

***Final Draft***  
**of the original manuscript:**

Retzmann, A.; Zimmermann, T.; Proefrock, D.; Prohaska, T.; Irrgeher, J.:  
**A fully automated simultaneous single-stage separation of  
Sr, Pb, and Nd using DGA Resin for the isotopic analysis of  
marine sediments**

In: Analytical and Bioanalytical Chemistry (2017) Springer

DOI: 10.1007/s00216-017-0468-6

# **A fully automated simultaneous single-stage separation of Sr, Pb and Nd using DGA Resin for the isotopic analysis of marine sediments**

Retzmann, A.<sup>1\*</sup>, Zimmermann, T.<sup>2,3\*</sup>, Pröfrock, D.<sup>2</sup>, Prohaska, T.<sup>1</sup>, Irrgeher, J.<sup>2</sup>

\*These two authors contributed equally as main authors to the presented work

corresponding author

Johanna Irrgeher (johanna.irrgeher@hzg.de, phone +49415287-1832)

<sup>1</sup> University of Natural Resources and Life Sciences Vienna, Department of Chemistry, Division of Analytical Chemistry, VIRIS Laboratory, Konrad-Lorenz-Str. 24, 3430 Tulln, Austria

<sup>2</sup> Helmholtz-Centre Geesthacht, Institute of Coastal Research, Marine Bioanalytical Chemistry, Max-Planck Str. 1, 21502 Geesthacht, Germany

<sup>3</sup> University of Hamburg, Department of Chemistry, Inorganic and Applied Chemistry, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

## **Abstract**

A novel fast and reliable sample preparation procedure for the simultaneous separation of Sr, Pb and Nd has been developed for subsequent isotope ratio analysis of sediment digests. The method applying a fully automated, low pressure chromatographic system separates all three analytes in a single-stage extraction step using self-packed columns filled with DGA Resin. The fully automated set-up allows the unattended processing of three isotopic systems from one sediment digest every two hours, offering for high sample throughput of up to 12 samples

per day and reduces substantially laboratory manpower as compared to conventional manual methods. The developed separation method was validated using the marine sediment GBW-07313 as matrix-matched certified reference material and combines quantitative recoveries (>90 % for Sr, >93 % for Pb and >91 % for Nd) with low procedural blank levels following the sample separation ( $0.07 \mu\text{g L}^{-1}$  Sr,  $0.03 \mu\text{g L}^{-1}$  Pb and  $0.57 \mu\text{g L}^{-1}$  Nd). The average  $\delta$ -values for Sr, Pb and Nd of the separated reference standards were within the certified ranges ( $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  of  $-0.05(28) \text{‰}$ ,  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  of  $-0.21(14) \text{‰}$ , and  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  of  $0.00(7) \text{‰}$ ).

The DGA Resin proved to be reusable for the separation of >10 sediment digests with no significant carry-over or memory effects, as well as no significant on-column fractionation of Sr, Pb and Nd isotope ratios. Additional spike experiments of NIST SRM 987 with Pb, NIST SRM 981 with Sr and JNdi-1 with Ce, revealed no significant impact on the measured isotopic ratios, caused by potential small analyte peak overlaps during the separation of Sr and Pb, as well as Ce and Nd.

## **Keywords**

isotopic analysis, automated sample matrix separation, Sr, Pb, Nd, DGA resin, MC ICP-MS

## 1. Introduction

Within the last decades, the analysis of systematic variations in the isotopic composition of strontium, lead and neodymium in the geosphere has been widely applied in geology and geochemistry. Isotopic analysis can be used for providing geochronological information of bedrock material, as well as for tracing various natural lithogenic and pedogenic but also anthropogenic processes. This is because of the variance in abundance of  $^{87}\text{Sr}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$  and  $^{143}\text{Nd}$  due to the radiogenic decay of their parent nuclides ( $^{87}\text{Rb}$  to  $^{87}\text{Sr}$ ;  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  to  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ;  $^{147}\text{Sm}$  to  $^{143}\text{Nd}$ ) as a function of geological age and original composition of the geological material. Strontium, lead and neodymium are released via weathering from the bedrock material and their isotopic signature is transported through and incorporated in the ecosphere. The resulting isotopic fractionations of these three isotopic systems within extracts and digests of soil, sediment and rock samples are typically analyzed by either thermal ionization mass spectrometry (TIMS) or multiple collector inductively coupled plasma mass spectrometry (MC ICP-MS). [1-3]

Apart from the issue of instrumental isotopic fractionation (IIF, *aka* mass bias or mass discrimination) [4,5], the accurate determination of the isotopic composition of these elements suffers from isobaric and polyatomic spectral interferences (e.g.  $^{84}\text{Kr}^+$ ,  $^{86}\text{Kr}^+$ ,  $^{87}\text{Rb}^+$ , doubly charged ions of rare earth elements (REE) as well as Ca-dimers and Ca-argides [6] on Sr isotopes ( $^{84}\text{Sr}^+$ ,  $^{86}\text{Sr}^+$ ,  $^{87}\text{Sr}^+$ ,  $^{88}\text{Sr}^+$ );  $^{204}\text{Hg}^+$ ,  $^{203}(\text{TiH})^+$  and  $^{205}(\text{TiH})^+$  on Pb isotopes ( $^{204}\text{Pb}^+$ ,  $^{206}\text{Pb}^+$ ),  $^{142}\text{Ce}^+$ ,  $^{142}(\text{PrH})^+$ ,  $^{143}(\text{CeH})^+$  and  $^{144}\text{Sm}^+$  on Nd isotopes ( $^{142}\text{Nd}^+$ ,  $^{143}\text{Nd}^+$ ,  $^{144}\text{Nd}^+$ )). Moreover, substantial amounts of matrix elements can lead to signal suppression and changes in the instrumental isotopic fractionation as compared to pure calibration solutions leading to loss in precision and shifts of the measured values. [7]

In general, low levels of interfering elements can be mathematically corrected for by estimating the content of the interfering isotope via peak stripping using the isotopic abundance of a simultaneously measured, non-interfered isotope of the same element. This

strategy works only sufficiently for minor interferences, but often goes along with an unsatisfactory increase of measurement uncertainty [8,9].

Commercially available sector field mass spectrometers offer a maximum achievable mass resolving power up-to  $(m/z)/\Delta(m/z) = 10,000$  [10,11]. This is sufficient to resolve for example double charged rare earth elements (REE) from Sr isotopes at medium mass resolution ( $(m/z)/\Delta(m/z) > 400$ ) or  $^{83,86}(\text{KrH})^+$  interferences on  $^{84}\text{Sr}^+$  and  $^{87}\text{Sr}^+$  at high mass resolution ( $(m/z)/\Delta(m/z) < 10,000$ ) (according to a 10 % valley definition [12]). Some (mainly isobaric) interferences addressed in this work would require a mass resolution of  $(m/z)/\Delta(m/z) > 10,000$  up to 500,000 (e.g.  $^{87}\text{Rb}^+$  from  $^{87}\text{Sr}^+$ ,  $^{204}\text{Hg}^+$  from  $^{204}\text{Pb}^+$ ,  $^{144,148,150}\text{Sm}^+$  and  $^{142}\text{Ce}^+$  from Nd isotopes). Nonetheless, in many MC ICP-MS applications, the use of low mass resolution is preferable for the benefit of precision caused by increased sensitivity and flat topped peak shape [13].

The approach of chemical resolution utilizing cell technologies to remove isobaric interferences ( $^{87}\text{Rb}^+$  on  $^{87}\text{Sr}^+$  and  $^{204}\text{Hg}^+$  on  $^{204}\text{Pb}^+$ ) has been applied successfully using particular cell gases (Sr:  $\text{CH}_3\text{F}/\text{He}$  mixture; Pb:  $\text{NH}_3/\text{He}$ ). Based on the highly effective and selective reactions (Sr: mass shift of +19; Pb: charge transfer on  $^{204}\text{Hg}^+$ ), the determination of  $n(^{87}\text{Sr})/n(^{86}\text{Sr})$  and  $n(^{204}\text{Pb})/n(^{206}\text{Pb})$  isotope ratios free from spectral overlaps ( $^{87}\text{Rb}^+$ ,  $^{204}\text{Hg}^+$ ) was possible with an external precision of  $\leq 0.05$  % RSD [14-16]. However, the total measurement uncertainty that can be obtained, using such approaches is significantly higher as compared to multi collector sector field mass spectrometers.

A number of spectral interferences still cannot be removed from the sample using either of the latter approaches. Thus, the method of choice in accurate isotope ratio determination is still based on analyte purification by means of chemical separation [17,18,9].

Extraction chromatography offers an attractive alternative to the traditionally used ion exchange, due to its improved elemental selectivity, more effective separation yields and the capability to separate multiple elements on one stage [19,20,17,18]. Several methods for the

simultaneous separation of two or more isotopic systems have been developed over the last 25 years. This is a major advantage as the complex and time consuming sample preparation still represents the main bottleneck in isotopic analysis. Table 1a summarizes the (since 1992) developed extraction chromatography methods for the separation of Sr, Pb and Nd from a single sample digestion based on manual separation. The primarily used resins were the Sr Resin (*aka* Sr.Spec), the TRU Resin and the LN Resin (all TrisKem International, Bruz, France) applied in column volumes between 150  $\mu$ L and 3.75 mL. Single-stage column set-ups for Sr and Pb, 2/3-stage column set-ups for Sr and Nd and up-to 4-stage column set-ups for all three systems together were developed. Many of these procedures were based on the Sr Resin, which suffers from significant memory effects when being re-used [21,22,19]. Furthermore, the Sr Resin is known for elevated Pb blank levels and the formation of “brownish, jam-like residues” [19] after evaporation of Pb fractions as well as the incomplete extraction when working with complex (rock) matrices [23]. General problems related to separation of Nd are the requirement of a two-stage separation for REE [24,25] and severe resin aging with changes in elution profiles on the LN Resin [24,20].

Several approaches were developed to provide reproducible automated single-stage separation of Sr, Pb and Nd (see Table 1b). Major drawbacks of the presented methods are the limitation in separation of only one isotopic system and the maximum number of processable samples (due to aging of the chosen resin), specific instrumental modifications (not commercially available), long instrument run times in the on-line set-up and isotopic fractionations in the transient signal. In 2012, a new automated sample preparation device has been presented to the public [26]. The prepFAST-MC<sup>TM</sup> (Elemental Scientific, Omaha, USA) is a fully automated low pressure ion exchange chromatography system which utilizes re-usable micro columns of 200  $\mu$ L to 3 mL volume. Depending on the complexity of the separation procedure, it can process up to 60 samples in unattended operation including a cleaning step between each new sample [27]. Elemental Scientific provides packed columns with specific

extraction resins and the associated separation protocols for U, B, Sr, Mg, Ca, Pb, Fe, Cu, Zn, and Cd [27-30]. The repertoire is continuously extended by the manufacturer (e.g. future applications for Pu [31]). So far, the commercially available prepFAST-MC<sup>TM</sup> has been successfully adopted for the isotopic analysis of Sr (+ Ca), Cu and Nd in a wide range of matrices (described in detail in Table 1c).

In the present study, we systematically developed a single-stage simultaneous separation procedure for Sr, Pb and Nd from sediment digest, based on the data published by Horwitz *et al.* [32] and Pourmand & Dauphas [33] describing the retention behavior of the DGA Resin (*N,N,N',N'*-tetra-*n*-octyldiglycolamide, TrisKem International) for Ca, Sr, Pb and REE. We aimed at the complete matrix removal along with high recovery rates and high sample throughput for accurate Sr, Nd and Pb isotope analysis.

**Table 1** a) Literature overview of different manual separation methods for simultaneous Sr, Pb, Nd isotopic analysis (note: some papers cite additional Hf separation within the procedure), b) Literature overview of different automated separations methods for Sr, Pb and Nd isotopic analysis, c) Literature overview of applications using the prepFAST-MC<sup>TM</sup> system.

a)

Analytes	Matrix/interference	Sample type	Separation technique	Resin	Eluents	Sample throughput (samples/24h)	Detection	Reference
Sr, Pb	Y, Rb, Ca, Ba, Pb, Na, K, Fe, Al	Environmental and biological samples	Manual, 1-stage, single-column, 1 elution Sr (3 mol L <sup>-1</sup> HNO <sub>3</sub> ), 2 elution Pb	Sr Resin	Sr: H <sub>2</sub> O, Pb: 0.1 mol L <sup>-1</sup> (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> *	-	ICP-AES**	[34]
Sr, Nd	Rb, Ba, Sm, Pb, rest LREE	Rock digest	Manual, 2-stage (tandem Sr Resin + TRU Resin) + extraction: 1 elution Sr (Sr Resin), 2 elution LREE (TRU Resin), extraction of Nd	Sr: Sr Resin; LREE: TRU Resin	Sr: 0.05 mol L <sup>-1</sup> <sup>1</sup> HNO <sub>3</sub> , LREE: 0.05 mol L <sup>-1</sup> HCl	-	TIMS	[22]
Sr, Pb	Ba, Rb, Hg, Tl, major matrix elements, REE, U, Th	Rock digest	Manual, 1-stage, single column: 1 elution of Sr, 2 elution of Pb	Sr Resin	Sr: 0.05 mol L <sup>-1</sup> <sup>1</sup> HNO <sub>3</sub> ; Pb: 8 mol L <sup>-1</sup> HCl	Complete separation in about 3 h	TIMS	[19]
Sr, Nd	Rb, Sm, Ce, Eu, Ba, major matrix elements	Rock digest	Manual, 3-stage (tandem Sr Resin + TRU Resin; TRU Resin+ LN Resin): 1 elution Sr (Sr Resin),	Sr: Sr Resin; Nd: LN Resin	Sr: 0.05 mol L <sup>-1</sup> <sup>1</sup> HNO <sub>3</sub> , Nd: 0.25 mol L <sup>-1</sup> HCl	Complete separation in about 1 day	TIMS	[20]

				2 elution LREE (TRU Resin), 3 elution Nd (LN Resin)					
Sr, Pb	Rb, Tl, Hg, Y, major matrix elements	Rock digest	Manual, 1-stage, single column: 1 elution of Sr, 2 elution of Pb	Sr Resin	Sr: H <sub>2</sub> O, Pb: 8 mol L <sup>-1</sup> HCl	4-5 hours for 20 samples	MC ICP-MS	[23]	
Sr, Nd, Hf	Rb, Sm, Ce, matrix elements	Dust LiBO <sub>2</sub> alkali flux	Manual, 3 step separation (tandem Sr Resin & DGA + DGA), 1 elution Sr, 2 elution Hf + REE, 3 elution Nd	Sr Resin, DGA	Sr: 0.01 mol L <sup>-1</sup> HNO <sub>3</sub> , Hf: 1 mol L <sup>-1</sup> HNO <sub>3</sub> + 0.1 mol L <sup>-1</sup> HF, REE: 0.01 mol L <sup>-1</sup> HCl, Nd: 0.0075 mol L <sup>-1</sup> HNO <sub>3</sub>	-	MC ICP-MS	[35]	
Sr, Pb, Nd	Rb, Sm, Hg, partly Ce, Tl, major elements (Al, Ca, Ba, Fe, Ti)	Rock digest	Manual, 3-stage without evaporation: 1 Sr+ Pb (Sr Resin), 2 Waste (TRU Resin), 3 Nd (LN Resin), 1+2 tandem column	Sr+Pb: Sr Resin; Nd: LN Resin	Sr: 0.05 mol L <sup>-1</sup> HNO <sub>3</sub> ; Pb: 6 mol L <sup>-1</sup> HCl; Nd: 0.25 mol L <sup>-1</sup> HCl	Complete separation in about 6 h	Sr: TIMS; Pb, Nd: MC ICP-MS	[18]	
Sr, Pb, Nd, Hf	Rb, Sm, Lu, Yb, Hg, Tl	Rock digest	Manual, 4-stage: 1 Pb (AG1X-8), 2 Waste (TRU-Resin), 3 Sr (Sr Resin), 4 Nd, Hf (LN Resin)	Sr: Sr Resin; Pb: AG1X-8; Nd: LN Resin	Sr: H <sub>2</sub> O; Pb: 6 mol L <sup>-1</sup> HCl; Nd: 0.22 mol L <sup>-1</sup> HNO <sub>3</sub> ; Hf: 6 mol L <sup>-1</sup> HCl+0.2 mol L <sup>-1</sup> HF	Complete separation in several days	Sr: TIMS; Pb, Nd, Hf: MC ICP-MS	[36]	
Sr, Pb, Nd, Hf	Rb, Sm, Yb, Lu, HREEs, major elements (K, Na, Al, Ti, Fe, Mg, Ba)	Rock digest	Manual, 2-stage tandem column: 1 Sr+Pb: Sr Resin, 2 Nd+ Hf: DGA	Sr+Pb: Sr Resin; Nd+ Hf: DGA Resin	Sr: 0.05 mol L <sup>-1</sup> HNO <sub>3</sub> ; Pb: 8 mol L <sup>-1</sup> HCl; Nd: 0.4 mol L <sup>-1</sup> HCl; Hf: 3.5 HNO <sub>3</sub> +1 mol L <sup>-1</sup> HF	8 hours for 25 samples	TIMS	[37]	

\*various reagents to elute Pb, \*\* no isotopic analysis

#### b) Automated separations

Analytes	Matrix/interference	Sample type	Separation technique	Resin	Eluents	Sample throughput (samples/24h)	Detector	Reference
Sr	Rb, Ca-rich matrix	Skeletal remains, soil	Automated (HPIC), on-line coupled	IonPac CS12A	Sr: 14 mol L <sup>-1</sup> HNO <sub>3</sub>	45 min per analysis/sample	ICP-SFMS	[38]
Sr	Rb, Ca-rich matrix	Environmental and biological samples	Automated (FI), on-line coupled	Sr Resin	Sr: H <sub>2</sub> O	< 10 min per analysis/sample	MC ICP-MS	[8,39]
Sr	Rb, Ca, Mg, Na, K	Environmental and food samples	Automated (HPLC), on-line coupled	IonPac CS2	Sr: 0.9 mol L <sup>-1</sup> HNO <sub>3</sub> + 18-crown-6 ether	< 20 min per analysis/sample	MC ICP-MS	[40,41]
Sr	Rb, salt matrix	Fresh and saline water	Automated (IC), on-line coupled	IonPac CS16	Sr: 46 mmol L <sup>-1</sup> methane-sulfonic acid	14 min per analysis/sample	MC ICP-MS	[42]

Pb	Salt matrix	Fresh and saline water	Automated (IC/ICP), on-line coupled	I-8-HOQ	El: 1 mol L <sup>-1</sup> NH <sub>3</sub> /NH <sub>4</sub> Cl (pH 9.2), E2: 2 mol L <sup>-1</sup> HCl/0.8 mol L <sup>-1</sup> HNO <sub>3</sub> , E3: H <sub>2</sub> O	< 45 min per analysis/ sample	ICP-MS	[43]
Pb	Salt matrix	Seawater	Semi-automated	Toyopearl AF-Chelate 650 M	Pb: 1.5 mol L <sup>-1</sup> HNO <sub>3</sub>	2.5 h for 50 mL, 6.5 h for 500 mL	MC ICP-MC	[44]
Nd	U, Pu, lanthanides, actinides	Nuclear fuel	Automated (HPLC), on-line coupled, 1 stage (gradient elution)	Dionex CS10	Nd: α-hydroxyisobutyric acid	30 min per analysis/ sample	(MC) ICP-MS	[45-47]
Nd	Ce, Sm, Mo, Ru, Gd, Eu, Cs, Pr, La, Sr	Nuclear fuel	Automated (HPLC), on-line coupled, 1 stage (gradient elution)	LUNA SCX	Nd: 2-hydroxy-2-methylbutyric acid	30 min per analysis/ sample	MC ICP-MS	[48]
Sr, Nd	Rb, Sm, REE	(Rb-Sr and Nd-Sm dating)	Automated (HPLC), on-line coupled	Sr: IonPac CS2, Nd: IonPac AG9-HC	Sr: 0.9 mol L <sup>-1</sup> HNO <sub>3</sub> + 18-crown-6 ether, Nd: 5 mmol L <sup>-1</sup> EDTA-Na <sub>2</sub>	Sr: < 20 min per analysis/ sample, Nd: < 22 min per analysis / sample	MC ICP-MS	[49]

### c) Applications prepFAST-MC™

Analytes	Matrix/interference	Sample type	Separation technique	Resin	Eluents	Sample throughput (samples/24h)	Detector	Reference
Sr, Ca	Rb, major matrix elements	Environmental and biological samples	Automated (prepFAST-MC™), 1 stage, single-column, 1 elution Sr, 2 elution Ca	CF-MC-Sr/Ca-1000 (ESI column)	Sr: 6 mol L <sup>-1</sup> HNO <sub>3</sub> , Ca: 12 mol L <sup>-1</sup> HNO <sub>3</sub>	32	MC ICP-MS	[50]
Nd	Ce, Sm, Pr, major matrix elements	Rock digest	Partly automated (prepFAST-MC™), 3-step: 1 removal of major matrix elements (AG 50W-X8), 2 oxidative removal of Ce (LN Resin), 3 removal Sm and Pr (LN Resin - prepFAST-MC)	Nd: AG 50W-X8 + LN Resin	Nd: 7 mol L <sup>-1</sup> HNO <sub>3</sub>	1	MC ICP-MS	[51]
Cu	Major matrix elements (Na, Mg, K, Ca, Mn, Fe, Zn, Se, P)	Biological sample	Automated (prepFAST-MC™), 1 stage	CF-MC-Cu-500 (ESI column)	Cu: 8 mol L <sup>-1</sup> HCl	36	MC ICP-MS	[52]
Sr, Pb, Nd	Rb, Ca, Hg, Tl, Ce, Sm, REE and major matrix elements	Rock digest	Automated (prepFAST-MC™), single stage	Sr, Pb, Nd: DGA Resin	Sr: 0.2 mol L <sup>-1</sup> HNO <sub>3</sub> , Pb: 5 mol L <sup>-1</sup> HNO <sub>3</sub> , Nd: 0.1 mol L <sup>-1</sup> HCl	12	MC ICP-MS	This study

## 2. Experimental

Experimental work was carried out at the Helmholtz-Centre Geesthacht and the University of Natural Resources and Life Science Vienna. All procedures were performed in clean rooms at both facilities.

### 2.1 Reference materials, reagents and solutions

#### *Procedures conducted at the Helmholtz-Centre Geesthacht, Germany*

Preparatory laboratory work was performed in a class 10,000 clean room inside a class 100 clean bench. Type I reagent-grade water (18.2 M $\Omega$  cm) was obtained from a Milli-Q Integral water purification system (Merck-Millipore, Darmstadt, Germany). Suprapur<sup>®</sup> nitric acid (65 % w/w, Merck-Millipore) and suprapur<sup>®</sup> hydrochloric acid (30 % w/w, Merck-Millipore) were further purified by double sub-boiling in quartz stills (AHF Analysentechnik, Tübingen, Germany). Tetrafluoroboric acid (38 % w/w, Chem-Lab, Zedelgem, Belgium) was used for sample digestion without any further purification. Polyethylene (PE) flasks, tubes and pipette tips (VWR International, Radnor, USA), as well as perfluoroalkoxy (PFA) screw cap vials (Savillex, Eden Prairie, USA) were pre-cleaned in a two-stage washing procedure using nitric acid (10 % w/w and 1 % w/w respectively).

#### *Procedures conducted at the University of Natural Resources and Life Science Vienna, Austria (VIRIS Laboratory)*

Preparatory laboratory work was performed in a class 100,000 clean room. Type I reagent-grade water (18 M $\Omega$  cm) (F+L GmbH, Vienna, Austria) was further purified by sub-boiling distillation (Milestone-MLS GmbH, Leutkirch, Germany). Analytical reagent-grade nitric acid (65 % w/w, Merck-Millipore) was purified by double sub-boiling using a DST-1000 sub-boiling distillation system (AHF Analysentechnik). Polyethylene (PE) flasks, tubes and pipette tips (VWR International, Radnor, USA), as well as perfluoroalkoxy (PFA) screw cap

vials (Savillex, Eden Prairie, USA) were pre-cleaned in a two-stage washing procedure using nitric acid (10 % *w/w* and 1 % *w/w* respectively).

1 - 5 g of the unbranched DGA Resin (part. no. DN-B25-S, TrisKem International) with a particle size of 50 - 100  $\mu\text{m}$  was soaked in 50 mL diluted nitric acid (2 % *w/w*) overnight and sonicated in an ultrasonic bath for at least 30 minutes. The resin was stored suspended in nitric acid (2 % *w/w*) in the refrigerator (8°C).

Single-element standards (1 g L<sup>-1</sup>) of Ca, Rb, Sr, Ce, Sm, Eu, In, Ir, Nd, Hg, Tl, and Pb were obtained from Merck-Millipore. Dilutions of multi-element stock solutions (Inorganic Ventures, Christiansburg, USA and ICP multi-element standard Merck VI, 10 mg L<sup>-1</sup>; Merck-Millipore) were used for external calibration.

Certified reference materials NIST SRM 987 (highly purified SrCO<sub>3</sub>, NIST, Gaithersburg, USA) and NIST SRM 981 (high purity lead metal, NIST) were used for Sr and Pb isotopic analysis [53]. JNdi-1 (high purity neodymium oxide, Geological Survey of Japan, Tokyo, Japan) [54] was used as reference material for Nd isotopic measurements. Solutions of these standards were prepared gravimetrically in nitric acid (2 % *w/w*) and diluted to final concentration of 50 - 100 ng g<sup>-1</sup> as isotopic reference for standard-sample bracketing (SSB). The commonly used reference marine sediment GBW-07313 (National Research Centre for Certified Reference Materials, Beijing, China) with a representative mass fraction of Sr compared to Pb ( $w(\text{Sr})/w(\text{Pb}) = 9.1$ ) was used for method validation, for further information see ESM table 1.

## **2.2 Sediment sample digestion**

About 50 mg of marine sediment reference material GBW-07313 was weighed into 55 mL TFM<sup>®</sup> bombs, submerged with 5 mL concentrated double sub-boiled nitric acid (65 % *w/w*), 2 mL concentrated double sub-boiled hydrochloric acid (30 % *w/w*) and 1 mL tetrafluoroboric

acid (38 % *w/w*). The dissolved samples were digested for 300 minutes at 180 °C with a MARS Xpress (CEM Corp., Kamp Lintfort, Germany) microwave. After digestion, the solution was transferred quantitatively to a 50 mL pre-cleaned DigiTUBE (SCP Science, Quebec, Canada) and diluted to a final volume of 50 mL with milli-Q water. 5 mL aliquots of the digested sediment were transferred to a pre-cleaned 15 mL PFA screw-cap beaker, evaporated to dryness and re-dissolved in 1 mL of 2 mol L<sup>-1</sup> nitric acid for subsequent separation. All microwave assisted digestions were performed at the Helmholtz-Centre Geesthacht.

## **2.3 Instrumentation, measurement routines and data processing**

### **2.3.1 Multi-elemental analysis**

Multi-elemental analyses of the samples were performed either using an ICP-MS/MS (Agilent 8800, Agilent Technologies, Tokyo, Japan) coupled to an ESI SC-4 DX FAST autosampler (Elemental Scientific) at the Helmholtz-Centre Geesthacht or an ICP-QMS (NexION 350D, PerkinElmer, Ontario, Canada) coupled to an ESI SC-2 DX FAST autosampler at the University of Natural Resources and Life Science Vienna. Both instruments were optimized in a daily routine using a tuning solution, containing Li, Y, Ce, Tl or Be, In, Ce and U to maintain a reliable day-to-day-performance. All samples were diluted by a factor of 10 prior to analysis using nitric acid (2 % *w/w*). Sr, Pb and Nd concentrations solutions covering a concentration range from 0.5 µg L<sup>-1</sup> to 100 µg L<sup>-1</sup> including 10 µg L<sup>-1</sup> iridium (Ir) as internal normalization standard (Merck-Millipore) were prepared from volumetrically custom made multi-element standards (Inorganic Ventures) for external calibration using the ICP-MS/MS for concentration screening. ICP-QMS measurements were accomplished performing a calibration in the range of 0.1 µg g<sup>-1</sup> to 150 µg g<sup>-1</sup> including 10 ng g<sup>-1</sup> indium (In) as internal normalization standard (Merck-Millipore), prepared gravimetrically from Merck multi-element standard VI.

General instrumental settings for the multi-elemental measurements are described in ESM Table 2.

### **2.3.2 Isotopic analysis**

Sr and Pb isotopic compositions were measured using a multi collector ICP-MS (Nu Plasma HR, Nu Instruments, Wrexham, UK) equipped with a desolvation nebulization membrane unit (Aridus II, Cetac) in combination with a PFA nebulizer (Microflow ST Nebulizer, Elemental Scientific) as sample introduction system at the VIRIS Laboratory, University of Natural Resources and Life Science Vienna, Austria. The instrument is equipped with 12 Faraday cups and 3 ion counters. Nd and Pb isotopic compositions were measured using a multi collector ICP-MS (Nu Plasma II, Nu Instruments) equipped with an APEX Q desolvation system (Elemental Scientific) in combination with a PFA nebulizer (Elemental Scientific) as sample introduction system at the Department of Marine Bioanalytical Chemistry, Helmholtz-Centre Geesthacht, Germany. The instrument is equipped with 17 Faraday cups and 5 ion counters. The instruments were optimized on a daily basis using the associated (certified) reference material (NIST SRM 987, NIST SRM 981, JNdi-1) for maximum intensity, signal stability and peak shape. All measurements were done in low mass resolution mode. General instrumental settings for the measurements are described in ESM Table 3.

Separated Sr fractions were directly diluted with nitric acid (2 % w/w). The separated Pb and Nd fractions were evaporated to dryness on a hot plate at 85°C and re-dissolved in nitric acid (2 % w/w) prior to isotopic analysis. Instrumental isotopic fractionation was corrected following an internal inter-elemental approach (combining standard sample bracketing and external calibration by Zr to account for time dependent and matrix dependent IIF variation between the samples) following standard measurement protocols [9,55-58]. Therefore, the diluted Sr fractions and the corresponding isotopic standard (NIST SRM 987) were spiked with Zr (Merck-Millipore), while the diluted Pb fractions and the corresponding isotopic

standard (NIST SRM 981) were spiked with Tl (Merck-Millipore). The diluted Nd fractions and the corresponding isotopic standard (JNdi-1) were spiked with Eu (Merck-Millipore) as internal standard. All Sr, Pb and Nd isotopic data were collected using static multi-collection with a corresponding detector configuration as shown in Table 2. Data collection was accomplished over a period of 300 s with an integration time of 10 s, resulting in a total of 60 measurements per sample. Blank correction was performed using the ‘measure zero’ method implemented in the Nu Plasma instrument software by aspirating solutions of nitric acid (2 % w/w) prior to every set of 5 samples. The samples and corresponding isotopic standards were introduced into the plasma in the following sequence: standard<sub>1</sub> - sample - standard<sub>2</sub>, to enable correction for time-dependent IIF via classical SSB [9]. Concentrations of sample and SSB standard were matched within 10 %.

The  $\delta$ -values (in ‰) for Sr, Pb and Nd isotope ratios were calculated relative to the average isotopic ratio of the used reference standard (std: NIST SRM 987, NIST SRM 981, JNdi-1) from the SSB in accordance with Eq.1:

$$\delta(^iE/^jE)_{std} = \left( \frac{R_{spl} - R_{std}}{R_{std}} \right) \cdot 1000 \quad [‰] \quad (1)$$

$\delta$ : delta value

$^iE, ^jE$ : isotopes  $i$  and  $j$  of element  $E$

$R$ : isotope ratio of sample ( $spl$ ) or standard ( $std$ ) after blank and interference correction

The upper and lower  $\delta$ -limits of the reference materials set as anchor for the delta values were calculated according to Eq. 1 with  $R_{spl}$  being the maximum and minimum absolute ratio defined by the uncertainty of the reference material and  $R_{std}$  being the certified/published absolute ratio.

**Table 2** Detector configurations for Sr, Pb and Nd isotopic analysis using Nu Plasma HR and Nu Plasma II

**Nu Plasma HR**

F	F	F	F	F	F	F	F	F	IC	F	IC	F	IC	F
<b>H6</b>	<b>H5</b>	<b>H4</b>	<b>H3</b>	<b>H2</b>	<b>H1</b>	<b>Ax</b>	<b>L1</b>	<b>L2</b>	<b>IC0</b>	<b>L3</b>	<b>IC1</b>	<b>L4</b>	<b>IC2</b>	<b>L5</b>
<sup>91</sup> Zr	<sup>90</sup> Zr	<sup>208</sup> Pb	<sup>207</sup> Pb	<sup>88</sup> Sr	<sup>206</sup> Pb	<sup>205</sup> Tl	<sup>204</sup> Pb	<sup>203</sup> Tl	<sup>202</sup> Hg	<sup>86</sup> Sr	<sup>85</sup> Rb	<sup>84</sup> Sr		

**Nu Plasma II**

F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
<b>H10</b>	<b>H9</b>	<b>H8</b>	<b>H7</b>	<b>H6</b>	<b>H5</b>	<b>H4</b>	<b>H3</b>	<b>H2</b>	<b>H1</b>	<b>Ax</b>	<b>L1</b>	<b>L2</b>	<b>L3</b>	<b>L4</b>
	<sup>153</sup> Eu	<sup>151</sup> Eu		<sup>149</sup> Sm	<sup>148</sup> Nd	<sup>147</sup> Sm	<sup>146</sup> Nd	<sup>145</sup> Nd	<sup>144</sup> Nd	<sup>205</sup> Tl	<sup>204</sup> Pb	<sup>203</sup> Tl	<sup>202</sup> Hg	<sup>140</sup> Ce

**2.3.3 Corrections for isobaric interferences**

Similar to Horsky *et al.* [55] and Irrgeher *et al.* [9], minor interferences of <sup>87</sup>Rb<sup>+</sup> on <sup>87</sup>Sr<sup>+</sup> arising from residual Rb (< 0.03 %, expressed as  $int(^{85}\text{Rb})/int(^{88}\text{Sr})$ ) in the purified sample solutions were corrected. Herein, <sup>87</sup>Rb ( $int(^{87}\text{Rb})_{spl}$ ) calculated via the simultaneously measured <sup>85</sup>Rb ( $int(^{85}\text{Rb})_{spl}$ ) signal and using  $n(^{87}\text{Rb})/n(^{85}\text{Rb})_{nat}$  (= 0.3856) recommended by IUPAC/CIAAW [59] for natural Rb, which was corrected for IIF via SSB with NIST SRM 987 of known isotopic compositions ( $n(^{87}\text{Sr})/n(^{86}\text{Sr})_{cert} = 0.71034(26)$ ) was subtracted from <sup>87</sup>Sr ( $int(^{87}\text{Sr})_{spl}$ ), assuming the same IIF for  $n(^{87}\text{Sr})/n(^{86}\text{Sr})_{spl}$  and  $n(^{87}\text{Rb})/n(^{85}\text{Rb})_{spl}$ , according to Eqs. 2a-c:

$$int(^{87}\text{Sr})_{spl} = int(^{87}\text{Sr})_{spl} - int(^{85}\text{Rb})_{spl} \cdot \left( \frac{n(^{87}\text{Rb})}{n(^{85}\text{Rb})} \right)_{nat} \cdot \left( \frac{M(^{87}\text{Rb})}{M(^{85}\text{Rb})} \right)^f \quad (2a)$$

$$f = \frac{f_{SSB1} + f_{SSB2}}{2} \quad (2b)$$

$$f_{SSB} = \ln \left( \frac{\left( \frac{n(^{87}\text{Sr})}{n(^{86}\text{Sr})} \right)_{cert}}{\left( \frac{n(^{87}\text{Sr})}{n(^{86}\text{Sr})} \right)_{SSB}} \right) / \ln \left( \frac{M(^{87}\text{Sr})}{M(^{86}\text{Sr})} \right) \quad (2c)$$

where all intensities correspond to blank corrected beam intensities,  $int(^{87}\text{Sr})/int(^{86}\text{Sr})_{\text{SSB}}$  was the measured raw ratio in the SSB standard, and  $M(X)$  were the atomic weights extracted from the IUPAC/CIAAW tables [60].

This strategy was also applied to correct  $^{204}\text{Pb}^+$  for minor interferences of  $^{204}\text{Hg}^+$  arising from residual Hg ( $< 0.02\%$ , expressed as relative ratio of  $int(^{202}\text{Hg})/int(^{208}\text{Pb})$ ) in the purified sample solutions. Here, the simultaneously measured  $^{202}\text{Hg}$  ( $int(^{202}\text{Hg})_{\text{spl}}$ ) signal and the IUPAC/CIAAW value [59] for  $n(^{204}\text{Hg})/n(^{202}\text{Hg})_{\text{nat}} (= 0.2293)$ , which was corrected for IIF via SSB with NIST SRM 981 of calculated isotopic compositions ( $n(^{206}\text{Pb})/n(^{204}\text{Pb})_{\text{cert}} = 16.937 (11)$ ), assuming the same IIF for  $n(^{206}\text{Pb})/n(^{204}\text{Pb})_{\text{spl}}$  and  $n(^{204}\text{Hg})/n(^{202}\text{Hg})_{\text{spl}}$ , was used to calculate the  $^{204}\text{Pb}$  ( $int(^{204}\text{Pb})_{\text{spl}}$ ), according to Eqs. 3a-c:

$$int(^{204}\text{Pb})_{\text{spl}} = int(^{204}\text{Pb})_{\text{SSB}} - int(^{202}\text{Hg})_{\text{spl}} \cdot \left( \frac{n(^{204}\text{Hg})}{n(^{202}\text{Hg})} \right)_{\text{nat}} \cdot \left( \frac{M(^{204}\text{Hg})}{M(^{202}\text{Hg})} \right)^f \quad (3a)$$

$$f = \frac{f_{\text{SSB}_1} + f_{\text{SSB}_2}}{2} \quad (3b)$$

$$f_{\text{SSB}} = \ln \left( \frac{\left( \frac{n(^{206}\text{Pb})}{n(^{204}\text{Pb})} \right)_{\text{cert}}}{\left( \frac{n(^{206}\text{Pb})}{n(^{204}\text{Pb})} \right)_{\text{SSB}}} \right) / \ln \left( \frac{M(^{206}\text{Pb})}{M(^{204}\text{Pb})} \right) \quad (3c)$$

where all intensities correspond to blank corrected beam intensities,  $int(^{206}\text{Pb})/int(^{204}\text{Pb})_{\text{SSB}}$  was the measured raw ratio in the SSB standard, and  $M(X)$  were the atomic weights extracted from the IUPAC/CIAAW tables [60].

In case of Nd, minor interferences of  $^{144}\text{Sm}^+$  on  $^{144}\text{Nd}^+$  arising from residual Sm ( $< 0.5\%$ , expressed as  $int(^{149}\text{Sm})/int(^{146}\text{Nd})$ ) in the purified sample solutions were corrected. Herein,  $^{144}\text{Sm}$  calculated via the simultaneously measured  $^{147}\text{Sm}$  ( $int(^{147}\text{Sm})_{\text{spl}}$ ) signal and using the IUPAC/CIAAW value [59] for  $n(^{144}\text{Sm})/n(^{147}\text{Sm})_{\text{nat}} (= 0.2053)$ , which was corrected for IIF,

was subtracted from  $^{144}\text{Nd}$  ( $int(^{144}\text{Nd})_{spl}$ ). Nd ratios are commonly corrected for IIF by internal normalization to  $n(^{146}\text{Nd})/n(^{144}\text{Nd})$ . However, as  $^{144}\text{Nd}^+$  is possibly interfered by  $^{144}\text{Sm}^+$ , and the Sm content of a separated samples is usually too low to use  $^{149}\text{Sm}/^{147}\text{Sm}$  via peak stripping for IIF correction, in this study an internal inter-elemental approach [9,55-58] was chosen. The IIF factor for Sm was determined applying a bracketing approach with JNdi-1 (of known Nd isotopic composition) spiked with Eu as externally added internal standard, assuming the same IIF for  $n(^{143}\text{Nd})/n(^{144}\text{Nd})$  and  $n(^{144}\text{Sm})/n(^{147}\text{Sm})$ , following Eqs. 4a-d

$$int(^{144}\text{Nd})_{spl} = int(^{144}\text{Nd})_{spl} - int(^{147}\text{Sm})_{spl} \cdot \left( \frac{n(^{144}\text{Sm})}{n(^{147}\text{Sm})} \right)_{nat} \cdot \left( \frac{M(^{144}\text{Sm})}{M(^{147}\text{Sm})} \right)^{f_{Eu}} \quad (4a)$$

$$f_{Eu} = \ln \left( \frac{\left( \frac{n(^{153}\text{Eu})}{n(^{151}\text{Eu})} \right)_{SSB1} + \left( \frac{n(^{153}\text{Eu})}{n(^{151}\text{Eu})} \right)_{SSB2}}{\left( \frac{n(^{153}\text{Eu})}{n(^{151}\text{Eu})} \right)_{spl}} \right) / \ln \left( \frac{M(^{153}\text{Eu})}{M(^{151}\text{Eu})} \right) \quad (4b)$$

$$\left( \frac{n(^{153}\text{Eu})}{n(^{151}\text{Eu})} \right)_{SSB} = \left( \frac{int(^{153}\text{Eu})}{int(^{151}\text{Eu})} \right)_{SSB} \cdot \left( \frac{M(^{153}\text{Eu})}{M(^{151}\text{Eu})} \right)^{f_{Nd}} \quad (4c)$$

$$f_{Nd} = \ln \left( \frac{\left( \frac{n(^{143}\text{Nd})}{n(^{144}\text{Nd})} \right)_{cert}}{\left( \frac{n(^{143}\text{Nd})}{n(^{144}\text{Nd})} \right)_{SSB}} \right) / \ln \left( \frac{M(^{143}\text{Nd})}{M(^{144}\text{Nd})} \right) \quad (4d)$$

where  $int(^{153}\text{Eu})/int(^{151}\text{Eu})_{spl}$ ,  $int(^{153}\text{Eu})/int(^{151}\text{Eu})_{SSB}$  and  $int(^{143}\text{Nd})/int(^{144}\text{Nd})_{SSB}$  were the already blank corrected measured raw ratio in the sample and the SSB standard,

$n(^{143}\text{Nd})/n(^{144}\text{Nd})_{cert}$  was the published value of Wakaki & Tanaka [61] (= 0.511592 (5),

which had been IIF corrected via  $n(^{146}\text{Nd})/n(^{144}\text{Nd})_{nat} = 0.72333$  [62]), and  $M(X)$  were the atomic weights extracted from the IUPAC/CIAAW tables [60].

The determination of absolute isotope ratio values of Sr, Pb and Nd included the interference corrected ratio of each system and subsequent correction for IIF via an internal inter-elemental approach using SSB with the corresponding isotopic standards (NIST SRM 987, NIST SRM 981, JNdi-1) and the spiked internal standard (Zr for Sr, Tl for Pb and Eu for Nd).

### **2.3.4 Uncertainty calculations**

The total combined uncertainty budget for each isotopic analysis (Sr, Pb, Nd) was calculated using a simplified Kragten approach according to the protocol of Horsky *et al.* [55]. As main contributors to the uncertainty the precision of the measured isotope ratio of the sample and the standards, as well as the within-run-repeatability of the measured isotope ratio in the bracketing standards as proxy for instrument stability were taken into account.

## **2.4 Extraction chromatography**

### **2.4.1 Chromatographic system**

All matrix separations were performed using the fully automated, low pressure chromatography sample preparation system prepFAST-MC<sup>TM</sup> (Elemental Scientific). The prepFAST-MC<sup>TM</sup> system consists of an autosampler, which can handle up to four standard racks, two 6-port-2-position valves, one 10-port-multi-position valve, a S400V syringe pump with a fill-dispense valve and a 13-mL sample loop. The syringe-driven system allows sample loading, multiple washing steps, column conditioning and elution cycles all at user-defined intervals (time, volume and flow rate) via the system's integrated software [27,50]. The prepFAST-MC<sup>TM</sup> system runs a custom arranged protocol consisting of sub methods provided by the ESI software for the automated separation of Sr, Pb and Nd. All valves and tubes, which get in contact with the different reagents, as well as the column consist of high purity PFA.

### **2.4.2 Column packing**

Various types of columns can be purchased from the manufacturer ESI, either pre-packed with specific resins for different applications (e.g. Sr/Ca, Pb, U/Th separation) or as empty columns with different dimensions in terms of i.d and length. Throughout this work empty columns with a bed volume of 1 mL (i.d 6.2 mm, length 33 mm, part. no. CF-1000) were

utilized and self-packed, using the DGA Resin (TrisKem International) with a mesh size of 50 - 100  $\mu\text{m}$  (part. no. DN-B25-S). Polyethylene frits with a diameter of 6 mm were purchased from Biotage (Biotage, Uppsala, Sweden, part. no. 120-1062-B).

In the first step the empty column was disassembled and rinsed with milli-Q water. A new acid leached frit was inserted and secured with one of the two column nuts. The outlet of the column was connected via a custom-made adapter to a 10-mL syringe that was used to induce a negative pressure to the column. The suspended resin was then filled into the column using a pipette. After the column had been filled completely with resin, a second frit was carefully inserted and positioned by the second nut. Finally, a 50-mL syringe filled with nitric acid (2 % *w/w*) was attached to the adapter and used for rinsing the new column. In addition, this testing step ensured the leak free reassembling of the self-packed column prior to its usage. All used columns were packed at the Helmholtz-Centre Geesthacht.

### **2.4.3 Description of the original ESI Sr/Ca method**

The present initial work was based on the separation protocol for Sr and Ca provided by ESI, which uses the DGA Resin (TrisKem). The DGA Resin is functionalized with *N,N,N',N'*-tetra-*n*-octyldiglycolamide groups and was initially synthesized and characterized by Horwitz *et al.* [32,63]. Originally designed for the separation of actinides from one another, especially the isolation of americium, the DGA Resin also allows a direct separation of Ca and Sr from each other in the presence of e.g. Na, Mg, Al, K, Ti, Fe, Rb, Zr, Ba in complex sample matrices.

The original separation protocol for Sr and Ca uses a rather high concentration of 5 mol L<sup>-1</sup> nitric acid for the elution of Sr. The corresponding elution parameters for this protocol are shown in Table 3.

#### **2.4.4 Calibration of the prepFAST-MC™**

The prepFAST-MC™ offers the possibility to separate sample solutions using the so called “calibration mode” allowing the evaluation/optimization of the elution parameters. In this mode, the stepwise elution of the separated elements from the column is achieved by pumping small, defined reagent volumes (e.g. 1 or 2 mL) through the column with respect to release the specific element fractions from the resin. Every fraction is automatically eluted into a separate vessel, which allows monitoring the elution profiles of each element during subsequent multi-element analysis of the different fractions. Calibration is recommended for any newly purchased or freshly in-house prepared column to optimize separation procedures. In this study, all eluates were diluted by a factor of 10 with nitric acid (2 % w/w) prior to their screening for Sr, Pb, Nd and their main interferences using either ICP-MS or ICP-MS/MS. Calibrations of the columns were done either using an in-house test solution (TS: containing NIST SRM 987, NIST SRM 981, JNdi-1, doped with Ca, Rb, Ce, Sm, Tl, and Hg) or using acid-digests of GBW-07313 to mimic effects of a complex sample matrix. The calibration steps were divided into aliquots of 1 mL, except for the washing of REEs with 0.1 mol L<sup>-1</sup> nitric acid, where 2 mL aliquots were sampled as well as the last washing step with 0.1 mol L<sup>-1</sup> hydrochloric acid, which consisted of one 10 mL aliquot. The elution profile was reconstructed from the multi-element data obtained for the 48 fractions collected by the prepFAST-MC™ system.

#### **2.4.5 Method development for Sr/Pb/Nd separation**

The original ESI separation protocol is unfavorable for the simultaneous analysis of Sr, Pb and Nd due to the fact that Sr and Pb co-elute when using 5 mol L<sup>-1</sup> nitric acid. But the column chemistry is flexible when taking into account that the distribution coefficients ( $K_d$ ) of Sr and Pb depend on the type of acid used as well as its concentration. The DGA Resin offers the possibility for the separation of Sr and Pb (+ Nd) from their isobaric interferences and

various other matrix elements by using different concentrations of nitric acid: Sr, Ca and Pb (+ REEs) are well retained in the concentration range for nitric acid from 2 - 4 mol L<sup>-1</sup> while other matrix elements like Al, Fe, Mg etc. are not retained by the resin under such conditions. The co-elution of Sr and Pb in 5 mol L<sup>-1</sup> nitric acid can be explained by their similar  $K_d$  values as published by Horwitz *et al.* [32], which are still tenfold lower than the one of Ca. While Sr shows similar  $K_d$  values in the concentration range for nitric acid of 0.1 - 0.5 mol L<sup>-1</sup>, Pb has  $K_d$  values two to fivefold higher [32]. Based on the systematic evaluation of the retention behavior of Sr and Pb when using lower concentrated nitric acid, a new separation protocol for sediment digests allowing a separation of Sr and Pb was established. Finally, the Sr fraction was eluted in 0.2 mol L<sup>-1</sup> nitric acid, which would allow the direct measurement of some of the elution solutions without any additional evaporation step, while Pb was eluted with 5 mol L<sup>-1</sup> nitric acid. The elution parameters (flow rates, volumes, acid concentrations) for sample loading and rinsing of the original ESI separation protocol were not changed, as shown in Table 3.

Within the method development a graded elution of rare earth elements (REE) during the column wash with 0.1 mol L<sup>-1</sup> hydrochloric acid (removal of Ca) was observed, when separating acid digests of the marine sediment GBW-07313. This led to the assumption that the DGA Resin would offer also the possibility additionally separate Nd in the developed procedure subsequent to Sr and Pb elution.

Comparing the  $K_d$  values of the REEs published by Pourmand & Dauphas [33] obtained when using diluted nitric acid for elution, it can be seen that La and Ce have significantly lower  $K_d$  values compared to the other REEs. In the presented work, when using 0.1 mol L<sup>-1</sup> nitric acid, their different elution behavior was sufficient for the quantitative removal of Ce and La, while Nd did remain on the column. In a second elution step with 2 mol L<sup>-1</sup> hydrochloric acid, the quantitative separation of Nd from Sm was achieved, as Sm has a significantly higher  $K_d$  value compared to Nd. After the elution of Nd, Sm and remaining REEs had to be sufficiently

stripped off from the resin, in order to minimize potential carry-over effects or any decrease in retention capacity of the resin. This was done in accordance with the original ESI separation protocol using 0.1 mol L<sup>-1</sup> hydrochloric acid. The final optimized separation protocol is shown in Table 3.

**Table 3** Comparison of the elution parameters of the original ESI Sr/Ca separation method and the new separation protocol of Sr, Pb and Nd using a self-packed 1 mL DGA column

Step	<u>Sr/Ca method* (ESI)</u>			<u>Sr/Pb/Nd method (this study)</u>		
	Purpose/ Analyte	Volume/flow rate	Acid	Purpose/ Analyte	Volume/flow rate	Acid
1	Condition column	6 mL / 2 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HNO <sub>3</sub>	Condition column	6 mL / 2 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HNO <sub>3</sub>
2	Load sample	1 mL / 1 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HNO <sub>3</sub>	Load sample	1 mL / 1 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HNO <sub>3</sub>
3	Elute matrix	5 ml / 2 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HNO <sub>3</sub>	Elute matrix	5 ml / 2 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HNO <sub>3</sub>
4	Elute Sr	15 mL / 1 mL min <sup>-1</sup>	5 mol L <sup>-1</sup> HNO <sub>3</sub>	Elute Sr	4 ml / 1 mL min <sup>-1</sup>	0.2 mol L <sup>-1</sup> HNO <sub>3</sub>
5				Elute Pb	5 ml / 1 mL min <sup>-1</sup>	5 mol L <sup>-1</sup> HNO <sub>3</sub>
6				Wash column (Ca, Ce)	30 ml / 1 mL min <sup>-1</sup>	0.1 mol L <sup>-1</sup> HNO <sub>3</sub>
7				Elute Nd	5 ml / 1 mL min <sup>-1</sup>	2 mol L <sup>-1</sup> HCl
8	Elute Ca/wash column	10 mL / 1 mL min <sup>-1</sup>	0.1 mol L <sup>-1</sup> HCl	Wash column (Sm, other REE)	10 ml / 1 mL min <sup>-1</sup>	0.1 mol L <sup>-1</sup> HCl

\* Elemental Scientific and Romaniello *et al.* [27,50]

## 2.5 Spiking, cut-off and carry-over experiments

### 2.5.1 Spiking experiments of NIST SRM 981 and NIST SRM 987 (matrix effects)

Due to the remaining small overlap of the Sr and Pb fractions during elution (chapter 3.2, Figure 1), the possible impact of any residual Pb and Sr in the recovered fractions on the determination of accurate  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  and  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  ratios of NIST SRM 987 and NIST SRM 981 was evaluated.

A solution of NIST SRM 987 (100 ng g<sup>-1</sup> Sr) was spiked with a single element ICP-MS standard of Pb (Merck-Millipore, residual Sr in standard stock solution <20 ng g<sup>-1</sup>) resulting in Pb concentrations of 1 ng g<sup>-1</sup>, 5 ng g<sup>-1</sup>, 10 ng g<sup>-1</sup>, 50 ng g<sup>-1</sup>, 100 ng g<sup>-1</sup> respectively, for

which the  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  value was determined. In the reversal set-up, a solution of NIST SRM 981 (100 ng g<sup>-1</sup> Pb) was spiked with single element ICP-MS standard of Sr (Merck-Millipore, residual Pb in standard stock solution <50 ng g<sup>-1</sup>) resulting in Sr concentrations of 1 ng g<sup>-1</sup>, 5 ng g<sup>-1</sup>, 10 ng g<sup>-1</sup>, 50 ng g<sup>-1</sup>, 100 ng g<sup>-1</sup> respectively, for which the  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  value was determined.

### 2.5.2 Spiking experiments of JNdi-1 (interferences)

The validity of the correction for the isobaric interference of Sm using Eqs. 4a-d. was evaluated by monitoring  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values from a series of solution containing 50 ng g<sup>-1</sup> JNdi-1 spiked with 0.05 ng g<sup>-1</sup>, 0.25 ng g<sup>-1</sup> and 0.5 ng g<sup>-1</sup> Sm (1 g L<sup>-1</sup>, Merck ICP standard) in three-time repetition. The lowest mass fraction of Sm ( $w(\text{Sm})/w(\text{Nd})$ ) of 0.001 was set at the average measured level of residual Sm in the Nd fractions, collected during the separation of GBW-07313 sediment digests and the in-house multi-elemental test solution (TS) (see chapter 2.5.4).

The possible influence of <sup>142</sup>CeH<sup>+</sup> on the determination of  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values was evaluated by monitoring  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values from a series of solution containing 50 ng g<sup>-1</sup> JNdi-1 and 0.05 ng g<sup>-1</sup> Sm (1 g L<sup>-1</sup>, Merck ICP standard) spiked with 1 ng g<sup>-1</sup>, 5 ng g<sup>-1</sup> and 10 ng g<sup>-1</sup> Ce (1 g L<sup>-1</sup>, Merck ICP standard) respectively in triplicates. The lowest mass fraction of Ce ( $w(\text{Ce})/w(\text{Nd})$ ) of 0.02 was set at the average measured level of residual Ce in the Nd fractions, collected during the separation of GBW-07313 sediment digests and the in-house multi-elemental test solution (TS) (see chapter 2.5.4).

### 2.5.3 Cut-off between Sr and Pb fraction

Since the overlap of Sr and Pb in the developed elution profile did not enable a 100 % yield of both analytes at the same time, their potential isotopic fractionation was evaluated for different cut-offs during separation. A mixture of NIST SRM 987 and NIST SRM 981 (1 ug g<sup>-1</sup> Sr and Pb) in 2 mol L<sup>-1</sup> nitric acid was separated following the developed separation

protocol (see Table 3) on an ESI Sr/Ca-1000 column (ESI part no. CF-MC-SrCa-1000) filled with the DGA Resin. This column showed broader peaks for Sr (6 mL elution volume) and Pb (3 mL elution volume) while using the calibration mode. This resulted in an overlap in the fractions at 5 mL to 6 mL, which corresponds to relative amounts of 3 % Sr and 12 % Pb. Hence, the cut-off was set after pooling 4 mL, 5 mL and 6 mL of the Sr fractions. The  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values of the pooled Sr fractions and  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values of the associated pooled Pb fractions were determined by MC ICP-MS.

#### **2.5.4 Recovery, blanks and carry-over**

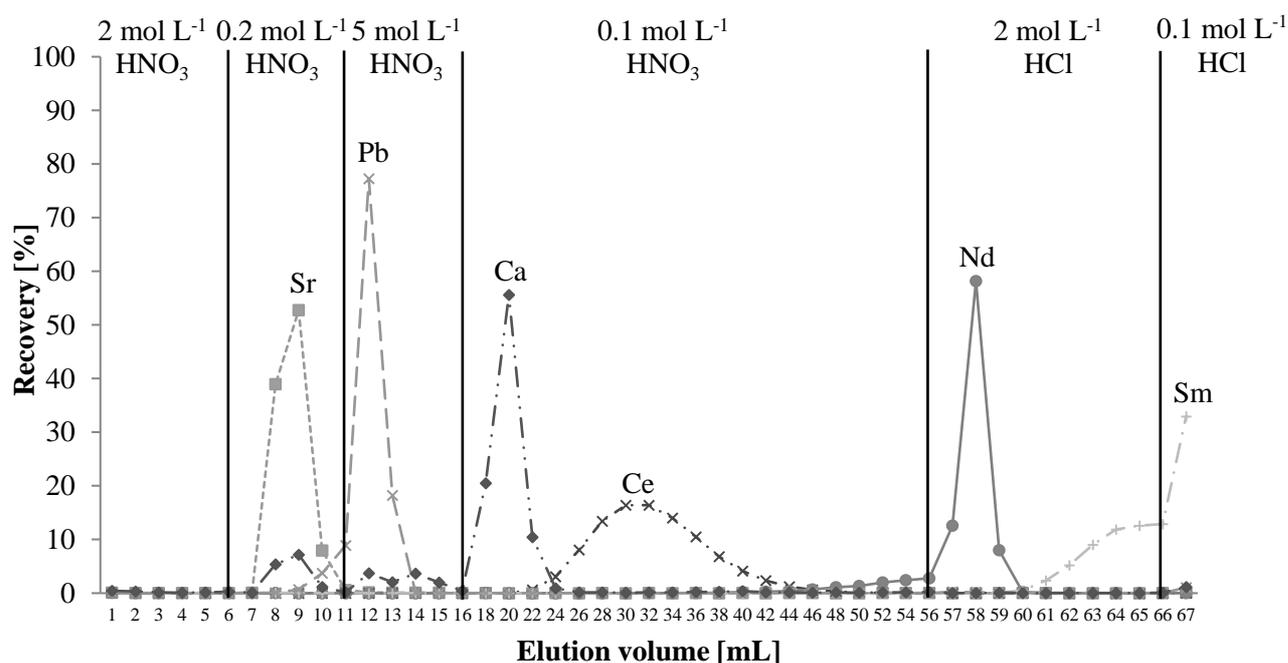
In order to evaluate recoveries, as well as to determine blank concentration levels and potential carry-over effects, an in-house multi-elemental test solution (TS) containing  $1 \mu\text{g g}^{-1}$  Sr (NIST SRM 987),  $0.1 \mu\text{g g}^{-1}$  Pb (NIST SRM 981),  $0.5 \mu\text{g g}^{-1}$  Nd (JNdi-1) and various matrix components ( $15 \mu\text{g g}^{-1}$  Ca,  $0.5 \mu\text{g g}^{-1}$  Rb,  $0.5 \mu\text{g g}^{-1}$  Ce,  $0.1 \mu\text{g g}^{-1}$  Sm,  $0.01 \mu\text{g g}^{-1}$  Tl and  $0.01 \mu\text{g g}^{-1}$  Hg) was prepared in  $2 \text{ mol L}^{-1}$  nitric acid. This solution was separated ten times alternately with a blank separation ( $2 \text{ mol L}^{-1}$  nitric acid) according to the separation scheme described in Table 3. Samples were prepared for measurements of elemental concentrations and isotopic analysis as described above.

The in-house multi-elemental test solution (TS) and the GBW-07313 sediment digest, having significantly different isotopic ratios for Sr, Pb and Nd, were used to evaluate possible shifts in isotopic composition of the separated samples occurring from memory and carry-over effects on the column as known from the Sr Resin [19]. Therefore, these solutions were separated in an alternating sequence with a blank separation in between each sample according to the separation scheme described in Table 3.

### 3. Results

#### 3.1 Optimized elution profile

Figure 1 shows elution profiles of various analytes, separated from the reference material GBW-07313, including Sr, Pb and Nd. The first step of the developed separation procedure after sample loading consisted of a column wash with 2 mol L<sup>-1</sup> nitric acid in order to elute major matrix components like Al, Fe or Ti. Furthermore, potential interferences like Rb, Ba or Hg were stripped off the resin during this rinse step as well, if they had been retained by the DGA Resin in the sample load step with 2 mol L<sup>-1</sup> nitric acid. (Please note that the unretained fraction of the sample matrix during the sample loading is not shown, since its collection via the prepFAST-MC<sup>TM</sup> is not possible). Afterwards, Sr was eluted with 0.2 mol L<sup>-1</sup> nitric acid. This part of the separation was crucial for a high recovery of Pb, since a small overlap between Sr and Pb could not be resolved by means of different concentrations of nitric acid. Therefore, the elution volume of Sr was decreased to 4 mL in the separation protocol shown in Table 3, which led to an increased recovery of Pb. Nevertheless, around 10 % of the total Pb content still eluted in the Sr fraction. A high Pb recovery is required not only because of potential on-column fractionation but also because of the much lower concentrations of Pb in typical sediment digests compared to Sr. In order to evaluate potential bias of the isotopic composition due to incomplete recoveries and presence of Sr in the Pb fraction or vice-versa caused by the overlap of Sr and Pb, cut-off experiments were done (see chapter 3.4). Subsequently, Ca and Ce were eluted with 0.1 mol L<sup>-1</sup> nitric acid. After this column rinse, Nd was eluted with 2 mol L<sup>-1</sup> hydrochloric acid, which sufficiently separated Nd from Sm. Finally, the column was rinsed with 0.1 mol L<sup>-1</sup> hydrochloric acid to remove Sm and potential other elements, which did not elute during the previous steps. The optimized separation protocol enables a sample throughput of ~ 12 samples per 24 h separated for isotopic measurements of Sr, Pb and Nd.



**Fig. 1** Elution profiles for Sr, Pb, Ca, Ce, Nd and Sm separated from the reference material GBW-07313 (marine sediment) using the prepFAST-MC™ calibration mode in combination with the developed separation protocol. 1 mL elution volume for each sampling point using 2 mol L<sup>-1</sup> HNO<sub>3</sub>, 0.2 mol L<sup>-1</sup> HNO<sub>3</sub>, 5 mol L<sup>-1</sup> HNO<sub>3</sub>, and 2 mol L<sup>-1</sup> HCl. 2 mL elution volume for each sampling point using 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 10 mL using 0.1 mol L<sup>-1</sup> HCl.

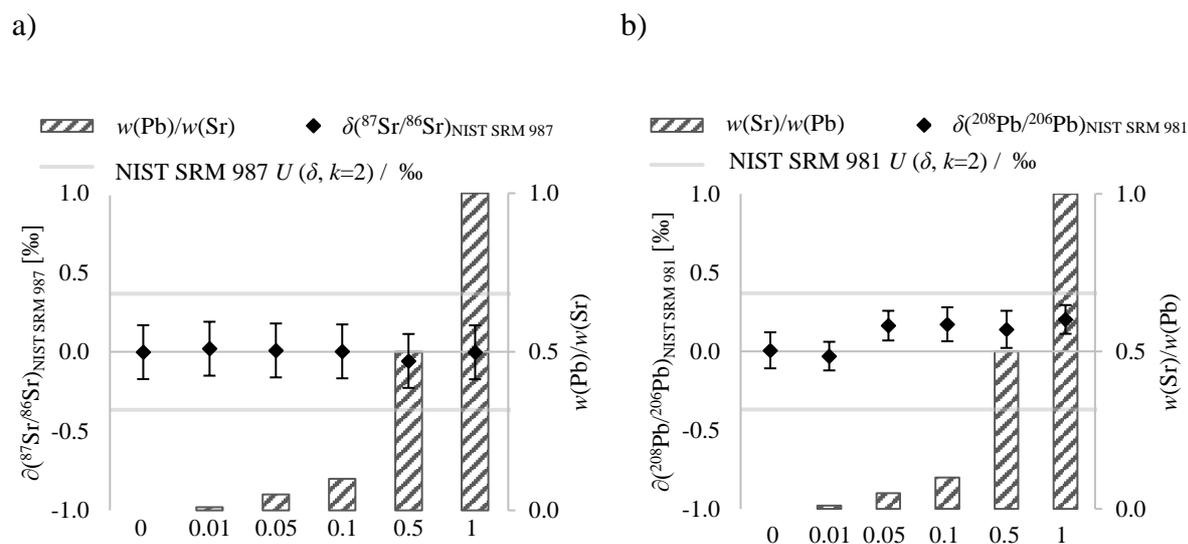
### 3.2 Impact of residual Sr and Pb on isotope ratio measurements

Since the elution overlap between Sr and Pb could not be completely resolved, the corresponding solutions would contain significant amounts of Pb or respectively Sr.

Measurements revealed that the mass fraction of Pb in the collected Sr fraction ( $w(\text{Pb})/w(\text{Sr})$ ) was around 0.01. Due to the much higher Sr concentration in sediment digests, the Sr mass fraction in the collected Pb fraction ( $w(\text{Sr})/w(\text{Pb})$ ) raised up to 0.5. To evaluate potential effects of residual Sr and Pb on isotope ratio measurements a spiking experiment was carried out.

The  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values of the Pb-spiked NIST SRM 987 solutions overlapped within their uncertainties with the un-spiked NIST SRM 987 solution ( $w(\text{Sr})/w(\text{Pb}) = 0$ ) and

are within the certified range of NIST SRM 987 even in presence of up-to the equal level of Pb and Sr, as shown in Figure 2a. Hence, no significant shifts in the  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values related to Pb were observed. In the reversal experiment, the  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values of the Sr-spiked NIST SRM 981 solutions in presence of Sr mass fraction between 0.05 and 1 showed a shift of about 0.2 ‰ towards higher values in comparison to the values of those with a Sr mass fraction of 0.01. The  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values of all Sr-spiked NIST SRM 981 solutions excepted for those with the same concentration level of Sr and Pb ( $w(\text{Pb})/w(\text{Sr}) = 1$ ) overlapped within the uncertainties with the value of the un-spiked NIST SRM 981 solution ( $w(\text{Pb})/w(\text{Sr}) = 0$ ). Still, all  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values are within the certified range of the NIST SRM 981 (Figure 2b). Hence, the shifts were considered as not significant.



**Fig. 2** a)  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values of Pb-spiked NIST SRM 987, b)  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values of Sr-spiked NIST SRM 981. Un-spiked solutions of NIST SRM 987 and NIST SRM 981 are represented as

$w(\text{Pb})/w(\text{Sr}) = 0$  and  $w(\text{Sr})/w(\text{Pb}) = 0$ . Horizontal grey lines show the upper and lower  $\delta$ -limited of the reference materials. Error bars correspond to expanded uncertainties  $U$  ( $k = 2$ ).

### **3.3 Evaluation of Sm correction strategies and impact of residual Ce for Nd isotope ratio measurements**

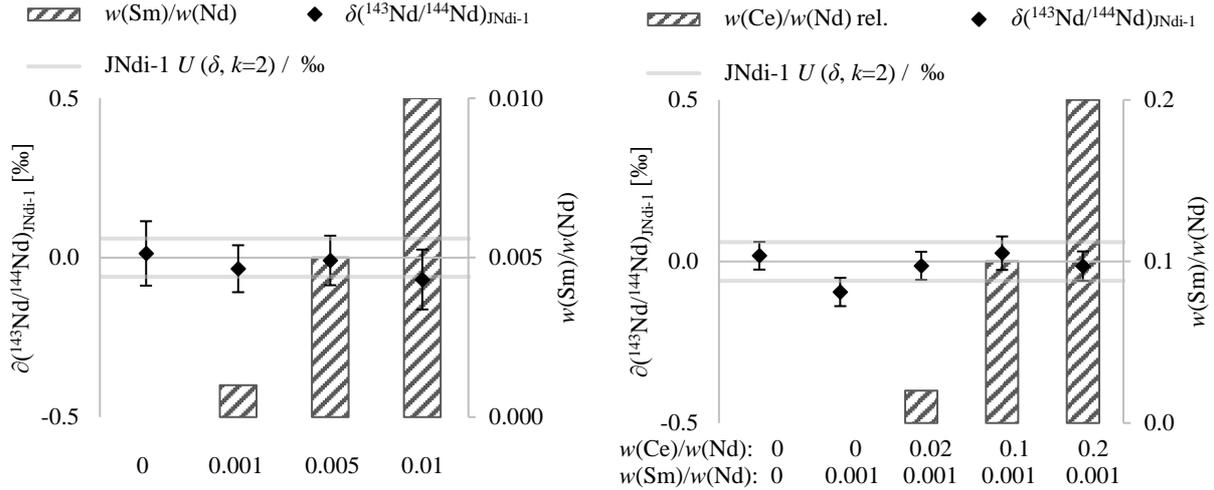
As described in chapter 3.5, separated Nd fractions contained Sm mass fraction of approximately 0.001, as well as mass fraction of Ce up-to 0.1. Thus, the efficiency of Sm correction and the influence of residual Ce on Nd ratio measurements was evaluated by spiking experiments.

The determined  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values of JNdi-1 in presence of Sm mass fraction up-to 0.01, utilizing the Sm correction as described above, overlapped within their uncertainties with the un-spiked values of JNdi-1 ( $w(\text{Sm})/w(\text{Nd}) = 0$ ) and laid within the uncertainty of the published value for JNdi-1, as shown in Figure 3a. Hence, it can be concluded that the  $^{144}\text{Sm}$  interference correction works sufficient for Sm mass fractions up-to 0.01.

The determined  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values of JNdi-1 spiked with Ce mass fraction up-to 0.2 in presence of Sm mass fraction of 0.001 overlapped within their uncertainties with the values of un-spiked JNdi-1 ( $w(\text{Ce})/w(\text{Nd}) = 0$ ) and laid within the uncertainty of the published value for JNdi-1. Therefore, no shifts in the isotopic composition caused by possible  $^{143}(\text{CeH})^+$  interferences were observed, as shown in Figure 3 b.

a)

b)



**Fig. 3** a)  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values of Sm-spiked JNdi-1 b)  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values of Ce-spiked JNdi-1 containing Sm mass fraction of 0.001. Un-spiked solutions of JNdi-1 are represented as  $w(\text{Sm})/w(\text{Nd}) = 0$  and  $w(\text{Ce})/w(\text{Nd}) = 0$ . Horizontal grey lines show the upper and lower  $\delta$ -limited of the reference materials. Error bars correspond to expanded uncertainties  $U (k = 2)$ .

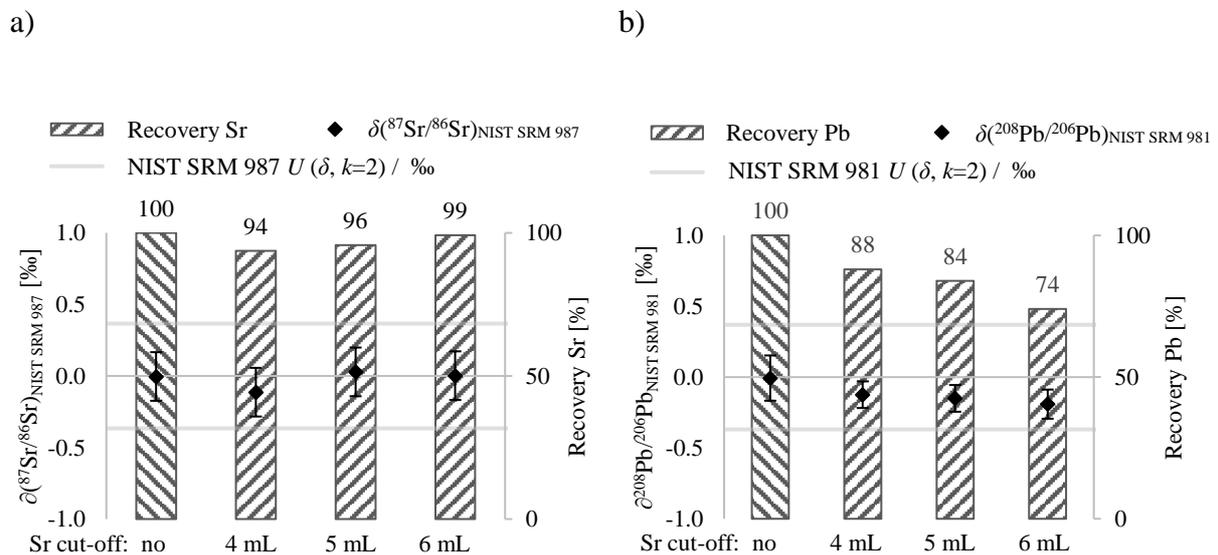
### 3.4 Cut-off between Sr and Pb fractions

Recent studies have revealed that the (extraction) chromatographic separation technique can cause isotopic fractionation of analytes [17,23,25,48] and therefore, a 100% yield should be targeted. Since the elution overlap of Sr and Pb in the developed elution profile did not enable a 100 % yield for both analytes at the same time, the potential isotopic fractionation was evaluated for different cut-offs volumes during separation.

The  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  value in the cut-off volume of 4 mL showed a shift towards lower values in comparison to those of 5 mL and 6 mL for Sr fraction, which would indicate a possible fractionation towards higher masses in the later elution fractions. These observations stand in contrast to the general observations of on-column fractionation in extraction chromatographic separations, where higher masses tend to elute first [17,23,25,48]. However, still, all three  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values overlapped within their uncertainties with the values of the un-processed NIST SRM 987 solution (Sr cut-off: no) and laid within the

uncertainty of the certified values of NIST SRM 987 (Figure 4a). Hence, the shifts were considered as not significant.

The  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values measured for the Pb fractions corresponding to the cut-off volumes 4 mL, 5 mL and 6 mL for the Sr fraction were all slightly shifted by about 0.15 ‰ to 0.2 ‰ towards lower values as compared to the value of the unprocessed NIST SRM 981, indicating a possible fractionation towards higher masses eluting first within the Sr fractions. However, all  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values of the three Sr cut-off volumes overlapped within the uncertainties with the value of the un-processed NIST SRM 981 solution (Sr cut-off: no) and laid within the certified range of NIST SRM 981, as shown in Figure 4b. Hence, the shifts were considered as not significant. In spite of these observations, the cut-off volume during Sr elution was set at 4 mL, favoring a quantitative yield of Pb for the expected low concentrations in sediment digests.



**Fig. 4** a)  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values of separated NIST SRM 987 with cut-off volumes 4 mL, 5 mL and 6 mL for Sr fraction and the corresponding Sr recovery, b)  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values of separated NIST SRM 981 with cut-off volumes 4 mL, 5 mL and 6 mL for Sr fraction and the corresponding Pb recovery. Un-processed solutions of NIST SRM 987 and NIST SRM 981 are represented as Sr cut-off: no. Horizontal grey lines show

the upper and lower  $\delta$ -limited of the reference materials. Error bars correspond to expanded uncertainties  $U$  ( $k = 2$ ).

### 3.5 Recovery, blanks and carry-over

To evaluate recoveries, blank concentration levels as well as potential carry over effects, the in-house multi-elemental test solution (TS) was separated ten times according to the separation scheme described in Table 3. The achieved recoveries are shown in Table 4a. Recoveries for all ten repetitions were  $> 90\%$  in case of Sr,  $>93\%$  in case of Pb and  $>91\%$  in case of Nd. All determined  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$  values for the ten-time-repetition overlapped within uncertainty with the certified value of NIST SRM 987, set as delta anchor ( $0\%$ ), and laid within the certified range of NIST SRM 987 ( $U_{\text{NIST SRM 987}}$ ), as shown in Table 4a. The  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  and  $\delta(^{207}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$  values for the ten-time-repetition showed a general negative off-set to the certified value of the NIST SRM 981, set as delta anchor ( $0\%$ ), while  $\delta(^{206}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$  values showed a general positive off-set to the delta anchor ( $0\%$ ). Nonetheless, the overall determined  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{207}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{208}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{207}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$  and  $\delta(^{206}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$  values overlapped within uncertainty with the certified range of NIST SRM 981 ( $U_{\text{NIST SRM 981}}$ ), as shown in Table 4a. The determined  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values for the ten-time-repetition overlapped within uncertainty with the reference values of JNdi-1 ( $U_{\text{JNdi-1}}$ ), set as delta anchor ( $0\%$ ), as shown in Table 4a. Potential procedural blanks were about  $0.07 \text{ ug L}^{-1}$  Sr,  $0.03 \text{ ug L}^{-1}$  Pb and  $0.57 \text{ ug L}^{-1}$  Nd for a sequence of 10 blanks. To evaluate memory and carry-over effects for the separation of sediment digests, an alternating sequence of in-house test solution (TS) and sediment digest of GBW-07313 was run. All determined  $\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST SRM 987}}$ ,  $\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{207}\text{Pb}/^{206}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{208}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{207}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$ ,  $\delta(^{206}\text{Pb}/^{204}\text{Pb})_{\text{NIST SRM 981}}$  and  $\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$  values of the separated in-house test solution (TS) overlapped within their uncertainty of 10-times-repetition measurements. Same goes for all values of the sediment

digests of the GBW-07313. In sum, this indicated no significant shifts in their isotopic composition related to possible memory or carry-over effects of the column, as shown in Table 4b. Based on these observations, no blank has to be separated between samples. During both experiments, backgrounds of approximately  $w(\text{Rb})/w(\text{Sr})$  of 0.0006 and  $w(\text{Ca})/w(\text{Sr})$  of 0.9 in Sr fractions,  $w(\text{Hg})/w(\text{Pb})$  of 0.01 in Pb fractions, and  $w(\text{Sm})/w(\text{Nd})$  of 0.001 in the Nd fractions were observed. This proved the suitability of the DGA Resin for repetitive usage after its regeneration by 0.1 mol L<sup>-1</sup> hydrochloric acid within an automated matrix separation approach. Meanwhile the background of Ce concentrations in Nd fractions generally increased with increasing number of samples processed. In the ten-time-repetition of the in-house standard, the concentrations of Ce in the Nd fractions raised from ( $w(\text{Ce})/w(\text{Nd})$ ) 0.01 to 0.04. The same effect was observed during the alternating separation of the in-house standard and the GBW-07313 sediment digest ( $w(\text{Ce})/w(\text{Nd})$  of 0.02 to 0.07). This indicates an aging process of the DGA Resin regarding special elements, which generally limits reusability. Nevertheless, the measurement protocol for Nd isotopic analysis showed to be robust up-to a mass fraction of Ce of 0.2 as shown earlier.

#### **4. Discussion**

The results clearly show the capability of the method to accomplish automated, simultaneous separation of Sr, Pb and Nd from sediment digests with respect to isotopic analysis within a single-stage separation using the extraction chromatography DGA Resin. Compared to previously published, manually operated methods [18,36,37], this automated approach has several distinct advantages: (1) the unattended processing of one sample every two hours. In comparison with the existing protocols, this drastically reduces laboratory manpower, consumption of expensive high purity acids and resin. In addition, the operation accuracy of the prepFAST-MC<sup>TM</sup> syringe pump system allows to maintain constant elution conditions resulting in high run-to-run-reproducibility and reduces human-operator-related errors; (2)

high recoveries for all three analytes > 90 %, while interfering elements such as Rb, Ca, Hg, Ce, and Sm are effectively removed from the solutions. This enables accurate isotope ratio analysis of Sr, Pb and Nd from one sample aliquot; (3) the low blank concentration levels of Sr, Pb and Nd, as well as the lack in memory or carry-over effects, allow at least ten times of re-use, which stands in agreement with the observations of Romaniello *et al.* [50] for Sr. This is a major leap forward in term of high sample throughput; (4) the use of highly diluted nitric acid for Sr elution enables the direct Sr isotope ratio analysis of the samples without the need for any further (error prone) sample handling steps such as evaporation and re-dissolution. Beside these advantages, some aspects and limitations of the presented method have to be considered: (1) the overlap of Sr and Pb elution limits the yields for both analytes, while separated at the same time. There is a need to set a cut-off favoring one of these two isotopic systems. While residual Pb in the Sr fraction show no impact on the Sr isotopic ratios, the Pb isotope ratios of NIST SRM 981 spiked with a mass fraction of Sr > 0.05 indicate a potential shift. The cut-off between the Sr and the Pb fractions indicated a potential shift in Pb isotopic composition with yields < 90%. Since all potential shifts were within the measurement uncertainty, a cut-off for Sr (higher yields of Pb, accepting residual Sr in the eluate) seems to be the favorable approach when considering the lower levels of Pb in contrast to Sr in sediment digests; (2) calibration of any freshly prepared column is highly recommended to adjust the elution volumes as slight changes in the elution profile are possible; (3) adaption and optimization of the separation scheme with changes in the sample matrix; (4) the Ce background on the column increases with increasing re-use of the DGA Resin, which might indicate resin aging. However, spiking experiments demonstrated, that the measurement routine for Nd isotope ratios is robust and does not show  $^{143}(\text{CeH})^+$  interferences on  $^{143}\text{Nd}^+$  in presence of a Ce mass fraction up-to 0.2. Therefore, a screening of the eluted fractions prior to analysis is recommended: Sr fraction for Rb, Ca and REE; Pb fraction for Hg; Nd fraction from Sm and Ce.

The developed method represents a step forward to facilitation of simultaneous and automated separation of multiple isotopic systems and offers opportunities for adaption to other matrices or also extension to additional isotopic systems being separated with modified protocols.

## **5. Acknowledgements**

The authors would like to acknowledge Paul Field together with Patrick Klemens from Elemental Scientific as well as Stephen Romaniello from Arizona State University for their input related to the prepFAST-MC<sup>TM</sup> system and Steffen Happel (Triskem) for providing a first version of a self-packed column. We would like to thank the Geological Survey of Japan (Hikari Kamioka) for providing us with an aliquot of JNdi-1 (neodymium oxide) standard as well as Anna Reese (Helmholtz-Centre Geesthacht) and Tine Opper (VIRIS laboratory) for their support in the lab.

## **Conflict of Interest**

The authors declare that they have no conflict of interest.

## **References**

1. DePaolo DJ (1988) Neodymium Isotope Geochemistry. An Introduction, vol 20. Minerals, Rocks and Mountains. Springer-Verlag Berlin Heidelberg. doi:10.1007/978-3-642-48916-7
2. Capo RC, Stewart BW, Chadwick OA (1998) Strontium isotopes as tracers of ecosystem processes: theory and methods. *Geoderma* 82:197–225
3. Faure G, Mensing TM (2005) *Isotopes: Principles and Applications*. 3rd edn. Wiley&Sons Inc., Hoboken
4. Irrgeher J, Prohaska T (2015) CHAPTER 6 Instrumental Isotopic Fractionation. In: *Sector Field Mass Spectrometry for Elemental and Isotopic Analysis*. The Royal Society of Chemistry, pp 107-120. doi:10.1039/9781849735407-00107
5. Meija J, Yang L, Mester Z, Sturgeon RE (2012) Correction of Instrumental Mass Discrimination for Isotope Ratio Determination with Multi-Collector Inductively Coupled Plasma Mass Spectrometry. In: *Isotopic Analysis*. Wiley-VCH Verlag GmbH & Co. KGaA, pp 113-137. doi:10.1002/9783527650484.ch5
6. Woodhead J, Swearer S, Hergt J, Maas R (2005) In situ Sr-isotope analysis of carbonates by LA-MC-ICP-MS: interference corrections, high spatial resolution and an example from otolith studies. *J Anal At Spectrom* 20 (1):22. doi:10.1039/b412730g

7. Prohaska T (2015) CHAPTER 7 Interferences. In: Sector Field Mass Spectrometry for Elemental and Isotopic Analysis. The Royal Society of Chemistry, pp 121-125. doi:10.1039/9781849735407-00121
8. Galler P, Limbeck A, Boulyga SF, Stingeder G, Hirata T, Prohaska T (2007) Development of an On-Line Flow Injection Sr/ Matrix Separation Method for Accurate, High-Throughput Determination of Sr Isotope Ratios by Multiple Collector-Inductively Coupled Plasma-Mass Spectrometry. *Anal Chem* 79:5023-5029
9. Irrgeher J, Prohaska T, Sturgeon RE, Mester Z, Yang L (2013) Determination of strontium isotope amount ratios in biological tissues using MC-ICPMS. *Anal Methods* 5 (7):1687. doi:10.1039/c3ay00028a
10. nu instruments (2016) Application note AN22: Capability in resolving anayte peaks from interferences for precise and accurate isotopic measurements Nu Plasma II - MULTI COLLECTOR ICP-MS. nu instruments, Wexham
11. Thermo Scientific (2016) Thermo Scientific Neptune Plus - Multicollector ICP-MS. Mass Spectrometry. Thermo Scientific, Bremen
12. Irrgeher J, Galler P, Prohaska T (2016)  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio measurements by laser ablation multicollector inductively coupled plasma mass spectrometry: Reconsidering matrix interferences in bioapatites and biogenic carbonates. *Spectrochim. Acta B* 125:31-42. doi:10.1016/j.sab.2016.09.008
13. Hanousek O, Rottmann L, Prohaska T (2015) CHAPTER 5 Mass Resolution. In: Sector Field Mass Spectrometry for Elemental and Isotopic Analysis. The Royal Society of Chemistry, pp 97-106. doi:10.1039/9781849735407-00097
14. Moens LJ, Vanhaecke FF, Bandura DR, Baranov VI, Tanner SD (2001) Elimination of isobaric interferences in ICP-MS, using ion–molecule reaction chemistry: Rb/Sr age determination of magmatic rocks, a case study. *J Anal At Spectrom* 16 (9):991-994. doi:10.1039/b103707m
15. Bolea-Fernandez E, Balcaen L, Resano M, Vanhaecke F (2016) Tandem ICP-mass spectrometry for Sr isotopic analysis without prior Rb/Sr separation. *J Anal At Spectrom* 31 (1):303-310. doi:10.1039/c5ja00157a
16. Woods G (2014) Lead isotope analysis: Removal of  $^{204}\text{Hg}$  isobaric interference from  $^{204}\text{Pb}$  using ICP-QQQ in MS/MS mode. Application note, Agilent Technologies.
17. De Muynck D, Huelga-Suarez G, Van Heghe L, Degryse P, Vanhaecke F (2009) Systematic evaluation of a strontium-specific extraction chromatographic resin for obtaining a purified Sr fraction with quantitative recovery from complex and Ca-rich matrices. *J Anal At Spectrom* 24 (11):1498. doi:10.1039/b908645e
18. Pin C, Gannoun A, Dupont A (2014) Rapid, simultaneous separation of Sr, Pb, and Nd by extraction chromatography prior to isotope ratios determination by TIMS and MC-ICP-MS. *J Anal At Spectrom* 29 (10):1858-1870. doi:10.1039/c4ja00169a
19. Deniel C, Pin C (2001) Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements. *Anal. Chim. Acta* 426 (1):95-103. doi:http://dx.doi.org/10.1016/S0003-2670(00)01185-5
20. Míkova J, Denková P (2007) Modified chromatographic separation scheme for Sr and Nd isotope analysis in geological silicate samples. *J. Geosci* 52:221-226. doi:10.3190/jgeosci.015
21. Pin C, Bassin C (1992) Evaluation of a strontium-specific extraction chromatographic method for isotopic analysis in geological materials. *Anal. Chim. Acta* 269 (2):249-255. doi:http://dx.doi.org/10.1016/0003-2670(92)85409-Y
22. Pin C, Briot D, Bassin C, Poitrasson F (1994) Concomitant separation of strontium and samarium-neodymium for isotopic analysis of silicates samples, based on specific extraction chromatography. *Anal. Chim. Acta* 298:209-217

23. Smet I, De Muynck D, Vanhaecke F, Elburg M (2010) From volcanic rock powder to Sr and Pb isotope ratios: a fit-for-purpose procedure for multi-collector ICP-mass spectrometric analysis. *J Anal At Spectrom* 25 (7):1025-1032. doi:10.1039/B926335G
24. Pin C, Zalduegui JS (1997) Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. *Anal. Chim. Acta* 339 (1):79-89. doi:http://dx.doi.org/10.1016/S0003-2670(96)00499-0
25. Ohno T, Hirata T (2013) Determination of Mass-Dependent Isotopic Fractionation of Cerium and Neodymium in Geochemical Samples by MC-ICPMS. *Anal. Sci.* 29 (1):47-53. doi:10.2116/analsci.29.47
26. Field P Elemental Scientific - Booth 918. In: AGU Fall Meeting, San Francisco, 3-7 December 2012 2012.
27. Field P (2015) prepFAST-MC™ - Automating Sample Purification - MC-ICPMS. Elemental Scientific, Omaha
28. Field P (2015) prepFAST-MC: Mg, Sr and Ca Isotopes. Elemental Scientific, Omaha
29. Field P (2015) prepFAST-MC : Lead Extraction for MC-ICP-MS. Elemental Scientific, Omaha
30. Field P (2015) prepFAST-MC: Fe, Cu, Zn and Cd Isotopes. Elemental Scientific, Omaha
31. Field P, Tevepaugh KN, Ticknor BW, Kim H, Bottorff SC, Hexel CR (2017) Advances in Nuclear Forensics. Paper presented at the European Winter Conference on Plasma Spectrochemistry St. Anton, Austria,
32. Horwitz EP, McAlister DR, Bond AH, Barrans RE (2005) Novel Extraction Chromatographic Resins Based on Tetraalkyldiglycolamides: Characterization and Potential Applications. *Solvent Extraction Ion Exch* 23 (219)
33. Pourmand A, Dauphas N (2010) Distribution coefficients of 60 elements on TODGA resin: Application to Ca, Lu, Hf, U and Th isotope geochemistry. *Talanta* 81:741-753. doi:10.1016/j.talanta.2010.01.008
34. Horwitz EP, Chiarizia R, Dietz ML (1992) A novel strontium-selective extraction chromatographic resin *Solvent Extraction Ion Exch* 10 (2):313-336. doi:10.1080/07366299208918107
35. Pourmand A, Prospero JM, Sharifi A (2014) Geochemical fingerprinting of trans-Atlantic African dust based on radiogenic Sr-Nd-Hf isotopes and rare earth element anomalies. *Geology* 42 (8):675
36. Jweda J, Bolge L, Class C, Goldstein SL (2016) High Precision Sr-Nd-Hf-Pb Isotopic Compositions of USGS Reference Material BCR-2. *Geostand. Geoanal. Res* 40 (1):101-115. doi:10.1111/j.1751-908X.2015.00342.x
37. Li C-F, Wang X-C, Guo J-H, Chu Z-Y, Feng L-J (2016) Rapid separation scheme of Sr, Nd, Pb, and Hf from a single rock digest using a tandem chromatography column prior to isotope ratio measurements by mass spectrometry. *J Anal At Spectrom* 31 (5):1150-1159. doi:10.1039/c5ja00477b
38. Latkoczy C, Prohaska T, Watkins M, Teschler-Nicola M, Stingeder G (2001) Strontium isotope ratio determination in soil and bone samples after on-line matrix separation by coupling ion chromatography (HPIC) to an inductively coupled plasma sector field mass spectrometer (ICP-SFMS). *J Anal At Spectrom* 16 (0):806-811. doi:10.1039/b102797m
39. Galler P, Limbeck A, Uveges M, Prohaska T (2008) Automation and miniaturization of an on-line flow injection Sr/matrix separation method for accurate, high throughput determination of Sr isotope ratios by MC-ICP-MS. *J Anal At Spectrom* 23 (10):1388. doi:10.1039/b803964j
40. García-Ruiz S, Moldovan M, García Alonso JI (2007) Large volume injection in ion chromatography Separation of rubidium and strontium for on-line inductively coupled plasma mass

- spectrometry determination of strontium isotope ratios. *J. Chromatogr. A* 1149:274-281. doi:10.1016/j.chroma.2007.03.048
41. Garcia-Ruiz S, Moldovan M, Garcia Alonso JI (2008) Measurement of strontium isotope ratios by MC-ICP-MS after on-line Rb-Sr ion chromatography separation. *J Anal At Spectrom* 23 (1):84-93. doi:10.1039/b708936h
42. Karasinski J, Bulska E, Wojciechowski M, Krata AA, Halicz L (2016) On-line separation of strontium from a matrix and determination of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio by Ion Chromatography/Multicollector-ICPMS. *J Anal At Spectrom*. doi:10.1039/C6JA00109B
43. Halicz L, Lam JWH, McLaren JW (1994) An on-line method for the determination of lead and lead isotope ratios in fresh and saline waters by inductively coupled plasma mass spectrometry. *Spectrochim. Acta B* 49 (7):637-647. doi:http://dx.doi.org/10.1016/0584-8547(94)80057-X
44. Zurbrick CM, Gallon C, Flegal AR (2013) A new method for stable lead isotope extraction from seawater. *Anal. Chim. Acta* 800:29-35. doi:10.1016/j.aca.2013.09.002
45. Röllin S, Kopajtjic Z, Wernli B, Magyar B (1996) Determination of lanthanides and actinides in uranium materials by high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection. *J. Chromatogr. A* 739 (1-2):139-149. doi:http://dx.doi.org/10.1016/0021-9673(96)00037-4
46. Günther-Leopold I, Wernli B, Kopajtjic Z, Günther D (2004) Measurement of isotope ratios on transient signals by MC-ICP-MS. *Anal Bioanal Chem.* 378 (2):241-249. doi:10.1007/s00216-003-2226-1
47. Günther-Leopold I, Kivel N, Kobler Waldis J, Wernli B (2008) Characterization of nuclear fuels by ICP mass-spectrometric techniques. *Anal Bioanal Chem.* 390 (2):503-510. doi:10.1007/s00216-007-1644-x
48. Guéguen F, Isnard H, Nonell A, Vio L, Vercoouter T, Chartier F (2015) Neodymium isotope ratio measurements by LC- MC-ICPMS for nuclear applications: investigation of isotopic fractionation and mass bias correction. *J Anal At Spectrom* 30:443-452. doi:10.1039/C4JA00361F  
10.1039/c4ja00361f
49. Rodríguez-Castrillón JÁ, García-Ruiz S, Moldovan M, García Alonso JI (2012) Multiple linear regression and on-line ion exchange chromatography for alternative Rb-Sr and Nd-Sm MC-ICP-MS isotopic measurements. *J Anal At Spectrom* 27 (4):611. doi:10.1039/c2ja10274a
50. Romaniello SJ, Field MP, Smith HB, Gordon GW, Kim MH, Anbar AD (2015) Fully automated chromatographic purification of Sr and Ca for isotopic analysis. *J Anal At Spectrom* 30 (9):1906-1912. doi:10.1039/c5ja00205b
51. Saji NS, Wielandt D, Paton C, Bizzarro M (2016) Ultra-high-precision Nd-isotope measurements of geological materials by MC-ICPMS. *J Anal At Spectrom* 31 (7):1490-1504. doi:10.1039/C6JA00064A
52. Enge TG, Field MP, Jolley DF, Ecroyd H, Kim MH, Dosseto A (2016) An automated chromatography procedure optimized for analysis of stable Cu isotopes from biological materials. *J Anal At Spectrom*. doi:10.1039/c6ja00120c
53. Brand WA, Coplen TB, Vogl J, Rosner M, Prohaska T (2014) Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). *Pure Appl. Chem* 86 (3):425-467. doi:10.1515/pac-2013-1023
54. Tanaka T, Togashi S, Kamioka H, Amakawa H, Kagami H, Hamamoto T, Yuhara M, Orihashi Y, Yoneda S, Shimizu H, Kunimaru T, Takahashi K, Yanagi T, Nakano T, Fujimaki H, Shinjo R, Ashara Y, Tanimizu M, Dragusanu C (2000) JNdi-1: a neodymium isotopic reference in consistency with LaJolla neodymium. *Chem. Geol.* 168:279-281
55. Horsky M, Irrgeher J, Prohaska T (2015) Evaluation strategies and uncertainty calculation of isotope amount ratios measured by MC ICP-MS on the example of Sr. *Anal Bioanal Chem.* doi:10.1007/s00216-015-9003-9

56. Yang L, Peter C, Panne U, Sturgeon RE (2008) Use of Zr for mass bias correction in strontium isotope ratio determinations using MC-ICP-MS. *J Anal At Spectrom* 23 (9):1269-1274. doi:10.1039/b803143f
57. Irrgeher J, Vogl J, Santner J, Prohaska T (2015) CHAPTER 8 Measurement Strategies. In: *Sector Field Mass Spectrometry for Elemental and Isotopic Analysis*. The Royal Society of Chemistry, pp 126-151. doi:10.1039/9781849735407-00126
58. Kramchaninov AY, Chernyshev IV, Shatagin KN (2012) Isotope analysis of strontium by multicollector inductively-coupled plasma mass spectrometry: High-precision combined measurement of  $^{88}\text{Sr}/^{86}\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios. *J Anal Chem* 67 (14):1084-1092. doi:10.1134/s1061934812140067
59. Meija J, Coplen TB, Berglund M, Brand WA, De Bièvre P, Gröning M, Holden NE, Irrgeher J, Loss RD, Walczyk T, Prohaska T (2016) Isotopic compositions of the elements 2013 (IUPAC Technical Report). *Pure Appl. Chem* 88 (3). doi:10.1515/pac-2015-0503
60. Meija J, Coplen TB, Berglund M, Brand WA, De Bièvre P, Gröning M, Holden NE, Irrgeher J, Loss RD, Walczyk T, Prohaska T (2016) Atomic weights of the elements 2013 (IUPAC Technical Report). *Pure Appl. Chem* 88 (3). doi:10.1515/pac-2015-0305
61. Wakaki S, Tanaka T (2012) Stable isotope analysis of Nd by double spike thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* 323–324:45-54. doi:<http://dx.doi.org/10.1016/j.ijms.2012.06.019>
62. Dubois JC, Retali G, Cesario J (1992) Isotopic analysis of rare earth elements by total vaporization of samples in thermal ionization mass spectrometry. *Int. J. Mass Spectrom. Ion Process.* 120 (3):163-177. doi:[http://dx.doi.org/10.1016/0168-1176\(92\)85046-3](http://dx.doi.org/10.1016/0168-1176(92)85046-3)
63. Eichrom Technologies (2016) DGA Resin Technical Info. [http://www.eichrom.com/products/info/dga\\_resin.aspx](http://www.eichrom.com/products/info/dga_resin.aspx). Accessed February 2016

**Table 4** a) Sr, Pb, and Nd recovery,  $\delta$ -values of Sr, Pb and Nd, and blank concentration levels of Sr, Pb, and Nd for ten-time repeated separation of a test solution (TS), b) Sr, Pb, and Nd recovery,  $\delta$ -values of Sr, Pb and Nd, and blank concentration levels of Sr, Pb, and Nd for alternating separation of TS and GBW-07313, c) absolute Sr, Pb and Nd isotopic ratios of GBW-07313. The uncertainty of the reference materials and those in brackets are the *expanded uncertainties*  $U$  ( $k = 2$ ).

Sample ID	Sr recovery		Sr content in Pb		$\delta$ -values					Pb content in Nd		Nd content	
	[%]	$\delta(^{87}\text{Sr}/^{86}\text{Sr})_{\text{NIST}}$	blank*	recovery	$\delta(^{208}\text{Pb}/^{206}\text{Pb})_{\text{NIST}}$	$\delta(^{207}\text{Pb}/^{206}\text{Pb})_{\text{NIST}}$	$\delta(^{208}\text{Pb}/^{204}\text{Pb})_{\text{NIST}}$	$\delta(^{207}\text{Pb}/^{204}\text{Pb})_{\text{NIST}}$	$\delta(^{206}\text{Pb}/^{204}\text{Pb})_{\text{NIST}}$	blank*	recovery	$\delta(^{143}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}$	in blank*
	SRM 987	SRM 987	[ug/L]	SRM 981	SRM 981	SRM 981	SRM 981	SRM 981	SRM 981	[ug/L]	SRM 981	SRM 981	[ug/L]
$U_{\text{NIST SRM 987}}$		$\pm 0.37$											
$U_{\text{NIST SRM 981}}$					$\pm 0.37$	$\pm 0.36$	***	***					
$U_{\text{Jndi-1}}$													$\pm 0.06$ ****
<b>a)</b>													
TS_1	100	0.00(27)	0.18	94	-0.25(11)	-0.38(23)	-0.04(16)	-0.21(26)	0.20(9)	<LOD	106	0.03(4)	0.67
TS_2	94	-0.07(27)	0.03	97	-0.27(11)	-0.72(23)	0.64(16)	0.22(26)	0.93(9)	<LOD	95	-0.08(4)	0.33
TS_3	93	-0.03(27)	0.07	101	-0.14(11)	-0.18(23)	0.28(16)	0.23(26)	0.42(9)	<LOD	98	-0.05(4)	0.43
TS_4	89	-0.16(27)	0.07	98	-0.09(11)	-0.10(23)	0.20(16)	0.17(26)	0.27(9)	<LOD	103	0.13(4)	0.52
TS_5	89	-0.00(27)	0.01	100	-0.13(11)	-0.11(23)	0.09(16)	0.19(26)	0.19(9)	<LOD	91	0.00(4)	0.56
TS_6	90	-0.02(27)	0.04	102	-0.07(11)	-0.14(23)	0.24(16)	0.07(26)	0.27(9)	<LOD	94	0.02(4)	0.71
TS_7	91	-0.06(27)	0.16	99	-0.22(11)	-0.33(23)	0.02(16)	-0.13(26)	0.23(9)	0.10	97	0.01(4)	0.59
TS_8	92	-0.00(27)	0.11	94	-0.30(11)	-0.24(23)	-0.04(16)	-0.05(26)	0.27(9)	0.21	107	-0.03(4)	0.75
TS_9	91	-0.06(27)	0.04	95	-0.28(11)	-0.80(23)	-0.13(16)	-0.69(26)	0.13(9)	<LOD	101	-0.04(4)	0.56
TS_10	90	-0.08(27)	0.00	93	-0.34(11)	-0.43(23)	-0.27(16)	-0.48(26)	0.05(9)	<LOD	98		0.56
<b>b)</b>													
TS_1	97	0.13(28)	0.28	82	-0.15(5)	-0.27(3)	0.36(25)	0.23(25)	0.49(25)	0.08	92	0.02(4)	0.40
GBW_1	97	1.21(28)	0.05	92	-43.24(5)	-85.80(3)	57.02(25)	1.00(25)	104.79(25)	0.09	98	0.51(4)	0.14
TS_2	97	0.09(28)	0.06	86						0.07			0.16
GBW_2	98	1.13(28)	0.02	96	-43.27(5)	-85.79(3)	56.87(25)	9.91(25)	104.69(25)		98	0.52(4)	0.17
TS_3	101	0.12(28)	0.02	84						0.06			0.24
GBW_3	100	1.13(28)	0.04	96	-43.21(5)	-85.74(3)	56.98(25)	9.99(25)	104.70(25)	0.05			0.44
TS_4	100	0.07(28)	0.03	93	-0.18(5)	-0.34(3)	0.39(25)	0.24(25)	0.58(25)	0.05	103	-0.04(4)	0.25
GBW_4	99	1.10(28)	0.05	99	-43.27(5)	-85.80(3)	56.95(25)	9.94(25)	104.72(25)	0.06	103	0.49(4)	0.43
TS_5	100	0.14(28)	0.03	93	-0.25(5)	-0.42(3)	0.43(25)	0.26(25)	0.68(25)	0.05	101	-0.02(4)	0.39
GBW_5	54	1.14(28)	0.03	105	-43.18(5)	-85.70(3)	56.92(25)	9.93(25)	104.61(25)	0.05	98	0.46(4)	0.62
av. GBW ( $n = 5$ )		1.14(28)			-43.23(6)	-85.77(5)	56.95(26)	9.95(25)	104.70(26)				0.50(5)
<b>c)</b>													
		$n(^{87}\text{Sr})/n(^{86}\text{Sr})$			$n(^{208}\text{Pb})/n(^{206}\text{Pb})$	$n(^{207}\text{Pb})/n(^{206}\text{Pb})$	$n(^{208}\text{Pb})/n(^{204}\text{Pb})$	$n(^{207}\text{Pb})/n(^{204}\text{Pb})$	$n(^{206}\text{Pb})/n(^{204}\text{Pb})$			$n(^{143}\text{Nd})/n(^{144}\text{Nd})$	
av. GBW ( $n = 5$ )		0.71109(23)			2.0742(1)	0.83617(5)	38.809(25)	18.710(11)	15.644(9)			0.51201(13)	

\*blank separated after sample, \*\*estimated from certified  $n(^{204}\text{Pb})/n(^{206}\text{Pb})$ , \*\*\*anchor values were calculated via certified masses, \*\*\*\*using values for  $n(^{143}\text{Nd})/n(^{144}\text{Nd})$  ratio determined by Wakaki & Tanaka [61] (= 0.511591, IIF corrected via  $n(^{146}\text{Nd})/n(^{144}\text{Nd}) = 0.72333$ )

