



Stable Sm isotopic analysis of terrestrial rock samples by double-spike thermal ionization mass spectrometry



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ABSTRACT

This study presents the first report on mass-dependent stable Sm isotopic variability in geological materials using the double-spike thermal ionization mass spectrometry (DS-TIMS). The precision of the stable Sm-isotopic-composition DS-TIMS analysis was ca. 0.5 ε/amu. The accuracy of the analysis was demonstrated by the consistent Sm isotope fractionation behavior observed during cation-exchange column chromatography. The Sm isotope fractionation factor between the cation-exchange resin (AG 50W X8) and alpha-hydroxyisobutyric acid (HIBA) at 22.6 °C was obtained from the experimental results to be $\alpha_{147} = (^{147}\text{Sm}/^{150}\text{Sm})_{\text{AG50WX8}} / (^{147}\text{Sm}/^{150}\text{Sm})_{\text{HIBA}} = 1.000076 \pm 0.000011$, which corresponds to a Sm isotopic difference of 0.25 ε/amu between the resin and HIBA under equilibrium condition. Mass-dependent Sm stable isotopic variations on the order of epsilon unit were observed among the analyzed geological rock samples. Six igneous rocks from various rock types showed no resolvable variation in their Sm isotopic compositions, whereas a Mesozoic seamount-type marine dolomite and an Archean banded ferruginous chert showed stable Sm isotopic compositions significantly enriched in heavy isotopes as compared to the igneous rocks. The range of the Sm isotopic variation among the geological materials herein studied was 0.9 ε/amu. Our results suggest that significant stable Sm isotope fractionation occurs in the marine environment at low temperatures and the stable Sm isotopic composition may thus be used to trace the Sm cycling in the ocean and earth surface environment.

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1. Introduction

Samarium is a rare earth element (REE) having seven naturally occurring isotopes, namely ¹⁴⁴Sm (3.07%), ¹⁴⁷Sm (14.99%), ¹⁴⁸Sm (11.24%), ¹⁴⁹Sm (13.82%), ¹⁵⁰Sm (7.38%), ¹⁵²Sm (26.75%), and ¹⁵⁴Sm (22.75%) [1]. Sm isotopic compositions in nature may change mass independently by nuclear reactions. Since ¹⁴⁹Sm has a very large neutron-capture cross-section, intensive neutron irradiation generates ¹⁵⁰Sm at the expense of consuming ¹⁴⁹Sm, thereby changing the abundance ratios of ¹⁴⁹Sm and ¹⁵⁰Sm against the other Sm isotopes. The mass-independent changes in the ¹⁴⁹Sm and ¹⁵⁰Sm abundance ratios in terrestrial (e.g. natural nuclear fission reactor samples) and extraterrestrial samples (e.g. meteorites) have been

used to estimate neutron fluxes in natural nuclear reactors and cosmic rays [2–4].

The other potential cause of variation in Sm isotopic composition in nature is mass-dependent isotope fractionation—which occurs through chemical reactions and physical processes, although the fractionation degree is likely to be low for a high-atomic-mass element such as Sm [5]. The potential mass-dependent variation in Sm isotopic compositions in geological materials may contain evidence of physicochemical reactions undergone by the material during various geochemical processes (e.g., igneous, sedimentary, and metamorphic processes). Sm isotopic compositions can thus be used to trace such geochemical processes and Sm source materials provided a measurable stable isotopic variation exists among various geological materials. In fact, mass-dependent stable isotopic variations have been reported for other REEs such as Nd and Ce in terrestrial rocks using an external normalization technique with multi-collector Inductively Coupled Plasma mass spectrometry (MC-ICP-MS) [6,7]. Moynier et al. have analyzed Sm stable isotopic compositions of three terrestrial sample as well as six extraterrestrial samples including chondrites and

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CAIs by MC-ICP-MS [8]. There Sm isotopic results were based on measurement of the Eu fraction that contained about half the Sm of the samples and no significant Sm stable isotopic variations were observed. Although Sm has the largest number of isotopes among the REEs covering a wide range of mass numbers, the stable isotopic variation of Sm in nature has not been reported so far.

This paper reports stable Sm isotopic compositions of several terrestrial rocks in order to determine whether a mass-dependent Sm isotopic variation exists among geological materials. With this aim, we developed a high-precision analytical technique, called double spike thermal ionization mass spectrometry (DS-TIMS), for analyzing the mass-dependent difference of stable Sm isotopic compositions in rock samples. To demonstrate the precision and accuracy of DS-TIMS analysis, Sm isotope fractionation experiments were performed using cation-exchange column chromatography. Finally, several igneous rocks with a wide variety of chemical compositions as well as some sedimentary rocks were analyzed for stable Sm isotopic compositions.

2. Materials and methods

2.1. Standard reagent and the double spike

A pure Sm oxide reagent (99.998%; Lot no. P4362, Alfa Aesar) was dissolved in a 0.5 M HNO₃ solution. This reagent (AA-STD) was used as an in-house standard for the stable Sm isotopic composition analysis. Aliquots of this reagent are available from the first author upon request.

The Sm spike reagent used herein was a ¹⁵⁰Sm-¹⁵⁴Sm double spike. The Sm double spike was prepared by mixing ¹⁵⁰Sm and ¹⁵⁴Sm single-spike solutions. The isotopic composition of the double spike was measured and calibrated against AA-STD. The calibration was carried out by inverse-double spike analysis, where the double spike was treated as the unknown natural sample and AA-STD was considered as the spike within the double-spike data analysis procedure. The isotope ratios of the double-spike and the double-spike AA-STD mixture were repeatedly measured for this purpose. Average Sm isotope ratios from multiple AA-STD measurements were used in the calibration.

2.2. Isotope fractionation experiments

The isotope fractionation during column chromatography has been studied theoretically and experimentally [9,10]. Isotopic fractionation of Sm in a liquid-liquid extraction system using a crown ether of dicyclohexano-18-crown-6 has been investigated by Fujii et al. [11]. In this study, the Sm isotope fractionation during cation-exchange column chromatography was investigated to demonstrate the degree of potential isotope fractionation and to assess the accuracy of the stable Sm isotopic analysis. The isotope fractionation experiment was performed as follows. A quartz column of 6 mm in diameter was filled (120 mm in height) with the cation-exchange resin (Biorad AG 50W X8). An alpha-hydroxyisobutyric acid (HIBA) solution was used as an eluent. HIBA was prepared as a stock solution of 2.5 M. The stock solution was adjusted to pH 4.5 using purified NH₃ solution. The working HIBA solution is diluted from the stock solution to 0.2 M by distilled and deionized water with no pH adjustment. The elution behavior of Sm was calibrated prior to the experiment and the sample collection interval was determined. Then, 0.5 ml of AA-STD, corresponding to 121.9 μg of Sm, was loaded on the column and subsequently eluted with the 0.2 M HIBA solution. The eluted Sm was successively divided into eight fractions in an interval from 19 ml to 49 ml. The temperature of the column during the experiment was measured to be 22.6 °C. The amount of Sm in each fraction was measured by

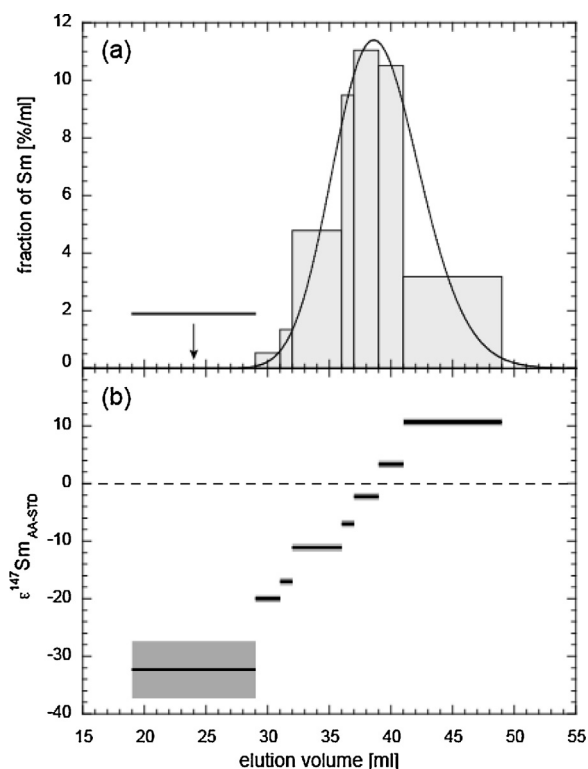


Fig. 1. (a) Elution profile of Sm during the isotope fractionation experiment by cation-exchange column chromatography. The eluted Sm was divided into eight fractions with different volumes of 0.2 M HIBA. The y-axis represents the fraction of Sm per unit volume. Thus, the fraction of Sm in each sample is represented by a gray box area. The solid curve represents the best-fit elution curve calculated with a peak elution volume of 38.6 ml, a maximum peak height of 11.4%/ml, and number of theoretical plates of 121 (see text for details). (b) Isotope fractionation profile of the eight eluted fractions. The $\epsilon^{147}\text{Sm}$ values of the eight fractions are plotted against the 0.2 M HIBA elution volume. Black lines and gray boxes represent $\epsilon^{147}\text{Sm}$ values and two sigma error ranges, respectively. The $\epsilon^{147}\text{Sm}$ value of the original material (AA-STD) is represented with a horizontal dashed line.

an isotope dilution technique using a ¹⁵⁰Sm spike prior to the stable isotopic analysis. The Sm elution profile obtained during this isotope fractionation experiment is shown in Fig. 1a.

2.3. Rock samples

Six bulk igneous rock samples and two bulk sedimentary rock samples were investigated for their stable Sm isotopic compositions. The igneous rocks included an alkali basalt (JB-1b), an island arc tholeiite (JB-2), a granodiorite (JG-1a), a granite (JG-2), an obsidian (JR-1), and a peralkaline rhyolite (JR-3). The sedimentary rocks included a Mesozoic seamount-type marine dolomite (JDo-1) and an Archean banded ferruginous chert (FBC) from the Barberton Greenstone belt [12]. All rock samples except FBC were international reference rocks from the Geological Survey of Japan. The chemical compositions of these international reference rocks can be found elsewhere [13–15].

2.4. Chemical separation of Sm

The silicate rock samples were decomposed with a mixture of HF-HClO₄-HNO₃. JDo-1 was leached by a 6M-HCl solution. The residues of the leached JDo-1 (very likely organic matter) were removed from the solution by using centrifugation prior to the column chemistry. Multiple aliquots of JB-1b, JB-2, and JDo-1 were separately decomposed, passed through the column chemistry, and finally analyzed. The concentrations of Sm were measured on a

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