Sr-Nd isolation procedure for subsequent isotopic analysis using multi-collector ICP – mass spectrometry in the context of provenance studies on archaeological glass

Monica Ganio^a, Kris Latruwe^b, Dieter Brems^a, Philippe Muchez^a, Frank Vanhaecke, Patrick Degryse^a

5

Sr and Nd isotopic analysis of glass can be relied upon to unravel the provenance of the flux component and the sand used in the manufacturing of archaeological glasses, respectively. For reliable isotopic analysis of the target elements using multi-collector ICP – mass spectrometry, the target elements need to be isolated from the matrix to permit adequate correction for instrumental mass discrimination. In this paper, a simple, fast and reliable analytical method for the isolation of Sr and Nd from complex sample matrixes such as archaeological glasses is proposed. Special attention is focused onto the Nd isolation protocol, with the definition of TRU-Spec and Ln-Spec resin bed volumes and of an appropriate HCl concentration to optimize Nd elution from the column.

Keywords: Nd isotopes, Sr isotopes, isolation procedure, TRU-Spec resin, Ln-Spec resin, archaeological glass

15

Introduction

Objective determination of provenance relies on the assumption that there is a scientifically measurable property that will link an artifact to a particular source or production site¹. In the field of ancient glass studies, both determining where the raw materials used in the production of glass may have come from, and where the glass may have been shaped are of prime importance. Since the elemental composition of Roman glass was found to be relatively uniform, it was proven very difficult to assign specific objects to their manufacturing site. Recent advances using isotopic analysis of elements containing a radiogenic isotope, in particular Sr and Nd, have allowed the development of new approaches in the provenance determination of primary glass^{2–6}. Due to their high masses and low relative mass differences, Sr and Nd isotopes are not measurably fractionated at the temperatures involved in glass melting, and therefore, their isotopic composition in a glass artifact will be identical to that in the raw materials from which it is derived. The Sr in glass is mainly incorporated with the lime-bearing constituents, being either shell or limestone, or lime-rich plant ash^{2–5}. When CaCO₃ was derived from Holocene beach shell, the ⁸⁷Sr/⁸⁶Sr ratio of the glass reflects that of modern seawater, whereas when the lime was derived from ‘geologically aged’ limestone, the signature of the glass reflects that of the limestone, possibly modified by diagenesis. For plant ash glass, the ⁸⁷Sr/⁸⁶Sr ratio will reflect that the bio-available strontium from the soils on which the plants grew. Nd comes from the non-quartz or heavy mineral fraction of the silica raw material⁶. The Nd isotopic composition of the sediment input of most rivers into the Mediterranean is relatively homogeneous. This is because it is the result of erosion of crustal material with similar compositions. However, in the Eastern Mediterranean, Nile sediments have an exceptional Nd isotopic composition due to the input from volcanic rocks from the Ethiopian Plateau. The Western Mediterranean on the other hand

also has inputs from wind-blown Saharan dust⁷. As a consequence, the east-west axis of the Mediterranean has a Nd isotopic gradient⁸, which allows tracing of the origin of the sand used in primary glass production^{9–11}.

55

Prior to mass spectrometric analysis using multi-collector ICP-MS, target element purification is needed to avoid potential spectral interferences and to allow for an accurate correction for instrumental mass discrimination¹². Whereas the extraction chromatographic separation of Sr from complex matrixes is relatively easy and well established¹³, this is less the case for Nd. Nd is conventionally separated from the concomitant matrix by a two-step extraction chromatographic separation using TRU and Ln resin^{14–24}. In a first step, the LREEs are separated from the matrix using TRU resin (Eichrom Technologies, Darien IL, USA). In a second step, Ln resin (Eichrom Technologies, Darien IL, USA) is used for sequential separation of the LREEs.

So far, little attention has been drawn to the definition of a specific Sr-Nd isolation protocol for the analysis of archaeological glass, despite the increasing number of provenance studies based on these isotopic systems^{2–6,25–30}. The aim of this work was to define a simple, rapid and practical analytical protocol for the isolation of Sr and Nd from complex glass matrixes. Special attention is focused onto the Nd isolation procedure. The following aspects were addressed: (i) dependence of the elution profile on the amount of resin and column type and (ii) selection of the HCl concentration best suited for Nd elution, (iii) definition of a Sr-Nd protocol for the sequential separation of both isotopes from the same sample digest.

80

Experimental

Reagents and materials

All sample preparation was performed in a class 10 clean lab at Ghent University, Belgium. *Pro analysi* nitric acid (14 M) and hydrochloric acid (12 M) (Panreac, Spain) were further purified by sub-boiling distillation in PFA and quartz equipment, respectively. Hydrofluoric acid (22 M, intra-analyzed) was bought from J.T. Baker Chemicals N.V., The Netherlands. Ultrapure water with a resistivity >18.2 MΩ cm was obtained from a Milli-Q Element system (Millipore, USA) and used throughout this work for diluting concentrated acids. Standard solutions for elemental analysis were prepared by diluting commercially available single element 1 g L⁻¹ stock solutions (Alfa Johnson-Matthey, Germany).

The two chromatographic resins used in the Nd separation tests, referred to as TRU-Spec and Ln-Spec, were purchased from Eichrom Technologies (Darien IL, USA). Information on the chemical properties of these extraction chromatographic resins can be found in the literature^{14–16,31,32}. Fresh resin was first dispersed in Milli-Q water, allowed to settle for a few minutes and the supernatant was decanted. Fresh Milli-Q water was added again to the resin and the resin was loaded into pre-cleaned columns.

As mentioned before, the isolation of Nd from any type of sample matrix usually involves a first separation step using TRU resin. During this step, the LREEs are separated from the bulk of the sample matrix. Most methods described in literature^{14–16,18,20} use 2 M HNO₃ to load the samples onto the TRU resin and to wash off the matrix elements, and 0.05 M HNO₃ to elute the LREEs. However, all these methods use varying amounts of resin (between 250 µl and 1 ml) and different volumes of the acids. In this study, three different TRU resin bed volumes were tested and the amounts of acids needed to remove the matrix elements from the columns and to collect the LREE fraction were determined. To this end, BioRad polypropylene Micro Bio-Spin columns, which can hold up to 800 µl of resin, were packed with TRU resin beds of 100, 250 and 600 µl.

A second extraction chromatographic separation step is needed to separate Nd from the rest of the LREEs. This can be done using Ln resin. Published methods^{16,19–24}, however, all use different volumes of resin (between 300 µl and 2 ml) and different volumes and concentrations of HCl to displace the LREEs. In

Table 1. Instrument settings and data acquisition parameters for the Thermo Element XR single-collector ICP-MS instrument

instrument settings	
RF power	1100 W
nebulizer gas flow rate	0.9 - 1.0 l min ⁻¹ (optimized daily)
plasma gas flow rate	15 l min ⁻¹
auxiliary gas flow rate	0.7 l min ⁻¹
sample uptake rate	0.2 ml min ⁻¹
sampling cone	Ni; 1.1 mm aperture diameter
skimmer	Ni; 0.8 mm aperture diameter
resolution	low (R = 300)
data acquisition parameters	

detector mode	triple
scan type	E-scan
sample time	0.01 s
sampling points per spectral peak	10
runs	3
passes	16
estimated total time	87 s

addition to the resin bed volume, the dependence of the elution profile on the features of the column used was also tested. For this purpose, two different types of columns were packed with Ln resin: a BioRad polypropylene Poly-Prep column, 9 cm long with a 0.8 cm inner diameter and a porous 1 mm polyethylene frit, and an Eichrom polypropylene column, 8 cm long with a 0.8 cm inner diameter and a porous 3 mm frit. Both column types were packed with 0.75, 1.5 and 2 ml of Ln resin. After filling the columns, the resins were cleaned with five 1 ml aliquots of Milli-Q H₂O.

Instrumentation

Elemental analysis

Semi-quantitative analysis was carried out at low mass resolution using a (single-collector) Thermo Scientific ELEMENT XR double-focusing sector-field ICP-MS instrument. The instrument was equipped with a self-aspirating MicroFlow PFA nebulizer with a declared sample uptake rate of 200 µl/min. The instrument settings and data acquisition parameters for this instrument are summarized in Table 1. Nd fractions were analyzed for Rb, La, Ce, Nd, Sm and Eu to (i) assess whether Nd was adequately separated from the other elements, with particular focus on Ce and Sm, and (ii) find out how fast Nd was eluted from the column.

Quantitative Nd determination was carried out using a Perkin-Elmer SCIEX Elan 5000 quadrupole-based ICP – mass spectrometer. The sampling introduction system consisted of a cross-flow nebulizer mounted onto a Scott-type spray chamber and sample solution was transported to the nebulizer at a flow rate of 1 ml/min with a multi-channel peristaltic pump. The instrument settings and data acquisition parameters for this instrument are summarized in Table 2.

Table 2. Instrument settings and data acquisition parameters for the Perkin-Elmer Sciex ELAN 5000 ICP-MS instrument

instrument settings	
RF power	1100 W
nebulizer gas flow rate	0.8-0.9 l min ⁻¹ (optimized daily)
plasma gas flow rate	15 l min ⁻¹
auxiliary gas flow rate	0.8 l min ⁻¹
sample uptake time	1 ml min ⁻¹
sampling cone	Ni; 1.0 mm aperture diameter
skimmer	Ni; 1.0 mm aperture diameter
data acquisition parameters	
detector mode	dual

scanning mode	peak hop transient
dwell time	50 ms
sampling points per spectral peak	1
sweeps/reading	40
readings/replicate	3
replicate time	6000 ms
number of replicates	4

Isotope ratio determination

Nd isotope ratio measurements were carried out using a Thermo Scientific Neptune multi-collector ICP-MS instrument. This instrument provides double-focusing with a Nier-Johnson geometry and was operated in low-resolution mode ($m/\Delta m=400$). Sample delivery was accomplished via an auto-aspirating low-flow (50 $\mu\text{l}/\text{min}$) PFA nebulizer, mounted onto a combined cyclonic/double-pass spray chamber made of quartz glass. The multi-collector arrangement consists of a fixed central Faraday cup along with 8 movable Faraday cups and 3 secondary electron multipliers. Instrument settings, data acquisition parameters and cup configurations used for Nd isotope ratio measurements are presented in Table 3. The intensities for $^{147}\text{Sm}^+$ and $^{149}\text{Sm}^+$ were measured to correct for the isobaric overlap of $^{144}\text{Sm}^+$, $^{148}\text{Sm}^+$ and $^{150}\text{Sm}^+$ and the corresponding isobaric Nd isotopes. Data acquisition was done in 30 cycles of 5 s integration, grouped in blocks of 5 cycles. Outliers were removed by the software on the basis of a 2s-test (95 % confidence interval). The JNdi-1 standard (Geological Survey of Japan) solution was measured after every two samples. After measurement of every sample or standard solution, the sample introduction system was rinsed for a few minutes with 0.42 M HNO_3 to allow the signal intensities to drop back to blank levels. Procedure blanks for Nd were negligible compared to Nd intensities for samples and standards.

To calculate the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, the measured intensities for $^{147}\text{Sm}^+$ and $^{149}\text{Sm}^+$ were used to correct for the contribution of Sm to the apparent intensity for the $^{144}\text{Nd}^+$ isotope, using $^{144}\text{Sm}/^{149}\text{Sm}$, $^{144}\text{Sm}/^{147}\text{Sm}$ and $^{147}\text{Sm}/^{149}\text{Sm}$ ratios of 0.22214, 0.20480 and 1.08466³³, respectively. To correct for instrumental mass discrimination, Nd isotope ratios were internally normalized using the Russell's law to the invariant $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ ³³. Repeated measurements of the JNdi-1 Nd standard yielded $^{143}\text{Nd}/^{144}\text{Nd} = 0.512098 \pm 0.000020$ (2σ , $n = 53$).

Table 3. Instrument settings, cup configuration and data acquisition parameters for the Thermo Scientific Neptune multi-collector ICP-MS

instrument settings	
RF power	1300 W
plasma gas flow rate	15 L min^{-1}
auxiliary gas flow rate	0.6 L min^{-1}
nebulizer gas flow rate	1.5 L min^{-1}
sampling cone	Ni, aperture diameter 1.1 mm
skimmer	Ni, aperture diameter 0.9 mm
extraction lens voltage	4 V
mass resolution	400
sample delivery	auto-aspiration

sample uptake rate			1 mL min ⁻¹						
cup configuration									
L4	L3	L2	L1	C	H1	H2	H3	H4	
¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁸ Nd	¹⁴⁹ Sm	¹⁵⁰ Nd	
¹⁴² Ce		¹⁴⁴ Sm							¹⁵⁰ Sm
data acquisition parameters									
magnet delay time			3 s						
integration time			5 s						
number of cycles			10 per block						
number of blocks			5						
measurement time			~200 s						

Samples and sample digestion

A standard solution containing Rb, La, Ce, Nd, Sm and Eu was prepared to have Nd, Ce and Sm concentrations of 500 $\mu\text{g}/\text{l}$, and Rb, La and Eu concentrations of 250 $\mu\text{g}/\text{l}$. These concentrations were selected in order to simulate the corresponding situation in a typical archaeological glass. Rb was added to the lanthanides in order to simulate a sample matrix.

To evaluate the method, the glass certified reference materials NIST SRM 610, NIST SRM 612 and NIST SRM 620, available from the National Institute for Standards and Technology (USA), the glass certified reference material SGT CRM 10, available from the Society of Glass Technology (UK), the granodiorite reference material GSJ JG-1 available from the Geological Survey of Japan (Japan), and the Neodymium isotopic reference material JNdi-1 available from the Geological Survey of Japan (Japan) were used. Depending on the Nd concentrations, 15 to 100 mg of powdered reference material was weighed into a 15 ml flat bottom Savillex PFA vial and subjected to digestion.

100 mg of powdered sample are weighed into a 7 ml flat bottom Savillex PFA screw-top beaker and subjected to a hotplate digestion procedure. In a first digestion step, 3 ml of 22 M HF and 1 ml of 14 M HNO_3 are added to the powdered sample. The beakers are closed and placed on a hotplate (110°C) overnight. Then the beakers are opened and the mixture is evaporated to near dryness on a hotplate. The residues are taken up in 3 ml of 12 M HCl + 1 ml of 14 M HNO_3 (aqua regia) and again, the closed beakers are heated on a hotplate overnight and evaporated to dryness.

Fig.1. Elution profile for the Micro-BioSpin column (BioRad) with 600 μ l of TRU resin

Fig.2. Elution profile for the BioSpin column (BioRad) packed with 0.75, 1.5 and 2 ml of Ln resin

Fig.3. Elution profile for the Eichrom column packed with 0.75, 1.5 and 2 ml of Ln resin

To assess the possibility of regenerating the resins after use, a 500 μ g/l solution of the Neodymium isotopic reference material JNdi-1 from the Geological Survey of Japan (Japan) has been chosen, together with an in-house Nd standard solution (500 μ g/l solution). The two solutions have been alternatively loaded onto column for a total of nine times, rinsing with Milli-Q H_2O in-between.

Results and discussion

Definition of the Nd isolation protocol

Dependence of the elution profile on the amount of resin and column type

To optimize the volume of resin in the columns, and define the best column type, three different bed volumes for each resin, and three different columns, were tested.

1 ml of standard solution in 2 M HNO_3 was loaded onto preconditioned columns (BioRad Micro Bio-Spin columns packed with 100, 250 or 600 μ l of TRU spec resin). The conditioning of the TRU resin was done with five 1 ml aliquots of water and 1 ml of 2 M HNO_3 . After sample loading, the TRU resin was washed with a total volume of 4 ml of 2 M HNO_3 to elute the unwanted matrix elements, while the LREE remain strongly held by the resin. During this phase, the individual 1 ml aliquots were collected separately. Subsequently, the LREE were eluted with 10 ml (arbitrary volume) of 0.05 M HNO_3 , and again every 1 ml aliquot was collected separately.

The resulting 15 (1 loading, 4 rinsing and 10 elution) aliquots were analysed for the presence of Rb, La, Ce, Nd, Sm and Eu. In the case of 100 μ l and 250 μ l of TRU resin, the Nd was eluting directly during the loading, and no separation from the complex glass matrix, simulated in the standard solution by the presence of Rb, was achieved. The 600 μ l TRU bed resin, instead, allowed a good separation of Nd and the other LREE from the Rb matrix (Fig. 1). The elution is achieved within the first 7 ml of 0.05 M HNO_3 .

1 ml of the standard solution in 0.05 M HNO_3 was loaded onto preconditioned columns (BioRad polypropylene Poly-Prep

columns and Eichrom polypropylene columns packed with 0.75, 1.5 or 2 ml of Ln spec resin) The conditioning of the Ln resin was done with five 1 ml aliquots of water, followed by 1 ml of 0.25 M HCl and 1 ml of 0.05 M HNO_3 . After loading the samples, the Ln resin was washed with 20 ml of 0.25 M HCl, divided into 1 ml aliquots, with every aliquot collected separately.

The resulting 20 aliquots were analysed for the presence of Rb, La, Ce, Nd, Sm and Eu. In this way, the elution profiles shown in Figs. 2 and 3 were obtained. The Ln resin elution profiles were clearly affected by both column type and resin amount. The use of the BioRad column (Fig. 2) did not lead to sufficient separation of Ce and Nd from one another and the Nd peak was spread over a larger effluent volume than with the Eichrom column. With the Eichrom column (Fig. 3), both 1.5 and 2 ml resin beds provided good separation of Ce, Nd and Sm. However, since the 2 ml resin bed required a larger volume of acid to displace Nd, 1.5 ml of resin is preferred. Sm, which gives rise to spectral overlap with ^{144}Nd , was not eluted after 20 ml of 0.25 M HCl.

Selection of HCl concentration best suited for Nd elution

The selection of the HCl concentration best suited for Nd elution is essential. The capacity factors of the LREEs on the Ln resin are strongly dependent on the HCl concentration ¹⁶. *Pro analysi* HCl (12 M) was further purified by sub-boiling distillation in quartz

Fig.4. Dependence of the elution profile on the HCl concentration

equipment. Different sub-boiled batches show slightly different final acid concentration, and replicates of the separation method showed a small variation in the amount of effluent needed to elute the Nd fraction. As this jeopardizes routine use, it was decided to determine the exact HCl concentration of every batch of purified HCl via acid-base titration and, based on the corresponding outcome, dilute the HCl to an appropriate extent with Milli-Q water.

After introduction of this approach, the efficiency of separating Nd from the other LREEs was tested for 3 different HCl concentrations (0.20, 0.25 and 0.30 M). As shown in Fig. 4, when using 0.3 M HCl, it is not possible to achieve a good separation of Ce and Nd. Both 0.25 and 0.20 M HCl provided acceptable separation. However, since a larger volume of 0.20 M HCl is required to fully elute the Nd fraction (up to 20 ml for each sample), 0.25 M HCl is preferred, and allows a good, even if not fully complete, separation of Ce and Nd. It was experimentally verified that the Ce remaining in the Nd fraction did not exert any noticeable influence on the Nd isotope ratio measurement result.

To evaluate and verify the method described above, replicate Nd isotopic analyses of four international glass reference materials (NIST SRM 610, NIST SRM 612, NIST SRM 620, SGT CRM 10), a granodiorite reference material (GSJ JG-1) and the Neodymium certified reference material (JNdi-1) were carried out using the Neptune MC-ICP-MS. The results, summarized in table 4, show a good reproducibility of the measurements, and are in agreement with the published data^{34,35}.

Regeneration of the TRU and Ln extraction chromatographic resins

An experiment was set up to assess the performance of both TRU and Ln resin after being regenerated and used multiple times to isolate Nd. The incautious reuse of resin can be an important source of cross-contamination between samples when the target element or the sample matrix is not completely removed.

The regeneration procedure put forward consisted of rinsing the resin with Milli-Q H₂O after use, followed by rinsing the TRU resin with 2 M HNO₃ and the Ln resin with 0.25 M HCl, the same procedure as was used in this work to pre-clean the resins before use.

Table 4. Evaluation of the method. Replicate measurements of four international glass reference materials (NIST SRM 610, NIST SRM 612, NIST SRM 620, SGT CRM 10), a granodiorite reference material (GSJ JG-1) and the Neodymium certified reference material (JNdi-1)

Evaluation of the method

	¹⁴³ Nd/ ¹⁴⁴ Nd			
	this study	average	2 st dev	reference value
NIST SRM 610	0.511932 ± 0.000033 0.511924 ± 0.000029 0.511946 ± 0.000037	0.511934	0.000022	0.511927 ± 0.000004
NIST SRM 612	0.511917 ± 0.000039 0.511937 ± 0.000050 0.511918 ± 0.000037	0.511924	0.000023	0.511930 ± 0.000004
NIST SRM 620	0.512122 ± 0.000073 0.512147 ± 0.000078 0.512159 ± 0.000079	0.512143	0.000038	
SGT CRM 10	0.511973 ± 0.000161 0.511946 ± 0.000041 0.511928 ± 0.000034	0.511949	0.000045	
JG-1	0.512382 ± 0.000029 0.512394 ± 0.000037 0.512378 ± 0.000032	0.512385	0.000016	
JNdi-1	0.512113 ± 0.000032 0.512103 ± 0.000034 0.512164 ± 0.000197 0.512102 ± 0.000031 0.512139 ± 0.000058	0.512124	0.000054	0.512115 ± 0.000007

The selected resin bed volume for TRU (600 µl) and Ln (1.5 ml) resins were submitted to regeneration and their re-use was evaluated via the JNdi-1 certified reference material and an in-house Nd standard solution. The results of the resin regeneration are summarized in Figs. 5 and 6. In a first batch, an amount of JNdi-1 certified reference material was loaded onto a new column. After Nd isolation, the column was washed with 10 ml of Milli-Q H₂O to regenerate the resin. In a second batch, a Nd in-house standard solution was loaded onto the regenerated resin. A second regeneration step using 10 ml of Milli-Q H₂O was applied, and in a third batch, again JNdi-1 certified reference material was loaded onto the column. The same procedure was repeated for 10 times, both on TRU and Ln resin columns. After the isolation procedures, the Nd isotope ratio was determined via MC-ICP-MS. No systematic difference is observed between the isotope ratio results obtained after use of a new column on the one hand, and after re-use of one that was used once or twice before, on the other. Moreover, the ¹⁴³Nd/¹⁴⁴Nd ratio obtained for every JNdi-1 certified reference material is, within experimental uncertainty, in agreement with the values reported for this reference material³⁵. It can be concluded that the regeneration of TRU and Ln resins using 10 ml milli-Q of H₂O, followed by a pre-cleaning treatment with 2 ml of 2 M HNO₃ and 2 ml of 0.25 M HCl, respectively, is efficient. The regeneration approach validated here allows using the resin at least 4 times.

Fig. 5. Regeneration of TRU resin. Replicate measurements of JNdi-1 and of a in-house standard solution

Fig. 6. Regeneration of LN resin. Replicate measurements of JNdi-1 and of a in-house standard solution

Sr-Nd isolation protocol

The Sr-Nd optimized separation protocol is schematically shown in Fig. 7. The typical Sr content of an archaeological glass varies between 200 and 600 $\mu\text{g/g}$; the Nd concentration is typically between 5 and 10 $\mu\text{g/g}$. The protocol defined here is suitable for a Sr concentration of 5 up to 35 $\mu\text{g/ml}$ ¹³, and for a Nd concentration of 300 $\mu\text{g/l}$ up to 1 $\mu\text{g/ml}$.

After the digestion procedure (described in an earlier section), the residue is dissolved in 1 ml of 7 M HNO_3 and Sr is isolated from the concomitant matrix using the extraction chromatographic method described in the literature¹³. Due to the high concentration of Sr in archaeological glasses, only 100 μl of sample solution is loaded onto a column. The Bio-Spin column (BioRad), packed with 400 μl of Sr-SpecTM resin (Eichrom), is previously cleaned with five 1 ml aliquots of milli-Q H_2O , followed by 1 ml of 6 M HCl (to eliminate any trace of Pb), 1 ml of milli-Q H_2O and then conditioned with 1 ml of 7 M HNO_3 . After rinsing with four 1 ml aliquots of 7 M HNO_3 to eliminate the matrix, the Sr fraction is eluted with 5.5 ml of 0.05 M HNO_3 .

The remaining 900 μl of sample digest are put on a hotplate and evaporated to dryness. The residue is dissolved in 1 ml of 2 M HNO_3 , and is loaded onto a preconditioned Micro Bio-Spin polypropylene column (Bio-Rad) containing 600 μl of TRU resin.

Sample digestion

~200 mg sample
6 ml 22M HF + 2 ml 14M HNO_3 , 24h on hotplate + evaporate to dryness
6 ml 12M HCl + 2 ml 14M HNO_3 , 24h on hotplate + evaporate to dryness

Sr isolation

a) Resin bed washing and conditioning

b) Sample loading and matrix elements elution

c) Sr elution

d) Washing

Nd isolation

a) Resin bed washing and conditioning

b) Sample loading and matrix elements elution

c) LREEs elution from TRU resin and loading on Ln resin

d) Nd elution

e) Washing

Fig. 7. Sr-Nd protocol

The conditioning of the TRU resin is done with five 1 ml aliquots of milli-Q H_2O and 1 ml of 2 M HNO_3 . After loading the samples, the TRU resin is washed with four 1 ml aliquots of 2 M HNO_3 to elute the unwanted matrix elements, while the LREEs remain strongly held by the resin. The TRU-Spec column containing the LREE is then placed above a pre-cleaned 2 ml

Eichrom polypropylene column containing 1.5 ml of Ln resin. The Ln resin is preconditioned with five 1 ml aliquots of H₂O, 1 ml of 0.25 M HCl, and 1 ml of 0.05 M HNO₃. The LREEs are eluted from the TRU resin with seven 1 ml aliquots of 0.05 M HNO₃ and immediately sorbed onto the Ln-Spec column. Then the columns are decoupled. The Ln resin is rinsed with two 2.5 ml aliquots of 0.25 M HCl, during which La and Ce are eluted. Then, the Nd fraction is collected using three 3 ml aliquots of 0.25 M HCl. This Nd-containing fraction is evaporated to dryness on a hotplate and redissolved in 1 ml of 0.42 M HNO₃. Although the Nd isolate contains minor amounts of Ce, this solution is suitable for isotopic analysis of Nd using MC-ICP-MS.

Both Sr and Nd fractions are checked for concentrations and diluted to 250 µg/l prior to multi-collector ICP-MS measurements.

Conclusions

In this paper, a simple, fast and reliable analytical method for the isolation of Sr and Nd from complex sample matrixes such as archaeological glasses is proposed.

100 mg of finely powdered glass are digested on hotplate in closed flat bottom Savillex PFA screw-top beakers, using, in a first step, a 3:1 mixture of 22 M HF and 14 M HNO₃ followed by evaporation to dryness, and, in a second step, aqua regia followed by evaporation to dryness. For the isolation of Sr ¹³, 100 µl of solution in 7 M HNO₃ are loaded onto a BioSpin column (BioRad) packed with 400 µl Sr-Spec resin (Eichrom Technologies). After rinsing with 4 ml of 7 M HNO₃ to eliminate the matrix, the Sr fraction is eluted with 5.5 ml of 0.05 M HNO₃. The isolation of Nd involved a 2-step chromatographic separation. The 900 µl of sample solution not used for Sr separation are dried, taken up in 1 ml of 2 M HNO₃, and loaded onto a Micro-BioSpin column (BioRad) filled with 600 µl TRU-Spec resin (Eichrom Technologies). After washing it with 4 ml of 2 M HNO₃, the Micro-BioSpin column is connected to an Eichrom column (0.8 cm inner diameter) packed with 1.5 ml of Ln-Spec resin (Eichrom Technologies), and is rinsed with 7 ml of 0.05 M HNO₃ in order to elute the LREE fraction from the TRU resin onto the Ln resin. The Ln resin is then washed with 5 ml of 0.25 M HCl, and the Nd fraction is stripped off using 9 ml of 0.25 M HCl.

Acknowledgements

The authors would like to thank the Geological Survey of Japan for providing the JNdi-1 certified reference material. The research is financially supported by the ERC Starting Grant ARCHGLASS Grant agreement no. 240750 and FWO projects no. 6.0864.09 and G002111N. Monica Ganio and Dieter Brems are currently working as Aspirant of the Research Foundation – Flanders (FWO).

Notes and references

- ^aDepartment of Earth and Environmental Sciences, Section Geology, Katholieke Universiteit Leuven, Celestijnenlaan 200E – bus 2410, BE-3001 Leuven, Belgium monica.ganio@ees.kuleuven.be
- ^bDepartment of Analytical Chemistry, Ghent University, Krijgslaan 281 - S12, BE-9000 Ghent, Belgium
1. Weigand, P. C.; Harbottle, G.; Sayre, E. V. In *Exchange Systems in Prehistory*; Earle, T. K.; Ericson, J. E., Eds.; Academic press: New York, 1977; pp. 15-34.
2. Wedepohl, K. H.; Baumann, A. *Die Naturwissenschaften* 2000, 87, 129-32.
3. Degryse, P.; Schneider, J.; Haack, U.; Lauwers, V.; Poblome, J.; Waelkens, M.; Muchez, P. *Journal of Archaeological Science* 2006, 33, 494-501.
4. Degryse, P.; Schneider, J.; Lauwers, V.; Muynck, D. De; Vanhaecke, F.; Waelkens, M.; Muchez, P. In *Annales du 17e Congrès de l'Association Internationale pour l'Histoire du Verre (Anvers, 2006)*; Janssens, K. H. ; Degryse, P.; Cosyns, P., Eds.; UPA University Press Antwerp: Brussels, 2006; pp. 564-570.
5. Freestone, I. C.; Leslie, K. A.; Thirlwall, M.; Gorin-Rosen, Y. *Archaeometry* 2003, 45, 19-32.
6. Degryse, P.; Schneider, J. *Journal of Archaeological Science* 2008, 35, 1993-2000.
7. Goldstein, S. L.; O'Nions, R. K.; Hamilton, P. J. *Earth and Planetary Science Letters* 1984, 70, 221-236.
8. Weldeab, S. *Chemical Geology* 2002, 186, 139-149.
9. Brems, D.; Ganio, M.; Walton, M.; Degryse, P. In *Annales du 18e Congrès de l'Association Internationale pour l'Histoire du Verre (Thessaloniki, 2009)*.
10. Brems, D.; Ganio, M.; Latruwe, K.; Balcaen, L.; Carremans, M.; Gimeno, D.; Silvestri, A.; Vanhaecke, F.; Muchez, P.; Degryse, P. *Archaeometry*.
11. Brems, D.; Ganio, M.; Latruwe, K.; Balcaen, L.; Carremans, M.; Gimeno, D.; Silvestri, A.; Vanhaecke, F.; Muchez, P.; Degryse, P. *Archaeometry*.
12. Vanhaecke, F.; Balcaen, L.; Malinovsky, D. *Journal of Analytical Atomic Spectrometry* 2009, 24, 863-886.
13. Muynck, D. De; Huelga-Suarez, G.; Heghe, L. Van; Degryse, P.; Vanhaecke, F. *Journal of Analytical Atomic Spectrometry* 2009, 24, 1498-1510.
14. Horwitz, E. P.; Chiarizia, R.; Dietz, M. L.; Diamond, H.; Nelson, D. M. *Analytica Chimica Acta* 1993, 281, 361-372.
15. Pin, C.; Briot, D.; Bassin, C.; Poitrasson, F. *Analytica Chimica Acta* 1994, 112, 209-217.
16. Pin, C.; Zalduegui, J. F. S. *Analytica Chimica Acta* 1997, 339, 79-89.
17. Gioia, S. M. C. L.; Pimentel, M. M. *Anais da Academia Brasileira de Ciências* 2000, 72, 219-245.
18. Mellado, J. *Analytica Chimica Acta* 2001, 443, 81-90.
19. Lefevre, B.; Pin, C. *Analytica Chimica Acta* 2005, 543, 209-221.
20. Míková, J.; Denková, P. *Journal of Geosciences* 2007, 52, 221-226.
21. Makishima, A.; Nath, B. N.; Nakamura, E. *Geochemical Journal* 2008, 42, 237-246.
22. Yang, Y.-heng; Zhang, H.-fu; Chu, Z.-yin; Xie, L.-wen; Wu, F.-yuan *International Journal of Mass Spectrometry* 2010, 290, 120-126.
23. Yang, Y.-heng; Chu, Z.-yin; Wu, F.-yuan; Xie, L.-wen; Yang, J.-hui *Journal of Analytical Atomic Spectrometry* 2011, 26, 1237-1244.
24. Pirlet, H.; Colin, C.; Thierens, M.; Latruwe, K.; Rooij, D. Van; Foubert, A.; Frank, N.; Blamart, D.; Huvenne, V. A. I.; Swennen, R.; Vanhaecke, F.; Henriët, J. P. *Marine Geology* 2011, 282, 13-25.
25. Degryse, P.; Schneider, J.; Lauwers, V.; Henderson, J.; Daele, B. Van; Martens, M.; Huisman, H. D. J.; Muynck, D. De; Muchez, P. In *Isotopes in Vitreous Materials*; Degryse, P.; Henderson, J.; Hodgins, G., Eds.; University Press (Studies in Archaeological Sciences): Leuven, 2009; pp. 53-72.
26. Degryse, P.; Boyce, A.; Erb-Satullo, N.; Eremin, K.; Kirk, S.; Scott, R.; Shortland, A. J.; Schneider, J.; Walton, M. *Archaeometry* 2010, 52, 380-388.
27. Degryse, P.; Schneider, J.; Lauwers, V.; Brems, D. *Journal of Cultural Heritage* 2008, 9, 47-49.
28. Freestone, I. C.; Degryse, P.; Shepherd, J.; Gorin-Rosen, Y.; Schneider, J. *Journal of Archaeological Science* in press.

-
29. Ganio, M.; Boyen, S.; Brems, D.; Scott, R.; Foy, D.; Latruwe, K.; Molin, G. ; Silvestri, A.; Vanhaecke, F.; Degryse, P. *European Journal of Glass Science and Technology part A* 2012, *accepted*.
30. Ganio, M.; Boyen, S.; Fenn, T.; Scott, R.; Vanhoutte, S.; Domingo, G.; Degryse, P. *Journal of Analytical Atomic Spectrometry* 2012, *27*, 743-753.
31. Horwitz, E. P. In *Presented at international workshop on the application of extraction chromatography in radionuclide measurement, IRMM, Geel, Belgium, 9-10 November 1996.*; 1996.
- 10 32. McAlister, D.; Horwitz, E. P. *Solvent Extraction and Ion Exchange* 2007, *25*, 757-769.
33. Laeter, J. R. de; Böhlke, J. K.; Bièvre, P. De; Hidaka, H.; Peiser, H. S.; Rosman, K. J. R.; Taylor, P. D. P. *Pure and Applied Chemistry* 2003, *75*, 683-800.
- 15 34. Woodhead, J. D.; Hergt, J. M. *Geostandards and Geoanalytical Research* 2001, *25*, 261-266.
35. 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.; Asahara, Y.; Tanimizu, M.; Dragusanu, C. *Chemical Geology* 2000, *168*, 279-281.
- 20