New sequential separation procedure for Sr, Nd and Pb isotope ratio measurement in geological material using MC-ICP-MS and TIMS

Akio Makishima,[1]* B. Nagender Nath[1,2] and Eizo Nakamura[1]

[1]The Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry (PML), Institute for Study of the Earth's Interior, Okayama University, Yamada 827, Misasa, Tottori 682-0193, Japan
[2]National Institute of Oceanography, Dona Paula, Goa 403 004, India

A new 3-step sequential separation chemistry for Sr, Nd and Pb from silicate samples, which is suitable for isotope analysis by MC-ICP-MS as well as TIMS, has been developed. The chemistry is designed to minimize the number of evaporation steps, enabling high throughput especially when MC-ICP-MS is employed. The sample solution in 0.5 mol l^{-1} HNO$_3$ after digestion with HF–HClO$_4$, which is prepared for trace element analysis, can be directly used in the new chemistry. In the first column using Sr resin, Sr and Pb are collected. The recovered solution for Sr can be directly aspirated into MC-ICP-MS. The Pb solution is dried, re-dissolved, separated into two aliquots and measured by double spike MC-ICP-MS. Subsequently, LREEs are collected by the second column packed with cation exchange resin. Finally, Nd was purified from Sm using Ln resin in the third column. The recovered Nd solution can also be directly nebulized into MC-ICP-MS. The Sr and Nd isotope ratios for the standard material JB-3 (basalt) from the Geological Survey of Japan by MC-ICP-MS and TIMS were reported to verify the chemistry and mass spectrometry developed in this study.

Keywords: Sr, Nd, isotope ratio, MC-ICP-MS, TIMS

INTRODUCTION

The ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios, which show variation by radioactive decay of long half life isotopes of ^{87}Rb, ^{147}Sm, ^{238}U, ^{235}U and ^{232}Th, respectively, are routinely used for basic description of natural rocks and detrital sediments in geochemistry, and to interpret the origin of oceanic island basalts, island arc basalts, evolution of continental crust, source provenance and paleoclimate as well as age determinations. These measurements were conventionally carried out using thermal ionization mass spectrometry (TIMS). However, for the Sr, Nd and Pb isotope analyses by TIMS, tedious column chemistry including many evaporation steps are required. Usually, multi-step column chemistry is used combining H$^+$-form cation exchange, NH$_4$$^+$-form cation exchange with HIBA (2-hydroxyisobutyric acid) (e.g., Walker et al., 1989; Makishima and Nakamura, 1991), extraction resin with HDEHP (bis-(2-ethylhexyl) hydrogen phosphate) (Richard et al., 1976) for Nd, pyridinium-form cation exchange with DCTA (trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid) (Birck and Allegre, 1978; Yoshikawa and

Nakamura, 1993) for Sr, or anion exchange with HBr medium (Manhes et al., 1978; Koide and Nakamura, 1990) for Pb. Recently, extraction resins, such as Sr, Pb and Ln resins, are commercially available and used for separation of Sr, Nd and Pb (e.g., Horwitz et al., 1991, 1994; Weiss et al., 2004).

Since its invention, multiple collector-inductively coupled plasma mass spectrometry (MC-ICP-MS) has begun to be widely used for Sr, Nd and Pb isotope analyses (Ehrlich et al., 2001; Thirlwall, 2002; Thirlwall and Anczkiewicz, 2004; Baker et al., 2004; Weiss et al., 2004; Balcaen et al., 2005; Foster and Vance, 2006). However, the chemistry is usually adopted from those developed for TIMS, and not modified for optimization for use with MC-ICP-MS.

The purpose of this study is to describe a newly developed sequential separation routine of Sr, Nd and Pb enabling higher throughput for data acquisition with MC-ICP-MS, especially by reducing the number of evaporation steps of solutions, which takes 8 hrs or one night. Under ideal working conditions, completion of column chemistry and obtaining isotopic ratios for about 20 solutions containing geological material can be accomplished in about 3 days with the new method described here in combination with MC-ICP-MS. It should be emphasized that the separated Sr, Nd and Pb can also be employed in TIMS. Furthermore, the chemistry is de-

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*Corresponding author (e-mail: max@misasa.okayama-u.ac.jp)

signed to utilize the sample solution aliquot in 0.5 mol l^{-1} HNO_3 prepared for elemental determination by Q-pole type ICP-MS (ICP-QMS) or sector field type ICP-MS (ICP-SFMS) after $HClO_4$ treatment (Makishima and Nakamura, 1997, 2006). The commonly used anion exchange column chemistry for Pb (Manhes et al., 1978; Koide and Nakamura, 1990) cannot be employed because of interference from $HClO_4$, therefore, Sr–Nd and Pb chemistry are carried out separately. As details for mass spectrometry and analytical performances using the Pb separated in the chemistry developed in this study are already demonstrated elsewhere (Makishima et al., 2007), this paper describes Sr and Nd separation, mass spectrometry (MC-ICP-MS and TIMS) and analytical performances.

EXPERIMENTAL

Reagents and silicate reference materials

Water, HF and HCl were purified as described elsewhere (Nakamura et al., 2003). EL-grade HCl and HNO_3 from Kanto Chemical Co. Inc. (Japan) and $HClO_4$ (TAMAPURE-AA-100) from Tama Chemicals Co. Ltd. (Japan) were directly used in sample digestion and column chemistry. The purified HCl by sub-boiling (denoted as 1D HCl) was used in the final elution of Pb.

Cation exchange resin of AG 50W-X10, which is made by mixing AG 50W-X8 and AG 50W-X12 (200–400 mesh, Bio-Rad Laboratories, USA), extraction resins of Sr resin and Ln resin (100–150 μm, Eichrom Technologies, Inc., USA) and Amberchrom CG-71C (Rohm and Haas Co., USA) were used. The cation exchange resin was alternately washed with HCl and water. The Sr and Ln resins were soaked with water, washed with 6M HCl, and stored in water. CG-71C was washed and stored in water.

The Sr standard solution prepared from NIST 987 (USA) and an in-house Nd standard solution, PML-Nd, which was prepared from 10000 μg ml^{-1} Nd plasma standard solution (Spex Inc., USA) were used as Sr and Nd isotope ratio standards in TIMS and MC-ICP-MS. 1000 μg ml^{-1} Rb, La, Ce, Pr and Sm standard solutions for atomic absorption spectrophotometry (Kanto Chemical Co. Inc., Japan) were used for interference tests.

The silicate reference material, JB-3 (basalt from Mt. Fuji) issued by Geological Survey of Japan was used. JB-3 was further pulverized to enhance homogeneity by the alumina swing mill (Makishima and Nakamura, 1997).

Sample decomposition

All experiments were carried out in a clean room at the Pheasant Memorial Laboratory (PML) (Nakamura et al., 2003). About 20 mg of JB-3 was weighed, and digested with HF and $HClO_4$ in an ultrasonic bath for 3 days. Then the digested sample was stepwise dried to decompose fluorides. To ensure the complete decomposition of fluorides, $HClO_4$ was further added and dried after Yokoyama et al. (1999). Following this, HCl was added and dried, and the sample was dissolved in 5 ml of 0.5 mol l^{-1} HNO_3. This method is the standard sample solution preparation procedure for trace element analysis used in our laboratory (Makishima and Nakamura, 1997, 2006). The decomposition blank was <30 and <2 pg for Sr and Nd, respectively, and ~10 pg for Pb (Makishima et al., 2007).

Purification of Sr, Nd and Pb

Pb, Sr and Nd for MC-ICP-MS and TIMS were purified by three step column separation procedure. In the first column, Sr and Pb were separated using a two-layered resin bed polyethylene column (23 mm length × 5 mm in diameter) packed with 0.30 ml of CG-71C (the bottom layer) and 0.15 ml Sr resin (the upper layer). In the second column, LREE were collected by a cation exchange resin bed polypropylene column (23 mm length × 5 mm in diameter) packed with 0.45 ml of AG50W-X10. In a third column, Nd was separated from Sm using an extraction resin bed polyethylene column (31 mm length × 3.5 mm in diameter) packed with 0.30 ml of Ln resin. Details of the Pb–Sr–Nd separation scheme are shown in Fig. 1. All resins were discarded after separation.

Sr and Nd concentrations of ~50 and ~100 ng ml^{-1} are required in the measurement solution to provide sufficient repeatability and intermediate precision of <0.004% in MC-ICP-MS. To achieve this, ~100 and ~120 ng of Sr and Nd were required, because the final elution volumes from the column are 2 and 1.2 ml, respectively. For Pb analysis, >25 ng are preferred to make the blank effect negligible and to achieve the intermediate precision of <0.009% ("intermediate precision" in this paper means "reproducibility" or "repeatability" in different analytical sessions but in the single laboratory; "repeatability" in this paper means "precision" in the single measurement) using double spike (DS) MC-ICP-MS method (Makishima et al., 2007).

Two types of separation methods have been developed depending on the concentration of Sr, Nd and Pb. When amounts of Sr, Nd and Pb are abundant in the initial 0.5 mol l^{-1} HNO_3 sample solution (>100, >30 and >25 ng ml^{-1} for Sr, Nd and Pb, respectively, in the ~5 ml sample solution), the Sr-Pb and the Nd column separations are performed separately (Case 1 in Fig. 1a). However, when the amounts of Sr, Nd and Pb are limited, the sample solution is passed through the Sr–Pb column to collect Sr and Pb, and then passed through the Nd column to collect Nd (Case 2 in Fig. 1b).

Separation of Sr and Pb The resin bed was washed and conditioned as shown in Fig. 1, and the sample solution was loaded. After sample loading and major element wash

with 1.4 ml of 3 mol l^{-1} HNO$_3$, Sr and Pb were recovered by subsequent addition of 2.0 ml of 0.05 mol l^{-1} HNO$_3$ and of 4 ml of 6 mol l^{-1} 1D HCl, respectively (see Fig. 1). This column chemistry is principally based on Horwitz *et al.* (1991) for Sr and Weiss *et al.* (2004) for Pb. In order to reduce organic materials from the Sr resin in the Sr fraction, and to reduce the flow rate resulting in better absorption of Sr and separation, CG-71C is used in the lower layer of the column.

In Case 1, the 1.2 ml loading solution in 3 mol l^{-1} HNO$_3$ was prepared by mixing of <1 ml of the sample solution and 16 mol l^{-1} HNO$_3$, and 3 mol l^{-1} HNO$_3$ if necessary. Recovery yields of Sr and Pb were ~90 and ~99% using JB-3 solution, respectively. In Case 2, the sample solution up to 4.5 ml in 0.5 mol l^{-1} HNO$_3$ was directly loaded into the column. All of the sample solution passed through the column was recovered and used in the Nd separation procedure in Case 2. Recovery yields of Sr and Pb were ~65 and ~99%, respectively, when the sample solution was 4.5 ml. The low Sr yield in Case 2 is caused by the lower K$_d$ of Sr in 0.5 mol l^{-1} HNO$_3$ (Horwitz *et al.*, 1991) than that in 3 mol l^{-1} HNO$_3$ in Case 1. However, as Pb has a similar and high K$_d$ (Horwitz, 1998) in both concentrations of HNO$_3$, the yield of Pb is ~99% in both cases. Practically, the lower Sr recovery yield of ~65% does not hinder the Sr measurement, because concentrations of Sr in silicate samples (as also carbonates) are usually >5 times higher than those of Nd and Pb. The blanks of Sr and Pb in this separation chemistry were ~6 pg (2–13 pg) and ~20 pg (16–27 pg), respectively. When the Pb blank in decomposition is taken into account, the total Pb blank was ~30 pg. The Nd blank from the first column chemistry in Case 2 was ~4 pg.

The HNO$_3$ concentration of the recovered 2 ml Sr fraction is calculated to be ~0.5 mol l^{-1} using the pore volume of the resins, which can be directly aspirated into MC-ICP-MS to measure ^{87}Sr/^{86}Sr. For TIMS analysis of Sr, this solution was dried and loaded on the filament. The Pb fraction was dried, re-dissolved, split, added with double-spike, and measured by DS-MC-ICP-MS (Makishima *et al.*, 2007). It should be noted that these Pb solutions with and without spike can also be employed in DS-TIMS measurement, which is described elsewehre (Nath *et al.*, in prep.).

Separation of Nd Details of the second and third column chemistry are also shown in Fig. 1. The second column chemistry for the Nd separation is principally the same as that of the conventional LREE separation described elsewhere (e.g., Makishima and Nakamura, 1991). The resin bed was washed and conditioned as shown in Fig. 1. The loading solution in mix acid of 2.1 mol l^{-1} HCl-0.3 mol l^{-1} HNO$_3$ was prepared by mixing of 6 mol l^{-1} HCl, the initial sample solution of 0.5 mol l^{-1} HNO$_3$ (Case 1) or the sample solution passed through the Sr–Pb col-

umn (Case 2), and additional 2.1 mol l^{-1} HCl-0.3 mol l^{-1} HNO$_3$ if necessary. After washing the column with 3.2 ml mix acid of 2.1 mol l^{-1} HCl-0.3 mol l^{-1} HNO$_3$ to remove major elements, the LREE fraction was recovered with 4.8 ml of 6 mol l^{-1} HCl. The LREE fraction was dried and re-dissolved with 0.1 ml of 0.06 mol l^{-1} HCl for the third column. The yield of Nd in the second column was ~85% obtained by JB-3 solution. The blank of Nd was <2 pg.

Ln resin was used in the third column (Pin and Zalduegui, 1997). The resin bed was washed and conditioned as in Fig. 1. After sample loading and washing the column with 0.6 ml of 0.25 mol l^{-1} HCl to remove La–Pr, Nd fraction was collected with 1.2 ml of 0.25 mol l^{-1} HCl. The yield of Nd in the third column was ~90% and the blank was 7 pg (3–12 pg). Although the separated Nd contains significant amounts of La, Ce and Pr compared to HIBA separation (Makishima and Nakamura, 1991), this column chemistry is suitable for MC-ICP-MS determination of Nd, because the 0.25 mol l^{-1} HCl Nd fraction can be directly introduced into MC-ICP-MS without further evaporation. For TIMS analysis of Nd, the Nd fraction was dried with nitric acid, and loaded on the Re filament. To make the loading spot on the filament as small as possible, we later found further addition and drying with HClO$_4$ would help by decomposing organic materials. However, this method was not employed in this study. In total, the yield and blank for Nd in the 3-step column chemistry were ~75% and ~20 pg, respectively.

Determination of Sr and Nd isotope ratios by MC-ICP-MS

A Neptune MC-ICP-MS, (Thermo Electron Corp., Germany) at the PML, was used for the analysis of Sr and Nd isotope ratios. Details of MC-ICP-MS operating conditions are shown in Table 1. For sample, carrier and washing solutions, 0.5 mol l^{-1} HNO$_3$ and 0.25 mol l^{-1} HCl were used for Sr and Nd analyses, respectively. Gains of amplifiers of each Faraday cup were calibrated once a day. ^{86}Sr/^{88}Sr = 0.1194 and ^{146}Nd/^{144}Nd = 0.7219 were used for normalization employing the exponential law. The solution sample nebulization into plasma was employed. On top zeros for Sr and Nd were measured as background for each sample. Especially, the background at mass 86, which was ^{86}Kr, was assumed to be constant during sample measurement and subtracted as the on top zeros. The background at mass 86 was <3 × 10^{-16} A with variation of <20% (RSD) during one analytical session. The Sr and Nd solutions containing 50 and 100 ng ml^{-1} were used for the sample and standard solution, which gave ~4 × 10^{-11} A for ^{88}Sr and ~1 × 10^{-11} A for ^{146}Nd, respectively. The standard solutions of NIST 987 for Sr and PML-Nd for Nd were measured before and after the analyses of every four samples during one analytical ses-
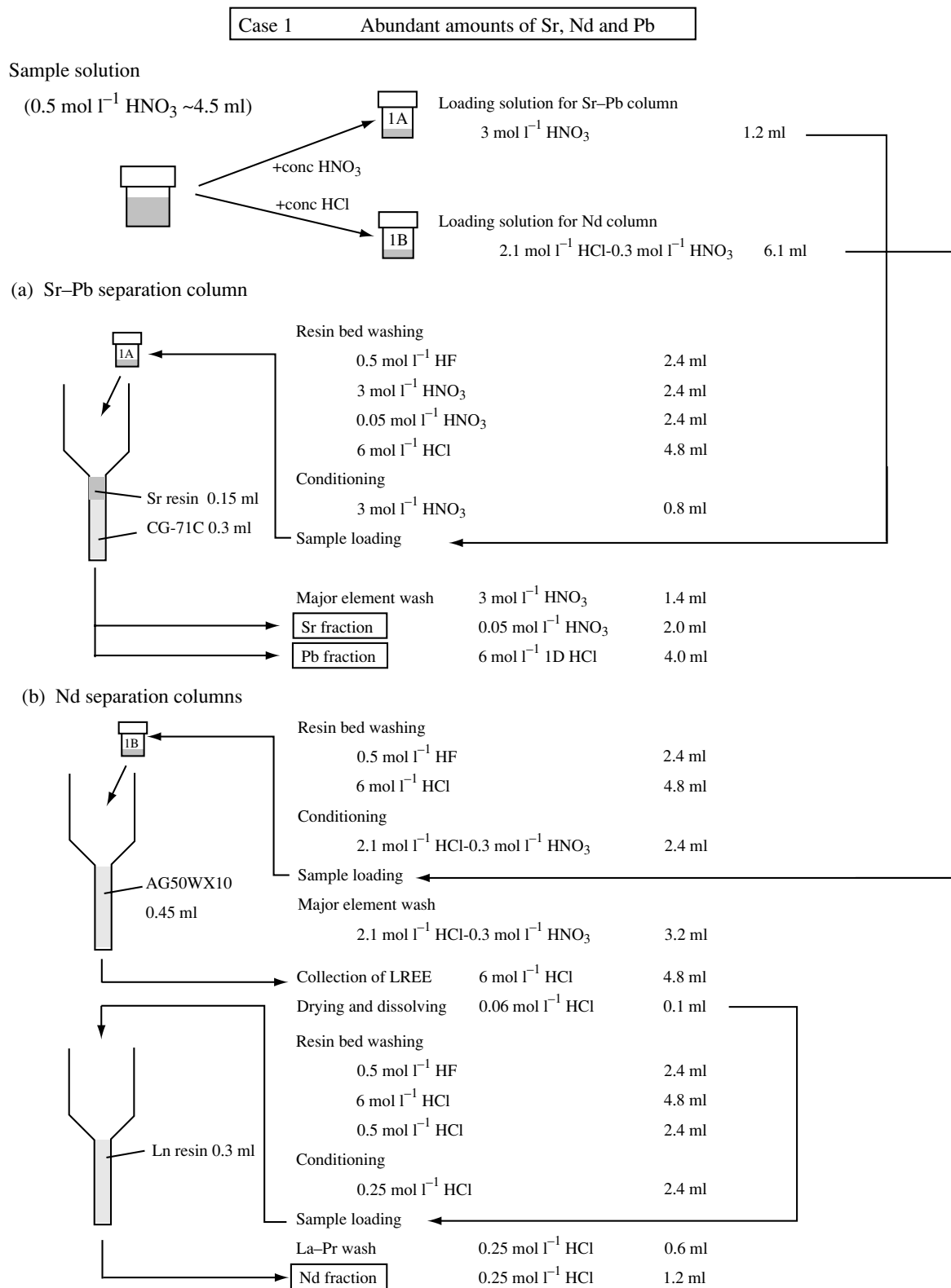
Fig. 1. Sequential Pb–Sr–Nd separation chemistry developed in this study. (a) The procedure when amounts of Sr, Nd and Pb are abundant in the sample solution (Case 1). (b) The procedure when amounts of Sr, Nd and Pb are limited in the sample solution (Case 2).
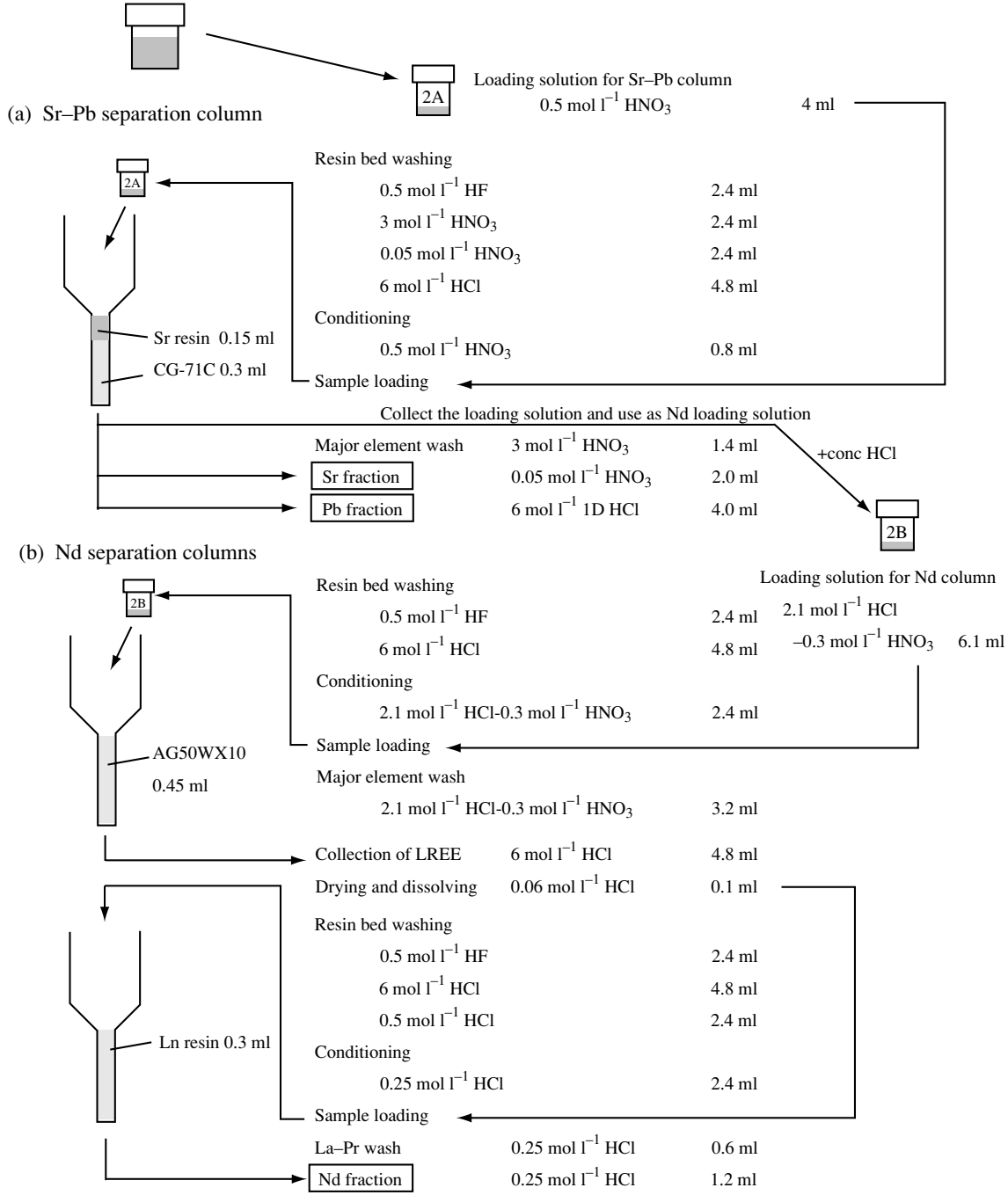
Fig. 1. (continued).

Table 1. MC-ICP-MS operating conditions for Sr and Nd analyses

1. ICP conditions							
Plasma power	1.2 kW						
Torch	Quartz glass torch with a sapphire injector						
Plasma Ar gas flow rate	$15 \ l \ min^{-1}$						
Auxiliary Ar gas flow rate	$0.80 \ l \ min^{-1}$						
Nebulizer Ar gas flow rate	$1.1 \sim 1.2 \ l \ min^{-1}$						
Spray chamber	Quartz cyclonic dual spray chamber at ambient temperature						
2. Interface							
Sampling cone	Made of Ni						
Skimmer cone	Made of Ni (X-skimmer)						
3. Data acquisition conditions							
Washing time	960 sec after measurement						
Uptake time	90 sec						
Background data integration	4 sec for 1 scan, 60 scans in one run						
Sample data integration	4 sec for 1 scan, 60 scans in one run						
4. Cup configuration							
	L4	L3	L2	L1	C	H1	H2	H3
Sr	82	83	84	85	86	87	88	
Nd	140	142	143	144	145	146	147	149

sion. The average of the standard solution in each analytical session was used to calculate a standardization factor for samples. The standardization factor for Sr was calculated to make $^{87}Sr/^{86}Sr$ of NIST 987 to be 0.710240. The standardization factor for Nd was calculated based on $^{143}Nd/^{144}Nd = 0.511724$ for PML-Nd, which corresponds to $^{143}Nd/^{144}Nd = 0.511860$ for the La Jolla Nd standard (see the next section).

In order to correct mass interference of ^{87}Rb on ^{87}Sr, the $^{87}Rb/^{85}Rb$ ratio of the Rb standard solution was measured at the beginning and the end of one analytical session, and the average was used in the isobaric interference correction of ^{87}Rb. The artificial mixture of the Rb standard solution and NIST 987 Sr standard showed that the Rb correction gives the accurate Sr ratio up to $^{87}Rb/^{87}Sr = \sim0.018$. After column chemistry, $^{87}Rb/^{87}Sr$ was usually <0.008 even for the sample with a high Rb/Sr ratio of ~1, which corresponds to the decrease of <1/1300 for Rb/Sr. Therefore, the Rb correction usually does not seem to affect our analytical results. When $^{87}Rb/^{87}Sr$ ratio is >0.018 during measurement, the analytical data is discarded.

For ^{144}Sm interference correction on ^{144}Nd, the mass discrimination factor per mass unit for Sm was assumed to be identical to that of Nd using the exponential law, and using a value of $^{144}Sm/^{147}Sm = 0.1995$. The artificial mixture of the Sm standard solution and PML-Nd standard indicated that the Nd isotope ratio is identical after Sm correction up to $^{144}Sm/^{144}Nd = \sim0.016$. After the column chemistry, $^{144}Sm/^{144}Nd$ was usually <0.00003 even

for JB-3 with the relatively LREE depletion with Sm/Nd = ~0.27. Therefore, Sm correction was usually very small and negligible.

Determination of Sr and Nd isotope ratios by TIMS

TIMS, MAT 262 (Finnigan, Germany) nicknamed as "SARU" in PML with 7 Faraday cups, was used for the Sr isotope ratio measurement. Sr of ~50 ng was loaded on to a single W filament with Ta activator, and the ^{88}Sr signal intensity was kept to $\sim3 \times 10^{-11}$ A. $^{86}Sr/^{88}Sr = 0.1194$ was used for normalization, assuming the power law. Five Faraday cups were used. Isotopes of ^{84}Sr, ^{85}Rb, ^{86}Sr, ^{87}Sr and ^{88}Sr were monitored using the COL7, COL6, COL5 (center), COL4 and COL3 Faraday cups, respectively. 110 ratios were obtained in 10 blocks. The repeated analysis of Sr standard, NIST 987 gave an average of 0.710241 ± 0.000028 ($n = 17$) during the course of this study. No standardization was performed for reported values.

Another TIMS, TRITON TI, (Thermo Electron Corp., Germany) housed in PML with 9 Faraday cups, was used for the Nd isotope ratio analysis. The Re double filament technique was employed using ~60 ng of Nd, and the ^{146}Nd signal intensity was kept to $\sim4 \times 10^{-12}$ A. $^{146}Nd/^{144}Nd = 0.7219$ was used for normalization employing the exponential law. Isotopes of ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd and ^{147}Sm were monitored using the L4, L3, L2, L1, C (center) and H1 Faraday cups, respectively. 112 ratios were obtained in 8 blocks with alternately changing amplifiers (virtual amplifier). The repeated analysis

(a)

Loading
& wash | Sr fraction | Pb fraction

(b)

Loading | Wash | LREE fraction

(c)
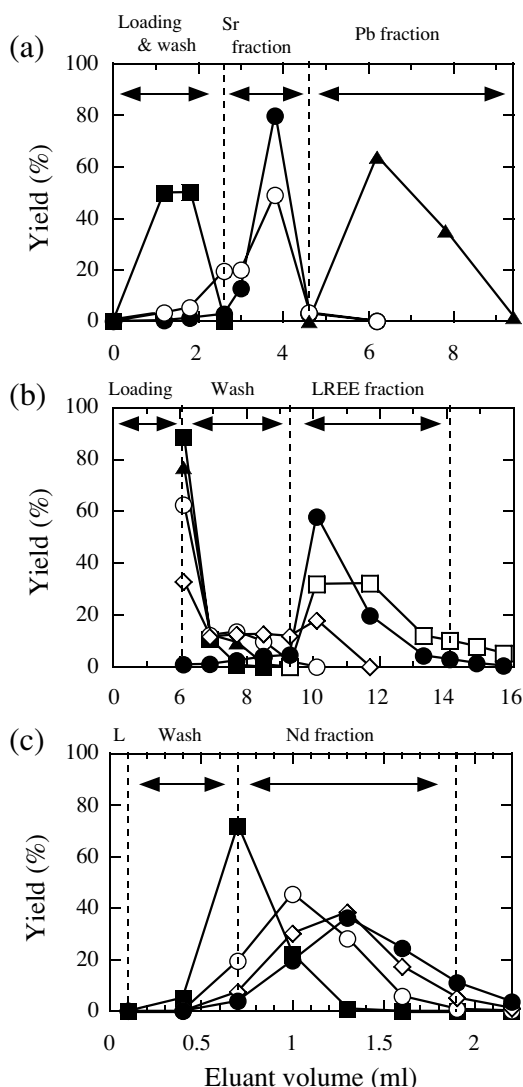
L | Wash | Nd fraction

Eluant volume (ml)

Fig. 2. Elution curves of 3-step column chemistry. (a) Elution curves of Sr (●), Ba (○), Nd (■) and Pb (▲) in the first column with Sr resin in Case 1. 3 mol l^{-1} HNO_3, 0.05 mol l^{-1} HNO_3 and 6 mol l^{-1} HCl are used for the loading and wash, Sr and Pb fractions, respectively. (b) Elution curves of Al (▲), Ca (○), Fe (■), La (□), Nd (●) and Lu (◇) in the second column with cation exchange resin. As all of La was not recovered even after addition of eluant of 16 ml, the actual recovery yield of La is slightly lower than that depicted in the figure. 2.1 mol l^{-1} HCl-0.3 mol l^{-1} HNO_3 and 6 mol l^{-1} HCl are used for the loading and wash, and LREE fraction, respectively. It should be noted that the horizontal axis during the loading step between 0 and 6 ml is compressed. (c) Elution curves of La (■), Ce (○), Pr (◇) and Nd (●) in the third column with Ln resin. The experiment was performed up to the total eluant volume of 5 ml (not shown). 0.06 mol l^{-1} HCl and 0.25 mol l^{-1} HCl are used for the loading (denoted as L in the figure), and wash and Nd fraction, respectively. No Sm appears in this eluant volume range.

Table 2. Sr isotope ratios of JB-3 by MC-ICP-MS and TIMS

(a) MC-ICP-MS

JB-3			NIST 987		
	$^{87}Sr/^{86}Sr$	2SE	$^{87}Sr/^{86}Sr$	2SE	n
#1-a	0.703456	20	0.710241	16	7
#1-b	0.703429	31			
#1-c	0.703416	22			
#2	0.703418	21	0.710233	27	5
#3	0.703446	24	0.710233	24	4
#4	0.703423	34	0.710244	30	7
#5	0.703432	23	0.710255	27	6
#6	0.703441	18	0.710257	19	4
	Average	2SD	Average	2SD	
	0.703432	28	0.710244	20	

(b) TIMS

JB-3			NIST 987	
	$^{87}Sr/^{86}Sr$	2SE	$^{87}Sr/^{86}Sr$	n
#1	0.703441	14		
#2	0.703451	16		
#3	0.703455	19		
#4	0.703443	15		
#5	0.703448	13		
	Average	2SD	Average	2SD	
	0.703448	11	0.710241	28	8

All 2SD and 2SE errors correspond to the last digit of each isotope ratio.
a, b and c indicate the different sample in the same analytical session.

of the in-house Nd standard, PML-Nd gave an average of 0.511704 ± 0.000008 (2SD, $n = 8$) with La Jolla Nd of 0.511840 ± 0.000010 (2SD, $n = 8$) during the course of this study. No standardization was performed for reported values.

RESULTS AND DISCUSSION

Elution curves for 3-step column chemistry

Elution curves for the first, second and third columns are shown in Fig. 2. The vertical axis is the recovery yield for each element calculated by normalizing the intensity of each fraction to the total intensity. Figure 2(a) shows the elution curves for Sr, Nd and Pb with the first column in Case 1 in Fig. 1a using the JB-3 solution. The elution curve of Case 2 is essentially same except for small break of Sr during sample loading because of lower K_d of Sr at low concentration of HNO_3 used in Case 2. During the loading and washing step, major elements behave like Nd in the figure. In the Sr fraction, ~70% of Ba is recovered.

Table 3. Nd isotope ratios of JB-3 by MC-ICP-MS and TIMS

(a) MC-ICP-MS

| JB-3 | | | PML-Nd | | |
	$^{143}Nd/^{144}Nd$	2SE	$^{143}Nd/^{144}Nd$	2SD	n
#1	0.513080	17	0.511735	22	5
#2	0.513097	18	0.511726	26	6
#3	0.513098	22	0.511722	29	5
#4	0.513081	11	0.511719	23	5
	Average	2SE	Average	2SD	
	0.513089	20	0.511726	14	

(b) TIMS

| JB-3 | | | PML-Nd | |
	$^{143}Nd/^{144}Nd$	2SE	$^{143}Nd/^{144}Nd$	n
#1	0.513048	8		
#2	0.513044	9		
#3	0.513064	19		
#4	0.513041	10		
#5	0.513052	12		
	Average	2SD	Average	2SD
	0.513049	18	0.511704*	8	8

All 2SD and 2SE errors correspond to the last digit of each isotope ratio.
*This value corresponds to 0.511840 for the La Jolla Nd standard.

If larger volume of Sr resin is used, Ba can be separated. However, to keep the HNO_3 concentration in the recovered Sr fraction to be ~0.5 mol l^{-1} HNO_3 with significantly small amount of solution (~2 ml) suitable to achieve higher intensity in MC-ICP-MS, the presence of Ba in the Sr fraction is compromised. The presence of Ba does not seem to affect the MC-ICP-MS measurement because the Sr isotope ratio of JB-3 is similar to that obtained using TIMS (see Table 2).

The elution curves for the second column are shown in Fig. 2(b). Most major elements, such as Al, Ca and Fe are removed in loading and washing steps. REE appears from HREE (Lu) to LREE (La). About 80% of Lu is lost in these steps. However, ~85% of Nd is recovered, though a large volume of 6.1 ml solution is loaded, compared to the resin volume of 0.45 ml.

The elution curves for the third column are shown in Fig. 2(c). In contrast to the second column, REE appears from LREE (La) to HREE (Lu). No Sm appears in this eluant volume range up to 2.2 ml with 0.25 mol ml^{-1} HCl. The Nd fraction contains not only Nd with the yield of ~90%, but also significant amounts of La (~20%), Ce

(~80%) and Pr (~90%). In order to achieve higher purity of Nd in the Nd fraction, larger amounts of Ln resin, e.g., 1 ml (Pin and Zalduegui, 1997) are required. However, as the resin volume is increased, the Nd elution volume also increases from 1.2 ml in this study to 2 ml (Pin and Zalduegui, 1997), requiring 1.7 times larger amounts of Nd to obtain the same Nd concentration in the solution. The effect of interferences from La, Ce and Pr is examined using MC-ICP-MS, by preparing and measuring the solution containing 100 ng ml^{-1} of La, Ce, Pr and PML-Nd. The ratio thus obtained was $^{143}Nd/^{144}Nd = 0.511744 \pm 0.000022$ (2SE), which is similar to the PML-Nd value of 0.511724 within error. Furthermore, as the analytical result of JB-3 is identical with those by TIMS (see Table 3), it is confirmed that the impurity (La to Pr) in the Nd fraction does not affect the accuracy in the MC-ICP-MS measurement. The Nd solution can also be employed in TIMS, because the impurity does not interfere with Nd isotope measurement for JB-3 by TIMS.

Analytical results of Sr by MC-ICP-MS and TIMS

Analytical results of Sr for JB-3 from different sample decomposition and column chemistry are shown in Table 2. The MC-ICP-MS and TIMS data were obtained using the Case 1 column chemistry in Fig. 1a. The MC-ICP-MS results for JB-3 in this study yielded intermediate precision of 0.703432 ± 0.000028 (2SD, $n = 8$) (see Table 2(a)). The typical repeatability (2SE) in each measurement was 0.000024, and comparable to the intermediate precision. The mean Sr isotope ratios of NIST 987 used for standardization in each analytical session are also shown in Table 2(a). The standardization factors are within the range of 0.999977–1.000010, and the typical intermediate precision (2SD) in each analytical session is 0.000024. The average of all NIST 987 analyses in all analytical sessions are 0.710244 ± 0.000020 (2SD, $n = 6$). This indicates that the variation in all analytical sessions is comparable to the intermediate precision in each analytical session.

The Sr isotope ratio of JB-3 measured by TIMS was 0.703448 ± 0.000011 (2SD, $n = 5$), as shown in Table 2(b). The grand averages of both JB-3 and NIST 987 by MC-ICP-MS are identical with those by TIMS within analytical errors, assuring the accuracy of MC-ICP-MS method, although the intermediate precision of MC-ICP-MS is twice as large as that of TIMS. It is also shown that the column chemistry developed in this study is suitable for the Sr isotope measurement by both MC-ICP-MS and TIMS. There are few reliable data for JB-3, but the Sr isotope ratio of 0.703446 ± 0.000006 (2SE) by Shibata *et al*. (2002) agrees with our result. Orihashi *et al*. (1998) reported 0.703414 ± 0.000032 (2SD, $n = 5$), slightly lower value of for JB-3 after normalization using NIST 987, but still within analytical errors.

Analytical results of Nd by MC-ICP-MS and TIMS

Analytical results of Nd for JB-3 from different sample decomposition and column chemistry are shown in Table 3. The MC-ICP-MS data and TIMS #1 data were obtained by the Case 1 chemistry in Fig. 1a, and TIMS #2–#5 data were obtained using the Case 2 chemistry. The MC-ICP-MS results for JB-3 in this study yielded a intermediate precision of 0.513089 ± 0.000020 (2SD, $n = 4$) (see Table 3(a)). The typical repeatability (2SE) in each measurement was 0.000017, and comparable to the intermediate precision. The mean Nd isotope ratios of PML-Nd used for standardization in each analytical session are also shown in Table 3(a). The standardization factors are within the range of 0.999980–1.000011, and the typical intermediate precision (2SD) in each analytical session is 0.000025. The grand average of PML-Nd in all analytical sessions is 0.511726 ± 0.000014 (2SD, $n = 4$). This indicates that the variation in all analytical sessions is comparable to the intermediate precision in each analytical session (2SD), which is similar to the case for Sr.

The Nd isotope ratio of JB-3 measured by TIMS is 0.513049 ± 0.000018 (2SD, $n = 5$) (see Table 3(b)). This value becomes 0.513069 when normalized to the La Jolla Nd = 0.511860. Thus, the grand averages of both JB-3 and PML-Nd by MC-ICP-MS are similar to those by TIMS within analytical errors, suggesting that the accuracy in MC-ICP-MS after the 3-step column chemistry is similar to that of TIMS and adequate enough to be routinely used in geochemistry. There are a few reliable results for JB-3, and Arakawa (1992), Orihashi *et al.* (1998) and Shibata *et al.* (2002) reported the Nd isotope ratios of JB-3 to be 0.513042 ± 0.000009 (2SE), 0.513069 ± 0.000012 (2SD, $n = 5$) and 0.513057 ± 0.000009 (2SE), respectively, after normalization using the La Jolla Nd standard. These values are consistent with our result when errors are taken into account.

Some remarks on the improvement of analytical throughput

It is difficult to discuss the improvement of the sample throughput which depends on the individual laboratory conditions. Factors such as the time available for machine use, availability of lab space, laboratory apparatus and chemicals, all of which are different for each laboratory. Under ideal conditions employing the chemistry described, when the sample solution in 0.5 mol l⁻¹ HNO_3 is already prepared, the first column for 12–20 samples can be undertaken in the morning on the first day, and the chemistry of the second column can be accomplished in the afternoon. During the night, Pb and the LREE fractions are dried. Simultaneously if MC-ICP-MS is available, Sr isotopes ratio can be measured automatically using an auto sampler by MC-ICP-MS. On the second day, the third column chemistry can be undertaken in the morning, and the Pb solution is prepared by adding spike and dilution in the afternoon and the Pb measurement by MC-ICPMS can be started with an autosampler. On the third day, the Nd solution is measured by MC-ICP-MS. Thus under ideal conditions, Sr–Nd–Pb data for ~20 samples can be obtained in 3 days. However, if TIMS is used for the Sr and Nd measurements, several additional days are required for drying the solution, loading the sample on the filament and measurement by TIMS. In any case, combined Sr–Nd–Pb isotope analysis for ~50 samples is practically possible in about one month which is a reasonably fast throughput.

REFERENCES

Arakawa, Y. (1992) $^{143}Nd/^{144}Nd$ ratios of twelve GSJ rock reference samples and reproducibility of the data. *Geochem. J.* **26**, 105–109.

Baker, J., Peate, D., Waight, T. and Meyzen, C. (2004) Pb isotopic analysis of standards and samples using a $^{207}Pb–^{204}Pb$ double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chem. Geol.* **211**, 275–303.

Balcaen, L., Dchrijver, I. D., Moens, L. and Vanhaecke, F. (2005) Determination of the $^{87}Sr/^{86}Sr$ isotope ratio in USGS silicate reference materials by multi-collector ICP-mass spectrometry. *Int. J. Mass Spectrom.* **242**, 251–255.

Birck, J. L. and Allegre, C. J. (1978) Chronology and chemical history of the parent body of basaltic achondrites studied by $^{87}Rb–^{87}Sr$ method. *Earth Planet. Sci. Lett.* **39**, 37–51.

Ehrlich, S., Gavrieli, I., Dor, L.-B. and Halicz, L. (2001) Direct high-precision measurements of the $^{87}Sr/^{86}Sr$ isotope ratio in natural water, carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). *J. Anal. Atom. Spectrom.* **16**, 1389–1392.

Foster, G. L. and Vance, D. (2006) *In situ* Nd isotopic analysis of geological materials by laser ablation MC-ICP-MS. *J. Anal. Atom. Spectrom.* **21**, 288–296.

Horwitz, E. P. (1998) Extraction chromatography of actinides and selected fission products: Principles and achievement of selectivity. *International Workshop on the Application of Extraction Chromatography in Radionuclide Measurement*, IRMM, Keel 9–10, Belgium.

Horwitz, E. P., Dietz, M. L. and Fisher, D. E. (1991) Separation and preconcentration of strontium from biological, environmental, and nuclear waste samples by extraction chromatography using a crown ether. *Anal. Chem.* **63**, 522–525.

Horwitz, E. P., Dietz, M. L., Rhoads, S., Felinto, C., Gale, N. H. and Houghton, J. (1994) A lead-selective extraction chromatographic resin and its application to the isolation of lead from geological samples. *Anal. Chim. Acta* **292**, 263–273.

Koide, Y. and Nakamura, E. (1990) Lead isotope analyses of standard rock samples. *Shitsuryoubunseki (Mass spectroscopy)* **38**, 241–252.

Makishima, A. and Nakamura, E. (1991) Precise measurement of cerium isotope composition in rock samples. *Chem. Geol. (Isot. Geosci.)* **94**, 1–11.

Makishima, A. and Nakamura, E. (1997) Suppression of matrix effects in ICP-MS by high power operation of ICP: Application to precise determination of Rb, Sr, Y, Cs, Ba, REE, Pb, Th and U at ng g^{-1} levels in milligram silicate samples. *Geostand. Newsl.* **21**, 307–319.

Makishima, A. and Nakamura, E. (2006) Determination of major, minor and trace elements in silicate samples by ICP-QMS and ICP-SFMS applying isotope dilution-internal standardization (ID-IS) and multi-stage internal standardization. *Geostand. Geoanal. Res.* **30**, 245–271.

Makishima, A., Nath, B. N. and Nakamura, E. (2007) Precise determination of Pb isotope ratios by simple double spike MC-ICP-MS technique without Tl addition. *J. Anal. Atom. Spectrom.* **22**, 407–410.

Manhes, G., Minster, J. F. and Allegre, C. J. (1978) Comparative uranium-thorium-lead and rubidium-strontium study of the saint severin amphoterite: consequences for early solar system chronology. *Earth Planet. Sci. Lett.* **39**, 14–24.

Nakamura, E., Makishima, A., Moriguti, T., Kobayashi, K., Sakaguchi, C., Yokoyama, T., Tanaka, R., Kuritani, T. and Takei, H. (2003) Comprehensive geochemical analyses of small amounts (<100 mg) of extraterrestrial samples for the analytical competition related to the sample-return mission, MUSES-C. Inst. Space Astron. Sci. Report, SP No. 16. 49–101.

Orihashi, Y., Maeda, J., Tanaka, R., Zeniya, R. and Niida, K.

(1998) Sr and Nd isotopic data for the seven GSJ rock reference samples; JA-1, JB-1a, JB-2, JB-3, JG-1a, JGb-1 and JR-1. *Geochem. J.* **32**, 205–211.

Pin, C. and Zalduegui, J. F. S. (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**, 79–89.

Richard, P., Shimizu, N. and Allegre, C. J. (1976) ^{143}Nd/^{146}Nd, a natural tracer: an application to oceanic basalts. *Earth Planet. Sci. Lett.* **31**, 269–278.

Shibata, T., Yoshikawa, M. and Tatsumi, T. (2002) An analytical method for determining precise Sr and Nd isotopic compositions and results for thirteen rock standard materials. *Frontier Research of Earth Evolution* (Kushiro, I., ed.), **1**, 363–367.

Thirlwall, M. F. (2002) Multicollector ICP-MS analysis of Pb isotopes using a ^{207}pb-^{204}pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization. *Chem. Geol.* **184**, 255–279.

Thirlwall, M. F. and Anczkiewicz, R. (2004) Multidynamic isotope ratio analysis using MC-ICP-MS and the causes of secular drift in Hf, Nd and Pb isotope ratios. *Int. J. Mass Spectrom.* **235**, 59–81.

Walker, R. J., Carlson, R. W., Shirey, S. B. and Boyd, F. R. (1989) Os, Sr, Nd and Pb isotope systematics of southern African peridotite xenoliths: Implications for the chemical evolution of subcontinental mantle. *Geochim. Cosmochim. Acta* **53**, 1583–1595.

Weiss, D. J., Kober, B., Dolgopolova, A., Gallagher, K., Spiro, B., Le Roux, G., Mason, T. F. D., Kylander, M. and Coles, B. J. (2004) Accurate and precise Pb isotope ratio measurements in environmental samples by MC-ICP-MS. *Int. J. Mass Spectrom.* **232**, 205–215.

Yokoyama, T., Makishima, A. and Nakamura, E. (1999) Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock dissolution by acid digestion. *Chem. Geol.* **157**, 175–187.

Yoshikawa, M. and Nakamura, E. (1993) Precise isotope determination of trace amounts of Sr in magnesium-rich samples. *J. Min. Petrol. Econ. Geol. (Ganko)* **88**, 548–561.