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An improved chromatographic separation technique of Nd with application to NdO^+ isotope analysis

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Abstract

Isotopic analysis by Thermal Ionization Mass Spectrometry (TIMS) requires efficient chemical separation of the element of interest. This statement is particularly true for NdO^+ measurements during which isobaric interferences must be minimized. Here, we present a new chromatographic procedure that efficiently separates Nd from other Light Rare-Earth Elements (LREE) and is ideal for NdO^+ measurements. After separation of the LREE fraction from the bulk matrix, Nd is chemically separated using a High Pressure Liquid Chromatographic (HPLC) technique, with Aminex resin (Bio-Rad©) and a CH_3OH–HAc–HNO_3 eluent. This simple and low blank (10–15 pg) separation technique efficiently reduces isobaric interferences so that $^{140}CeO^+/^{144}NdO^+$ and $^{141}PrO^+/^{144}NdO^+$ ratios are generally below recommended values, ensuring no significant contribution from isobaric interferences.

The NdO^+ analytical technique also requires accurate determination of the oxygen isotope composition in TIMS since it is used to recalculate the Nd isotope composition of the samples. The results of a series of measurements performed to determine the oxygen isotope ratios ($^{18}O/^{16}O = 0.002040$ and $^{17}O/^{16}O = 0.000386$) were used to constrain the parameters influencing the measurements. Loading technique and running conditions greatly affect measured oxygen isotope ratios. Guidelines to help accurately determine the oxygen isotope ratios are also presented. Combining the Aminex chromatographic separation with NdO^+ measurements and accurately determined oxygen isotope ratios allows high precision measurements. A wide range of low abundance samples can be analyzed to a precision similar to that obtained on larger samples with conventional Nd^+ technique (± 0.000020, 2σ). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Neodymium; Chromatography; REE; NdO^+ technique; Oxygen isotope

1. Introduction

The rationale for using the NdO^+ technique to measure Nd isotope compositions is based on the ability to ionise Nd more efficiently as NdO^+ than as Nd^+. This permits the precise measurement of Nd isotope compositions on samples smaller than 50 ng. The NdO^+ technique was developed in the 1970's and initially used to measure the Nd isotope composition of extraterrestrial material (e.g., Lugmair and Marti, 1977, 1978). In spite of its potential, this technique has not been widely applied. This is due to a combination of problems, such as the uncertainty in the oxygen isotope ratios, the long acquisition time needed on single collector mass-spectrometers to monitor potential interfering masses and the need

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for a good chromatographic separation of Nd. Following the development of multi-collector mass-spectrometers and growing interest in samples with low rare-earth element (REE) abundances, there has been a renewed interest in the technique. The increasing number of recent publications (Reisberg and Zindler, 1986; Thirlwall, 1991b; Sharma et al., 1995; Gruau et al., 1998; Amato et al., 1999; Griselin et al., 1999; van Soest, 2000) presenting data acquired using the NdO^+ technique stresses the need to develop a routine low blank chemical separation that allows accurate and highly precise measurements of Nd isotope compositions on 1–5 ng Nd samples.

Efficient chromatographic extraction is necessary before most thermal ionization mass spectrometer (TIMS) isotopic analysis. This statement is particularly true when measuring Nd isotope ratios using the NdO^+ technique. Since oxygen has three stable isotopes, the signal intensity on any mass is the "sum" of three isobaric molecules: $Nd^{16}O$, $REE^{17}O$ and $REE^{18}O$. Significant isobaric interferences on the NdO masses of interest are therefore possible from other REE like ^{140}Ce and ^{141}Pr. ^{139}La and ^{138}Ba in turn create interferences on ^{140}Ce and ^{141}Pr. These interferences can be monitored during measurements and corrected for in an online or off-line program. These corrections, however, can increase the uncertainty of the measurements. Consequently, to ensure high precision measurements with only 1–5 ng of Nd, it is necessary to minimise isobaric interferences (Thirlwall, 1991b). Since the measured oxygen isotope ratios are constants in isobaric interferences correction programs used to recalculate the different Nd isotope ratios, it is also necessary to determine accurately the oxygen isotope composition. Indeed, Wasserburg et al. (1981) and Thirlwall (1991b) showed that the uncertainty of the oxygen isotope ratios could lead to high-error propagation. In order to obtain good quality NdO^+ ratios it is therefore imperative to accurately determine the oxygen isotope composition in the TIMS.

Several methods of REE separation have been described in the literature (Hooker et al., 1975; Richard et al., 1976; Dosso and Murthy, 1980; Cassidy and Chauvel, 1989). Most of them are specifically designed to separate Nd from Sm, whereas other light rare-earth elements (LREE) remain, at least in part, in the Nd fraction. The α-hydroxyiso-

butyric acid technique (HIBA) effectively separates Nd from other REE (Eugster et al., 1970). Use of the HIBA technique, however, requires a good control of solution pH and needs to be done in an acid-free environment. This paper describes a simple and low blank chromatographic technique that uses a High-Pressure Liquid Chromatography (HPLC) column with an eluent containing mainly dilute methanol. It efficiently separates Nd from the other LREE and is ideal for use with the NdO^+ technique. Moreover, it achieves an excellent separation of all LREE and is suitable for other applications such as Ce isotope geochronology.

We also present a compilation of oxygen isotope ratios, both measured at the Vrije Universiteit and published in the literature, that are used to address the question of how to best determine the oxygen isotope ratios. The NdO^+ technique is applied to low-Nd abundance samples such as highly depleted peridotites and foraminifera to test the reproducibility of the entire technique.

2. Chromatographic separation

The Nd extraction procedure described below is a low blank (Table 1), high-yield (∼ 80%), three-step chromatographic separation. Prior to chromatographic separation, samples were dissolved in a conventional low blank procedure using Teflon©-distilled HF and concentrated HNO_3 and thoroughly cleaned Savillex© PFA beakers. Once free of precipitate, the sample solutions were dried down and prepared for the sequential chemical separation.

Table 1
Average Nd blank value

Sample	Foraminifera	Whole rock peridotite
Weight of sample processed (g)	0.002	0.8
Total procedure blank (pg)	16	48
Blank of the three different columns (pg)		
Tru-resin column	5	
Aminex column	4	
Small HDEHP column	2	

2.1. Separation of REE fraction

REE are separated from the bulk matrix using the specific chromatographic resin known as TRU-resin (EIChroM©, 100–125 μm). This resin was preferred to the traditional cationic resin due to the smaller volume of resin and eluent needed ($\sim 50 \times$ less), which therefore ensures low blanks (< 10 pg). The columns, made of quartz (32 mm long, 3.5 mm diameter), were filled with 0.3 ml of resin and
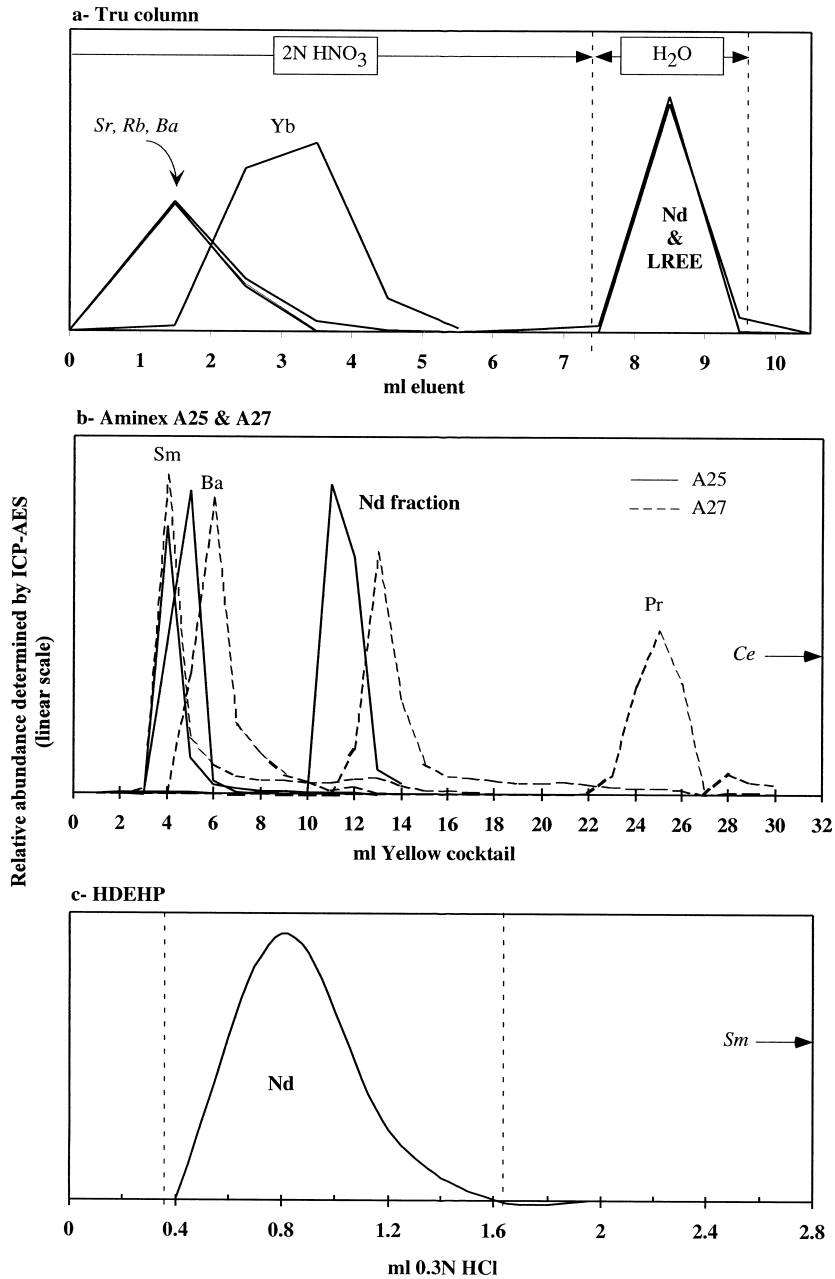

Fig. 1. Elution curve for (a) Tru-resin column, (b) Aminex A27 and A25 columns and (c) small HDEHP clean-up column.

cleaned several times, alternating MilliQ-water with 2 N HNO_3. The samples dissolved in 2 N HNO_3 (1.5 ml/100 mg sample) were centrifuged before being loaded onto the columns. The major elements and heavy REE were first eluted with 25 column volumes (cv) of 2 N HNO_3. The LREE fraction (La, Ce, Pr, Nd Sm and Gd) was then collected with 10 cv of MilliQ-water (Fig. 1a).

The maximum loading capacity of a 0.3 ml column is 0.2 g of whole rock. Low Nd abundances may require working with large amounts of sample (0.8–4 g). Several options were considered to overcome the potential problem of overloading: increasing the column volume, which significantly increases the blank and the cost per sample, or pre-concentrating the REE before ion-chromatography. The latter, based on the ability of iron to form oxy–hydroxide complexes with the lanthanides was first described by Goldberg et al. (1963) and then widely used by marine geochemists to pre-concentrate REE and other elements in water samples (Piepgras et al., 1979; Piepgras and Wasserburg, 1980). More recently, Chen et al., (1986) and Sharma and Wasserburg (1996) have applied the technique to geological samples such as carbonates and peridotites. Nevertheless, the total procedure blank can be significantly increased during the coprecipitation technique, which also does not ensure 100% yield. To date, we have chosen to pass larger samples through the same column in several aliquots. After a first REE separation, the same column is rinsed and re-conditioned before another aliquot is loaded. The total procedure blank increases by 10% if the sample size is larger than 2 g.

2.2. Separation of the Nd fraction

The HPLC grade Aminex anion exchange resins A25 and A27 (Bio-Rad©) are spherical beads of styrene divinylbenzene copolymer derived with quaternary ammonium functional groups. The resin has chemical and physical properties similar to those of the better-known AG1-X8 anion exchange resin (Bio-Rad©) but is specifically designed for HPLC. The columns are made of borosilicate glass and were thoroughly cleaned in sub-boiling 7 N HNO_3 before use. The first series of chromatographic separations were performed using 100 mm-long, 3 mm-diameter

columns (Omnifit©), filled with 0.7 ml of Aminex-A27 resin (referred to as A27). A second set of columns 150 mm long, 3 mm diameter was filled with 1 ml of Aminex-A25 (referred to as A25). Both resins have the same chromatographic specification but have different beads sizes: 18 and 22 μm, for A27 and A25, respectively. Due to the small size of the resin beads and the large aspect ratio of the columns, it is necessary to force the sample solution through the column. This is achieved by connecting a compressed air tap with a pressure regulator (Fig. 2). The system is thus entirely closed and only opened (via valves in the lid) during acid replenishment. The solutions used to clean and elute are contained in clean 1 l Savillex© PFA jars. Teflon tubes, pre-cleaned in hot acid, are used to carry the acids and sample solutions. During chromatographic separation and cleaning (using 1 N HNO_3 and MilliQ-water) a series of taps allow choice of the appropriate eluent. Further information about the over pressure system is available on request.

The solution that is used for the elution of the different REE (referred to as yellow cocktail) is a mixture of concentrated acetic acid (6.45 wt.%), water (21.65 wt.%), methanol (69.30 wt.%) and concentrated HNO_3 (2.60 wt.%). The recipe was modified from the original formulas of Hooker et al., (1975) and O'Nions et al., (1977). Samples are dissolved in 0.45 ml of yellow cocktail and placed in an ultrasonic bath to enhance the dissolution. The centrifuged samples are not loaded directly onto the column but into 0.45 ml removable Teflon© tubes. Once these tubes are filled, using a pipettor, they are re-attached to the columns and used to store the sample solutions until the HPLC system is switched on (see Fig. 2 for details).

The Aminex columns were calibrated at room temperature. They show good reproducibility over a range of temperature (20–25°C) and over time (the columns have been in use for over a year). Controlling the temperature to ±0.1°C using a water bath (O'Nions et al., 1977) is therefore not necessary. Nevertheless, according to Bio-Rad specifications, a major temperature increase (> 10°C) will significantly influence element retention times. The quality of the peak resolution is mainly dependent on the flow rate (the slower the elution the better the resolution). The optimum peak resolution is obtained with
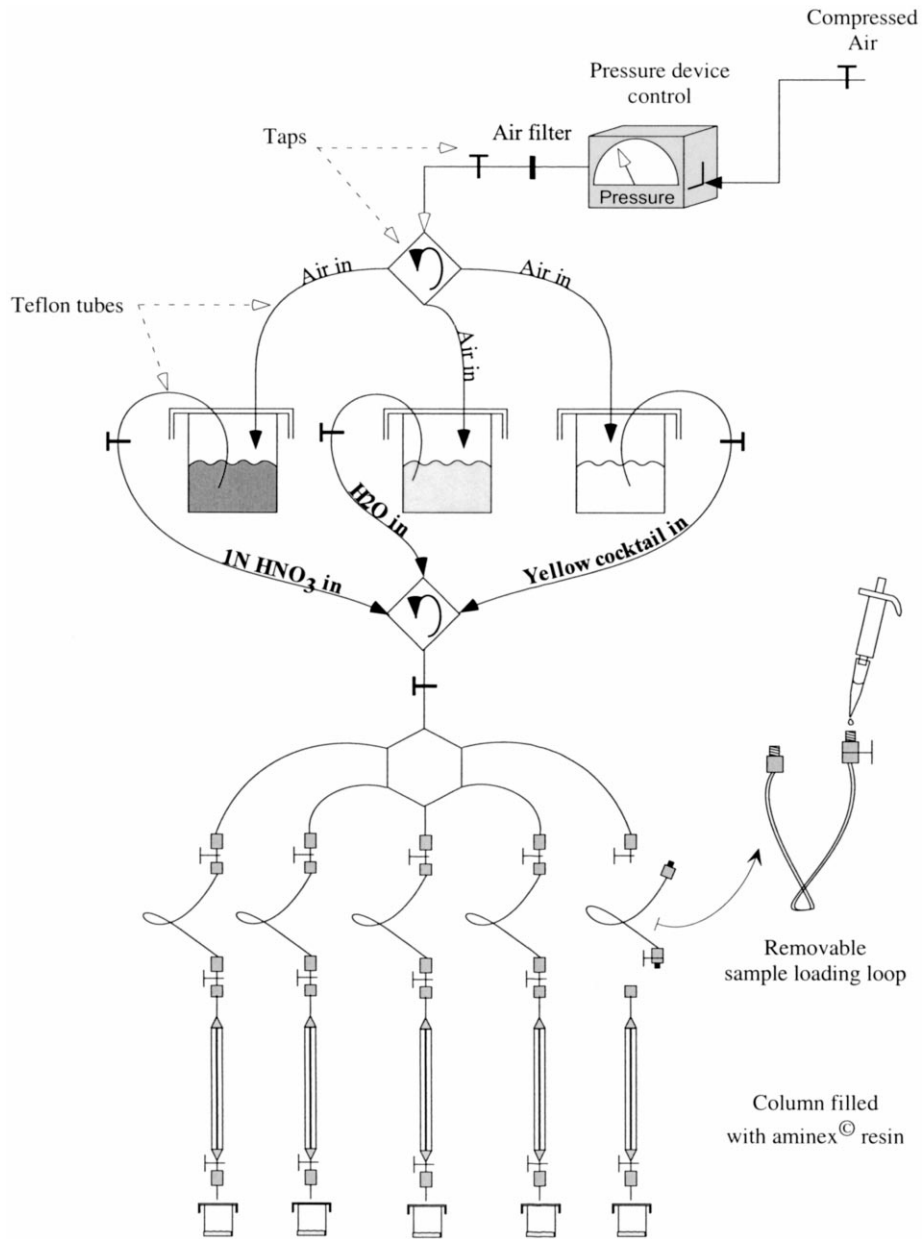
Fig. 2. Schematic diagram of the Aminex column set up.

a flow rate between 0.03 and 0.04 ml/min, which corresponds to a pressure of about 15–30 psi. A higher flow rate can be used for cleaning of the column. On both A25 and A27 columns the heavy REE are eluted first but less yellow cocktail is needed to elute and collect Nd fraction with the A25

than with the A27 (10 ml vs. 11 ml for pre-fraction and 4 ml vs. 5 ml for Nd fraction). The main difference between the two types of columns is in the shape of the peaks of the elution curve (Fig. 1b). The A25 columns have better-defined peaks with less tailing than the A27 columns. This difference

has no effect on the quality of the separation between Ce and Nd because Ce is eluted well after Nd. In both separations, some Pr is present in the Nd fraction but not in sufficient amounts to create significant interferences during the TIMS measurements. In general, the A25 columns provided the best quality of separation between Pr and Nd and are now routinely used at the Vrije Universiteit.
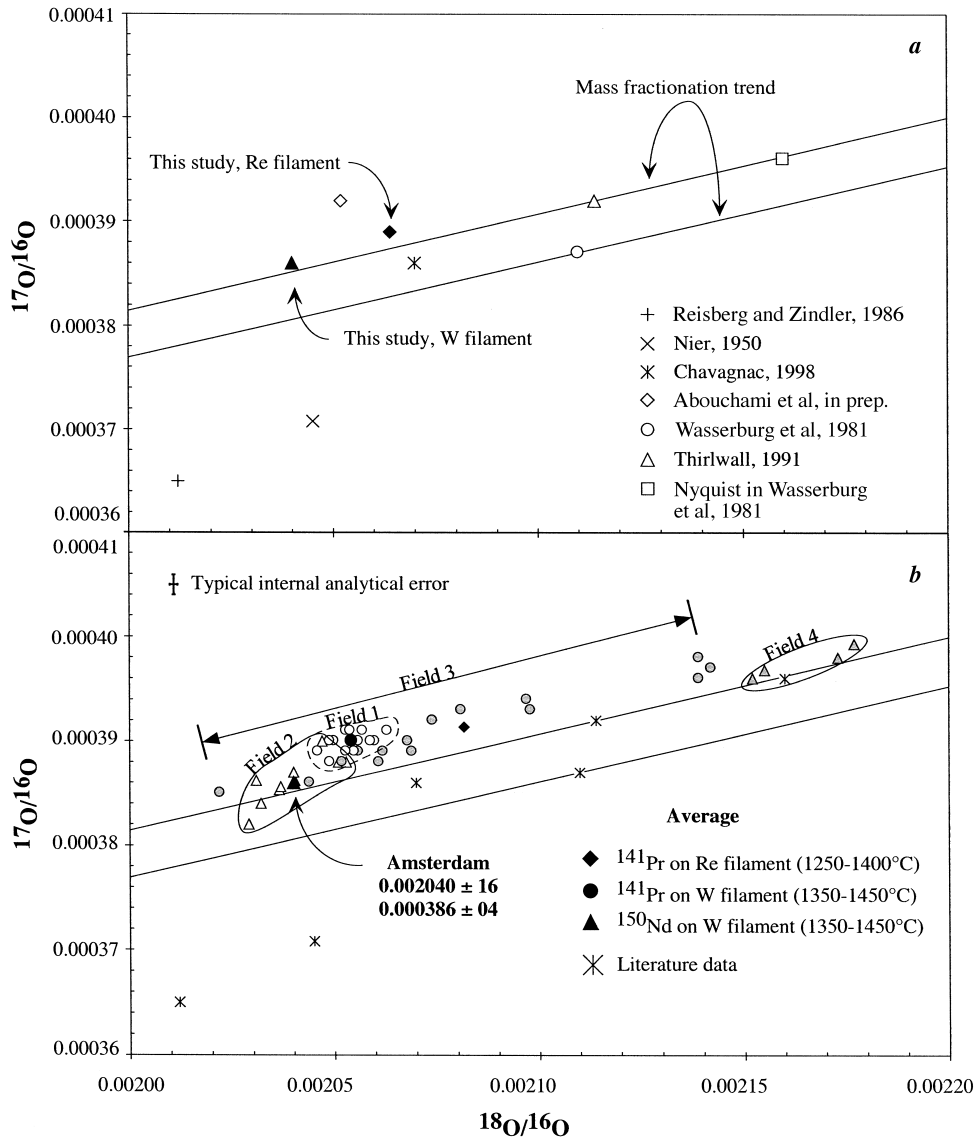

Fig. 3. (a) Compilation of oxygen ratios published in the literature — (b) Oxygen isotope ratios measured at the Vrije Universiteit. The fields define the oxygen isotope ratios measured using different loading techniques for a defined range of temperature. Field 1, ^{141}Pr on W filament between 1350°C and 1450°C; Field 2, ^{150}Nd on W filament between 1350°C and 1450°C; Field 3: ^{141}Pr on Re filament between 1250°C and 1400°C; Field 4, ^{150}Nd on Re filament between 1400°C and 1450°C. The typical internal analytical error on individual measurements is in the order of ± 0.000001 ($2\sigma_m$). The errors (2σ) on the average values defined and used in Amsterdam are ± 0.000016 and ± 0.000004 for the ^{18}O/^{16}O and ^{17}O/^{16}O, respectively. See text for further explanation.

2.3. Small clean up column or HDEHP

The direct consequence of the tailing effect mentioned above is the presence of Sm in the Nd fraction. Enough Sm is present to induce significant interferences on ^{144}Nd during TIMS measurements (Table 3). To solve this problem, one can monitor Sm (mass 170, ^{154}Sm^{16}O) during the measurements so that the relevant corrections can be applied (Thirlwall, 1991b). However, this significantly increases the acquisition time, making it difficult to achieve high-precision measurements (internal $2\sigma_m$ of ± 0.000020) on small sample (1–5 ng). Moreover, it adds another correction leading to larger error propagation. For these reasons, enhancing the separation between Sm and Nd in the chemistry is the preferred option.

Twenty five millimeter long, 3 mm diameter columns were filled with 0.2 ml of Bio-beads S-X8 (200–400 mesh) coated with HDEHP (1.2 g HDEHP/10 g Bio-beads, see Sochacka and Siekierski (1964) for more details). The columns were cleaned alternating MilliQ-water with 6 N HNO_3. After loading the sample in 0.150 ml 0.3 N HCl and elution with 0.250 ml 0.3 N HCl, the Nd fraction was collected in 1.2 ml of 0.3N HCl, while Sm was retained on the column (Fig. 1c; see Richard et al. (1976) for more details). The HDEHP column blank is very low (< 2 pg) and does not significantly increase the total blank procedure (Table 1).

3. Determination of the oxygen isotope composition

The oxygen isotope ratios, ^{18}O/^{16}O and ^{17}O/^{16}O, are constants used for the isobaric interference correction when recalculating the different Nd isotope ratios. Fig. 3a demonstrates that the oxygen ratios published in the literature cover a wide range (corresponding to a 7% variation). Clearly, the oxygen isotope composition determined in one laboratory will not necessarily apply to all mass spectrometers. The observed scatter in the data is big enough to significantly influence the REEO$^+$ correction on NdO$^+$ isotope ratios, and therefore, the accuracy and precision of the ^{143}Nd/^{144}Nd values (Wasserburg et al., 1981; Thirlwall, 1991b). Below, possible explanations for the observed variation are discussed and guidelines are proposed to help accurately determine oxygen isotope ratios.

The variation in the oxygen isotope ratios appears to be mainly due to different loading techniques (Table 2). The source of oxygen, the nature of chemical emitter and the type of ionization filament are all parameters that will influence the measured oxygen isotope ratios. Chavagnac (1998) demonstrated a difference in the measured values depending on the chemical emitter used on the filament (HCl or HNO_3). In this study the oxygen isotope ratios were measured statically, using both ^{141}Pr solution and ^{150}Nd spike and the same two loading

Table 2
Compilation of the oxygen isotope ratios published in the literature

References	Oxygen ratios		Remarks
	^{18}O/^{16}O	^{17}O/^{18}O	
This study [*]	0.002040	0.000386	Multicollector, W filament
Nier (1950)	0.002045	0.000370	Gas spectrometer
Nyquist in Wasserburg et al. (1981)	0.002160	0.000396	flow of oxygen to the source
Wasserburg et al. (1981)	0.002110	0.000387	Single collector, flow of oxygen
Reisberg and Zindler (1986)	0.002012	0.000365	Flow of oxygen to the source
Thirlwall (1991b)	0.002114	0.000392	Multicollector, Re filament
Chavagnac (1998)	0.002070	0.000386	Single collector, flow of oxygen
Abouchami et al. (in preparation)	0.002052	0.000392	Multicollector, W filament

[*] 2σ errors on the average values are ± 0.000016 and ± 0.000004 for ^{18}O/^{16}O and ^{17}O/^{16}O, respectively.

techniques used to measure the NdO^+ ratios (Re + silicagel or W + TaCl; Abouchami et al, in preparation). The oxygen isotope ratios measured using ^{141}Pr solution are significantly different depending on the type of ionization filament used; i.e. Re or W (Fig. 3b, compare the average of fields 1 and 3). The different work function of the ionization filament seems to significantly influence the fractionation of the oxygen isotopes during the measurements. A 5.9% increase of the $^{18}O/^{16}O$ over 150°C (Fig. 3b, field 3) was observed when measuring the oxygen isotope ratios using Pr solution loaded on Re filament. In contrast, similar measurements performed using W filaments are more reproducible, with only a 1.2% variation (Fig. 3b, field 1).

The measurements performed with W filament over the same range of temperature, but using the ^{150}Nd spike or the ^{141}Pr solution, yield distinct results. We noticed a significant difference between average value for the ^{150}Nd spike and ^{141}Pr solution: $^{18}O/^{16}O = 0.002040$ and $^{17}O/^{16}O = 0.000386$ vs. $^{18}O/^{16}O = 0.002054$ and $^{17}O/^{16}O = 0.000390$, respectively (Fig. 3b, compare fields 1 and 2). This difference may be related to the element specific properties and/or the impurities of La, Ce and Nd present in the Pr ICP standard used in this study. These elements created substantial interferences during the analysis, which may produce less-accurate data than with ^{150}Nd spike.

It is clear, from the above observations, that the same loading technique should be used for both NdO^+ and oxygen isotope measurements. Moreover, the temperature range over which the NdO^+ isotope composition is measured must be well controlled.

Finally, using a ^{150}Nd spike to determine the oxygen isotope ratios seems more appropriate than ^{141}Pr solution.

With the increasing number of data now available, it appears that all modern measurements are within error of a single mass fractionation trend (Fig. 3a). The observation that some older isotope data plot well outside this mass fractionation trend may be due to analytical problems such as decreased abundance sensitivity, a common issue in older single collector mass spectrometer particularly when O_2 is bled into the source.

4. Applications and results

The Nd isotope compositions were measured on a MAT-Finnigan 262 RPQ-plus multicollector mass spectrometer at the Vrije Universiteit (Amsterdam). The four interfering masses (154 to 157) and the five NdO masses (158 to 162) were determined using a multidynamic routine including two jumps (or magnetic field setting; Table 3). Mass 170 ($^{154}Sm^{16}O$) was monitored prior to acquisition. In all the measurements performed during this study, the $^{154}Sm^{16}O$ peak intensity was below 100 cps, implying that insufficient Sm was present to generate a significant isobaric interferences on ^{144}Nd. $^{140}CeO^+/^{144}NdO^+$, $^{141}PrO^+/^{144}NdO^+$ ratios were measured in order to monitor the extent of the isobaric interferences. Thirlwall (1991b) calculated that there would be no error contribution of the isobaric interferences if the ratios were better than 0.00035 and 0.020, respectively. So far, over 70 samples have been analysed

Table 3

Masses measured during acquisition and possible isobaric interferences. The Nd isotope ratios were measured at the Vrije Universiteit on a multicollector Finnigan-Mat 262 RPQ-plus mass spectrometer. During data acquisition, the masses are monitored using seven Faraday cups in a dynamic routine (two magnetic field setting). n.m., not monitored

Mass	154 $^{138}Ba^{16}O$	155 $^{139}La^{16}O$	156 $^{140}Ce^{16}O$	157 $^{141}Pr^{16}O$	158 $^{142}Nd^{16}O$	159 $^{143}Nd^{16}O$	160 $^{144}Nd^{16}O$	161 $^{145}Nd^{16}O$	162 $^{146}Nd^{16}O$
Faraday cups									
Setting 1	9	n.m.	8	7	6	5	4	3	n.m.
Setting 2	n.m.	9	n.m.	8	7	6	5	4	3
Possible isobaric interferences		$^{138}Ba^{17}O$ $^{137}Ba^{18}O$	$^{139}La^{17}O$ $^{138}Ba^{18}O$	$^{140}Ce^{17}O$ $^{139}La^{18}O$	$^{141}Pr^{17}O$ $^{140}Ce^{18}O$	$^{142}Nd^{17}O$ $^{142}Ce^{17}O$ $^{141}Pr^{18}O$	$^{144}Sm^{16}O$ $^{143}Nd^{17}O$ $^{142}Nd^{18}O$ $^{142}Ce^{18}O$	$^{144}Nd^{17}O$ $^{143}Nd^{18}O$	$^{145}Nd^{17}O$ $^{144}Nd^{18}O$

and the $^{140}CeO^+/^{144}NdO^+$ and $^{141}PrO^+/^{144}NdO^+$ measured are a factor 3 to 10 below the recommended values. These ratios also guarantee that Ba and La isobaric interferences are insignificant. The data clearly show the efficiency of the chromatographic separation described above. More importantly, it ensures that the error introduced by the interference correction will be insignificant in comparison to other measurements errors. Consequently, it is not required to monitor La and Ba during the analysis and it is therefore possible to measure Nd isotope ratios, as NdO^+, statically using seven collectors.

In the present study, all the measurements were made by dynamic data collection and all Nd isotope ratios were recalculated off-line using a software written for Finnigan-Mat 262 mass spectrometer (Koppers, 1998). The isobaric interference corrections were performed on individual scans before correcting for mass fractionation (Thirlwall, 1991a). The averages of the measured Nd isotope ratios and the analytical errors were then statistically calculated.

The accuracy and precision of the $^{143}Nd/^{144}Nd$ isotope data obtained for replicate measurements of standards and samples are discussed below and pre-

sented in Table 4. For this study, an initial series of samples and standards were loaded on Re filament following the procedure described by Thirlwall (1991a) using the silicagel developed by Gerstenberger and Haase (1997). Five-nanogram Nd internal (IGO) and international (La Jolla) standards were measured with ion beams of ~ 0.5 V of $^{142}Nd^{16}O$ giving the following average values for the $^{143}Nd/^{144}Nd$ isotope ratio: 0.511327 ± 0.000022 (2σ) and 0.511833 ± 0.000023 (2σ), respectively. The same standards measured as Nd metal (> 1.5 V of $^{142}Nd^{16}O$) yield 0.511338 ± 0.000016 (2σ) for IGO and 0.511850 ± 0.000022 (2σ) for La Jolla. Typical samples (1–5 ng), measured on Re filament produced very small beam intensities (< 0.1 V of $^{142}Nd^{16}O$ at 1350°C), that are insufficient to achieve precision better than ± 0.000050 (2σ). An alternative approach was adopted using W filaments and a TaCl emitter following the loading technique described by Abouchami et al. (in preparation). In this case, typical ion beam intensities of 1–1.5 V (on mass $^{142}Nd^{16}O$, lasting 1 h and 30 min) with 5-ng standard and 0.7–1 V with 1–5 ng samples were produced. The average measured values for the internal and La Jolla standards are 0.511345 ± 0.000017 (2σ) and 0.511864 ± 0.000020 (2σ), respectively.

Table 4
Precision obtained for different samples and standard depending of the amount of loaded Nd

Sample	NdO$^+$ technique			Nd$^+$ technique (100 ng)	
	Nanograms of Nd	Measured values[a]	Analytical error (10^{-6})	Measured values[a]	Analytical error (10^{-6})
			External[b]		External[b]
La Jolla	5	0.511864 (10)	20	0.511850 (43)	22
Internal standard	1	0.511347 (10)	16	/	/
Internal standard	5	0.511345 (15)	17	0.511338 (50)	16
Harzburgite 80L	5	0.513390 (8)	12	/	/
Foraminifera	0.5–2	0.511743 (6)	19	0.511738 (3)	07
Arc samples			Internal[c]		
Whole Rock	50	0.512827–0.513010	10	/	/
Olivine	20–40	0.512838–0.512996	12	/	/
Clinopyroxene	n.d.	0.512832–0.512992	08	/	/
Tibetan peridotites					
Whole Rock	1–5	0.512483–0.514272	30	/	/
Clinopyroxene	1–5	0.513419–0.514563	27	/	/

n.d. = not determined.

[a] The number of replicate analyses is indicated in brackets.

[b] 2σ.

[c] Typical internal analytical error expressed as $2\sigma_m$, where $2\sigma_m = 2\sigma/(\sqrt{n})$ with n representing the number of scans (~ 100).

One harzburgite (sample 80L) was also used as an additional "internal standard" to assess the reproducibility of the measurements under full analytical conditions: 0.513390 ± 0.000012 (2σ). It is important to point out that the 2σ external precision of the NdO^+ measurements (of standards and small size samples) are comparable to that routinely obtained on several tens of nanograms of Nd measured as Nd^+ (Table 4).

The driving force behind establishing this method was the desire to obtain large numbers of high quality Nd isotope ratios from mantle-derived peridotites. As shown below, the chemical extraction combined with the NdO^+ technique can also be applied to other geological materials and offers new opportunities in a wide range of Earth Science disciplines.

4.1. Highly depleted Tibetan peridotites, study of mantle processes

Even though peridotites are a key in understanding mantle processes, REE and Nd isotope studies of highly depleted harzburgites are not common. Peridotites have been neglected because of their extremely low trace-element abundances. The samples studied were highly depleted Tibetan peridotites (Nd < 0.01 ppm) from the Yarlung–Zangbo suture zone and ideal to fully test the capability of the entire technique. Over 20 whole rocks (WR) and mineral phases (clinopyroxene and orthopyroxene) were prepared and analyzed following the above procedure (Griselin et al., 1999). The internal analytical precision varies between ± 0.000015 and ± 0.000051 ($2\sigma_m$; Table 4) depending on the size of the measured sample (1–5 ng). The use of the NdO^+ technique could provide new constrains on the nature of partial melting and melt/rock interaction during melt extraction.

4.2. Mineral–mineral and mineral–WR disequilibria: evaluating crustal contamination at arcs

Distinguishing between crustal and subducted contributions in island-arcs is an issue that is still the subject of debate. Recently, Sr isotope studies on feldspars have shown that there can be significant disequilibria between feldspar phenocrysts and WR and within different areas of large feldspar phenocrysts themselves (Davies et al., 1994; Feldstein et al., 1994; Davidson and Tepley III, 1997; Davidson et al., 1998; Davies and Halliday, 1998). These disequilibria imply that, during at least part of its history, the magma experienced open system differentiation. The NdO^+ technique offers the opportunity to obtain Nd isotope data on additional mineral phases, such as olivine and (clino/ortho) pyroxene, that have specific positions in the crystallisation sequence of a magma. Such results could put constraints on the isotopic evolution of the magma as it traverses the crust and the presence, timing, and nature of crustal contributions to the magma. A pilot study on a set of thoroughly leached olivine and pyroxene separates from lavas of the Lesser Antilles arc yielded high quality Nd isotope ratios (Table 4; van Soest, 2000). The data imply that the NdO^+ technique could be a powerful tool for providing information to assess the role of crustal contamination in arc lava petrogenesis.

4.3. Nd isotope composition in foraminifera as a proxy of water mass movement

In individual ocean basins, different water masses identified by temperature and salinity have distinct neodymium isotope compositions (Bertram and Elderfield, 1992; Piepgras and Wasserburg, 1987). Planktonic and benthic foraminifera tests potentially record isotope composition of the water masses they lived in and consequently may provide a high resolution record of changing continental erosion and ocean circulation (Elderfield and Greaves, 1982).

To identify the different water masses, a $2\sigma_m$ external analytical precision of 0.5 ε_{Nd} units is required. Nd concentrations in foraminifera range from 0.03 to 1 ppm (Elderfield and Greaves, 1982; Shaw and Wasserburg, 1985). Nd isotope analyses of planktic foraminifera were recently performed using Nd^+ technique on 3.3 to 77 mg of foraminifera (Vance and Burton, 1999). With the NdO^+ technique, 1 to 10 mg are sufficient for one analysis. Living foraminifera sampled in sediment traps or benthic foraminifera sampled in sediment cores can therefore be analysed. Handpicked and carefully cleaned (Boyle, 1981 and 1983; Hastings et al., 1996) foraminifera species were prepared and analysed fol-

lowing the above procedure. External reproducibilities of 0.1 and 0.3 ε_{Nd} (Table 4) were obtained from repeated analyses of an internal standard ($n = 10$) and a foraminifera sample ($n = 6$), respectively.

4.4. Ce geochronology and ^{146}Sm–^{142}Nd chronometry

Ce isotope compositions are measured as CeO^+. Therefore, Ce must be separated from other REE to avoid isobaric interferences (such as $Nd^{16}O$, $Pr^{17}O$ and $Ba^{16}O$) during TIMS measurements. The chromatographic extraction presented in this paper is an alternative to the HIBA procedure (Makishima and Nakamura, 1991) or to the chemical separation described by Rehkämper et al. (1996). With the Aminex column Nd and Ce can be separated from the same aliquot and on the A25, the 4 ml Ce fraction can be collected after eluting approximately 25 ml of Yellow cocktail.

Harper and Jacobsen (1992) and others have shown that the ^{146}Sm–^{142}Nd system can be used to investigate the early stage of Earth History and also constrain the time of differentiation processes of the Moon and Mars. Here, again the chromatographic separation described above could be used to enhance the separation of Ce and Nd and therefore reduce interferences of ^{142}Ce on ^{142}Nd during measurements.

5. Conclusion

This paper describes a simple and highly efficient chromatographic extraction procedure of Nd from other LREE. This procedure is a reproducible, low blank and high-yield chemical separation that significantly reduces isobaric interferences during mass spectrometry measurements. Hence, it offers the opportunity to measure Nd isotope ratios on very low abundance and/or small size samples (1–5-ng Nd loaded on the filament). External precision comparable to that obtained on several tens of nanograms of Nd measured as Nd^+ (± 0.000020 2σ) are commonly achieved. Combining the present chemical separation with the NdO^+ technique potentially has a wide range of applications and offers the opportu-

nity to address many geological problems using samples that cannot be analyzed using conventional methods.

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