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Isotope analysis of nanogram to sub-nanogram sized Nd samples by total evaporation normalization thermal ionization mass spectrometry

Shigeyuki Wakaki*, Tsuyoshi Ishikawa

Kochi Institute for Core Sample Research, Japan Agency of Marine-Earth Science and Technology (JAMSTEC), 200 Monobe Otsu, Nankoku 783-8502, Japan

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ABSTRACT

This paper presents $^{143}Nd/^{144}Nd$ analysis of nanogram to sub-nanogram sized Nd samples using total evaporation normalization thermal ionization mass spectrometry (TEN-TIMS) with Nd^+ ions. Total integration of high and stable Nd^+ ion signals produced by dynamic filament-current control until sample burnout in combination with a long baseline measurement achieved reasonably high signal to noise ratios even for very small samples. Repeated analyses of an Nd isotopic reference material JNdi-1 with Nd sample sizes of 2, 1, 0.5, and 0.1 ng all yielded consistent $^{143}Nd/^{144}Nd$ values with external precisions of 42, 62, 93, and 184 ppm (2RSD), respectively. Errors were as small as analytical error limits defined by counting statistics. Repeated analyses of basalt (JB-2) and coral (JCp-1) samples with 0.6–1.2 ng of Nd after processing with low-blank Nd separation chemistry designed for small samples also gave $^{143}Nd/^{144}Nd$ values consistent with those given by large-sized sample analyses, and the external precisions were comparable to the JNdi-1 analyses. The TEN-TIMS technique was capable of analyzing $^{143}Nd/^{144}Nd$ ratios of geological materials with sample sizes as small as 0.5 ng of Nd with a precision of ± 1 ε-unit or better.

1. Introduction

The long-lived radionuclide ^{147}Sm (half-life = 1.06×10^{11} yr) decays to ^{143}Nd over geological time scales and produces variations of $^{143}Nd/^{144}Nd$ ratios in geological materials. The radiogenic $^{143}Nd/^{144}Nd$ ratio is one of the major isotopic tools used for elucidation of petrogenesis, source materials and evolution of various sedimentary, metamorphic, and igneous rocks. Recently, geochemical application of $^{143}Nd/^{144}Nd$ ratios has been expanded into various materials with very low levels of Nd. For example, the $^{143}Nd/^{144}Nd$ ratio of seawater is useful to distinguish between different water masses, to trace the ocean circulation, and to estimate the contributions of Nd from different sources (ca. [1–5]). Secular variation of seawater Nd isotopic composition estimated by analyses of calcareous/phosphorous microfossils, such as foraminifera and fish teeth preserved in marine sediments, possibly provides important information for understanding ocean water mass distribution and oceanic circulation changes related to climate changes in the past [5]. Due to the very low Nd concentration and/or quite limited sample availability, these studies require precise $^{143}Nd/^{144}Nd$ analysis of nanogram to sub-nanogram-sized Nd.

One of the most commonly used techniques for Nd isotopic analysis has been thermal ionization mass spectrometry (TIMS) using Re-double or Re-triple filament settings and an Nd^+ ion beam. Chu et al. [6] reported external precisions of 103 and 78 ppm (2RSD) for $^{143}Nd/^{144}Nd$ analysis of standard reagents with 5 and 10 ng of Nd, respectively. Shibata and Yoshikawa [7] and Aciego et al. [8] reported Nd isotope analyses of smaller sample sizes in which external precisions were 80 and 82 ppm for 2 and 1 ng of Nd, respectively. Generally, the sample size limit for precise and accurate Nd isotope analysis by TIMS using an Nd^+ ion beam is several to 10 ng of Nd.

For TIMS, ionization of Nd oxide (NdO^+) is more efficient compared with that of Nd metal ions (Nd^+) and has been used to analyze $^{143}Nd/^{144}Nd$ ratios of small amounts of Nd. Using a Re- or W-single filament settings and activators such as SiO_2 gel, Ta_2O_5, and TaF_5, external precisions of 88–21 ppm for 0.3–4 ng of Nd and up to 30% ion yield were achieved for $^{143}Nd/^{144}Nd$ analyses [6,9,10]. However, the NdO^+ method is sensitive to complex isobaric interference by oxide ions and oxygen isotope ratio correction, which can affect the accuracy of the analysis.

Multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is also capable of analyzing $^{143}Nd/^{144}Nd$ ratios of a

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* Corresponding author.
E-mail address: wakaki@jamstec.go.jp (S. Wakaki).

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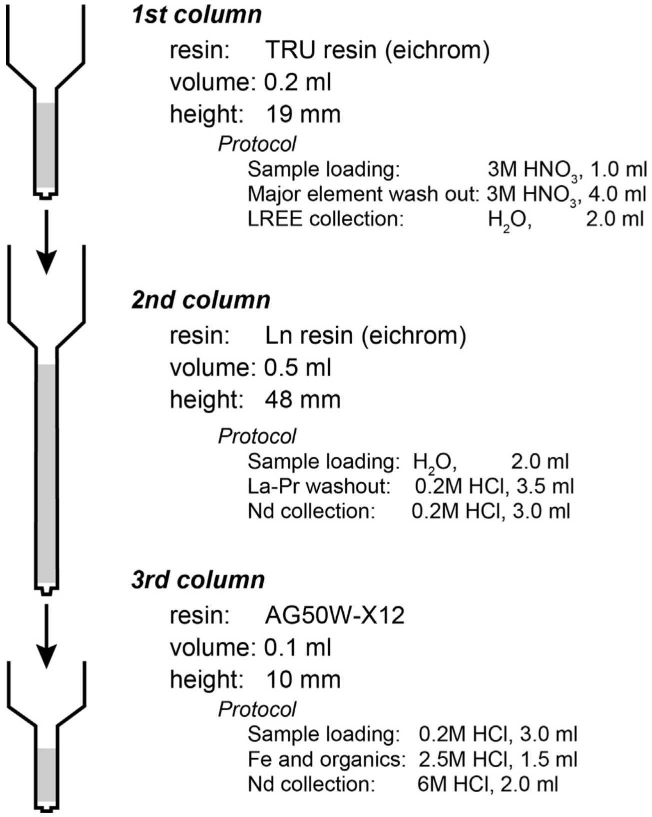
small amounts of Nd when special devices for improving the signal to noise ratio are installed. High-sensitivity desolvators and high efficiency interfaces enable MC-ICP-MS to analyze $^{143}Nd/^{144}Nd$ ratios for 1 and 0.5 ng of Nd with external precisions of 39 and 57 ppm, respectively [11].

The introduction of high-sensitivity Farady-cup amplifiers also enlarges the ability of TIMS and MC-ICP-MS in analyzing low-levels of Nd. Koornneef et al. [12,13] analyzed 0.1 ng of Nd samples and obtained external precisions of 176 and 125 ppm by TIMS using Faraday-cup amplifiers equipped with $10^{12}\,\Omega$ and $10^{13}\,\Omega$ resistors, respectively, instead of conventional amplifiers with $10^{11}\,\Omega$ resistors.

The current paper proposes the total evaporation normalization TIMS (TEN-TIMS) using Nd^+ ions as an alternative technique to analyze Nd isotopes for small sample sizes. Total evaporation was originally developed as an instrumental mass fractionation technique [14] and mainly used in the nuclear industry. It is characterized by total integration of all ion beams generated in a short time until burnout of the sample. The resultant high-intensity ion beams are advantageous for analyzing small-sized samples with relatively high signal to noise ratios. Wakaki et al. [15] first introduced TEN-TIMS using Nd^+ ions to analyze $^{143}Nd/^{144}Nd$ ratios and reported 140 ppm external precision for 0.5 ng of Nd. The current study presents further improved Nd isotope analysis by TEN-TIMS using a new procedure of Faraday-cup noise correction. Performance of the new TEN-TIMS technique was evaluated by analyzing nanogram to sub-nanogram sized Nd for an Nd isotopic reference material JNdi-1. A method for chemical separation of Nd, optimized for analysis of geological samples with small sample sizes, is also presented. The Nd separation chemistry using small-sized columns and minimal dry-up procedures enables low procedural blanks, high recovery yields, and high purity of Nd. The overall performance of the Nd isotope analysis including both the Nd separation chemistry and the TEN-TIMS measurement was demonstrated by analyzing basalt and coral standard samples with nanogram- to sub-nanogram sized Nd.



1st column

resin: TRU resin (eichrom)
volume: 0.2 ml
height: 19 mm

Protocol

Sample loading:	3M HNO_3,	1.0 ml
Major element wash out:	3M HNO_3,	4.0 ml
LREE collection:	H_2O,	2.0 ml

2nd column

resin: Ln resin (eichrom)
volume: 0.5 ml
height: 48 mm

Protocol

Sample loading:	H_2O,	2.0 ml
La-Pr washout:	0.2M HCl,	3.5 ml
Nd collection:	0.2M HCl,	3.0 ml

3rd column

resin: AG50W-X12
volume: 0.1 ml
height: 10 mm

Protocol

Sample loading:	0.2M HCl,	3.0 ml
Fe and organics:	2.5M HCl,	1.5 ml
Nd collection:	6M HCl,	2.0 ml

Fig. 1. Schematic diagram of the Nd separation chemistry.

2. Materials and methods

2.1. Reagents, samples, and standards

Ultra-pure water produced by a Milli-Q Element system (Millipore, USA) was used throughout this study. HNO_3, HCl, $HClO_4$ and HF acids were prepared from TAMAPURE AA-100 grade high purity reagents (Tama Chemicals Co., Ltd.). Geochemical reference samples, JB-2 (basalt) and JCp-1 (modern coral), issued from the Geological Survey of Japan (GSJ) were used as proxy samples for silicate and carbonate samples. An Nd isotopic reference material JNdi-1 [16] was used as a reference for Nd isotope ratio measurements. Solutions of JNdi-1 with 0.1, 0.5, 1, and 2 ppm of Nd were used to load 0.1, 0.5, 1, and 2 ng of Nd on the filament, respectively.

2.2. Nd separation chemistry

About 50 mg of JB-2 was dissolved in mixed HNO_3, $HClO_4$, and HF acids in a PFA vial at 120 °C and then dried at 180 °C. The sample was then redissolved with 6 M of HNO_3 and dried again at 180 °C. This procedure was repeated two times to completely remove remaining $HClO_4$ from the sample. The sample was finally dissolved with 3 mL of 3 M HNO_3 to make up the JB-2 stock solution. About 500 mg of JCp-1 was dissolved in 5 mL of 3 M HNO_3 in a PFA vial and dried at 120 °C. The sample was then dissolved with 6 mL 3 M HNO_3 to make up the JCp-1 stock solution. Nd concentrations of the stock solutions were measured using ICP-MS (Agilent 7700), which gave bulk-rock Nd concentrations of 6.0 and 0.027 ppm for JB-2 and JCp-1, respectively. Aliquots of the JB-2 solution containing 0.6, 1.2, and 100 ng of Nd and the JCp-1 solution containing 0.6, 1.1, and 6.8 ng of Nd were independently processed using Nd separation chemistry described below.

Nd in the samples was chemically separated and purified using three-step extraction and ion exchange column chromatography (Fig. 1). First, Nd was separated from coexistent major elements and the other rare earth elements (REEs) by two-step column chromatography using TRU and Ln resins (Eichrom, USA) with a procedure modified from Pin et al. [17]. Sample solutions were loaded into a 3.66 mm inner diameter Teflon column filled with 0.2 mL of TRU resin (column height ca. 19 mm). Major elements were washed out with 4 mL of 3 M HNO_3 and light REEs (LREEs) were subsequently eluted with 2 mL of H_2O. The eluted LREE solution was directly introduced into a second Teflon column (3.66 mm inner diameter) filled with 0.5 mL of Ln resin (column height of ca. 48 mm). La, Ce, and Pr were washed out with 3.5 mL of 0.2 M HCl, and the Nd fraction was subsequently collected with 3 mL of 0.2 M HCl. Finally, the separated Nd fraction was directly introduced to a third Teflon column (3.66 mm inner diameter) filled with 0.1 mL of cation exchange resin Bio-rad AG50W-X12 (column height ca. 10 mm) for Nd purification. Impurities, remaining major cations, and organic materials that may affect Nd ionization by TIMS were washed out with 1.5 mL of 2.5 M HCl, and the purified Nd fraction was finally collected with 2 mL of 6 M HCl. The total recovery yield of Nd was 92% and the total procedural blank was 1 pg. This blank value is lower than the most of the previous studies [6,9–11] and compares with the lowest total procedual blank reported [7].