Chapter 3
Analytical Methods

This chapter is divided into two parts: 3.1 Chemistry and 3.2 Mass Spectrometry. Section 3.1 discusses the details of the protocol developed for the chemical separation and purification of Nd. All reagents used were ultrapure in grade, including water that was de-ionized Milli – Q (resistivity 18.2MΩ. cm). HCl used for column chemistry was prepared in the laboratory by distilling commercial grade acid twice in a Savillex® PFA (Teflon) distillation unit. Section 3.2 gives details of the mass spectrometry employed to obtain high precision Nd isotopic ratios. I have compared the most commonly used data acquisition and reduction methods for their effects on the accuracy of Nd isotopic ratios. All isotopic investigations were carried out on a Triton (TIMS) at the Department of Earth Sciences, Pondicherry University, Puducherry, India. Measurements for column calibrations were carried out using a Q-ICP-MS (Quadrupole - Inductively Coupled - Mass Spectrometer) at Geosciences Division, Physical Research Laboratory, Ahmedabad, India.

3.1 Chemistry

In this section I present details of the chemical separation protocol developed to obtain a pure Nd fraction from the rock matrix. Rock samples were broken into smaller chips with the help of a jaw crusher and powdered using tungsten – carbide TEMA® mill. Kimberlite samples, for which sample amount was limited, were powdered using an agate mortar and pestle.

3.1.1 Sample Dissolution

Standard dissolution protocol for silicates/carbonates was modified depending upon the mineralogical composition of the rock. Carbonatites were analysed in two separate fractions; as carbonate and silicate. The carbonate fraction was leached from a sample using 6N HCl and the residual silicate fraction was dissolved following the dissolution protocol for silicate rocks. Since carbonate rich carbonatites generally have higher REE contents compared to carbonate poor carbonatites (Ray et al. 2013), the weight of the samples dissolved was varied between 60 mg to 200 mg depending on the carbonate content. In the case of very low concentrations of Nd (< 0.1 ppm) in samples like mantle xenoliths (peridotites), 1 – 2 g of sample powder was taken. A powdered sample was dissolved in a concentrated mixture of HF and HNO_3 (2:1). Complete dissolution was achieved through ~1 hour of ultra-sonication and heating at 60^oC with closed cap for ~12 hours. After two rounds of 8N HNO_3 treatment and drying, the sample was converted to chloride form using 6N HCl (two rounds of 0.5 ml) and 2N HCl (two rounds of 0.5 ml) and the final solution was prepared in 1ml of 1N HCl for

column chemistry. The sample dissolution procedures constitute the *Step – 1* in the chemical protocol (Figure 3.1).

3.1.2 Column Chemistry

Various elements of interest were separated from matrix of a sample solution in the different stages of column chromatography. The flowchart (Figure 3.1) gives an overview of the stages of column chemistry routines those were followed in this work with an emphasis on the protocol followed for Ce and Sm free Nd purification process. The various steps as shown in Figure 3.1 are described below in detail.

Step – 2 (Primary Column Procedure)

1. The final solution of the rock sample in 1 ml of 1N HCl was loaded onto the pre-conditioned AG-50W-X8 resin in the primary column. The column was pre-calibrated for Rb, Sr and REE separation.
2. Elution Protocol:
    i. 10 ml of 2N HCl – Elute and discard
    ii. 4 ml of 2N HCl – Elute and collect for Rb
    iii. 10 ml of 2N HCl – Elute and discard
    iv. 8 ml of 2N HCl – Elute and collect for Sr
    v. 18 ml of 6N HCl – Elute and collect for collecting REEs
    vi. 40 ml of 6N HCl – twice for column wash
    vii. Regeneration of the resin by Milli-Q water

Step – 3 (REE separation column procedure)

1. REE cuts in 100µl of 0.18N HCl was loaded onto the pre-conditioned Ln spec resin in column. Another 100µl of 0.18N HCl was added by washing the sample vial.
2. Elution Protocol:
    i. 18 ml of 0.18N HCl – Elute and discard
    ii. 8 ml of 0.3N HCl – Elute and collect for Nd
    iii. 7 ml of 0.3N HCl – Elute and discard
    iv. 7 ml of 0.4N HCl – Elute and collect for Sm.
    v. Full column reservoir volume 6N HCl – Wash
    vi. Full volume Milli Q water – Wash

Step – 4 (Micro column procedure with α–HIBA)

This step is critical for our experiment since here we ensure separation of pure Nd, devoid of any trace of Ce in the fraction. Every time the column chemistry was done, fresh batches of acids were prepared, and columns were loaded with fresh resin, maintaining the pH. Fresh calibration was done for every batch of acid and resin. Figure 3.3 shows a typical calibration curve obtained by us for our columns. The procedural details are described below.

α-HIBA column chemistry
Resin Preparation 1) Take AGW – X4 resin in a Teflon container. Clean it with Milli-Q water. 2) Add 6N HCl to this resin and ultra-sonicate for 60 minutes. 3) Discard the acid and store the resin in 6N HCl overnight. 4) Following day repeat steps 2 and 3, twice. 5) Wash the resin with Milli-Q water thoroughly (three times at least). 6) Carefully add a few drops of liquid NH_4 onto the resin in Milli-Q untill its pH becomes 7. 7) Resin is now ready to be used.
Preparation of α-HIBA 1) This acid is prepared by dissolving alpha-HIBA crystals in Milli-Q water. 2) 0.15M acid is prepared by calculating the required weight needed to be dissolved in required volume of the acid to be prepared. For example, to prepare 1L or 1000ml of 1M acid dissolve the weight equal to the molecular weight of the alpha – HIBA crystals. 3) The pH is adjusted to 4.8 by adding NH_4 to the acid. The acid is ready to be used.

Once the resin and acid were ready, the columns were calibrated. Teflon columns of dimension 9 cm × 0.25 cm (internal diameter) were used. Resin filled column was used only once, after which the resin was thrown and column was filled again with the new resin before a new experiment. The Nd eluted and collected in this stage is Ce – free, however, in alpha-HIBA medium. To remove α-HIBA the collected eluent was reacted with aqua-regia (mixture of concentrated HCl-HNO_3 in 3:1 proportion) at temperatures of around 120 – 150 °C.

3.2 Mass Spectrometry

In this section I discuss the details of the mass spectrometric methods used for Nd isotope data acquisition and reduction, starting with the details of the optimization of the ion current and run conditions.

3.2.1 Run Conditions for Nd Isotope Analyses on TIMS

Neodymium was measured as Nd^+ ions on a *Triton* TIMS at the Department of Earth Sciences, Pondicherry University, India. For each sample about 400 ng of Nd was loaded onto the degassed zone refined Re double filament assembly. The evaporation filament was heated to 1000-1500 mA, at a rate of 20 mA/min and the ionization filament to 4000-4300 mA, at a rate of 150 mA/min. This heating of the filaments was carried out in two steps. The first step involved heating of ionization filament to 3500 mA while evaporation filament was heated to 800 mA. Once current in the ionisation filament reached 3500 mA, the second step heating of the evaporation filament was initiated. The Nd^+ signal for 142 mass appeared only after the evaporation filament reached 1000 mA and the corresponding ionization filament current was 4000 mA. The data acquisition was initiated when Nd^+ (for 142 mass) reached about 2.5 - 4.0 V ($R = 10^{11}$ Ω). The Nd was maintained in a window of 80 % to 200 % of the original signal using *Triton* software. Details of the run conditions are given in Table 3.1. Ames Nd standard was analysed (using both 3- and 2- sequence multi-dynamic modes of data acquisition methods; Table 3.1) routinely with each batch of samples. For the 3-sequence data acquisition scheme, each run lasted for about 6-7 hours and that for the 2-sequence data acquisition scheme, around 5 hours. Isobaric interferences on Nd isotopes from Sm and Ce were monitored by measuring ^{147}Sm and ^{140}Ce, respectively.

3.2.2 Data Acquisition and Reduction Methods

High precision isotopic ratio measurements by TIMS often requires data acquisition through a multi-dynamic mode, wherein differences in collector efficiencies/factors can be nullified by measuring individual ion beams in multiple Faraday Cups through peak jumping. The Zoom Optics, a feature of *Triton* TIMS, helps in precise co-incidence and centring of peaks for various masses when magnet settings are changed during multi-dynamic data acquisition. In addition, the amplifier rotation, another feature of *Triton,* helps in minimising the errors, if any, due to unequal amplifier efficiencies.

For the present study, I have carried out the Nd isotopic ratio analyses using a multi-dynamic mode of data acquisition. The two most commonly employed multi-dynamic methods for Nd isotopic investigations: (1) 3-sequence method (as used by Upadhyay et al., 2009) and (2) 2-sequence method (as used by Roth et al., 2014b), were used to obtain data. A comparative analysis of the two methods was done by me to understand the effect of data acquisition method on the accuracy of the $^{142}Nd/^{144}Nd$ isotopic values. The results obtained are described in Chapter 4. The details of the two methods along with their run conditions are given in Table 3.1 and 3.2.

Data reduction includes correction for isobaric interferences and mass fractionation corrections, the details of which are discussed in Chapter 4. Table 3.3 provides the details of the two commonly used fractionation correction methods employed for data reduction in the present study, viz. *exponential law* and *power (law) – normalised exponential law* (Thirwall, 1991; Upadhyay et al., 2009; Gautam et al., 2017).

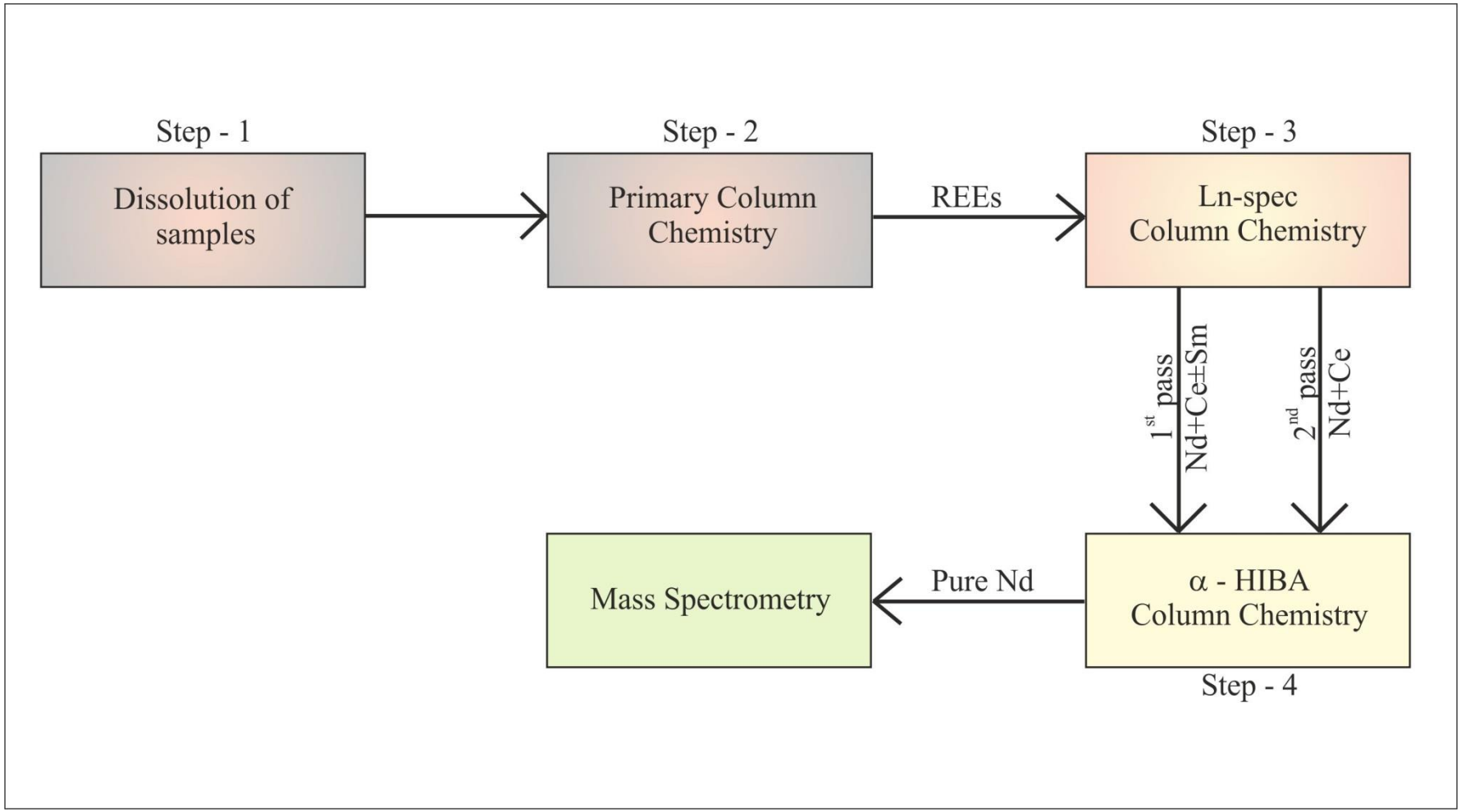

Figure 3.1 *Flowchart showing various stages of the protocol developed for extraction of pure Nd from samples.*

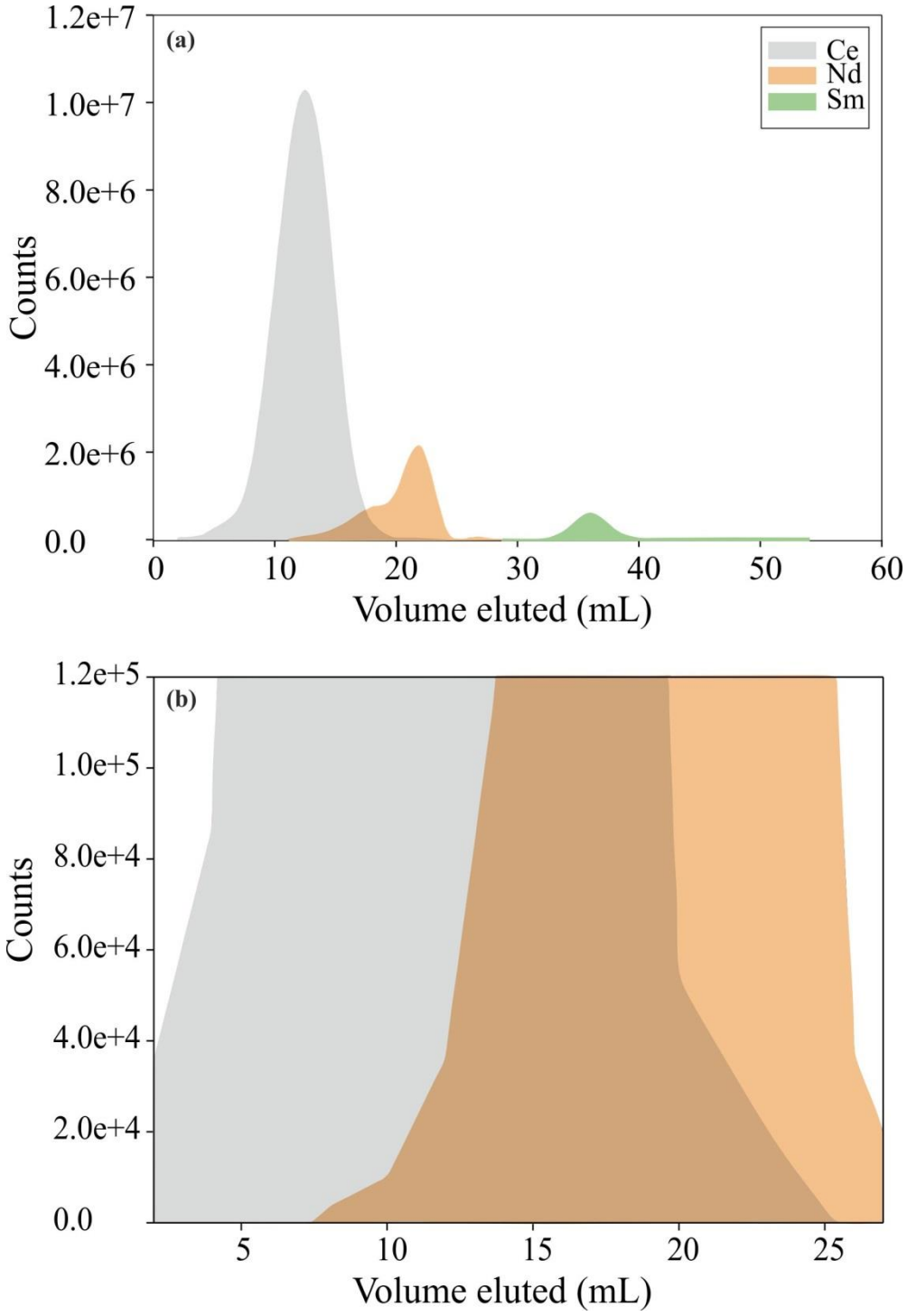

Figure 3.2 *Calibration curve for Nd – Sm separation using Ln spec resin, obtained by analyses of calibration cuts in a Q-ICP-MS (a) Separation of Sm from Nd during Step -2 of the element separation protocol: Ce elutes with Nd; (b) shows an enlarged view of the Nd elution.*

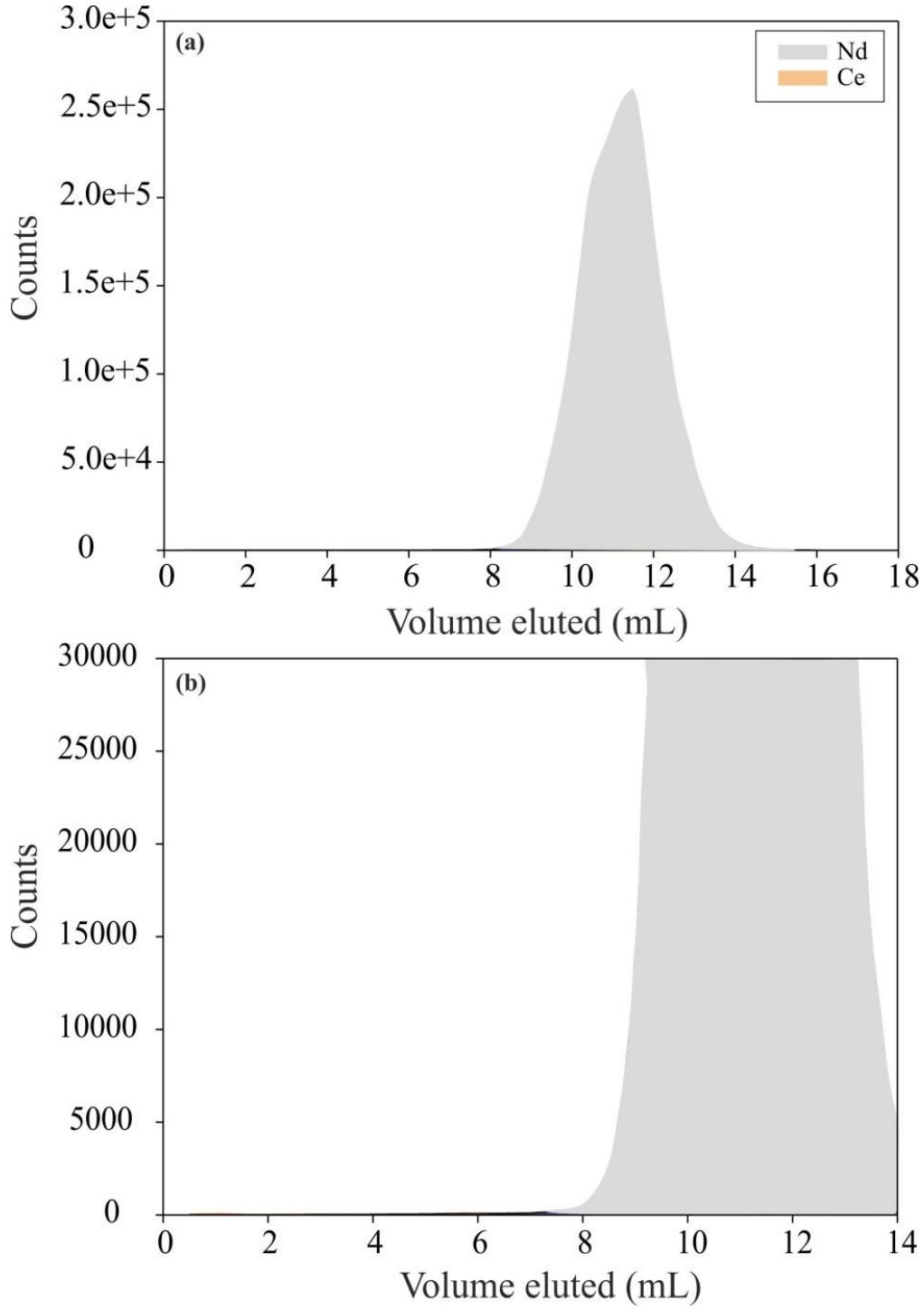

Figure 3.3 *Calibration curves for a-HIBA column chemistry. (a) shows Ce free Nd elution (b) enlarged view of the Nd elution, which shows no trace of Ce.*

Table 3.1

Cup configuration and run conditions used in this study for Nd isotopic ratios measurements on a Triton

a) Three-sequence method

											Zoom optics	
Cup	**L4**	**L3**	**L2**	**L1**	**C**	**H1**	**H2**	**H3**	**H4**	Integration time [sec]	Focus [V]	Dispersion [V]
Sequence 1	^{140}Ce	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{148}Nd	^{150}Nd	8.389	0.0	0.0
Sequence 2			^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{149}Sm	8.389	0.0	6.0
Sequence 3		^{140}Ce		^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	8.389	0.0	8.0

b) Two-sequence method

											Zoom optics	
Cup	**L4**	**L3**	**L2**	**L1**	**C**	**H1**	**H2**	**H3**	**H4**	Integration time [sec]	Focus [V]	Dispersion [V]
Sequence 1	^{140}Ce	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{148}Nd	^{150}Nd	8.389	0.0	0.0
Sequence 2		^{140}Ce		^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	8.389	0.0	8.0

Note: Number of blocks = 54, No. of cycles per block = 10, Amplifier rotation to left, Baseline after every 2 blocks, Peak centring after every 8 blocks, Lens focusing after every 4 blocks, No. of integrations = 1, Idle time (sec) = 3, Cycles filtered at 2σ.

Table 3.2
Comparison of various data acquisition and reduction procedures followed by Upadhyay et al. (2009) and Roth et al. (2014b)

Parameter	**Upadhyay et al. (2009)**	**Roth et al. (2014 b)**
Number of sequences in multi-dynamic mode	Three	Two
Fractionation correction law	Power-law normalized exponential law	Exponential law
Fractionation factor	Average of all sequences : $(\beta_1+ \beta_2+ \beta_3)/3$	Calculated from sequence 1: β_1
Cup factors	Get cancelled	Do not get cancelled*
Multi-dynamic correction for ratios	^{142}Nd/ ^{144}Nd, ^{143}Nd/ ^{144}Nd, ^{145}Nd/ ^{144}Nd, ^{148}Nd/ ^{144}Nd	^{142}Nd/ ^{144}Nd
Static correction for ratios	^{150} Nd/ ^{144}Nd	^{143}Nd/ ^{144}Nd, ^{145}Nd/ ^{144}Nd, ^{148} Nd/ ^{144}Nd, ^{150} Nd/ ^{144}Nd

*As described in Roth *et al*. (2014 b), the cup factors do not affect the exponential law corrected ^{142}Nd/^{144}Nd by more than 5ppm if the difference in relative cup efficiency is less than 370ppm. The relative cup efficiency is calculated by taking the difference of static ^{142}Nd/^{144}Nd measured in sequence 1 and 2.

Table 3.3

Details of fractionation correction methods used in the present study

Isotope ratio	Power law normalised exponential law	Simple exponential law
$^{142}Nd/^{144}Nd$	$[(^{142}Nd/^{144}Nd)_3\times(^{146}Nd/^{144}Nd)_1/0.7219]\times (141.907731/143.910096)^{\beta} \times (1+f)^2$	$[(^{142}Nd/^{144}Nd)_2]\times (141.907731/143.910096)^{\beta}{}_1$
$^{143}Nd/^{144}Nd$	$[\{(^{143}Nd/^{144}Nd)_2\times(^{143}Nd/^{144}Nd)_3\}/\{(^{144}Nd/^{146}Nd)_1\times 0.7219\}]^{0.5}\times (142.909823/143.910096)^{\beta} \times (1+f)^1$	$[(^{143}Nd/^{144}Nd)_1]\times (142.909823/143.910096)^{\beta}{}_1$
$^{145}Nd/^{144}Nd$	$[\{(^{145}Nd/^{144}Nd)_2\times(^{145}Nd/^{146}Nd)_1\times 0.7219\}]^{0.5}\times (144.912582/143.910096)^{\beta} \times (1+f)^{-1}$	$[(^{145}Nd/^{144}Nd)_1]\times (144.912582/143.910096)^{\beta}{}_1$
$^{148}Nd/^{144}Nd$	$[\{(^{148}Nd/^{146}Nd)_1\times(^{144}Nd/^{146}Nd)_3\times(0.7219)^2\}]\times (147.916901/143.910096)^{\beta} \times (1+f)^{-4}$	$[(^{148}Nd/^{144}Nd)_1]\times (147.916901/143.910096)^{\beta}{}_1$
$^{150}Nd/^{144}Nd$	$[(^{150}Nd/^{144}Nd)_1]\times (149.9209/143.910096)^{\beta}$	$[(^{150}Nd/^{144}Nd)_1]\times (149.9209/143.910096)^{\beta}{}_1$

Here $\beta = \frac{(\beta_1+\beta_2+\beta_3)}{3}$ and f = $\frac{(f_1+f_2+f_3)}{3}$ are the average mass fractionation factors from the three sequences

$\beta_i = \ln\{(0.7219)/(^{146}Nd/^{144}Nd)_i\}/\ln(145.913126/143.910096)$

$f_i = \{(0.7219)/(^{146}Nd/^{144}Nd)_i\}^{1/(145.913126 - 143.910096)} - 1$

i = 1, 2, 3 which refers to the sequence number