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Isotope ratio measurements of trace Nd by the total evaporation normalization (TEN) method in thermal ionization mass spectrometry

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Abstract

Isotope ratios of very small Nd samples (0.1–5 ng) are measured by the total evaporation normalization (TEN) method. Samples as small as 0.5 ng can be measured with an external precision of 140 ppm by this method. The average ^{143}Nd/^{144}Nd ratio of the samples with the measured electric charge Q (^{143}Nd) = 10–50 × 10^{-11} corresponds roughly to 0.5 ng JNdi-1, is 0.51214 ± 0.00007 ($n = 7$) and is coherent with the values obtained by conventional dynamic multi-collection thermal ionization mass spectrometric measurements. The precision of 0.5 ng Nd measurements is sufficient for the application of the ^{143}Nd/^{144}Nd ratio as a geochemical tracer. The precision of TEN measurements for samples smaller than 5 ng is superior to that of the conventional method.

Keywords: Total evaporation normalization; Nd isotope ratio; Thermal ionization mass spectrometry; Small sample; High precision

1. Introduction

The samarium–neodymium isotope system is widely used in geochemical and cosmochemical studies. The radioactive decay of ^{147}Sm to ^{143}Nd, with a half-life of 106 billion years (Gy), produces variations in the ^{143}Nd/^{144}Nd isotopic ratio. The isotopic ratio of Nd can be measured very precisely by present-day thermal ionization mass spectrometry (TIMS). There are three essential points in achieving high precision in isotope ratio measurements. The first is the use of an internal normalization technique for instrumental mass fractionation correction. Instrumental mass fractionation is the primary source of imprecision in isotope ratio measurements, and normalization is known to be the best way to correct for it when the element under consideration has two or more nonradiogenic isotopes [1]. The second point is the high ion current during measurement to keep the signal-to-noise ratio of the faraday cup high. The third point is the long data acquisition time. Typical Nd isotopic measurements by TIMS require approximately 3 h. Long data acquisition reduces random error due to ion counting statistics. The latter two points require large samples (e.g., 100–300 ng of Nd for a single measurement) to achieve good precision; decreasing the sample size decreases the ion current and shortens the data acquisition time. Thus, the precision of the measurement of a very small sample is usually poor compared to that obtained with large samples.

Many advances have been made in isotope geochemistry to improve analytical precision with very small samples. Many studies have focused on the enhancement of ionization efficiency to increase the sensitivity of elements in thermal ionization. For example, silica gel activator + phosphoric acid is known to improve the ionization efficiency of Pb [2], and Ta emitter is known to increase the sensitivity of Sr severalfold [3]. Neodymium is more efficiently ionized as the NdO$^+$ ion than as the Nd$^+$ ion. Thirlwall [4] reports that the silica gel + phosphoric acid technique promotes the ionization of NdO$^+$. However, NdO$^+$ measurement is not preferred because of the uncertainty in oxygen isotope ratio correction. To the best of our knowledge, no activator has yet been reported for Nd$^+$ ionization enhancement.

The total evaporation method [5], which is used primarily in nuclear industry, was developed as an instrumental mass fractionation correction technique for the measurement of U and Pu

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Table 1
Faraday cup configuration of the Sector 54-30

Collector	L2	L1	Axial	H1	H2	H3	H4
Mass	140	142	143	144	145	146	147
Isotope	^{140}Ce	^{142}Ce + ^{142}Nd	^{143}Nd	^{144}Nd + ^{144}Sm	^{145}Nd	^{146}Nd	^{147}Sm
Baseline	139.5	141.5	142.5	143.5	144.5	145.5	146.5

in which normalization cannot be applied. The principle of the total evaporation method is that no mass fractionation will occur if the entire sample is evaporated and ionized with a constant yield and the ion beams of the element are totally integrated [6]. The distinctive feature of the total evaporation method is the "burn out" of a very small amount of the sample in a very short time. There are a number of problems in applying the total evaporation method to geochemical isotope ratio measurements. First, the instrumental mass fractionation effect cannot be totally eliminated because the ionization yield of an element is easily biased during the short measurement time by slight changes in the focus potential, by changes in the ionization efficiency of the oxide ions, etc [7]. Second, the observed isotope ratios are not coherent with that measured by the conventional normalization technique. Dubois et al. [8] measured 20 ng of Nd using the total evaporation method, obtaining a mean ^{146}Nd/^{144}Nd value of 0.72333, which is considerably distinct from the value 0.7219 [9] used for normalization in geochemical studies.

In seeking a new method for the isotopic measurement of very small Nd samples, we have experimented with the idea of combining the total evaporation method with the normalization technique. With the total evaporation normalization (TEN) method presented in this paper, small amounts of the sample are measured by a total evaporation procedure. The obtained isotope ratios subsequently undergo the normalization calculation to correct for relict instrumental mass fractionation and to obtain the "geochemically accurate" isotope ratio. This paper presents the procedure and the results of Nd isotope ratio measurement of very small samples (0.1–5 ng Nd) by the TEN method. The present results are compared with those obtained by conventional dynamic multi-collector thermal ionization mass spectrometry (MC-TIMS).

2. Materials and methods

2.1. Apparatus and reagents

Neodymium isotopic reference reagent JNdi-1 [10] dissolved in diluted HNO_3 was used as a sample. Nd was measured with triple Re filaments (one ionization filament and two evaporation filaments). Small amounts (0.1, 0.5, 1 and 5 ng Nd) of the JNdi-1 were loaded on one of the evaporation filaments with 1 μl 2 M-H_3PO_4 and evaporated to dryness. Isotope ratio measurements were performed at Nagoya University on a VG Sector 54-30 equipped with seven faraday cups. Table 1 shows the configuration of the seven faraday cups.

2.2. Faraday cup efficiency calibration

Amplifier gains for the faraday cups were calibrated prior to each analytical session. In addition, efficiencies for faraday cups L1, Ax and H3 were calibrated relative to H1. Relative efficiency calibration for the other cups was not been carried out because the effect of the different efficiencies is negligible (L2 and H4) and because ^{145}Nd data is not used in ^{143}Nd/^{144}Nd ratio determination (H2). Efficiency factors for the faraday cups were measured by symmetrical peak jumping [11] using a ^{142}Nd ion beam with an intensity of 1V (= 10^{-11} A). Each calibration cycle consisted of 100 replicate measurements of the efficiency factors. Several calibration cycles were carried out each day, and the results were averaged to determine the efficiency factors for each analytical session. The results of the faraday cup efficiency calibration are shown in Table 2.

2.3. Mass spectrometry

Nd isotope ratios were measured using a total evaporation procedure. To the best of our knowledge, there is no software available for total evaporation measurements of Sector 54-30. Therefore, we controlled the filament current manually and used the software for dynamic measurement for the acquisition of "raw intensity data" during measurement.

2.3.1. Step 1: adjustment phase

First, the ionization filament was heated to a filament current of 4.6 A and stabilized for approximately 10 min. The ion beam of ^{187}Re from the ionization filament was then used to optimize the focus settings of the ion source. The intensity of the ^{187}Re ion beam was around 10–100 mV, which corresponds to an ion beam current of 10^{-13} to 10^{-12} A.

Table 2
Results of the faraday cup efficiency calibration

Session	L1	Axial	H1	H3	*n*
1	1.00014 ± 3	1.00025 ± 2	1	1.00005 ± 3	8
2	1.00038 ± 10	1.00032 ± 7	1	0.99994 ± 10	3
3	1.00034 ± 5	1.00038 ± 2	1	0.99996 ± 5	8

Errors are 2S.E.

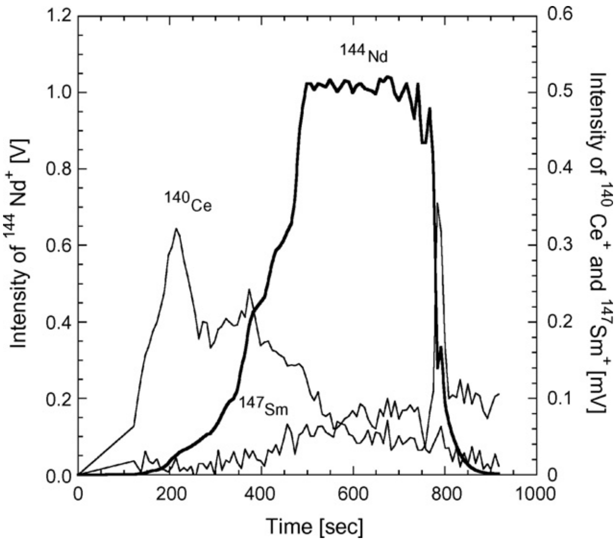

Fig. 1. Typical ion beam intensity profiles of ^{144}Nd, ^{140}Ce and ^{147}Sm during total evaporation normalization measurement plotted as a function of measurement time.

Next, evaporation filaments were slowly heated until the ion beam intensity of ^{142}Nd reached 1 mV. The evaporation filament current at this point was 1.6–1.7 A. Focus settings were optimized again using a ^{142}Nd ion beam. After the focus adjustment, the evaporation filament current was decreased to 1.0 A to avoid consumption of the sample during baseline measurement.

2.3.2. Step 2: data acquisition phase

The baseline was measured prior to the data acquisition. The integration time for the baseline was 30 s. The measured masses and corresponding collectors are shown in Table 1. Ion beam measurement was initiated immediately after baseline measurement. Ion beam integration of 8 s was repeated during measurement. As the data acquisition started, the evaporation filament current started to increase until the ion beam intensity of ^{144}Nd reached the target intensity. The target intensity of ^{144}Nd, which depended on the sample size, was 1 V, 500 mV and 100 mV, for 5, 0.5–1 and 0.1 ng of Nd, respectively. The evaporation filament current was then controlled to keep the ion beam intensity constant. As the sample had been consumed, the evaporation filament current was finally raised to 4.4 A. When the ion beam intensity of ^{144}Nd had fallen below 1 mV, data acquisition was terminated. A typical time profile of a ^{144}Nd ion beam for a 5 ng sample is shown in Fig. 1; the intensity profiles of ^{140}Ce and ^{147}Sm ion beams are also plotted in mV scale. The typical data acquisition time was 15, 11, 7 and 4.5 min for 5, 1, 0.5 ng and 0.1 ng of Nd, respectively.

2.4. Data processing

The VG software outputs "raw intensity data" from which baseline are subtracted for each integration. For every isotope measured, "raw intensity data" were summed and converted to measured electric charge Q by

$$Q[C] = \Sigma I \times t \times R \tag{1}$$

where I is the "raw intensity data" of a integration, t the integration time (8 s) and R is the resistance of the faraday cup amplifier ($\times 10^{11}$ Ω). The isobaric interferences of Ce and Sm were corrected on Q (^{142}Nd) and Q (^{144}Nd), using Q (^{140}Ce) and Q (^{147}Sm) and the reported natural isotope ratios for Ce [12] and Sm [13], respectively. Raw isotope ratios of Nd were calculated from Q (Nd) with reference to ^{144}Nd:

$$^{i}\mathrm{Nd}/^{144}\mathrm{Nd}_{\mathrm{raw}} = Q(^{i}\mathrm{Nd})/Q(^{144}\mathrm{Nd})$$
$$(i = 142, 143, 145 \text{ and } 146) \tag{2}$$

These raw isotope ratios were then corrected for instrumental mass fractionation by internal normalization using an exponential law [14] and the commonly used ratio ^{146}Nd/^{144}Nd = 0.7219 [9].

The error of the isotope ratio was estimated as follows. The number of ions counted in each faraday cup can be calculated from the measured electric charge Q:

$$N = Q \times N_{\mathrm{A}}/F \tag{3}$$

where N_{A} is the Avogadro's number and F is the Faraday constant. Applying the counting statistics, the standard deviation of N can be estimated:

$$\sigma N = \sqrt{N}/N \tag{4}$$

The error of the normalized ^{143}Nd/^{144}Nd ratio can then be calculated by propagating the errors σN of isotopes ^{143}Nd, ^{144}Nd and ^{146}Nd.

3. Results and discussion

3.1. Results

The results of the Nd isotope ratios of 0.1–5 ng JNdi-1 samples measured by the TEN method are shown in Table 3 and Fig. 2. The raw isotope ratios ^{142}Nd/^{144}Nd$_{\mathrm{raw}}$, ^{143}Nd/^{144}Nd$_{\mathrm{raw}}$, ^{145}Nd/^{144}Nd$_{\mathrm{raw}}$ and ^{146}Nd/^{144}Nd$_{\mathrm{raw}}$ in which the ratio was not normalized to ^{146}Nd/^{144}Nd = 0.7219, are also shown in Table 3. The raw ^{146}Nd/^{144}Nd ratio obtained in the present measurement is 0.7234 ± 15 (2S.D., n = 38). Excluding the three obviously fractionated data (Fig. 3), average raw ^{146}Nd/^{144}Nd ratio in this study is 0.7232 ± 6 (2S.D., n = 35). This is in agreement with the previously reported ^{146}Nd/^{144}Nd ratio of 0.72333 [8] measured by the total evaporation method. However, it differs significantly from the normalizing value 0.7219 used in geochemical studies (Fig. 3). The ^{146}Nd/^{144}Nd value of 0.7219, initially used by O'Nions et al. [9], is stated as the mean of large number of Nd analysis at that time [15]. Wasserburg et al. used ^{146}Nd/^{142}Nd = 0.636151, which is mentioned as an average of 10 Nd mass spectrometric runs in 1976, for normalization in NdO$^+$ measurements and reported ^{146}Nd/^{144}Nd = 0.724134 ± 0.000010 [16] in that normalization scheme. Taking an average of a large number of measurements is not sufficient to eliminate the bias due to instrumental mass fractionation, leading to the inconsistent results between different laboratories. The value 0.7219 seems to be rather inaccurate

Table 3
Results for the total evaporation normalization measurements of JNdi-1

Sample size	Q^{143}Nd[a] × 10^{11} (C)	Ionization efficiency (%)	^{142}Nd/ ^{144}Nd$_{raw}$[b]	^{143}Nd/ ^{144}Nd$_{raw}$[b]	^{145}Nd/ ^{144}Nd$_{raw}$[b]	^{146}Nd/ ^{144}Nd$_{raw}$[b]	^{143}Nd/^{144}Nd normalized	2S.D.
(a)								
5 ng	491.3	1.26	1.1396	0.511601	0.348834	0.723244	0.512070	±8
5 ng	468.6	1.34	1.1398	0.511698	0.348834	0.723211	0.512134	±8
5 ng	441.3	1.14	1.1398	0.511679	0.348784	0.723079	0.512100	±8
5 ng	267.2	0.69	1.1395	0.511634	0.348830	0.723190	0.512095	±11
5 ng	263.1	0.68	1.1397	0.511671	0.348799	0.723113	0.512105	±11
5 ng	200.3	0.52	1.1397	0.511784	0.348674	0.722943	0.512157	±12
5 ng	191.6	0.49	1.1394	0.511578	0.348846	0.723403	0.512115	±13
5 ng	177.5	0.46	1.1397	0.511761	0.348742	0.722993	0.512151	±13
5 ng	174.2	0.45	1.1397	0.511646	0.348832	0.723132	0.512086	±13
5 ng	164.0	0.42	1.1394	0.511595	0.348794	0.723271	0.512085	±14
5 ng	154.4	0.40	1.1400	0.511778	0.348729	0.722921	0.512143	±14
1 ng	117.8	1.52	1.1395	0.511610	0.348850	0.723222	0.512082	±16
5 ng	103.5	0.27	1.1404	0.511836	0.348621	0.722763	0.512145	±17
(b)								
1 ng	82.9	1.07	1.1396	0.511631	0.348807	0.723196	0.512094	±19
1 ng	79.2	1.02	1.1398	0.511671	0.348811	0.723048	0.512081	±20
1 ng	74.3	0.96	1.1393	0.511539	0.348888	0.723367	0.512064	±20
1 ng	66.0	0.85	1.1395	0.511669	0.348837	0.723225	0.512142	±22
1 ng	65.9	0.85	1.1388	0.511542	0.348902	0.723490	0.512110	±22
0.5ng	52.9	1.36	1.1403	0.511766	0.348817	0.722928	0.512133	±24
(c)								
1 ng	47.5	0.61	1.1388	0.511629	0.348818	0.723406	0.512168	±25
0.5 ng	42.4	1.09	1.1398	0.511681	0.348828	0.722993	0.512072	±27
5 ng	33.1	0.09	1.1364	0.511010	0.349257	0.724999	0.512116	±30
0.5 ng	26.9	0.69	1.1399	0.511681	0.348913	0.723249	0.512163	±34
0.5 ng	17.5	0.45	1.1393	0.511651	0.348844	0.723330	0.512162	±42
0.5 ng	14.1	0.36	1.1356	0.511475	0.348927	0.723708	0.512121	±47
0.5 ng	12.9	0.33	1.1397	0.511742	0.348924	0.723072	0.512161	±49
(d)								
0.5 ng	6.3	0.16	1.1372	0.510986	0.349157	0.724710	0.511989	±70
0.1 ng	5.7	0.73	1.1394	0.511571	0.348904	0.723521	0.512150	±74
0.1 ng	3.9	0.51	1.1397	0.511591	0.349139	0.723608	0.512202	±89
0.1 ng	3.6	0.46	1.1394	0.511690	0.349011	0.723533	0.512274	±92
0.1 ng	3.0	0.39	1.1410	0.511708	0.348891	0.722723	0.512003	±100
0.1 ng	2.7	0.35	1.1396	0.511412	0.349322	0.724018	0.512169	±106
0.1 ng	2.3	0.29	1.1374	0.511719	0.348865	0.723483	0.512285	±117
0.5 ng	2.2	0.06	1.1320	0.510324	0.349912	0.726924	0.512113	±117
0.1 ng	1.9	0.25	1.1398	0.511593	0.348650	0.722981	0.511979	±127
0.1 ng	1.9	0.24	1.1394	0.511546	0.348758	0.723463	0.512104	±128
0.1 ng	1.8	0.23	1.1409	0.511851	0.349009	0.722746	0.512153	±132
0.1 ng	1.2	0.16	1.1388	0.511647	0.348982	0.722996	0.512039	±159
Average		0.61	1.1391	0.51158	0.34890	0.7234	0.51212 ($n = 38$)	
2S.D.			0.0032	0.00055	0.00045	0.0015	0.00013	
2R.S.D.			0.281	0.107	0.129	0.207	0.025 (%)	

[a] These data are divided into four sections by means of integrated ^{143}Nd (see text).

[b] Isotope ratios obtained only by the total evaporation procedure.

estimation of ^{146}Nd/^{144}Nd ratio. However, despite the inaccuracy discussed above, we chosed ^{146}Nd/^{144}Nd = 0.7219 for normalization by convention.

The ^{143}Nd/^{144}Nd ratio obtained by the TEN method in the present study (0.51212 ± 0.00013 (2S.D.), $n = 38$) is consistent within analytical uncertainty with the ratio obtained at Nagoya University by the conventional dynamic MC-TIMS method (0.512101 ± 0.000012 (2S.D.), $n = 37$). The relative external precision of the ^{143}Nd/^{144}Nd ratio (0.025%, 2S.D.) is four times smaller than that of the raw ^{143}Nd/^{144}Nd ratio (0.107%, 2S.D.) in the same data set. The reproducibility of the measurement is improved significantly by the normalization procedure. The improvement of the reproducibility indicates that the continuation of the effect of instrumental mass fractionation on the raw data obtained by the total evaporation procedure (Fig. 3), and that the remaining instrumental mass discrimination is properly corrected by the normalization procedure.

The ionization efficiency of each sample (Table 3) can be calculated from the measured numbers of ions (Eq. (3)) and the amount of sample loaded on the filament. The ionization

Table 4
Average ^{143}Nd/^{144}Nd ratios measured by total evaporation normalization

$Q^{143}\mathrm{Nd} \times 10^{11}$ (C)	Average ^{143}Nd/^{144}Nd$_{\mathrm{raw}}$	2S.D.	2R.S.D. (ppm)	Average ^{143}Nd/^{144}Nd$_{\mathrm{normalized}}$	2S.D.	2R.S.D. (ppm)	n
(a) 100–500	0.51168	0.00017	327	0.512113	0.000060	116	13
(b) 50–100	0.51164	0.00017	337	0.512104	0.000061	118	6
(c) 10–50	0.51155	0.00051	991	0.512138	0.000072	140	7
(d) 1–10	0.51147	0.00084	1642	0.512122	0.000209	407	12

efficiencies of the 38 measurements in the present study vary largely from 0.06% to 1.52%. The measured numbers of ions do not correlate exactly with the sample amount because of the different ionization efficiency between different measurements. Therefore, in the present study, we grouped the data into four sections based on the measured electric charge Q instead of classifying the data by sample size (Table 3). The four sections, which have Q (^{143}Nd) ranges of $1–10 \times 10^{-11}$, $10–50 \times 10^{-11}$, $50–100 \times 10^{-11}$ and $100–500 \times 10^{-11}$ (Table 3) correspond roughly to Nd amounts of 0.1, 0.5, 1 and 5 ng, respectively.

The average ^{143}Nd/^{144}Nd ratios of the four sections are shown in Table 4; they do not differ significantly between the four sections and are consistent with the values obtained by the conventional method (Fig. 4). The external errors of the four sections shown in Table 4 and Fig. 2 are about 1.3–7.5 times large as the internal errors of a single run in each section. It is likely that internal error of a run is underestimated since not all the possible sources of error (e.g., amplifier noise) are taken into account in our error estimation. Therefore, external error should be used as a representative of the uncertainty of the measurement. The external standard deviation for each section increases as the measured electric charge decreases. For sections (a)–(c), the external standard deviations (116–140 ppm) do not differ significantly despite the large difference in the measured electric charge and the sample size. The precision of these measurements shown by these external standard deviations corresponds to an uncertainty of 1.2–1.4 in epsilon scale (parts per 10^4) for the ^{143}Nd/^{144}Nd ratio. The precision of the measurements with Q (^{143}Nd) $>10 \times 10^{-11}$, corresponds roughly to Nd > 0.5 ng, is sufficient for the application of the ^{143}Nd/^{144}Nd ratio as a geochemical tracer. The external precision for section (d) (407 ppm) is three to four times larger than those of sections (a) to (c). Additionally, the internal errors of the samples in section (d) are larger than the external precisions of sections (a) to (c) (Tables 3 and 4). The precision of the 0.1 ng sample measurements is limited by the large error due to the small number of ions measured. The measured electric charge Q (^{143}Nd) $= 10 \times 10^{-11}$ is likely to be the lower limit of the range in which an external precision better than 140 ppm can be obtained. To measure the 0.1 ng sample with Q (^{143}Nd) $>10 \times 10^{-11}$, enhancement of the ionization efficiency of Nd to at least 1.3% is required.

3.2. Comparison with the conventional dynamic MC-TIMS technique

The data of the JNdi-1 measurements carried out at Nagoya University between July 2004 to May 2006 by conventional

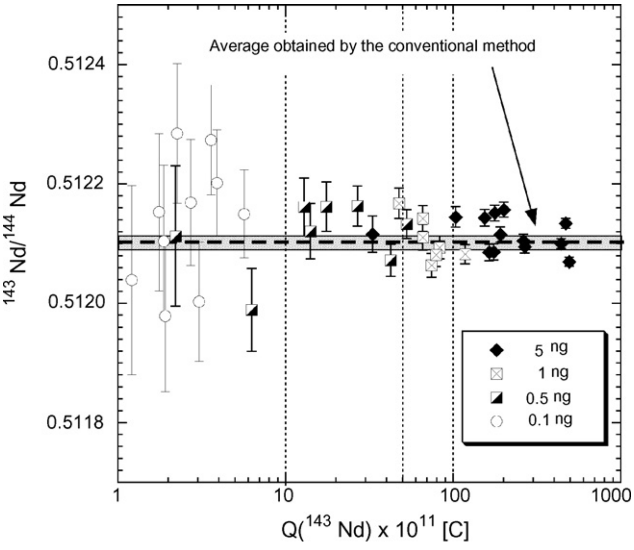

Fig. 2. Results of total evaporation normalization measurements of ^{143}Nd/^{144}Nd for samples of 0.1–5 ng JNdi-1. The horizontal axis shows the measured electric charge Q of ^{143}Nd in each run. The horizontal dashed line and the shaded area show the mean value and the reproducibility (0.512101 ± 0.000012 (2S.D.), $n = 37$) of the large sample measurements of JNdi-1 by conventional dynamic MC-TIMS at Nagoya University.

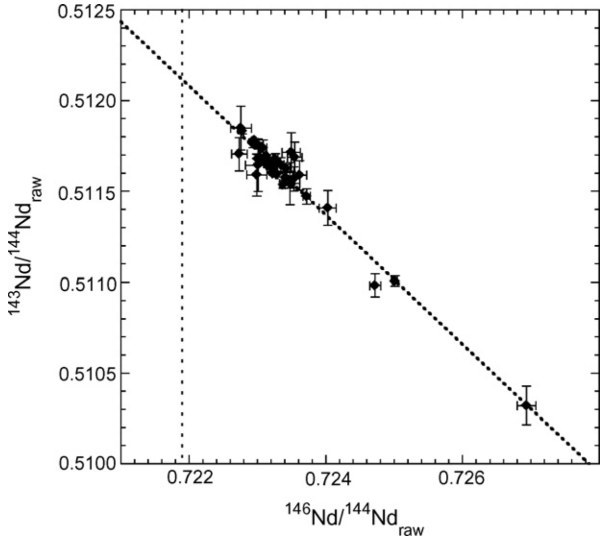

Fig. 3. Correlation plots of the raw ^{146}Nd/^{144}Nd and raw ^{143}Nd/^{144}Nd ratios of 0.1–5 ng JNdi-1 measurements, showing the remaining mass discrimination of the non-normalized isotope ratios. The diagonal dashed line indicates the theoretical mass fractionation trajectory. The vertical dashed line indicates the normalizing ratio ^{146}Nd/^{144}Nd = 0.7219.

Table 5
The ^{143}Nd/^{144}Nd ratios of JNdi-1 obtained by dynamic MC-TIMS measurement performed at Nagoya University

^{144}Nd intensity (V)	Ratios[a]	Q^{143}Nd[b] × 10^{11} (C)	^{143}Nd/^{144}Nd	2S.D.	2R.S.D. (ppm)	*n*
0.5	200	1587.5	0.512101	0.000011	22	37
0.25	200	793.8	0.512108	0.000020	40	4
0.1	300	471.1	0.512110	0.000041	81	8
0.05	300	235.6	0.512088	0.000054	105	10
0.01	400	62.5	0.512085	0.000169	329	10
0.005	400	31.2	0.512037	0.000666	1300	9
0.003	400	18.7	0.512450	0.001371	2675	16

[a] Number of ratios taken for a single measurement.

[b] Calculated with the average time of the measurement. Note that the ion beam consumed during the warm-up procedure is not included.

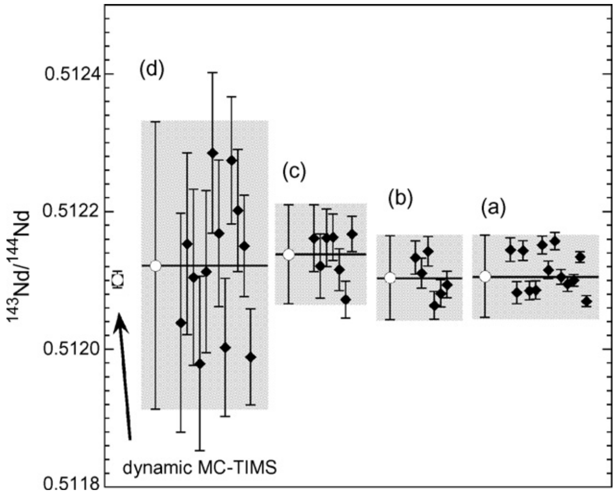

Fig. 4. Mean values (horizontal lines) and external standard deviations (shaded areas) of ^{143}Nd/^{144}Nd for four sections: (a) Q (^{143}Nd) = 100–500 × 10^{-11}, (b) Q (^{143}Nd) = 50–100 × 10^{-11}, (c) Q (^{143}Nd) = 10–50 × 10^{-11} and (d) Q (^{143}Nd) = 1–10 × 10^{-11}. The mean values and 2S.D. of the dynamic MC-TIMS measurements are also plotted.

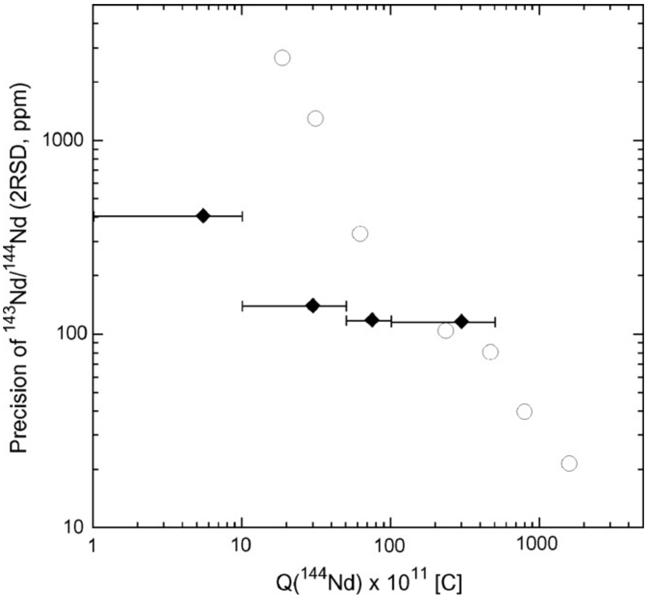

Fig. 5. Relative external standard deviations of the ^{143}Nd/^{144}Nd ratio by the total evaporation normalization measurements (diamonds) are compared with those of conventional dynamic MC-TIMS measurements (open circles).

dynamic MC-TIMS using Sector 54-30 were compiled for comparison (Table 5). The measured electric charge Q for the conventional measurements was estimated from the ion current and the average measurement time. Ion beam consumption during the filament warm-up procedure was not taken into consideration in the estimation of Q.

The relative external standard deviation of ^{143}Nd/^{144}Nd ratio measurements by dynamic MC-TIMS increased significantly as the measured electric charge decreased (Fig. 5). The increase of the uncertainty is likely to reflect a decrease in the signal-to-noise ratio of the faraday cups and an increase in the random error due to ion counting statistics. Only the measurement with a ^{144}Nd intensity over 0.05 V, which corresponds to Q (^{143}Nd) >236 × 10^{-11}, gives an external precision (2S.D.) of approximately 100 ppm or better.

In contrast, the degradation of the relative external standard deviations by TEN is gradual. The precision of the TEN measurement for Q (^{143}Nd) values of less than 100 × 10^{-11} is remarkably better than that of the conventional measurement. The external precision of the TEN measurements is better than 140 ppm for Q (^{143}Nd) values as small as 10 × 10^{-11}.

4. Conclusions

The neodymium isotope ratio of very small samples (0.5–5 ng) was measured precisely by the proposed TEN method. The external precision achieved for measurements with Q (^{143}Nd) = 100–500 × 10^{-11}, which corresponds to 5 ng samples, was 116 ppm (2S.D.). Using our proposed method, samples as small as 0.5 ng can be measured with an external precision of 140 ppm (2S.D.). Samples of 0.1 ng Nd can be measured with such precision if the ionization efficiency of Nd is over 1.3%. The precision of the total evaporation normalization method is superior to that of the conventional method for isotope ratio measurements of samples smaller than 5 ng.

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