *ratio measurement using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The effect of sample composition on the accuracy was investigated and optimized. Matching of the sample to the bracketing standard was necessary to obtain accurate results. The method was validated by the measurement of standard reference materials (IAEA-S-2, IAEA-S-3 and IAEA-S-4) and the* δ^{34}S *value could be determined with an uncertainty between* 0.45‰ *and* 1.9‰ *expressed with a coverage factor of 2. The method was then applied for the analysis of uranium ore concentrates of world-wide origin. In the studied materials distinct* ^{34}S/^{32}S *isotope ratios could be observed, which can be a promising signature for the nuclear forensic investigations to identify the source of unknown nuclear materials.*

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5.1. INTRODUCTION

As a response to the increased illicit trafficking of nuclear materials in the 1990s, a new scientific discipline emerged, now commonly referred to as nuclear forensics . The aim of the nuclear forensic analysis is to identify the hazard and origin of the seized or found nuclear materials and ultimately to strengthen security measures and prevent nuclear terrorism thereafter. Over the last few years several signatures of nuclear materials have been investigated and developed to establish the links between the origin of the nuclear materials (source of uranium ore or other feed materials, process methodology and identification of production facility) and the measurable parameters of the material in question. These measurable parameters, often referred to as signatures, include the measurement of elemental or anionic impurities [2–5], isotopic composition [4, 6–9], structural analysis [10, 11], morphology [12] or age determination [13, 14], and they can give information about the source of uranium ore or feed materials, process and production facility. Uranium ore concentrate (commonly known as yellow cake) has a special role among the investigated nuclear materials, as it is the first intermediate product of nuclear fuel fabrication, and thus it is highly useful to identify the source and propagation of various signatures.

Chemical impurities in various uranium products are generally considered as a signature, which may reveal information about the process used for the production. However, earlier studies have shown that isotope composition of various elements is a more robust signature of the origin than the concentration of the impurities, as the production route and the added chemicals can highly influence the impurity content [15–17]. Isotopic composition in uranium products are generally less affected by the process, as chemical separation itself causes a negligible isotopic fractionation. However, the addition of chemicals to the process stream can also result in the alteration of the isotopic composition of certain elements in the final product. So far several elements, such as U, Pb, Sr or O, with sufficiently high isotope variation in nature have been identified as a possible signature to provenance nuclear materials [4, 6, 9, 18]. It has also been demonstrated, however, that due to their relatively high variability in the ore and their contribution from various chemicals added during the process none of the isotopic composition can be used as an exclusive signature for origin assessment, thus further parameters are required to reliably trace unknown nuclear materials.

The sulphur isotope abundance shows relatively high variation in nature due to the large relative mass difference between its isotopes, the variety of chemical forms and the widespread occurrences in nature [19, 20]. Therefore the investigation of its isotope fractionation has been used in many geological, biological and environmental studies [5]. Several techniques are available for the sulphur isotope ratio measurements, such as gas-source mass spectrometry, multi-collector thermal ionization mass spectrometry, or multi-collector inductively coupled plasma mass spectrometry [19–22]. The sulphur variation is generally expressed as the amount ratio of $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ of the two principal sulphur isotopes relative to the IAEA V-CDT (Vienna Cañon Diablo Troilite meteorite) standard in parts per thousand (permil, ‰) [23]. The δ^{34}S values of samples relative to the V-CDT scale in ‰ are calculated using the following equation:

$$\delta^{34}\mathrm{S} = \left[\frac{\left({}^{34}\mathrm{S}/{}^{32}\mathrm{S}\right)_{sample}}{\left({}^{34}\mathrm{S}/{}^{32}\mathrm{S}\right)_{V-CDT}} - 1 \right] \times 10^{3} \tag{5.1}$$

where $\left({}^{34}\mathrm{S}/{}^{32}\mathrm{S}\right)_{sample}$ and $\left({}^{34}\mathrm{S}/{}^{32}\mathrm{S}\right)_{V-CDT}$ are the $n\left({}^{34}\mathrm{S}\right)/n\left({}^{32}\mathrm{S}\right)$ of ratio of sample and IAEA V-CDT standard, respectively. The $\left({}^{34}\mathrm{S}/{}^{32}\mathrm{S}\right)_{V-CDT}$ is defined as 0.0441626 pm 0.0000078 ($k = 2$) [20, 24]. Typically, natural materials with oxidized sulphur have $\delta^{34}\mathrm{S}$ values between +5 ‰ and +25 ‰, while for materials with reduced sulphur it ranges between -5 ‰ and +15 ‰.

The sulphur isotope ratio in uranium ore deposits is also reported to exhibit large variation. Sulphide minerals associated with sandstone-type uranium deposits of the Colorado Plateau and Wyoming have sulphur isotope ratios highly enriched in the lighter isotope (-20.5 to -17.8 ‰) [25], similarly to the second-stage sulphides related to processes that formed the uranium roll-type deposit in South Texas, USA (-25 to -40 ‰) [26]. Hydrothermal uranium deposits derived from residual magma are reported to have $\delta^{34}\mathrm{S}$ values approximately the same as meteorite sulphur (-2.6 to +2 ‰) [27], while high $\delta^{34}\mathrm{S}$ values were measured in the ore horizon of the Tono sandstone type-deposit (+10 to +43 ‰) due to a large extent of bacterial seawater sulphate reduction [28], or at several districts of the Colorado Plateau uranium mining area (-5 to +26 ‰) [29]. The variation of sulphur isotope ratio in uranium deposits is caused by a variety of inorganic chemical reactions and equilibria present at highly variable redox and temperature conditions as well as the occurrence of biological sulphur cycle and bacterial activity [19]. However, as the sulphur content in the nuclear material derives not only from the feedstock (ore), but is also introduced into the process stream as process chemical (e.g. as H_2SO_4 with an approximate $\delta^{34}\mathrm{S}$ value of -5 to +15 ‰) [19, 20], its contribution to the final $\delta^{34}\mathrm{S}$ value in the product has to be considered. The typical concentration of total sulphur in uranium ore concentrates varies highly between 100 and 30 000 µg g, which is comparable to that of the uranium ores [17, 30]. Therefore, it is expected that sulphur isotopic composition can be indicative both for the process (chemicals used) and the ore type.

The aim of the present study was to develop an effective sample preparation method for the recovery of sulphate from uranium ore concentrates and the subsequent sulphur isotope ratio analysis by MC-ICP-MS technique. Ion chromatography (IC) was used to optimize the sample preparation method. The applicability of the sulphur isotope ratio as a possible signature for nuclear forensics was tested by the measurement of several UOCs of world-wide origin.

Table 5.1: Operating parameters of the ion chromatograph

Parameters	
Eluent composition	$3.2\,\mathrm{mmol\,L^{-1}}$ Na_2CO_3 + $1.0\,\mathrm{mmol\,L^{-1}}$ $NaHCO_3$
Eluent flow rate	$0.7\,\mathrm{mL\,min^{-1}}$
Sample injection volume	20 µL
Column pressure	≤ 9 MPa
Suppressor regeneration	$50\,\mathrm{mmol\,L^{-1}}$ H_2SO_4
Typical run time	18 min

5.2. EXPERIMENTAL

5.2.1. INSTRUMENTATION

The anion (sulphate) measurements were performed by ion chromatography (Advanced Compact IC 861, Metrohm, Switzerland). The ion chromatograph is equipped with a chemical suppressor (Module MSM II) and a conductivity detector. The separation of sulphate was carried out using an anion exchange column (METROSEP A supp 5, 150 × 4.0 mm I.D.) preceded with a guard column (METROSEP Anion Dual 1, 50 × 4.6 mm I.D.). Before use the $Na_2CO_3/NaHCO_3$ eluent was filtered using 0.45 µm cellulose nitrate filter (Nalgene, USA). The operating parameters of the ion chromatograph are listed in Table 5.1.

A NuPlasma^{TM} (NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled mass spectrometer (MC-ICP-MS), equipped with 11 Faraday collectors and 3 discrete dynode electrode multipliers was used for the sulphur isotope ratio measurements. The instrument was operated at low mass resolution mode ($R = 300$). The samples were introduced into the plasma using a low-flow Teflon microconcentric nebulizer 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 used are summarised in Table 5.2. The tuning parameters were adjusted on a day-to-day basis to optimize the sensitivity and stability of the signals. Prior to analysis of samples the instrument was tuned using a $2\,\mathrm{\mu g\,g^{-1}}$ $SO_4{}^{2-}$ anion standard solution (Merck, Darmstadt, Germany). The optimization was carried out with respect to maximum sensitivity. The sensitivity was approximately 2 V for $1\,\mathrm{\mu g\,g^{-1}}$ ^{34}S.

5.2.2. REAGENTS AND MATERIALS

For dilutions ultra-pure water was used (UHQ System, USF Elga, Germany). Suprapur grade nitric acid (Merck, Darmstadt, Germany) was used for the sample preparation. All other reagents used were of analytical grade. To prevent anionic contamination during the measurement, all lab ware was washed three times with ultra-pure water, dried in a laminar flow bench and stored in clean zipped bags. New and cleaned labware was used for each sample. Ag ICP standard solution was purchased from Alfa Aesar (Specpure®, Karlsruhe, Germany), a sulphate anion standard (Certipur® grade, Merck, Darmstadt, Germany) was used for MC-ICP-MS optimization.

To validate the developed method, sulphur isotope ratio certified reference materials purchased from the International Atomic Energy Agency (IAEA) were used. For the analysis approximately 80 mg of the IAEA standards (S-1, S-2, S-3, S-4) were weighed into a screw-cap Teflon vial and dissolved in 5 mL of nitric acid while heating to 95 °C on a hotplate for 6 hours. After cooling to room temperature, sulphate concentrations in these stock solutions were measured by IC. These stock solutions were subsequently diluted to $2\,\mu g\,mL^{-1}$ (expressed as sulphur) in 1% HNO_3 for the sulphur isotope ratio measurement.

A total of 18 uranium ore concentrates originating from different mines were included in this study. The chemical compositions of the investigated uranium ore concentrates vary depending on the milling process applied in the different facilities [6, 10, 30].

Table 5.2: Optimised MC-ICP-MS instrumental setting and data acquisition parameters

MC-ICP-MS instrumental settings	
Forward power (W)	1300
Cooling gas flow rate ($L\,min^{-1}$)	13
Auxiliary gas flow rate ($L\,min^{-1}$)	0.75
Cones	Ni
Sample introduction conditions (DSN-100)	
Solution uptake rate ($\mu L\,min^{-1}$)	Approx. 100
Spray chamber temperature (°C)	106
Membrane temperature (°C)	110
Hot gas flow rate ($L\,min^{-1}$)	0.26
Membrane gas flow rate ($L\,min^{-1}$)	4.2
Nebulizer pressure(psi)	33.5
Data acquisition	
Mass resolution	300
Number of spectra acquired	3 × 10
Magnet delay between blocks (s)	2
Scan type	static multi-collection
Cup configuration for S measurements:	^{32}S: L4; ^{33}S: L1; ^{34}S: H5

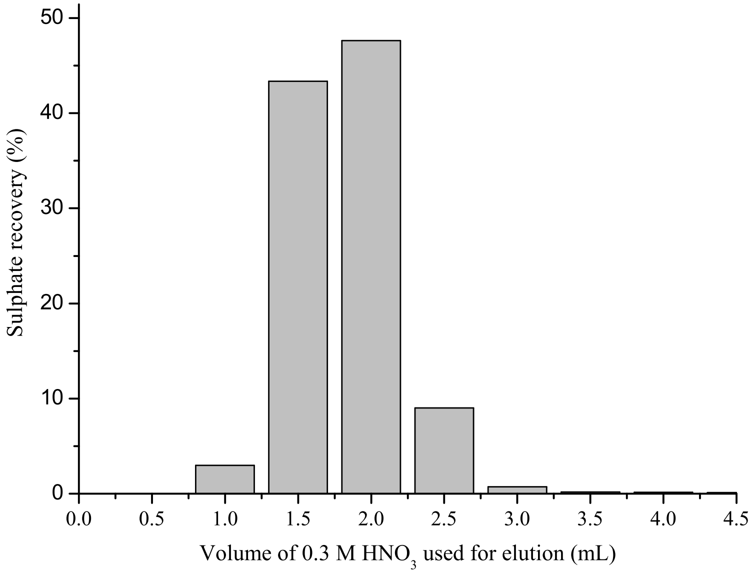

Figure 5.1: Elution curve of SO_4^{2-} ion during ion exchange sample preparation method (AG 1-X4).

5.2.3. SEPARATION OF SULPHATE BY ION EXCHANGE

100 – 300 mg of sample depending on the sulphur concentration was taken and 10 mL ultra-pure water was added in pre-cleaned plastic bottle. The samples were leached for 24 hours at room temperature and filtered with pre-rinsed 0.45 µm cellulose acetate syringe filters (Nalgene, USA) before the ion exchange separation.

For the separation of SO_4^{2-} from the leaching solution anion exchange resin (AG 1-X4, Cl^- form, 100 – 200 mesh, Bio-Rad Laboratories, USA) was applied. A new column was used for every sample to avoid the risk of cross-contamination. For the column preparation, 1 mL of the resin was placed in a poly-prep column (0.8 × 4 cm, Bio-Rad Laboratories, USA) and porous polyethylene frit (120 µm pore size, Reichelt Chemietechnik Heidelberg, Germany) was placed on the top to avoid mixing. Before use, the resin was converted into nitrate form by elution with 10 mL of 3 M HNO_3 and pre-conditioned with 10 mL of 0.03 M HNO_3. The flow rate for the resin column was about 0.6 - 0.7 mL min^{-1}. Before loading, the resin was conditioned again with 10 mL of 0.03 M HNO_3. After loading, the resin was washed with 10 mL of 0.03 M HNO_3 and subsequently SO_4^{2-} was eluted using 3 mL of 0.3 M HNO_3. An aliquot was taken for the recovery measurement of SO_4^{2-} by ion chromatography.

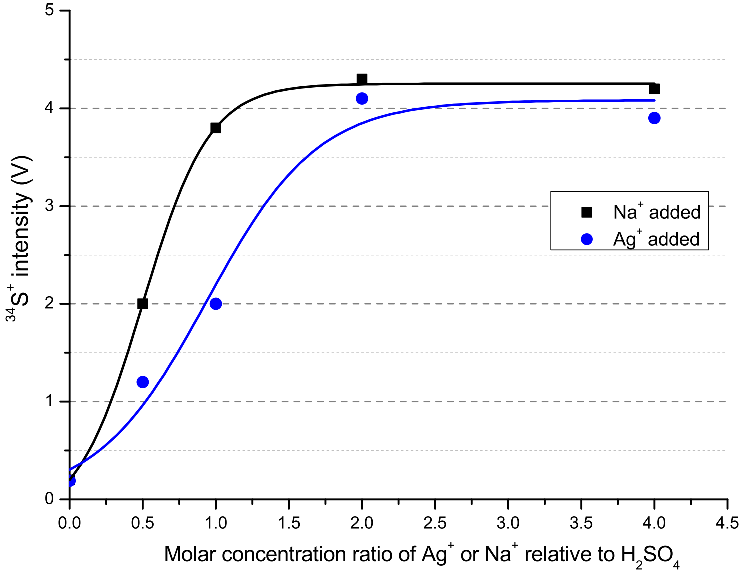

Figure 5.2: Intensity dependence of sulphur signal (as H_2SO_4) in the presence of a metal ion (Na^+ or Ag^+) using desolvation. The H_2SO_4 concentration was kept constant at 2 µg mL^{-1}. Sigmoidal function is fitted over the measured data points.

5.2.4. MEASUREMENT OF $^{34}S/^{32}S$ BY MC-ICP-MS

During the sulphur isotope ratio ICP-MS analysis dominantly two types of isobaric interferences need to be taken into account to achieve accurate results: doubly charged metals ions (e.g. $^{64}Ni^{2+}$, $^{64}Zn^{2+}$ or $^{68}Zn^{2+}$) and oxide/hydrate molecular ions (e.g. $^{16}O_2{}^+$, $^{1}H^{16}O_2^+$ or $^{16}O^{18}O^+$). Doubly charged isobaric interferences can be efficiently removed by using a prior chemical separation by the ion exchange process [31]. On the other hand, the significant interferences by oxygen and hydrogen containing polyatomic ions cannot be eliminated using only chemical separation. In our method the oxide and hydrate species were eliminated by the application of a desolvation system.

The background intensities for 1% HNO_3 solution at m/z = 32 and m/z = 34 were about 0.2 V and 0.006 V, respectively. In comparison, the intensities of 2 µg mL^{-1} S standard were 4 V and 0.19 V at m/z = 32 and m/z = 34, respectively. The contribution of blank for a 2 µg mL^{-1} S solution is estimated to be approximately 5%. As the blank intensity and the instrumental mass discrimination can change during the measurement sequence, a blank1–standard–blank2–sample bracketing procedure was used for the measurements. To correct for mass discrimination, the IAEA-S-1 standard was used, and 1% HNO_3 solution was used for background correction. The sulphur concentration of the standards and samples for the MC-ICP-MS measurement was adjusted to approximately 2 µg mL^{-1} by dilution with 1% HNO_3. For the IAEA-S-4 and the separated uranium samples, Ag standard solution was added to obtain a final Ag concentration of 27 µg mL^{-1} (equivalent to 4:1 molar ratio of $Ag^+/SO_4{}^{2-}$). By this means the HNO_3 and Ag^+ concentrations are matched for the standards and samples during the measurement.

5.2.5. DATA EVALUATION

The measured raw intensities were corrected for the background using the preceding blank sample. Then the obtained net ^{34}S/^{32}S isotope ratio of the sample was corrected for the instrumental mass discrimination using the bracketing IAEA-S-1 standard (external standardisation). For the correction the ^{34}S/^{32}S isotope abundance ratio of the IAEA-S-1 is $0.0441493 \pm 0.0000080, (k = 2)$ used [23]. Finally, the δ^{34}S values related to the V-CDT scale were calculated using Eq. 1. Three replicates were measured for each sample. For the estimation of the measurement uncertainty the ISO GUM (Guide to the Expression of Uncertainty in Measurements) approach was adapted. The calculation was performed with the GUM Workbench software [**?**]. The model developed was based on Eq. 5.1., taking into account the uncertainty contributions from the measured ^{34}S/^{32}S isotope ratios of the IAEA-S-1 bracketing standard and the sample, the isotope abundance ratio of the IAEA-S-1 $(0.0441493 \pm 0.0000080, k = 2)$, and the uncertainty of the assigned V-CDT δ^{34}S value $(0.0441626 \pm 0.0000078, k = 2)$ [23, 32]. All uncertainties are reported as expanded uncertainties (U) with a coverage factor $k = 2$.

5.3. RESULTS AND DISCUSSION

5.3.1. OPTIMIZATION OF THE SEPARATION PROCEDURE FOR SULPHUR ANALYSIS

The sulphur content of the UOC samples was recovered using water leaching. By the comparison of IC and ICP-MS results it was found that aqueous leaching is sufficient to recover sulphur almost quantitatively (i.e. sulphur is present as water leachable sulphate) [30]. However, in order to eliminate matrix constituents that can interfere with the ICP-MS analysis, an ion exchange separation method was developed. Our approach is a modified procedure developed by Das et al. [31]. The separation conditions were optimized using a Na_2SO_4 standard solution followed by IC measurement: after loading 100 µg of $SO_4{}^{2-}$, the matrix constituents not retained on the column were removed by washing with 10 mL of 0.03 M HNO_3. The elution behaviour of sulphate is shown in Fig. 5.1. Sulphate can be quantitatively eluted with 3 mL of 0.3 M HNO_3. The recovery of $SO_4{}^{2-}$ for this column condition is calculated to be higher than 96%. The eluted $SO_4{}^{2-}$ was diluted with 1% HNO_3 for approximately 2 µg mL^{-1} sulphur concentration for the isotopic measurement.

Table 5.3: Measurement results of the IAEA sulphur standards. For the IAEA-S-4 standard in different matrices (Na_2CO_3, NaOH, $AgNO_3$), the sulphur concentration was kept constant at $2\,\mu g\,mL$. The $Na^+/SO_4{}^{2-}$ or $Ag^+/SO_4{}^{2-}$ molar ratio was 4:1 in case of the IAEA-S-4 standard. Sulphur reference values are taken from Coplen et al. [20]

	IAEA-S-2	IAEA-S-3	IAEA-S-4		
			Na_2CO_3	NaOH	$AgNO_3$
Reference $\delta^{34}S_{V-CDT}$ (‰)	22.67 ±0.24	-32.55 ±0.30	16.90 ±0.30	16.90 ±0.30	16.90 ±0.30
Measured average (‰)	22.30 ($n = 5$)	-32.62 ($n = 5$)	15.5 ($n = 4$)	14.6 ($n = 5$)	17.20 ($n = 5$)
Expanded uncertainty ($k = 2$, ‰)	0.36	0.65	1.1	1.7	0.5
Deviation (‰)	-0.37	-0.07	-1.41	-2.31	0.30

5.3.2. EFFECT OF MATRIX CONSTITUENTS ON THE DESOLVATION PROCESS

In order to find the optimal conditions for the sulphur isotope ratio analysis by the MC-ICP-MS, the sensitivity of sulphur measurement was investigated. Initially, the analysis was performed with a sulphate anion standard in the form of Na_2CO_3, and it resulted in a sensitivity of approximately 2 V for $1\,\mu g\,g^{-1}$ ^{34}S. The intensity of the $^{34}S^+$ signal is in linear correlation with the S concentration ($R^2 > 0.99$) if Na_2SO_4 solution is used for the measurement. Surprisingly, however, no sulphur peak could be detected if a diluted H_2SO_4 solution was measured using the DSN-100 system coupled to the MC-ICP-MS. This phenomenon was also reported recently by Paris et al. using Aridus desolvator with a PTFE membrane [33]. In the present study, the desolvation membrane applied is likewise made of PTFE. A possible explanation also suggested by Paris et al. is the loss of $SO_4{}^{2-}$ via the desolvation process in case no additional cation is added to the sulphuric acid. We experienced the same effect, also for the dissolved IAEA standards, where no signal could be observed for IAEA-S-4 (dissolved elemental sulphur) in contrast to the other IAEA standards used, which are in Ag_2S form. It is noteworthy that the loss of sulphur has not been reported for other desolvation systems (e.g. MCN-6000 [22]), so this effect can be specific for certain membrane types and/or temperature used.

As the effect is related only to the use of desolvation, we postulate that the sulphur loss occurs through the semi-permeable membrane, if sulphate is present as sulphuric acid in the absence of other cations. In order to investigate the effect of counter-cations on the sulphur sensitivity, sodium (as NaOH) and silver (as $AgNO_3$) was added in increasing concentration to the sulphuric acid solution. The H_2SO_4 solution was prepared by dilution with 1% HNO_3, and its concentration was kept constant at $2\,\mu g\,mL^{-1}$ (expressed as S). The sulphur intensity as a function of the molar ratio of $Na^+/SO_4{}^{2-}$ or $Ag^+/SO_4{}^{2-}$ is shown in Fig. 5.2. The sensitivity reaches a maximum if the $Na^+/SO_4{}^{2-}$ or $Ag^+/SO_4{}^{2-}$ molar concentration ratio was higher than approximately 2. The saturation curve and the difference in the Na and Ag ionization energy suggest that the possible loss of sul-

Table 5.4: Measurement of the IAEA standards after chemical separation using the applied ion exchange method and measurement by MC-ICP-MS. Sulphur reference values are taken from Coplen et al.[20]

	IAEA-S-1	IAEA-S-2	IAEA-S-3	IAEA-S-4
Reference $\delta^{34}S_{V-CDT}$ (‰)	-0.30 (exactly)	22.67 ± 0.30	-32.55 ± 0.24	16.90 ± 0.30
Measured average (‰) ($n = 2$)	-0.12	23.05	-32.84	17.1
Expanded uncertainty ($k = 2$, ‰)	0.45	0.58	0.58	1.9
Deviation (‰)	0.18	0.38	-0.29	0.18

phur takes place in the desolvation unit, and that the absence of sulphur signal is not the result of the incomplete ionization of sulphur in the plasma.

The difference in the standard (IAEA-S-1 as dissolved Ag_2S) and sample composition can also lead to bias and variation in the isotope ratio [33]. When Na is added to the IAEA-S-4 standard in different forms as Na_2CO_3 (6.6 µg mL^{-1}) or NaOH, the measured S isotope ratio varies leading to inaccurate results (Table 5.3). The sulphur concentration and the $Na^+/SO_4{}^{2-}$ molar ratio were kept constant at 2 µg mL^{-1} and 4:1, respectively. The 4:1 molar ratio of Ag^+ to $SO_4{}^{2-}$ assures that sulphur isotope ratio was measured on the plateau of the sensitivity vs. Ag^+-concentration curve (Fig. 5.2), thus not influencing significantly the accuracy. For bracketing the IAEA-S-1 standard was used, and a respective matrix was used for background correction. By the addition of Ag to the IAEA-S-4, and thus approximately matching the IAEA-S-4 to the bracketing standard, accurate sulphur isotope ratio could be obtained. Matching the standard and the sample composition can also result in accurate results and can be a reason why discrepancy was found between external standardization by bracketing and internal standardization using Si ratios for mass bias correction [32]. In case of the IAEA-S-2 and IAEA-S-3 standards, where there is no need for matrix-matching due to the similar chemical composition of the standard and the sample, the measured values agreed with the reference value within uncertainty and no discrepancy was observed (Table 5.3).

In order to minimize matrix effects and avoid inaccuracy, the Ag concentration (the matrix in this case) in the measured samples has to be matched with the matrix and the intensity to the bracketing IAEA-S-1 standard. Thus, Ag standard solution was added to each sample to obtain a final Ag concentration of 27 µg mL^{-1} (equivalent to 4:1 molar ratio of $Ag^+/SO_4{}^{2-}$), while keeping the S concentration constant at 2 µg mL^{-1}. A higher $Ag^+/SO_4{}^{2-}$ ratio was chosen in order to completely eliminate the effect of cation concentration on the sulphur signal. As the ion exchange separation effectively eliminates the other matrix constituents (e.g. cations), accurate results could be achieved.

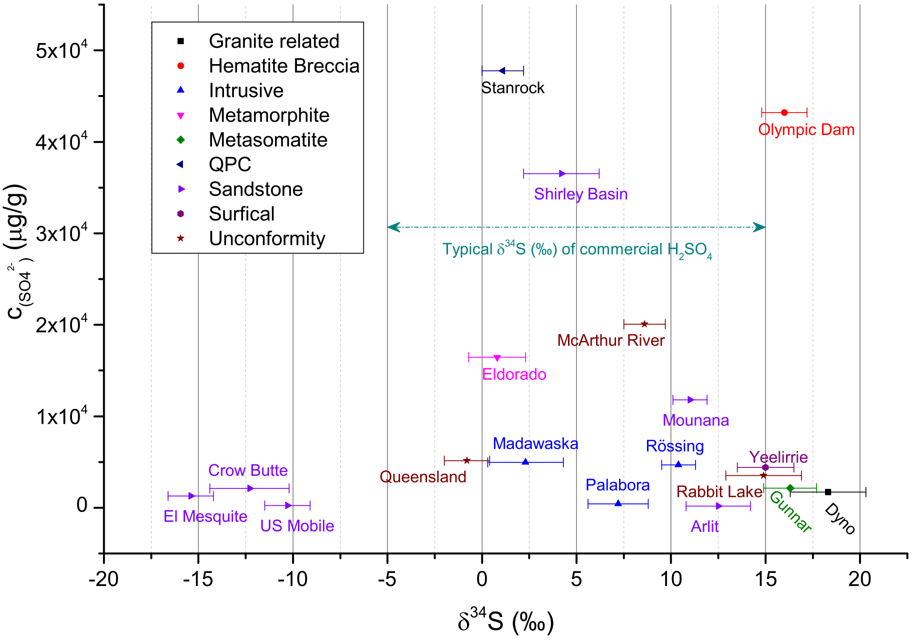

Figure 5.3: Distribution of δ^{34}S(‰) and sulphate concentration of the analysed uranium ore concentrates. The relative combined standard uncertainty of the sulphate determination by ion chromatography is less than 10%.

5.3.3. VALIDATION OF THE ^{34}S/^{32}S ANALYSIS

In order to validate the method, the dissolved IAEA sulphur standards were subjected to the ion exchange separation procedure, and the δ^{34}S values were determined by MC-ICP-MS.

The measured results are summarized in Table 5.4. The measured results agree well with the certified values as well as with the previously reported results [23, 31, 32, 34].The expanded uncertainties of the standard measurements vary between 0.45‰ and 1.9‰ with a coverage factor of 2. The dominant sources of uncertainties derive from the measured ^{34}S/^{32}S isotope ratios of the IAEA-S-1 bracketing standard, the repeatability of the measured ^{34}S/^{32}S isotope ratios of the sample and the uncertainty of the assigned V-CDT δ^{34}S value, contributing to about 45%, 45% and 5% relative to the combined standard uncertainty, respectively.

5.3.4. ^{34}S/^{32}S IN NUCLEAR MATERIALS

The developed method was applied for the measurement of uranium ore concentrates. The results are summarized in Table 5.5 and depicted in Fig 5.3 together with the sulphate concentrations measured by ion chromatography. Clear differences in the δ^{34}S

Table 5.5: δ^{34}S (‰) values for various uranium ore concentrate samples ($n = 2$). Uncertainties are expressed as expanded uncertainties with a coverage factor of 2.

Uranium ore concentrate sample	δ^{34}S (‰)	SO_4^{2-} concentration (µg g^{-1})
Gunnar (Canada)	16.3 ± 1.4	2136
Rabbit Lake (Canada)	14.9 ± 2.0	3529
Madawaska (Canada)	2.3 ± 2.0	4958
Queensland (Australia)	−0.8 ± 1.2	5150
Olympic Dam (Australia)	16.0 ± 1.2	43206
Stanrock (Canada)	1.1 ± 1.1	47780
El Mesquite (USA)	−15.4 ± 1.2	1268
US Mobile (USA)	−10.3 ± 1.2	230
Shirley Basin (USA)	4.2 ± 2.0	36530
Crow Butte (USA)	−12.3 ± 2.1	2115
Yeelirrie (Australia)	15.0 ± 1.5	4402
Dyno (Canada)	18.3 ± 2.0	1710
Eldorado (Canada)	0.8 ± 1.5	16445
Rössing (Namibia)	10.4 ± 0.9	4675
Palabora (South Africa)	7.2 ± 1.6	410
Arlit (Niger)	12.5 ± 1.7	190
McArthur River (Canada)	8.6 ± 1.1	20053
Mounana (Gabon)	11.0 ± 0.9	11793

values of the uranium ore concentrates can be observed. As the δ^{34}S value differs in several cases from the reported average δ^{34}S value in sulphuric acid (-5 to +15 ‰ [20]), it suggests that the sulphur content of the uranium ore can significantly contribute to the sulphur content of the final product, thus the measured δ^{34}S value is indicative of the uranium ore. Since the δ^{34}S values of several samples from different origin overlap, the sulphur isotopic composition can be used only as a comparative signature for the origin assessment, i.e. to use the parameter to verify or exclude of an assumed (declared) origin of a nuclear material by the measurement of a comparison sample [15, 16].

Moreover, in a few cases the δ^{34}S values can indicate a predictive nature: the El Mesquite, Crow Butte and US Mobile samples are recovered by in-situ leaching from sandstone-type deposit using carbonate leaching agent, followed by ion exchange separation. As sulphuric acid is not used in these processes in high amount compared to other metallurgical processes (e.g. acidic leaching with H_2SO_4, or use of H_2SO_4 for the solvent extraction purification), and the sulphide minerals associated with sandstone-type uranium have significantly low δ^{34}S values [25, 26], we can assume that the low δ^{34}S value together with the low sulphate content can be a useful predictive signature for uranium ore concentrates produced by in-situ leaching from sedimentary sandstone-type deposits, which are one of the major sources for uranium production (approximately 18% of world uranium resources).

5.4. CONCLUSION

A novel method has been developed and validated for the measurement of $n\left({}^{34}\mathrm{S}\right)/n\left({}^{32}\mathrm{S}\right)$ isotope ratio in uranium ore concentrates (yellow cakes). The ion exchange separation method effectively separates and pre-concentrates sulphate from uranium and the possibly interfering matrix components, such as cations. It was found that sulphur can be lost via the applied desolvation system coupled to the MC-ICP-MS, which can be overcome by adding Ag^{+} to the measured sample. This approach also provides matching the sample to the bracketing standard, thus assures accurate results. Determination of $n\left({}^{34}\mathrm{S}\right)/n\left({}^{32}\mathrm{S}\right)$ ratio in uranium ore concentrates of world-wide origin showed significant differences between the samples. This variation can be exploited to differentiate samples of different origin, for instance to verify or exclude a declared origin. Moreover, as the $n\left({}^{34}\mathrm{S}\right)/n\left({}^{32}\mathrm{S}\right)$ ratio can be indicative of the feed ore used for the production in several instances, the uranium ore deposit type can be identified, which can make this signature highly valuable to provide clues on the provenance of unknown nuclear materials, and thus trace them back to their source. Further studies are on-going to reveal further correlations between the $\delta^{34}\mathrm{S}$ value in the ore concentrate and the deposit type (geolocation).

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6

INVESTIGATION OF SULPHUR ISOTOPE VARIATION DUE TO DIFFERENT PROCESSES APPLIED DURING URANIUM ORE CONCENTRATE PRODUCTION

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The applicability and limitations of sulphur isotope ratio as a nuclear forensic signature have been studied. The typically applied leaching methods in uranium mining processes were simulated for five uranium ore samples and the $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ *ratios were measured. The sulphur isotope ratio variation during uranium ore concentrate (UOC) production was also followed using two real-life sample sets obtained from industrial UOC production facilities. Once the major source of sulphur is revealed, its appropriate application for origin assessment can be established. Our results confirm the previous assumption that process reagents have a significant effect on the* $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ *ratio, thus the sulphur isotope ratio is in most cases a process-related signature.*

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6.1. INTRODUCTION

SEVERAL new nuclear forensic signatures have been developed during the last years [2, 3]; however their routine application for real life investigation often leads to inconclusive decision except few notable ones, such as rare earth elements (REE) and isotope ratios of the major elements. This might be due to the fact that the persistence of most of these signatures during UOC processing has not been demonstrated or their variation in the course of the process has not been well understood. A more thorough study, however, would require a comprehensive set of samples from different origins following each process step and would limit conclusion to known processes. In chapter 5 the development of a novel method for the measurement of the $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ ratio in uranium ore concentrate (yellow cake) samples has been presented [4]. Sulphate content of UOC samples was leached with UP water then pre-concentrated by anion exchange separation. Afterwards 34S/32S ratio was measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). By the application of the method for real UOC samples from different origins, the usefulness of sulphur isotope ratio as a nuclear forensic signature was investigated. Variations in sulphur isotope ratio is generally expressed as δ^{34}S, the amount ratio of $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ of the sample relative to the IAEA V-CDT (Vienna Canyon Diablo Troilite) standard, expressed in ‰ and calculated using the following equation:

$$\delta^{34}\mathrm{S} = \left[\frac{\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{sample}}{\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{V-CDT}} - 1 \right] \times 10^3 \tag{6.1}$$

where $\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{sample}$ and $\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{V-CDT}$ are the $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ of ratio of the sample and IAEA V-CDT standard, respectively. The $\left(^{34}\mathrm{S}/^{32}\mathrm{S}\right)_{V-CDT}$ is defined as 0.0441626 ± 0.0000078 ($k = 2$) [5–7].

Our previous findings showed that δ^{34}S value combined with $\mathrm{SO_4}^{2-}$ concentration can be a useful signature only for UOC samples originating from those sandstone type uranium deposits, where the uranium is leached with alkaline leaching agent (typically by in-situ leaching), and not with sulphuric acid. Due to this process both their sulphate concentration and δ^{34}S value are significantly lower, appearing as an individual group well separated from other UOC samples [4]. It was also observed that the majority of the investigated UOC samples have a δ^{34}S value in the range of -5 to +15‰, which is consistent with the typical range of commonly used H_2SO_4 reagent [7]. It was also showed that in several cases the δ^{34}S value differs from the sulphuric acid value, which suggests that the uranium ore can also contribute to the sulphur content of the final product. Nevertheless, for the majority of the samples, they cannot be distinguished from each other exclusively based on the difference in sulfur isotope ratio.

Comparison between results of UOC samples and literature values of corresponding ore deposits offers the possibility to identify potential correlations. In these considerations, however, a number of factors need to be taken into account. Several previous studies have been performed on the measurement of sulphur isotopic variation related to uranium deposits in order to reveal ore forming processes. However, they focused on the analysis of sulphur minerals (e.g.: pyrite, galena, sphaleryte) associated with uranium minerals or originating from the mineralised zone of the deposit, which may be different than the chemically processed UOC samples. Further complexity arises from the fact that such deposits may show largely varying sulphur isotope ratio throughout the ore body. This is due to biological and inorganic reactions involving chemical transformation of sulphur compounds leading to variations between -40 and +50 ‰ in different deposit types [8]. Several studies have been performed to find systematic changes in sulphur isotopic variation of different U-deposit [8–13], however the following overview will concentrate only on those deposit types where the samples used in this study originate from.

Most of the publications [14–25] on sulphur isotope ratio variation in uranium deposits are related to sandstone-type deposits, in which pyrite plays an essential role in the uranium mineralization process. Sandstone-type deposits and in particular the roll-front subtype in Nebraska and Wyoming has been extensively studied by A. Meek [18]. Comparison with our study may be possible as her analysed samples were taken along the roll-front of the Three Crow deposit (7 km away from Crow Butte deposit – involved in present study), and represent the basal sands of the Lower Chadron Member, which hosts both uranium deposits. Very fine-grained pyrite, that is spatially associated with fine-grained coffinite crystals, has a wide range of δ^{34}S values, from -43 to -16 ‰ and it is consistent with biological reduction or biologically induced chemical reduction. These are essential to the formation of this type of U deposits as e.g.: biogenically precipitated aqueous sulphides and pyrite transformed from iron oxides serve as the principal reductant of U(VI) to U(IV) in the Three Crow roll-front. In general, this range of δ^{34}S value seems to be characteristic to the roll front type U-deposits [23, 26]. Northrop et al. [24] measured the δ^{34}S values of sulphides from the Henry Basin, Utah, and showed that pyrite associated with mineralized samples has an average $\delta^{34}S_{\text{sulphide}}$ value of -39.6 ‰, whereas Warren [21] measured an average -33‰ δ^{34}S value of pyrite from the ore zone of Shirley Basin deposit, Wyoming. Fewer studies can be found on samples originating from unconformity type uranium deposits. The majority of these publications are related to the Pine Creek Geosyncline in Australia and only some to the Athabasca basin, Canada. The geochemistry of Australian Pine Creek Geosyncline has been widely studied in the 1980´s. Unconformity type uranium deposits of South Alligator uranium district have been investigated by several research groups. Ayres and Eadington [26] measured sulphur isotopic variation in the Rockhole and El Sherana mine. δ^{34}S values of minerals associated with pitchblende ores spread from -5.9 to + 12.3‰. Donelly and Ferguson [27] measured sulphur isotopic variation in samples originating from three uranium deposits, Jabiluka I-II, Kongarra and Ranger I. They found that sulphide samples present in ore zones have a range of δ^{34}S values from -6 to +7‰, indicative of low-temperature biological sulphate reduction processes.

Alexandre et al. [28] analysed stable isotope variations (e.g.: N, C, S) in uraniferous bitumen originating from a sediment hosted unconformity type deposit in Southwest Athabasca. The measured δ^{34}S varies from –4.2 to –2.7 ‰. Kotzer and Kyser [29] measured various sulphides and sulphates associated with U minerals from the Athabasca Basin. Isotopic results suggest mixing of basement fluid (δ^{34}S values near 0) and basin fluid (near + 15 ‰) during uranium mineralisation. However, late sulphides, developed during re-activation and incursion of low-temperature meteoritic waters, has highly variable δ^{34}S values ranging from -25 to -57‰ and +15 to +40‰. In particular, J. Emberley et al. [30] investigated the petrography and chemistry of pyrite from the McArthur River uranium deposit. These samples were classified into six categories according to geological occurrence; in particular "ore-hosted pyrite" represents pyrite grains associated with uraninites. There is a large variation in S-isotopic compositions for pyrite within the deposit, δ^{34}S varying from -30 to + 40 ‰, but the values for pyrite associated with the U mineralization exhibit a fairly narrow, restricted range of δ^{34}S values from 0 to + 15 ‰, regardless of its occurrence. For ore-hosted pyrite this value was found to be -3 to +7 ‰.

Available sulphur isotope results related to quart-pebble conglomerate (QPC) deposits are much more limited compared to sandstone and unconformity type deposits. Pyrite crystals of various size and morphologies from Stanleigh mine (Canada) shows wide range between -9.0 to +5.5 ‰ [31]. Watanabe et al. investigated samples from the Kaapvaal Craton (South Africa) and found that bulk-rock sulphides (mostly pyrite) range from +2.7 to +7.4 ‰[32]. Isotope analyses of rounded pyrite grains from conglomerates of southern Africa (Zimbabwe, South Africa) indicate typically a small range of δ^{34}S values close to that of igneous rocks (0 ± 5 ‰) with outliers having more positive values up to 16 ‰[33]. To reveal further correlations between the δ^{34}S value of the UOC and the uranium ore (or the respective deposit type), the major source of sulphur during the different uranium production steps should be understood. First, uranium ore is extracted from the deposit by traditional excavation (underground or open pit) or by alternative extraction method like "in-situ leaching" (ISL).

The subsequent leaching of uranium from the ore can be either acid or alkaline depending on the gangue constituents. For acid leaching typically H_2SO_4 (10 - $100\,\mathrm{kg\,t^{-1}}$ ore) is used in the presence of an oxidant such as manganese dioxide or sodium chlorate to enhance solubility. Uranium is recovered from the leachate by ion-exchange (IX), solvent-extraction (SX) or direct precipitation. Uranium is obtained by eluting or stripping with an inorganic salt solution, such as sodium chloride or ammonium sulphate. When the carbonate content of ore makes acid leaching uneconomic, alkaline leaching is performed with sodium carbonate and bicarbonate solution. Uranium is recovered from the pregnant solution e.g. by sodium hydroxide precipitation [34, 35]. For ISL, both carbonate and acid leaching (dilute H_2SO_4) can be used depending on chemical and physical characteristic (e.g. permeability) of the ore horizon. Most frequently hydrogen-peroxide and oxygen are applied as oxidants, and uranium is recovered from the leach solution by ion exchange [36]. Subsequently the precipitate is filtered, dried and packaged for further processing.

Sulphate is introduced into the uranium hydrometallurgical process during the acid leaching (as H_2SO_4), elution of ion exchange or during back extraction following solvent extraction. Therefore it can be assumed that significant alteration both in the δ^{34}S value and sulphate concentration in uranium ore concentrate samples arise from these steps. In order to evaluate the applicability and limitations of sulphur isotope ratio as a nuclear forensic signature, we decided to carry out a thorough investigation involving five uranium ore samples, whose corresponding UOC samples had been analyzed in our previous study. Different leaching methods typically applied in uranium mining industry were simulated for these five ore samples in order to (a) investigate the major source of the sulphur in the UOC samples, (b) to clarify whether the isotope ratio is indicative of the process and/or of the geological origin. The $n(^{34}\mathrm{S})/n(^{32}\mathrm{S})$ ratio of the sulphuric acid used for the leaching was also measured in order to later estimate its contribution to the results. In addition, the sulphur isotope ratio variation was followed through two industrial sample sets from actual UOC production, in order to assess and compare the simulation results with real world samples.

6.2. EXPERIMENTAL

6.2.1. INSTRUMENTATION

A NuPlasma™ (NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), equipped with 11 Faraday collectors and 3 discrete dynode electrode multipliers was used for the sulphur isotope ratio measurements. The instrument was operated at low mass resolution mode ($R = 300$). The samples were introduced into the plasma using a low-flow Teflon microconcentric nebulizer operated in a self-aspirating mode in combination with a desolvation unit (DSN-100, NU Instruments, Oxford, United Kingdom).

The sulphate measurements were performed by ion chromatography (IC). The ion chromatograph (Advanced Compact IC 861, Metrohm, Switzerland) is equipped with a chemical suppressor (Module MSM II) and a conductivity detector. The separation of sulphate was carried out using an anion exchange column (METROSEP A supp 5, 150× 4.0 mm I.D.) preceded by a guard column (METROSEP Anion Dual 1, 50× 4.6 mm I.D.).

Operating parameters of the ion chromatograph and optimized MC-ICP-MS instrumental settings with data acquisition parameters are given in Chapter 5 [4].

6.2.2. REAGENTS AND MATERIALS

Ultra-pure water (UHQ System, USF Elga, Germany) was used for dilutions. Suprapur grade nitric acid (Merck, Darmstadt, Germany) was further purified by subboiling distillation and used for the sample preparation. All other reagents were of analytical grade. To prevent anionic contamination during the measurement, all lab ware was washed three times with ultra-pure water, dried in a laminar flow bench and stored in clean zipped bags. New and pre-cleaned labware was used for each sample.

The applied method was fully validated in Chapter 5. [4]; however silver sulphide reference materials (S-1, S-2, S-3) certified for sulphur isotope ratio, obtained from the International Atomic Energy Agency (IAEA) [6], were used as bracketing standard for sulphur isotope ratio measurement by MC-ICP-MS. For the analysis approximately 80 mg of each of the IAEA standards were weighed into a screw-cap Teflon vial and dissolved in 5 mL of nitric acid while heating to 95 °C on a hotplate for six hours. After cooling to room temperature, sulphate concentrations in these stock solutions were measured by IC. The stock solutions were subsequently diluted to 2 $\mu\mathrm{g\,mL^{-1}}$ (expressed as sulphur) in 1% $\mathrm{HNO_3}$ for the sulphur isotope ratio measurement.

Five uranium ore samples (Table 6.1) originating from different mines were included in this study in order to investigate the variation of sulphur isotope ratio when applying different leaching methods. For leaching suprapur grade sulphuric acid (Merck, Darmstadt, Germany) was used. All samples were finely ground and carefully homogenized.

Table 6.1: Description of the investigated samples

Mine	Deposit type	Subtype	Country	Mining
McArthur River (McA)	Proterozoic unconformity	Basement-hosted	Canada	Underground
Rabbit Lake (RL)	Proterozoic unconformity	Basement-hosted	Canada	Open pit
Ranger (R)	Proterozoic unconformity	Basement-hosted	Australia	Open pit
Crow Butte (CB)	Sandstone	Rollfront	USA	ISL
SA Nufcor (SA)	Quartz-pebble conglomerate	Quartzitic gold ore	South Africa	Underground

6.2.3. ORE LEACHING METHODS AND SEPARATION OF SULPHATE

For the analysis of uranium ore concentrate samples, aqueous leaching was found sufficient to recover sulphur almost quantitatively [4]. In uranium ore samples, however sulphur can be present both as water leachable sulphate and non-soluble sulphur compounds. To account for this, three different leaching methods (Method I, II and III) were used to investigate the sulphur isotopic composition variation introduced by the process.

Method (I): approximately 200 mg of sample was taken and 10 mL ultra-pure water was added to it in a pre-cleaned plastic bottle.

Method (II): approximately 200 mg of sample was taken and 10 mL ultra-pure 0.01M HNO_3 was added to it in a pre-cleaned plastic bottle.

Method (III): approximately 300 - 500 mg of sample was weighed into a Teflon vial and leached in 7 mL 8 M ultra-pure nitric acid while heating to 90 °C on a hot-plate for 24 hours. Approximately 200 µL of supernatant was weighed into a Teflon vial and evaporated to dryness. Afterwards the residue was dissolved in 3 mL of ultra-pure water.

In order to measure the effect of chemical leaching on the original sulphur isotope ratio, industrial leaching methods were simulated (referred to later as **Method IV**) based on the real industrial conditions (Table 6.2).

All the samples were leached for 24 hours at room temperature, centrifuged if necessary, and filtered with pre-rinsed 0.45 µm surfactant free cellulose acetate (SFCA) syringe filters (Nalgene, USA) before the ion-exchange separation. For the separation of SO_4^{2-} from the leaching solution anion exchange resin (AG 1-X4, Bio-Rad Laboratories, USA) was used. A complete description of applied anion exchange separation can be found in Chapter 5. [4].

Table 6.2: Conditions for the simulated industrial leaching (Method IV). δ^{34}S values of corresponding UOC samples were obtained from Chapter 5. [4] using Method I.

Ore	Leaching	Oxidant	T (°C)	δ^{34}S UOC [4]
McArthur River [37]	5% H_2SO_4	O_2	Ambient then 60	8.6 ± 1.1
Rabbit Lake [38, 39]	5% H_2SO_4	$NaClO_3$	65-75	14.9 ± 2.0
Ranger [39]	5% H_2SO_4	MnO_2	ambient	7.25 ± 0.35
Crow Butte [40]	0.001% $NaHCO_3$	O_2	ambient	-12.3 ± 2.1
Nufcor	10% H_2SO_4	MnO_2	50-60	n.d.

6.2.4. MEASUREMENT OF $SO_4{}^{2-}$ CONCENTRATION AND $n\left(^{34}S\right)/n\left(^{32}S\right)$ RATIO

100 µL of the filtered leachate solutions were diluted to 10 mL with ultra-pure water. Approximately 0.5 mm was injected in the ion chromatography for the determination of $SO_4{}^{2-}$ concentration in the samples. The relative combined uncertainty ($k = 2$) of the sulphate concentration by ion chromatography was less than 10%.

Sulphur isotope ratio was measured by MC-ICP-MS with blank1–standard–blank2 –sample bracketing procedure. Silver (Ag) ICP standard solution, purchased from Alfa Aesar (Specpure®, Karlsruhe, Germany), served as (a) matrix matching for the bracketing standard as well as (b) avoiding the loss of sulphur via the applied desolvation system coupled to the MC-ICP-MS. Metal ions were removed from the sample solution by ion exchange separation prior to the mass spectrometric measurement in order to avoid isobaric interferences caused by doubly charged metals ions (e.g. $^{64}Ni^{2+}$, $^{64}Zn^{2+}$ or $^{68}Zn^{2+}$). The use of the desolvating nebuliser system minimized the formation of oxide and hydrate species in the ICP-MS.

All the other uncertainties are reported as expanded uncertainties (U) with a coverage factor $k = 2$. Uncertainty contributions from the measured $n\left(^{34}S\right)/n\left(^{32}S\right)$ isotope ratios of the bracketing standard (IAEA-S-1) and the sample, the isotope abundance ratio of the IAEA-S-1 ($0.0441493 \pm 0.0000080, k = 2$), and the uncertainty of the assigned V-CDT δ^{34}S value ($0.0441626 \pm 0.0000078, k = 2$) [6] has been taken into account to calculate measurement uncertainty.

6.3. RESULTS AND DISCUSSION

6.3.1. THE VARIATION OF $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ RATIO IN URANIUM ORES

Sulphur isotope ratio and sulphate concentration results are summarised in Table 6.3 and depicted on Fig. 6.1. With regard to the different leaching methods, we can observe for all samples significant differences in the measured δ^{34}S value between Method IV and the other three (Method I-III) when using H_2SO_4 leaching. It is apparent from Fig. 6.1 that the measured δ^{34}S and sulphur concentration values of Method I-III are scattered close to each other. As it was expected samples from MethodIV have δ^{34}S values close to that of sulphuric acid (7.96 ± 0.19 ‰) used for leaching, which also explains the higher sulphur quantity. In case of the Crow Butte sample there is a small, but observable difference in the isotope ratio between Method I-II and Method III-IV. As during the process of Crow Butte there is no sulphuric acid added to the sample, we can assume that variation of δ^{34}S value is likely caused by the different solubility of various sulphur minerals.

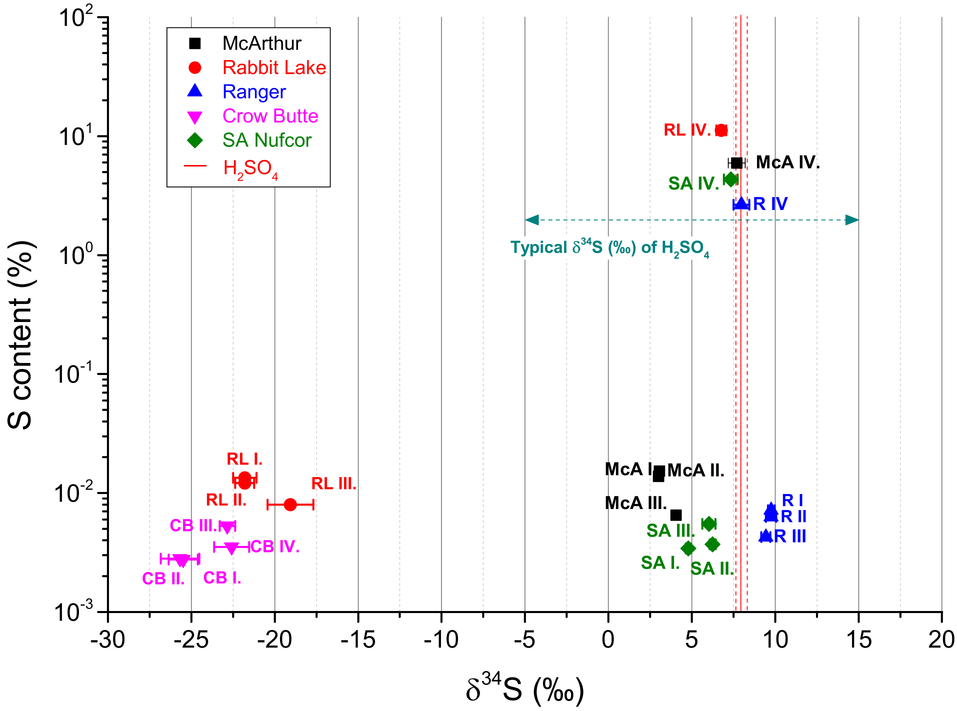

Figure 6.1: Distribution of δ^{34}S (‰) and sulphate concentration of the analysed uranium ore leachate samples. δ^{34}S (‰) value of sulphuric acid used for leaching in this study as well as typical δ^{34}S (‰) value of commercial sulphuric acid are also shown.

Table 6.3: Measured δ^{34}S results by the different leaching methods and the calculated process contribution of sulphuric acid.

Ore samples	$SO_4{}^{2-}$ in leachate ($\mu g\, g^{-1}$)	δ^{34}S (‰)	$\alpha_{process}$ (%)
McArthur I	138	3.01 ± 0.16	95 ±12
McArthur II	153	3.07 ± 0.16	
McArthur III	65	4.06 ± 0.24	
McArthur IV	59300	7.70 ± 0.51	
Rabbit Lake I	135	-21.8 ± 0.70	96 ±4
Rabbit Lake II	122	-21.8 ± 0.57	
Rabbit Lake III	78	-19.1 ± 1.4	
Rabbit Lake IV	111500	6.77 ± 0.30	
Ranger I	72	9.76 ± 0.20	99 ±30
Ranger II	63	9.75 ± 0.30	
Ranger III	43	9.44 ± 0.27	
Ranger IV	26500	6.93 ± 0.40	
Crow Butte I	28	-25.7 ± 1.2	
Crow Butte II	28	-25.5 ± 0.87	
Crow Butte III	53	-22.8 ± 0.47	
Crow Butte IV	35	-18.5 ± 7.0	
SA Nufcor I	34	4.80 ± 0.16	80 ±15
SA Nufcor II	37	6.25 ± 0.19	
SA Nufcor III	55	6.03 ± 0.40	
SA Nufcor IV	43300	7.01 ± 0.29	

Further evaluation was carried out, in order to estimate quantitatively the alteration of the δ^{34}S value by the process reagents. Previous research on application of Pb isotope ratio as nuclear forensic signature showed a similar problem, namely that radiogenic lead in the U ore was first separated during purification steps and later diluted with natural lead originating as contaminant of the process. Varga et al. demonstrated however, that by calculating the contribution of natural lead to the sample, one can partly overcome this problem [41]. In analogy, we built a model where we assumed that original δ^{34}S value of the ore deposit is close to the result obtained by leaching (Method I). For samples for which H_2SO_4 was used for leaching (Method IV), the δ^{34}S is expected, and as it was proven, to be different from the original value and closer to the value of the used sulphuric acid.

The relative contribution of "process contamination" during sulphuric acid leaching for each sample ($\alpha_{process}$) has been estimated using the following equation (Eq. 6.2):

$$\alpha_{process} = \left[\frac{\delta^{34}S_I - \delta^{34}S_{IV}}{\delta^{34}S_I - \delta^{34}S_{H_2SO_4}} \right] \times 10^2 \tag{6.2}$$

where $\delta^{34}S_I$ and $\delta^{34}S_{IV}$ are the measured $\delta^{34}S$ values of samples leached with Method I and Method IV, while $\delta^{34}S_{H_2SO_4}$ is the average isotope ratio value (7.96 ± 0.19 ‰) (n=4) of sulphuric acid applied as leaching reagent in our experiments. Results showed that contribution of sulphuric acid reagent on McArthur River, Rabbit Lake and Ranger samples is between 95-99 %, while in case of South African ore the process contribution is about 80% (Table 6.3). Therefore, one can conclude that for samples where H_2SO_4 leaching is used, the determined $\delta^{34}S$ value reflects largely, if not fully, the $\delta^{34}S$ value of used sulphuric acid.

Measurement of McArthur River samples resulted in $\delta^{34}S$ values between +3 and +4. This finding is in good agreement with the measured $\delta^{34}S$ values for ore-hosted pyrite (-3 to +7‰) from McArthur River deposit [30]. Moreover, previously measured UOC samples [4] showed a value of 8.6 ± 1.1 ‰, hence in good agreement with the result of 7.7 ± 0.51 ‰ obtained by the Method IV (industrial leaching) (Table 6.2 and 6.3). This finding indicates that $\delta^{34}S$ values of sulphur bearing process chemicals might be close to that we used for our simulations.

Our findings for the other unconformity type mines (Rabbit Lake and Ranger by Method I-III) are also in accordance with the previous studies confirming the relative large range of $\delta^{34}S$ values from -25 to 40 ‰ found earlier [8, 27, 28]. The results on Crow Butte samples are also consistent with results of previous studies on roll-front type U deposits [18, 21, 24]. Moreover, it could be demonstrated that the industrial leaching (Method IV) does not largely affect the original $\delta^{34}S$ value as no H_2SO_4 is applied.

Results of Nufcor samples shows $\delta^{34}S$ values between 4.8 and 6.25 ‰. However the H_2SO_4 value is quite close to the values of Nufcor ore (Method I-III), it still has significant effect during the leaching shifting towards its $\delta^{34}S$ value to 7.01 ‰ (Method IV). By comparing results with literature data we can conclude that they are consistent with general QPC trends for southern African samples, namely having more positive values between -5 to 16 ‰ [32, 33].

6.3.2. THE VARIATION OF $n(^{34}S)/n(^{32}S)$ RATIO IN UOC PRODUCTION

Aqueous leaching (i.e., method I) was also applied for the measurement of intermediate products in the course of UOC production. The aim was to support our results of different leaching tests by the measurement of samples coming from industrial processes and facilities. The samples originate from Nufcor, South Africa and Olympic Dam, Australia. Below are summaries of the applied processes in both UOC production facilities, respectively.

UOC is produced in the Nufcor facility by the following process: Uranium ore is leached with sulphuric acid. Ion exchange (IX), followed by solvent extraction (SX) are used to purify the acidic leachate. For the elution (IX) and the back-extraction (SX) of the

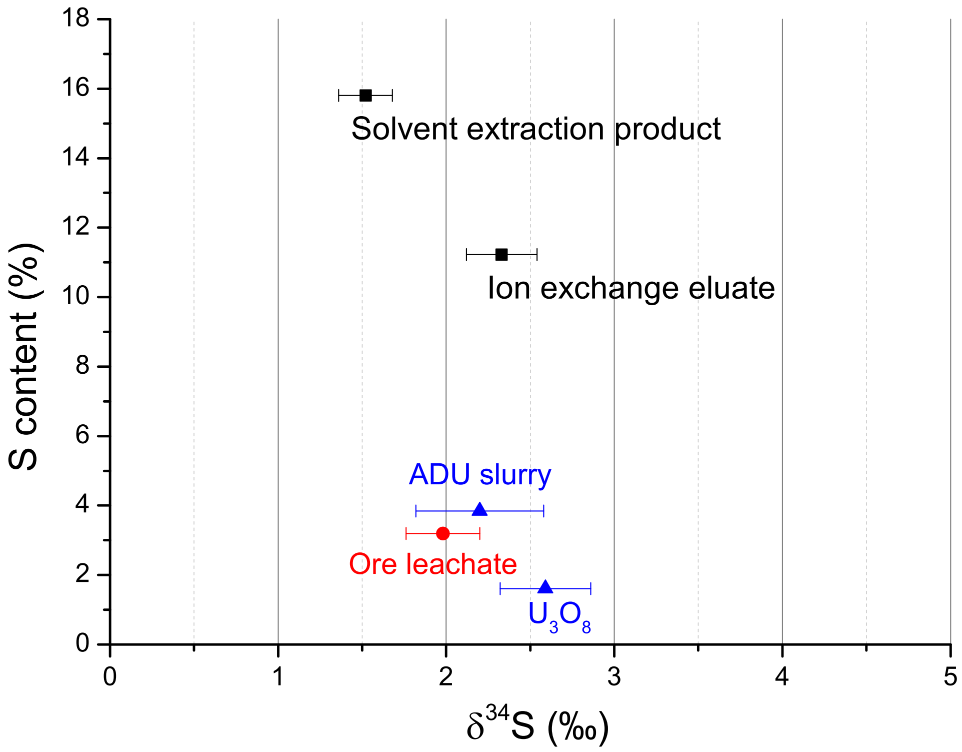

Figure 6.2: Distribution of δ^{34}S (‰) and sulphate concentration of the Nufcor samples during the UOC production.

uranium 12% sulphuric acid and ammonium sulphate is used, respectively. In the presence of ammonia, uranium is precipitated as ammonium di-uranate (ADU). The ADU slurry (15 wt% U_3O_8) is then filtered and dried to ADU powder, which is finally calcined to U_3O_8 at 490 °C. Samples were collected at each stage of the process in order to follow the flow of material originating from the same feed.

At Olympic Dam site, after crushing and grinding, the ore is subjected to a flotation circuit, where uranium containing ore is separated from tailings with approximately 90% efficiency. The uranium is leached with sulphuric acid in the presence of $NaClO_3$ oxidant at approximately 50 °C. After residual copper is separated, uranium is further purified by SX circuits. Stripping is done with ammonium sulphate and precipitated as ammonium di-uranate (ADU). The final oxide product (U_3O_8) is obtained by calcination of dried ADU at about 760 °C [39]. The investigated samples include uranium ore, ADU and calcined U_3O_8. Samples were collected during fall of 2001 and are assumed to represent consecutive production steps.

The sulphur concentration and the $n\left({}^{34}\mathrm{S}\right)/n\left({}^{32}\mathrm{S}\right)$ were measured on the respective samples using aqueous leaching (hence, Method I) and the results are shown in Figs. 6.2 and 6.3. As can be seen in Fig. 6.2, the sulphur concentration in the investigated Nufcor samples is significantly increasing from the ore to the samples representing solvent and

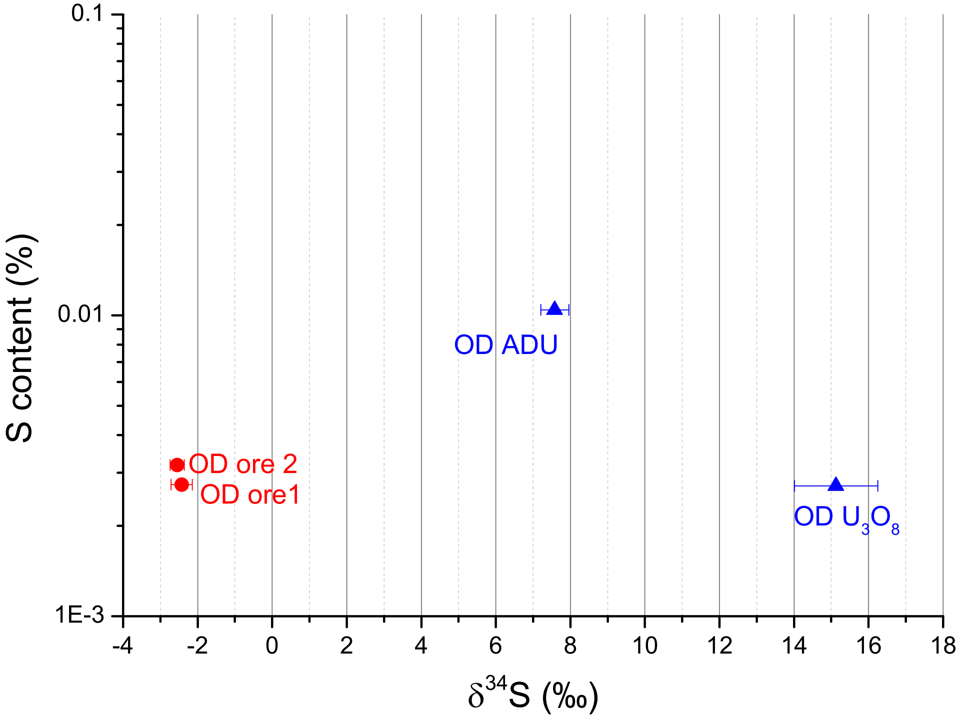

Figure 6.3: Distribution of δ^{34}S (‰) and sulphate concentration of the Olympic Dam (OD) samples during the UOC production.

ion extraction stages. This is obviously due to sulphur containing reagents added in large amounts during leaching, IX and SX circuits. During any of these steps $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$ value does not change notably, whilst the sulphur concentration is later significantly reduced by the precipitation of ADU and by the calcination of ADU to the final oxide product (U_3O_8).

When we compare the simulated leaching results (Table 6.3) and the real industrial samples of Nufcor, we can see that the initial δ^{34}S value of the ore measured by Method I-III is 5.69 ± 0.25 ‰. In the real samples we can see that the ore leachate is 1.98 ± 0.22 ‰, while IX and SX is 2.33 ± 0.21 ‰ and 1.52 ± 0.16 ‰, respectively. This result supports our finding that leaching is the step which significantly changes the initial ore value. Moreover, the results clearly show the change, in both the δ^{34}S value and sulphate concentration, caused by sulphur bearing solvents during IX and SX.

The results for sample set originating from Olympic Dam are shown in Figure 6.3. As expected, the sulphur contribution of process chemicals has an obvious effect on the sulphur isotope ratio in ADU and U_3O_8 products, resulting in a shift towards positive δ^{34}S values. The sulphate concentration increases from the ore to ADU and decreases then again once the material is calcined from ADU to U_3O_8. Associated with the latter process step we observe also a shift towards higher δ^{34}S values. This change might attributed to isotopic fractionation occurring during calcination (at high temperature) involving the preferential evaporation of the lighter (sulphur) isotope.

In summary the results of both real sample sets support the results obtained from our leaching studies in which we demonstrated that the sulphur isotopic signature of the ore is altered due to the high amount of sulphur containing reagents added to the material flow during the UOC production process, thus reflecting at the end the δ^{34}S value in the used sulphur containing reagents.

6.4. CONCLUSION

The present study was undertaken to further evaluate the suitability of the sulphur isotope ratio as indicator of the origin or processing history of uranium ore concentrates, hence as a nuclear forensic signature. In particular, we investigated the impact of sulphur isotope alteration caused by process chemicals used for the production of uranium ore concentrates. The findings of this investigation complement those of our earlier studies [4] and the following conclusions can be drawn:

In case uranium leaching is performed in the absence of sulphuric acid (e.g. in in-situ leaching where $NaHCO_3$ is used as leaching agent), the sulphur isotope ratios measured in the ore concentrate samples reflect the values observed for the ore. Hence, in this case the sulphur isotope ratio provides an additional hint on the geological origin of the uranium. When sulphuric acid is used as leaching agent (or for back-extraction of uranium during purification), the sulphur isotope ratio will essentially reflect the values of the sulphur containing reagents used for processing the ore.

The findings of this study, based on a combination of different leaching tests and the investigation of the sulphur isotope ratio variation during UOC production from ore to U_3O_8 product in real industrial samples, showed that process reagents have a significant effect on the $n\left(^{34}\mathrm{S}\right)/n\left(^{32}\mathrm{S}\right)$, thus the sulphur isotope ratio is largely a process-related signature.

Acknowledgement

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7

DISCUSSION AND CONCLUSION

"Although it is unlikely that any single isotope system will provide sufficient information to uniquely locate the source location of an interdicted UOC sample of unknown origin among the hundreds of currently and historically active uranium mines, the application of multiple isotopic systems will dramatically restrict the number of possible sources and prove invaluable in this endeavour."

dr. Gregory A. Brennecka [1]

7.1. SUMMARY OF THE RESULTS

EXPANDING the nuclear forensic toolset by investigating new nuclear forensic signatures is one of the most important tasks of nuclear forensic researchers. Published case studies clearly show that no single signature serves as a "silver bullet" [2–4] that can lead to a reliable, credible conclusion on the history and origin of nuclear material. This means that several parameters of the material have to be measured and combined to a "signature" until the circle of e.g. potential provenances can be narrowed down and a conclusion with high confidence can be drawn (Fig. 7.1). In the more than 20 years since nuclear forensic research emerged as a new branch of science, several groups worldwide (ITWG Nuclear Forensics Laboratories (INFL)) have engaged in research and development of new signatures to support nuclear forensic investigations [5]. During this time dedicated methodologies for analysing nuclear material, a systematic approach and the scientific basis for nuclear forensic investigations have been developed, validated and established.

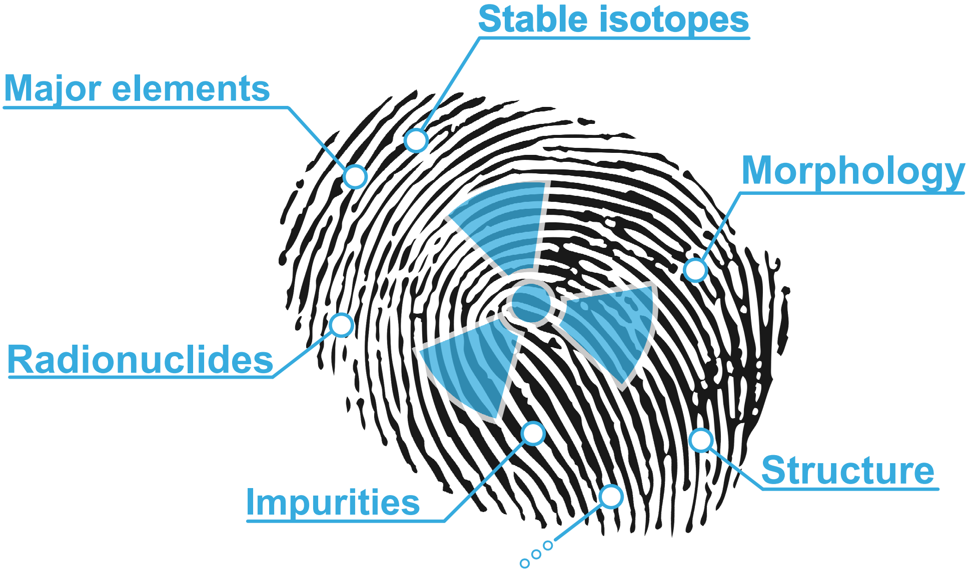

Figure 7.1: Nuclear forensic signatures

The aim of this work was to further support nuclear forensic research by evaluating new promising candidate signatures in natural uranium compounds, namely sulphur and neodymium isotope ratio, alongside with the development of optimized analytical methods. Therefore the thesis can be separated into two parts.

In the **first part**, (Chapter 2-4) the usefulness of the neodymium (Nd) isotope ratio as a nuclear forensic signature for provenance analysis is demonstrated and the analytical methodology developed is presented. Although there are several published papers on the separation of Rare-Earth Elements (REEs) from uranium matrix and on the sequential separation of Rare-Earth Elements REEs from each other, the methodologies had to be further developed and adapted to be suitable for our purposes. First of all, in natural uranium-based nuclear materials REEs are present at trace levels (below $\mu g\,g^{-1}U$), which immediately raised an analytical challenge, namely the development of a method to separate and preconcentrate the REEs from the high purity uranium matrix (Chapter 2). Secondly, as the mass spectrometric analysis of Nd isotope ratios may suffer from isobaric interferences of Ce and Sm isotopes, it is prerequisite to separate these from Nd prior to the mass spectrometric measurements. Straightforward separation and preconcentration of trace-level Nd from other heavier REEs has been established in order to perform precise $^{143}Nd/^{144}Nd$ isotope ratio measurements by MC-ICP-MS in various uranium ore and uranium ore concentrate (UOC) samples (Chapter 3-4).

To overcome the first analytical challenge explained above, a new pre-concentration method was developed for the analysis of trace-level amounts of REEs in high purity uranium (U) samples. As REEs are present in trace level in nuclear grade uranium products, a relatively high sample amount (100 mgU/samples) had to be processed. The developed method is a combination of co-precipitation and extraction chromatographic (EXC) separation and it is followed by the measurement of the purified REE fractions using inductively coupled plasma mass spectrometry. Co-precipitation was found to be the most suitable chemical separation technique which is capable of handling such a high amount of sample whilst still being very selective for the elements of interest. Subsequent EXC ensured the almost complete separation of REEs from the uranium matrix. The achievable cumulative uranium decontamination factor was about 10^8 - 10^9, which is high enough to avoid matrix effects (i.e. decrease in sensitivity) during the ICP-MS measurement.

For the measurement of the ^{143}Nd/^{144}Nd isotope ratio in various uranium-bearing materials, an improved extraction chromatographic procedure has been developed. A coupled extraction chromatographic procedure has been used for the lanthanide group separation from the uranium matrix and the subsequent separation of Nd from Sm and heavier lanthanides. High precision and accuracy measurements of ^{143}Nd/^{144}Nd isotope ratio were performed by MC-ICP-MS. Validation of the method was achieved by measuring standard reference materials (La Jolla, BCR-2, JB-2), while applicability of the method has been demonstrated by the measurement of uranium ore and uranium ore concentrates (UOC). Samples containing a few hundred nanograms of Nd per gram sample could be measured with a sufficiently low uncertainty (0.05 %) to distinguish between different samples. The investigated samples showed distinct ^{143}Nd/^{144}Nd ratios depending on the ore type and on the Sm/Nd ratio; for certain deposit types (e.g. intrusive or quartz-pebble conglomerate) grouping could be observed when ^{143}Nd/^{144}Nd ratio was plotted against the Sm/Nd ratio. The ^{143}Nd/^{144}Nd isotope ratio in the investigated samples has also smaller within mine variation compared to other isotope ratios (e.g.: Sr, Pb) studied previously for nuclear forensic purposes (Table 1).

The benefit of the combination of the developed methodologies explained above has been demonstrated in Chapter 3. Previously analyzed samples of very low REE concentration (< 1- 200 $\mathrm{ng_{Nd}}$ /$\mathrm{g_{sample}}$) in which the REE elemental pattern and Nd isotope ratio results had suffered from large uncertainties were re-measured resulting in significantly improved uncertainty. Based on the present work precise Nd isotopic data could be established and compiled in a comprehensive database for supporting nuclear investigations (Fig.7.2). This latter point is essential for increasing confidence in interpretational results and for accelerating the investigative process [6].

Table 7.1: Within-mine variation calculated for different isotopic signatures in 4 parallel samples originating from Beverley mine

Deposit	Mine	$^{143}Nd/^{144}Nd$	$^{87}Sr/^{86}Sr$	$^{207}Pb/^{206}Pb$
Sandstone	Beverley A1	0.511935 ± 0.000059	0.71775 ± 0.00003	0.23332 ± 0.0252
	Beverley A2	0.511657 ± 0.000026	0.71852 ± 0.00024	0.14298 ± 0.0007
	Beverley A3	0.511826 ± 0.000033	0.71758 ± 0.00001	0.1765 ± 0.0011
	Beverley A4	0.511849 ± 0.000025	0.71781 ± 0.00001	0.1379 ± 0.0029
	Average ± RSD	0.511817 ± 0.05%	0.71792 ± 0.12%	0.17268 ± 50.86%

For most of the signatures their persistence during UOC processing has not yet been demonstrated or their variation in the course of the process has not always been well understood. The results of this thesis demonstrate the persistence of the Nd isotope ratio throughout chemical processing of natural uranium at the front end of the nuclear fuel cycle.

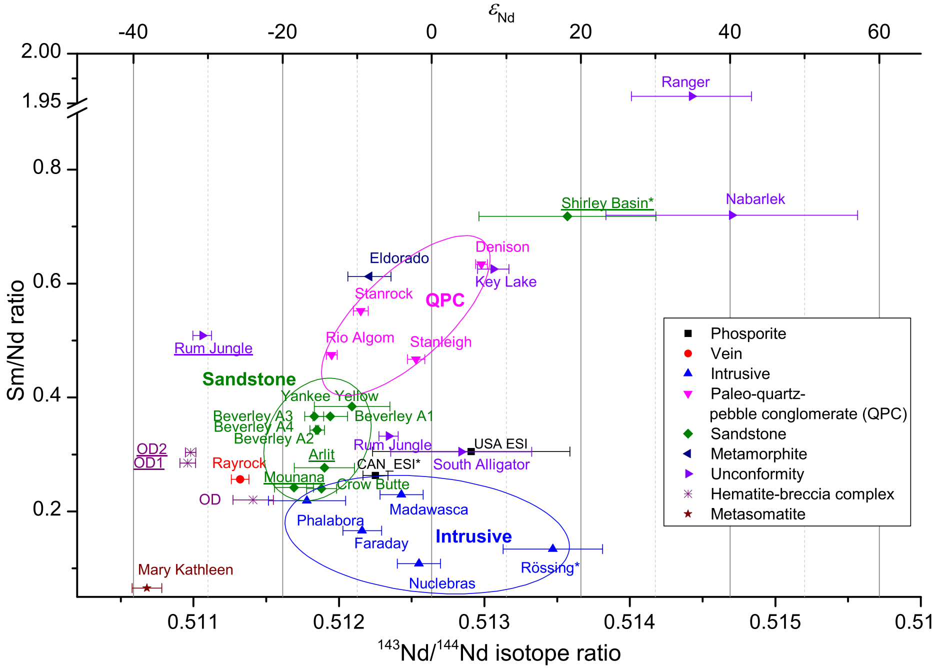

Figure 7.2: Variation of the $^{143}Nd/^{144}Nd$ ratio as a function of Sm/Nd ratio in the investigated uranium ore and ore concentrate samples with methods developed in Chapter 3. OD – Olympic Dam; underlined labels correspond to ore samples, while labels with $*$ stand for results achieved by coupled separation method (Chapter 3-4).

The **second part**, (Chapter 5-6) describes the evaluation of the Sulphur isotope ratio as a potential nuclear forensic signature, in particular for the origin assessment of natural uranium products. In contrast to the REE pattern, the sulphur isotope ratio has never been investigated with regard to its nuclear forensic significance. The sulphur content in uranium ore concentrates and in uranium ores is at similar level (varying between 100 and 30 000 $\mu g\,g^{-1}$). However, as sulphur is also introduced into the process stream as a chemical reagent or solvent (e.g. as H_2SO_4), the sulphur isotopic composition might be indicative both of the process (chemicals used) and the ore type . Similar to the structure of the first part of this thesis, first the procedure and method for the separation of sulphur from the uranium matrix was developed and a measurement protocol was established for the subsequent mass spectrometric determination of the sulphur isotope ratio. Then, the developed method was applied for the measurement of a set of UOC samples from worldwide origin (Chapter 5-6) in order to identify correlations between the $^{34}S/^{32}S$ ratio and the origin of the investigated samples (Chapter 6). Results are shown in Fig.7.3.

Separation of sulphate from uranium matrix was performed in two steps. First, the sulphate inventory of UOC samples was leached by water for 24 hours at room temperature and then the sulphate was further purified and preconcentrated from the filtered leachate by an ion exchange separation step. The recovery of $SO_4{}^{2-}$ for the procedure is calculated to be higher than 96%. The sulphur isotope ratio ($^{34}S/^{32}S$) was measured by MC-ICP-MS, where measurement phenomena (arising from the sample introduction system) posed some challenges. The sulphate signal intensity of $SO_4{}^{2-}$ in the mass spectrometer decreased significantly due to the desolvation process. This effect might be specific for certain membrane types (e.g.: PTFE membrane) and/or temperature applied, consistent with the explanation by Paris et al. who reported the same problem [7]. We could solve the problem by adding Ag^+ (in the form of $AgNO_3$) as additional counter-cation to the sulphuric acid. The method was validated by the measurement of IAEA sulphur standards (IAEA –S1, -S2, -S3, -S4), bracketing the sample measurements. The analysis results of UOC samples, originating from almost 20 different mines, showed significant differences between the samples. In most cases the $\delta^{34}S$ value is in the range of the reported average $\delta^{34}S$ value in sulphuric acid (-5 to +15 ‰) [8] which suggest that acid leaching during UOC production significantly changes the initial isotope ratio of the ore. However, in case of samples, which were treated with carbonate leaching agent, sulphur isotope ratio is indicative to the geological origin (e.g.: sandstone type uranium deposits).

Further study was undertaken to investigate the impact of sulphur isotope alteration caused by process chemicals used for the production of uranium ore concentrates. A total of 5 uranium ore samples originating from different mines were included in this study. In order to investigate the variation of sulphur isotope ratio different industrial leaching techniques were simulated in the laboratory, respectively, according to conditions found in literature. The sulphur isotope ratio variation during uranium ore concentrate (UOC) production, from ore to uranium ore concentrate product, was also followed using two sample sets obtained from two facilities. The findings of this study showed that process reagents have a significant effect on the $n(^{34}S)/n(^{32}S)$. Even if original $n(^{34}S)/n(^{32}S)$ is extremely low (e.g.: Rabbit Lake – around -20 ‰ $\delta^{34}S$), it is replaced by the values of sulphur containing chemicals applied during the process. Thus, it is proven that the sulphur isotope ratio is largely a process-related signature. These findings complement those of our earlier studies (Chapter 5).

The main goal of the current study was to determine the usefulness of Nd and S isotope ratios as nuclear forensic signatures for origin assessment. The results of our experiments confirmed that $^{143}Nd/^{144}Nd$ ratio belongs to the material inherited signatures because it is not altered during uranium processing. $^{143}Nd/^{144}Nd$ isotope ratio and Nd/Sm elemental ratio show a strong correlation with certain deposit types (e.g. intrusive or quartz-pebble conglomerate). Moreover, comparison to other isotope ratios (e.g.: Pb,

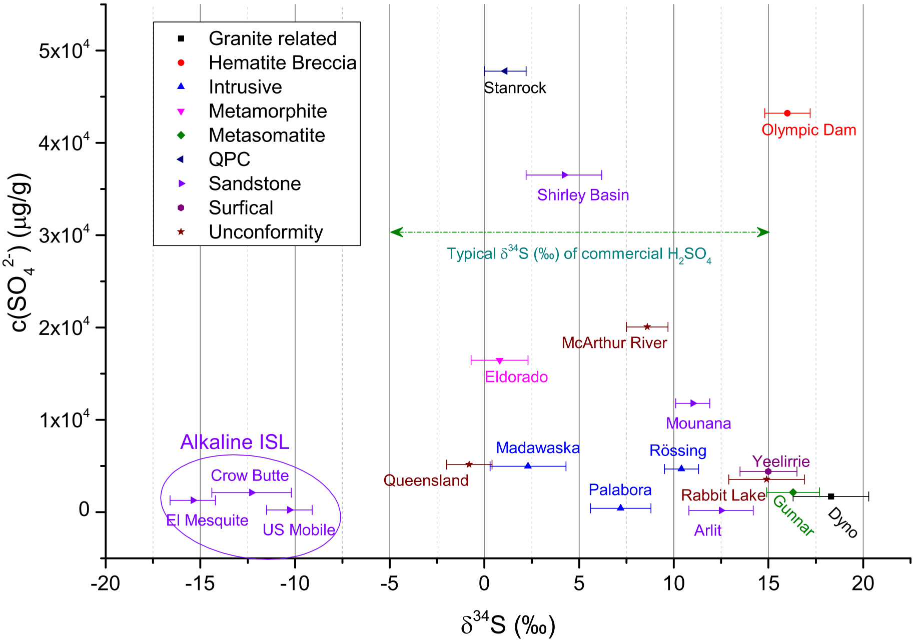

Figure 7.3: Distribution of δ^{34}S)(‰) and sulphate concentration of the analysed uranium ore concentrates (Chapter 5).

Sr) demonstrated that the ^{143}Nd/^{144}Nd isotope ratio in the investigated samples shows smaller within mine variation (Table 7.1).

The research has also shown that the ^{34}S/^{32}S ratio belongs to both material and process related signatures. When carbonate is used as leaching agent the sulphur isotope ratio is indicative of the geological origin (e.g.: sandstone type uranium deposits). However, the ^{34}S/^{32}S ratio in the majority of UOC samples was found to be largely a process-related signature as production often involves sulphur bearing chemicals and consequently significantly changes the initial sulphur isotope ratio significantly. Although isotopic signatures have been assumed to be more robust during the UOC production than elemental content, this thesis has demonstrated that process reagents can have significant effect on isotopic signatures too.

Table 7.2: Summary of investigated isotopic signatures for nuclear forensic purposes

Isotope ratios (IR)				
Major Isotopic Composition	Minor isotope ratio	Trace elements	Stable isotopes	Parent-daughter ratio
^{238}U, ^{235}U	$^{235}U/^{234}U$, $^{234}U/^{238}U$, $^{236}U/^{238}U$	$^{87}Sr/^{86}Sr$, $^{207}Pb/^{206}Pb$ $^{143}Nd/^{144}Nd$	$^{18}O/^{16}O$, $^{34}S/^{32}S$	$^{230}Th/^{234}U$, $^{228}Th/^{232}Th$, $^{231}Pa/^{235}U$
Enrichment–intended use/reactor type, nuclear fuel type, weapon type, and device type	Possible identification of origin of mine & type of depositional settings	Possible identification of origin of mine and the ore type	Possible indication of processing history of UOC & location of the facility	Production Date

It can be concluded that the two new nuclear forensic signatures, investigated in this thesis, expand the group of characteristic properties (Fig. 7.1.), which support the investigation of unknown nuclear materials. They belong to the group of stable isotopic signatures, which have been summed up in Table 7.2., and provide information on the provenance of the material. However, to identify seized samples unambiguously, the combination of the available signatures is necessary. Therefore coupling e.g. the REE pattern with the Nd data is an obvious choice. REE pattern has been found to be a strong indicator on the deposit type of the uranium ore, although it is not to differentiate between ores from different mines in a straightforward manner. By the combination of these two signatures (Nd and REE pattern) the geological origin of the sample can be traced back with higher reliability. Following the reasoing, the application of sulphur isotopic signature with the anionic impurity ratios (e.g. $SO_4{}^{2-}/Cl^-$, $NO_3{}^-/F^-$ can provide deeper understanding on the process the sample went through, thereby narrowing down the possible sources of the sample.

Furthermore the signatures developed in this thesis allow the possibility of combining not just the information they provide but they can also be based on common separation procedures. This means that from the same sample aliquot the above mentioned coupled signatures can be reached. For example anionic impurities from UOC samples are leached by deionised water. Splitting this stock solution into two aliquots one part can be used to measure full anionic pattern, while other part can be used to perform sulphur isotope ratio measurement.

7.2. OUTCOME

The main outcome of the thesis can be summarized as follows:

- New analytical methodologies have been developed for the pre-concentration and purification of the elements of interest.
    - By the application of the preconcentration method we could extend the range of applicability of the REE pattern to high purity refined uranium-oxides, thus REE pattern can be followed along the front-end of the nuclear fuel cycle (Chapter 1).
    - By the application of the sequential extraction chromatographic separation Nd isotope ratios of uranium ore concentrate samples could be measured with high accuracy.
    - The combination of the two developed methods was successfully applied for the measurement of Nd isotope ratio in samples having very low Nd content (< 1-200 ng_{Nd} /g_{sample}).
    - Furthermore, the combination of the two developed methods allows using a single sample aliquot and a straightforward sample preparation to reach several nuclear forensic signature such as REE pattern, Sm/Nd elemental ratio combined with the $^{143}Nd/^{144}Nd$ isotope ratio.

- New nuclear forensic signatures were investigated and evaluated for provenance analysis.
    - The $^{143}Nd/^{144}Nd$ isotope ratio was found to be indicative of certain ore deposit types, thus it is a signature pointing at the geological origin of natural uranium.
    - The within-mine variability of the $^{143}Nd/^{144}Nd$ isotope ratio was also investigated and found to be smaller than other previously investigated isotopic signatures such as Pb and Sr.
    - The $^{34}S/^{32}S$ isotopic ratio was found to be indicative for the geological origin only for ore concentrate samples gained by in-situ carbonate leaching.
    - When sulphuric acid is used as leaching agent, the $\delta^{34}S$ values between samples of different origins were found to be overlapping and lying in the range reported for commercial sulphuric acid, i.e. at $\delta^{34}S$ values of -5 to +15‰.
    - In extended studies the effect of different dissolution techniques on the $\delta^{34}S$ value as compared to the original value of the ore was investigated. Wherever sulphuric acid is applied at some point in the process, the $\delta^{34}S$ value of UOC product reflects the process applied and not the geological provenance of the material. Thus, sulphur isotope ratio is in most cases a process-related signature.

- Both ^{143}Nd/^{144}Nd and δ^{34}S values were found to be useful comparative signatures. Therefore the results obtained on a variety of samples can be considered as an essential contribution for a data base (nuclear forensic library) required for the comparative evaluation of results in support of nuclear forensic investigations.

7.3. OUTLOOK

Isotopic signatures have been increasingly used for nuclear forensic purposes. The studies in this thesis resulted in the identification of new signatures and in the development of respective analytical techniques. The signatures and methods were applied to a sample set reflecting a large part of the UOC production sites worldwide and to selected samples from few mining/milling facilities to understand the propagation and robustness of these signatures throughout the process. In particular the understanding of the latter could be further improved by samples from a larger number of facilities.

One chapter of this thesis has been devoted to demonstrate the advantage of combining the different separation procedures developed. The combined method, however, has also promising potential to measure additional elements of interest, such as Pu, Th, or Am, if they are present in the sample. This would be a fruitful area for further work.

There are also other potential isotopic signatures which might be worth being investigated. Sm, and Rb could be useful to supplement existing Nd and Sr results and measure the ^{147}Sm/^{144}Nd and ^{87}Rb/^{86}Sr isotope systems, respectively, in order to provide an even better indication of the mineralogy of the original uranium ore. From analytical point of view it is also straightforward, as the chemical separation method developed for the Nd can be extended for the separation of Sm.

Furthermore recent studies showed that Rb–Sr/Sm–Nd isotopes can be simultaneously measured by laser ablation (LA) ICP-MS in natural minerals [8]. However achieved accuracy of this study is comparable to measurements with solution methods, their samples were limited to natural minerals with enriched Sr and Nd contents, such as apatite, perovskite, loparite and eudialyte. Therefore, another possible area of future research would be to investigate the applicability of this technique for the above mentioned purpose. It might be very advantageous as not only sample separation time could be decreased but as LA-MC-ICP-MS is quasi a non-destructive technique therefore the required sample amount might be less as well.

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SUMMARY

Nuclear forensic is a young and complex branch of science. The easiest way to have an idea about nuclear forensic is to imagine it as television series CSI (series of Crime Scene Investigation) dealing with radioactive material. The science of nuclear forensics is aimed at solving questions like, 'where does the material come from?' and 'what is the intended use?' To solve this question the science uses nuclear forensics tool kits. Currently, much work is done by researchers into the expansion of nuclear forensics tool kits that support the successful identification of seized material. The expansion of the toolkit is mainly focussed on (1) the development of classical and radio-analytical techniques and methods (2) building of comprehensive databases and (3) the investigation and validation of new forensic signatures. Nuclear forensics signatures can both be physical and chemical properties of the material under investigation. Physical properties include properties such as visual appearance and geometry. Chemical properties include properties such as chemical/isotopic composition and impurities. These measurable parameters originate either from the feed material used or are incorporated during the production process and provide a hint on the age, intended use and the origin of the investigated material. In particular the origin assessment of the nuclear materials is complex as there is no single method or single signature to identify it exclusively. Several signatures such as rare earth element (REE) pattern, isotopic ratios need to be measured to differentiate between samples. However, there still exists a great lack of reference data in literature on these forensic signatures, and especially for isotopic ratios. It is for this reason that the research for this thesis was proposed.

The aim of this research was to determine the usefulness and applicability of isotopic ratios of ^{143}Nd/^{144}Nd and ^{34}S/^{32}S as a forensic signature in an origin assessment. In addition, the research looked into the propagation and the robustness of the isotopic ratios during uranium production. For both isotopic ratios we, firstly, developed a method for the separation of the element of interest from the matrix and for the measurement of the isotope. Secondly, we validated the method using reference materials and lastly, we evaluated the isotopic ratios, as a nuclear forensics signature, by applying the methods that we developed onto different real samples, uranium ores and uranium ore concentrate products.

In addition, a novel method has been developed for the pre-concentration and measurement of REE from high purity uranium oxide (UO_2 and UO_3) originating from an undisclosed refining and conversion facility. Although, the REE are found to be less prone to change during the chemical process of uranium production, their robustness has been only evaluated in uranium ore concentrate (UOC) products. In the later stages UOC samples are mixed and further purified (refined) to be made into an appropriate form for the enrichment or for the direct application as nuclear fuel in energy producing reactors. At this stage the REE concentration in uranium products reach $\mathrm{ng\,g^{-1}}$ – $\mathrm{pg\,g^{-1}}$ level, which could be one of the possible reasons for the lack of experimental results related to these samples.

The obtained REE patterns have been compared to REE patterns of feed materials and similarities can still be recognised. Because the measured patterns of the samples and the feed material show close similarities, it can be concluded that the feed matetial can be traced vi athe REE pattern. Furthermore, as the feed material was mixed from four different UOC sources, deposit type of the main contributor of REE impurity in the feed material could be traced back.

For the investigation of Nd as a nuclear forensic signature, a combination of an extraction chromatographic separation has been developed to separate Nd from the other interfering elements, and the uranium matrix. The isotope ratio has been measured with a multi-collector ICP-MS. After the validation of the method, it has been used to measure ^{143}Nd/^{144}Nd isotope ratio in uranium ore and ore concentrate samples of different origins. Results showed that the Nd isotope as a function of Sm/Nd ratio can be a useful signature, as samples shows grouping according to their deposit types when they are plotted as a function of these two parameters. These findings confirm that ^{143}Nd/^{144}Nd isotope ratio belongs to the group of origin related signatures.

The second section of this thesis describes the potential of the S isotope ratio as a nuclear forensic signature. Ion exchange separation method has been developed to separate sulphur from uranium matrix. The results of this study show that the sulphur isotope ratio is a straightforward indicator of the geological origin in case of samples originating from sandstone type deposits and processed with alkaline leaching agent. In case of other samples the application of sulphur isotope ratio as a function of sulphur concentration was not found to be effective enough to differentiate between the origin or deposit type of the investigated samples.

Therefore an extended study was made with the aim of assessing the persistence of the sulphur isotope ratio throughout the course of uranium ore concentrate production. Unprocessed uranium ore samples have been leached with different methods to estimate their original sulphur isotope ratio, while industrial leaching has been simulated to reveal any change in the isotope ratio during the process. According to assumptions, this study revealed a significant difference in the sulphur isotope ratio between the values of original and industrially processed ore. It has been proven that sulphuric acid applied during chemical leaching can change original ore values up to 90%. Therefore ^{34}S/^{32}S can be classified as a process related isotopic signature.

By the measurement of Nd and S isotopic data of uranium ore samples originating from five different mines and uranium ore concentrates originating from twenty different mills, this thesis contributed to complement the literature on isotopic signatures and expands both the nuclear forensic toolkit and library. Although none of the investigated isotopes can serve as a “silver bullet” in the nuclear forensic investigation, they are still useful when complemented with each other and other characteristics of the materials, such as Sr, Pb, or REE pattern, in order to differentiate material that shows similar source or production histories but is derived from unrelated sites.

SAMENVATTING

Het nucleaire forensische onderzoek is een jonge tak binnen de wetenschap. Het laat het zich het makkelijkst vergelijken met de televisieserie CSI “Crime Scene Investigation”, maar dan toegespitst op nucleair en radioactief materiaal. Het onderzoek is erop gericht vragen zoals, ’waar komt het materiaal vandaan?’ en ’wat is het beoogd gebruik?’ te beantwoorden. Om deze vragen op te lossen wordt er veelal gebruikt gemaakt van nucleair forensische "gereedschappen". Momenteel wordt er veel onderzoek verricht om het nucleair forensische "gereedschappen", dat wordt gebruikt om in beslag genomen materiaal te identificeren, uit te breiden. Dit onderzoek richt zich voornamelijk op de volgende drie zaken: de ontwikkeling van klassieke chemische en radiochemische analysetechnieken en -methoden, het samenstellen van databanken en ten slotte op het onderzoeken en valideren van nieuwe forensische signaturen. Deze nucleair forensische signaturen zijn chemische of fysische kenmerken van het gebruikte moedermateriaal of sluipen erin tijdens het productieproces, voorbeelden zijn uiterlijk, afmetingen, chemische samenstelling, isotopenverhouding en onzuiverheden. Door het analyseren van deze kernmerken kan de leeftijd van het materiaal, het beoogd gebruik en de herkomst van het materiaal worden achterhaald.

Vooral het herleiden van de herkomst van het materiaal is ingewikkeld, dit omdat er niet één enkele specifieke methode of één enkele forensische signatuur bestaat om een materiaal mee te identificeren. Er zullen dus altijd meerdere signaturen met elkaar vergeleken moeten worden, zoals de patronen van zeldzame aardmetalen en isotopenverhoudingen van bijvoorbeeld O, Pb en Sr. Referentiegegevens voor deze isotopenverhoudingen ontbreken echter nog grotendeels in de literatuur. Het doel van dit proefschrift is dan ook om op zoek te gaan naar nieuwe nucleaire forensische signaturen, die kunnen worden gebruikt voor de herkomstanalyse van een nucleair of radioactief materiaal. In dit proefschrift is de bruikbaarheid van isotopenverhoudingen van ^{143}Nd/^{144}Nd en ^{34}S/^{32}S als forensische signaturen voor een herkomstanalyse onderzocht. Naast hun bruikbaarheid in een herkomstanalyse, is er ook gekeken naar de robuustheid en eventuele veranderingen in de isotopenverhoudingen van ^{143}Nd/^{144}Nd en ^{34}S/^{32}S tijdens de uraniumproductie (het begin van de nucleaire splijtstofketen). Voor beide elementen is eerst een methode ontwikkeld om de isotopen te scheiden van de matrix en om de isotopen te meten. Vervolgens is de scheidingmethode gevalideerd aan de hand van referentiematerialen. Ten slotte zijn de isotopenverhoudingen van ^{143}Nd/^{144}Nd en ^{34}S/^{32}S geëvalueerd als forensische signaturen door ze te testen op ‘echte’ monsters – uraniumertsen en ertsconcentraten.

Aanvullend is er een methode ontwikkeld voor de preconcentratie en voor het meten van zeldzame aardmetalen in zuiver uraniumoxide (UO_3 en UO_2). Hoewel isotopenverhoudingen van zeldzame aardmetalen minder vatbaar zijn voor veranderingen tijdens het chemische proces van de uraanproductie, is hun robuustheid alleen onderzocht in geconcentreerde uraanerts producten. In latere stadia van de uraanproductie worden geconcentreerde uraanertsen gemengd en gezuiverd, om ze zo geschikt te maken voor verrijking of voor splijtstof in een nucleaire plant. In dit stadium, zijn de zeldzame-aardmetalen concentraties in de uraniumproducten in de orde van $\mathrm{ng\,g^{-1}}$ – $\mathrm{pg\,g^{-1}}$ wat een verklaring kan zijn voor het gebrek aan experimentele data voor deze monsters. Voor de ontwikkeling van de preconcentratie en het meten van zeldzame aardemetalen zijn monsters gebruikt van een niet-verder-gespecifieerde-raffinaderij. Na het ontwikkelen van de methode zijn de monsters gemeten op hun zeldzame-aardmetaalpatronen. Deze patronen zijn hierna vergeleken met de zeldzame-aardmetaalpatronen in het moedermateriaal. Aangezien de patronen van de monsters en van het moedermateriaal goede overeenkomst vertonen,kan dus aan de hand van de zeldzame-aardmetaalpatronen het moeder materiaal worden herleid. Bovendien is niet alleen het moedermateriaal te herleiden aan de hand van de zeldzame aardmetalenpatronen, maar kan ook het specifieke erts dat de patronen veroorzaakte worden achterhaald wanneer verschillende uraniumerts concentraten worden gemengd.

Voor het onderzoek naar Nd als een forensische signatuur is er een nieuwe methode ontwikkeld om Nd van andere storende elementen en van het uranium matrix te scheiden. De ^{143}Nd/^{144}Nd isotopenverhoudingen zijn na deze scheidingstap gemeten met een Multi-collector ICP-MS. Nadat de methode is gevalideerd, zijn de isotopenverhoudingen van uraniumertsen en ertsconcentraten gemeten. De behaalde resultaten laten zien dat het verband tussen Nd isotopenverhouding en de Sm/Nd-verhouding bruikbaar is als een forensische marker, aangezien de resultaten clusters vormen voor monsters van hetzelfde type erts. Deze resultaten bevestigen dat de isotopenverhouding van ^{143}Nd/^{144}Nd kan worden gebruikt als een forensische marker voor de herkomstanalyse.

Voor het onderzoek naar zwavel (S) als een forensische signatuur, is eveneens een nieuwe scheidingsmethode ontwikkeld. Met behulp van een ionenwisselaar is het gelukt om zwavel uit de uraniummatrix te scheiden. Na deze stap is de isotopenverhouding van ^{34}S/^{32}S in bijna twintig uranium erts monsters gemeten. De resultaten van dit onderzoek laten zien dat zwavel enkel als een forensische marker voor een herkomstanalyse kan worden gebruikt als er aan de volgende twee voorwaarden wordt voldaan: ten eerste, moet het erts van het zandsteen type zijn en ten tweede, moet er tijdens het productieproces voor het uitlogen een alkaline uitloogmiddel (en geen zwavelzuur) zijn gebruikt. Aangezien S niet in alle gevallen als forensische marker voor een herkomstanalyse kan worden gebruikt, is gekeken of zwavel wel kan worden gebruikt als forensische marker voor het productieproces dat het materiaal heeft ondergaan. Dit is gedaan door te kijken naar de ontwikkeling van de ^{34}S/^{32}S isotopen verhouding tijdens de uraniumproductie. Hiervoor zijn onbewerkte uraniumerts monsters uitgeloogd met verschillende methodes om hun oorspronkelijke isotopenverhouding te achterhalen. Daarnaast is industrieel uitlogen nagebootst om de verandering in isotopenverhouding door deze processtap te onderzoeken. Zoals verwacht, bestaat er een significant verschil in de isotopenverhouding van de originele en industrieel uitgeloogde ertsen. Het is bewezen dat gebruik van een zwavelhoudend uitloogmiddel tijdens het productieproces de oorspronkelijke isotopenverhouding tot 90% kan veranderen, daarom moet de isotopenverhouding van ^{34}S/^{32}S als een proces gerelateerd forensische marker worden geclassificeerd.

Door de isotopenverhoudingen van Nd en zwavel van vijf verschillende mijnen en twintig verschillende verwerkingsinstallaties te meten, heeft dit proefschrift een bijgedragen geleverd om het scala van nucleaire forensische signaturen uit te breiden. De gegenereerde technieken gegevens kunnen worden opgenomen in het nucleaire forensische "gereedschappenën in de bijbehorende databanken. Hoewel geen van de onderzochte isotopenverhouding de magische forensische signatuur levert, zijn ze zeer bruikbaar in combinatie met andere forensische signaturen, zoals Sr, Pb of zeldzame aardpatronen, om verschillen te achterhalen tussen materialen van vergelijkbare bron of productieproces, maar van niet gerelateerde productieplaatsen.

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