

Precise Determination of Isotopic Compositions for Lanthanum, Samarium, Gadolinium, Dysprosium, Erbium, Ytterbium and Lutetium by Thermal Ionization Mass Spectrometry

By

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Abstract

Techniques have been developed for the precise isotopic measurement of lanthanum, samarium, gadolinium, dysprosium, erbium, ytterbium and lutetium by use of a thermal ionization mass spectrometer with multi-collector. The use of the static multi-collector system can offer isotopic data with a high precision and with quick measurements. As the results from isotopic analyses of commercial reagents, major isotopic ratios have measured within 0.005% precision at the 95% of confidential level.

1. Introduction

The isotopic abundances of rare earth elements (REE) in cosmo- and geochemical materials are useful in determining possible formation processes of the meteorites as well as terrestrial planets on the basis of elemental fractionation and differentiation. Isotopic data of some REE like Ce and Nd have been widely applied to the determination of sample formation ages. Few isotopic studies of REE other than Ce and Nd have been carried out yet, and studies of these may provide useful information on nuclear phenomena such as the following:

(1) ^{138}La is a rare nuclide, because its nucleus consists of an odd number of neutrons and odd protons. ^{138}La requires a rare nucleosynthetic process. Isotopic studies of ^{138}La in meteorites may be a useful indicator to find a nucleosynthesis in a stellar origin in the solar system (SHEN *et al.*, 1994).

(2) ^{149}Sm , ^{155}Gd and ^{157}Gd have very large thermal neutron capture cross sections with 4.2×10^4 , 6.1×10^4 and 2.55×10^5 barns, respectively (LEDERER and SHIRLEY, 1978). Information on neutron irradiation in nature can be obtained from isotopic ratio measurements of ^{149}Sm – ^{150}Sm , ^{155}Gd – ^{156}Gd and ^{157}Gd – ^{158}Gd (RUSS *et al.*, 1971; MAAS

and McCULLOCH, 1990; HIDAHA *et al.*, 1995).

(3) La, Sm, Gd, Dy, Er and Yb contain at least one rare p-process nuclide amongst their isotopes. Although p-isotopes are generally present in very low abundances, precise isotopic data of them may provide clues for understanding of this nucleosynthetic process.

In order to determine possible isotopic deviations of cosmo- and geochemical samples, the reference isotopic values for comparison purposes are required. Thermal ionization mass spectrometry is one of best methods to obtain isotopic data with high reproducibilities and sensitivity. Because REE such as Sm, Gd, Dy, Er and Yb have 6 or 7 isotopes including low abundance isotopes, those elements can be good samples to check the abilities for mass spectrometric measurements. Here, we report a technique for the isotopic measurements of REE using a commercially available multi-collector thermal ionization mass spectrometer which has been installed in the National Science Museum since early 1994. Our aim in this study is to establish methods for determining the precise isotopic compositions of La, Sm, Gd, Dy, Er, Yb and Lu.

2. Experimental Procedures

2.1 Terrestrial Standard Samples

For standard isotopic reference materials, commercial REE reagents of La, Sm, Gd, Dy, Er, Yb and Lu (Shin-etsu Chemical Co., Ltd., 99.9% grade as oxide compounds; La_2O_3 , Sm_2O_3 , Gd_2O_3 , Dy_2O_3 , Er_2O_3 , Yb_2O_3 and Lu_2O_3) were used. Each reagent was heated to 1000°C in an electric oven until a constant weight of each reagent was reached. Working solutions were prepared by dissolving the above REE reagent in 5 wt.% of HNO_3 .

2.2 Mass Spectrometry

The primary analytical instrument used in this study was a thermal ionization mass spectrometer (VG Sector 54-30) equipped with a 30-cm-radius electro-static filter (ESF) following a 54-cm-radius magnet. Seven isotopes could be simultaneously detected by use of seven Faraday cup collectors.

About $1\text{ }\mu\text{g}$ of standard reagent was loaded onto the metal filament of a filament assembly. All filaments used in this study were degassed at 4.7 A for 20 minutes before loading of sample.

Data for Sm, Gd, Dy, Er and Yb were collected by static multi-collector mode with seven collectors (Sm and Gd: HIDAHA *et al.*, 1995). Before each static analysis was commenced, the collector gains were routinely calibrated. The gain calibration consisted of 2 blocks of 5 cycles with 10-s integrations for each produced less than 2 ppm uncertainties (2σ). La and Lu were measured with a single collector. Instrumental mass fractionation during the analysis was significant for precise isotopic composition determinations. Exponential law was temporarily applied for the correction of mass fractionation in this study (HART and ZINDLER, 1989; RUSSELL *et al.*, 1978). During the measurements, we always monitored the possible isobaric mass interferences mainly

from contamination in REE reagents.

2.2.1 Lanthanum

Since La is preferably ionized as LaO^+ rather than La^+ , an oxygen leak into ion source chamber of mass spectrometer is useful to enhance the intensity of the LaO^+ ion beam. The pressure of ion source chamber was maintained below 5×10^{-7} mbar during the isotopic measurements. 6×10^{-11} A of $^{139}\text{La}^{16}\text{O}$ was produced from $1 \mu\text{g}$ of La loaded onto a Re single filament assembly at the current of 2.1–2.3 A.

The analytical procedures using single collector for La is as following: monitoring of interference $^{137}\text{Ba}^{16}\text{O}$, $^{138}\text{La}^{16}\text{O}$, $^{139}\text{La}^{16}\text{O}$ and interference $^{142}\text{Ce}^{16}\text{O}$.

2.2.2 Samarium

Using $1 \mu\text{g}$ of sample loaded onto a Re side filament of a triple Re assembly, filament currents of 4.3 A for centre and 2.2–2.4 A for side were sufficient to obtain 2×10^{-11} A ion beam for $^{152}\text{Sm}^+$ for more than 3 hours.

The analytical procedures using static multi collector system for Sm consist of the following two sequences: monitoring of ^{144}Sm , interference ^{146}Nd , ^{147}Sm , ^{148}Sm , ^{149}Sm , ^{150}Sm and ^{152}Sm for the first sequence, and interference ^{146}Nd , ^{147}Sm , ^{149}Sm , ^{150}Sm , ^{152}Sm , ^{154}Sm and interference ^{155}Gd for the second.

2.2.3 Gadolinium

Previous studies on Gd isotopic measurement have mainly utilized the GdO , since it is easily ionized as the oxide ion rather than the metal ion (EUGSTER *et al.*, 1970; LUGMAIR and MARTI, 1971). Unfortunately the oxygen isobaric interferences from Gd^{16}O , Gd^{17}O and Gd^{18}O interfere with neighboring isotopes of GdO while any EuO and TbO also interfere with GdO . Thus, the recalculation of isotopic abundances for Gd from those of GdO is not a simple matter. It is preferable to directly detect Gd^+ . According to our previous study (HIDAKA *et al.*, 1995), the use of Ta-Re-Ta filament system is effective in producing intense Gd^+ ion beam. 2×10^{-11} A of ^{158}Gd was obtained for one hour from $1 \mu\text{g}$ of Gd on conditions of 2.6–2.7 A for Ta side filaments and 4.4 A for a Re centre filament.

The analytical procedures using static multi collector system for Gd consist of the following two sequences: for the first monitoring of interference ^{150}Sm , ^{152}Gd , ^{154}Gd , ^{156}Gd , ^{158}Gd , ^{160}Gd and interference ^{161}Dy , and for the second, ^{154}Gd , ^{155}Gd , ^{156}Gd , ^{157}Gd , ^{158}Gd , ^{160}Gd and interference ^{161}Dy .

2.2.4 Dysprosium

$1 \mu\text{g}$ of sample loaded on the Re side filament of a Re triple filament assembly, with a side filament current of 2.6 to 2.7 A and a centre filament of 4.4 A will produce 2×10^{-11} A of ^{164}Dy for more than 2 hours.

The analytical procedures using static multi collector system for Dy consist of the following two sequences: for the first monitoring of ^{156}Dy , interference ^{157}Gd , ^{158}Dy , ^{160}Dy , ^{161}Dy , ^{162}Dy and ^{163}Dy , and for the second, ^{158}Dy , ^{160}Dy , ^{161}Dy , ^{162}Dy , ^{163}Dy , ^{164}Dy and interference ^{166}Er .

2.2.5 Erbium

3×10^{-11} A for ^{166}Er is produced for more than 2 hours from $1 \mu\text{g}$ of sample at 2.8

A of Re side and 4.4 A of Re centre filaments.

The analytical procedures using static multi collector system for Er consist of the following two sequences: for the first monitoring of ^{162}Er , interference ^{163}Dy , ^{164}Er , ^{166}Er , ^{167}Er , ^{168}Er and ^{170}Er , and for the second, interference ^{163}Dy , ^{164}Er , ^{166}Er , ^{167}Er , ^{168}Er , ^{170}Er and interference ^{171}Yb .

2.2.6 Ytterbium

2×10^{-11} A for ^{174}Yb is obtained for more than 6 hours from 1 μg of sample at 2.4 A of Re side and 4.4–4.6 A of Re centre filaments.

The analytical procedures using static multi collector system for Yb consist of the following two sequences: for the first monitoring of interference ^{167}Er , ^{168}Yb , ^{170}Yb , ^{171}Yb , ^{172}Yb , ^{173}Yb and ^{174}Yb , and for the second, ^{170}Yb , ^{171}Yb , ^{172}Yb , ^{173}Yb , ^{174}Yb , interference ^{175}Lu and ^{176}Yb .

2.2.7 Lutetium

5×10^{-11} A for ^{175}Lu is obtained for 3 hours from 1 μg of sample at 2.9–3.0 A of Re side and 4.2–4.4 A of Re centre filaments.

The analytical procedures using single collector for Lu is as following: monitoring of interference ^{174}Yb , ^{175}Lu and ^{176}Lu .

3. Results and Discussion

The results obtained in this study are summarized in Tables 1 to 7. The uncertainties obtained for all data in the tables are shown as 2σ of the means. Some previous results for these elements are also compiled in these tables. The data of IUPAC in the tables are cited from Isotopic Compositions of the Elements 1989 (BARNES *et al.*, 1991).

No corrections for isotopic fractionation were made for La and Lu, because both are two-isotope elements. SHEN *et al.* (1994) have made a correction for isotope fractionation of $^{138}\text{La}/^{139}\text{La}$ by use of $(^{139}\text{La}^{18}\text{O})/(^{139}\text{La}^{16}\text{O})=0.002045$. However, in their correction method, the precise oxygen isotopic composition is also required. We

Table 1. La isotopic compositions.

	$^{138}\text{La}/^{139}\text{La}$ ($\times 10^{-4}$)
MAKISHIMA <i>et al.</i> * (1987)	9.025 ± 0.005
SHEN <i>et al.</i> ** (1992)	9.079 ± 0.002
This work*	9.038 ± 0.003

*The correction for mass fractionation is not made.

**The data are normalized to $(^{139}\text{La}^{18}\text{O})/(^{139}\text{La}^{16}\text{O})=0.002045$.

Table 2. Sm isotopic compositions.

	$^{144}\text{Sm}/^{152}\text{Sm}$	$^{148}\text{Sm}/^{152}\text{Sm}$	$^{149}\text{Sm}/^{152}\text{Sm}$	$^{150}\text{Sm}/^{152}\text{Sm}$	$^{154}\text{Sm}/^{152}\text{Sm}$
RUSS et al. (1971)	0.11499 ± 1	0.42045 ± 2	0.51686 ± 2	0.27600 ± 2	0.85079 ± 3
MAAS and McCULLOCH (1990)	0.114956 ± 13	0.420447 ± 5	0.516839 ± 9	0.276005 ± 2	0.850813 ± 35
This work	0.114962 ± 2	0.420456 ± 4	0.516862 ± 3	0.276002 ± 2	0.850824 ± 6

The data are normalized to $^{147}\text{Sm}/^{152}\text{Sm}=0.56083$.

Table 3. Gd isotopic compositions.

	$^{152}\text{Gd}/^{160}\text{Gd}$	$^{154}\text{Gd}/^{160}\text{Gd}$	$^{155}\text{Gd}/^{160}\text{Gd}$	$^{157}\text{Gd}/^{160}\text{Gd}$	$^{158}\text{Gd}/^{160}\text{Gd}$
RUSS et al. (1971)	0.009285 ± 8	0.09974 ± 3	0.67687 ± 5	0.71588 ± 4	1.13582 ± 5
MAAS and McCULLOCH (1990)	not analyzed	0.099706 ± 60	0.676909 ± 16	0.715875 ± 15	1.135886 ± 20
This work	0.009263 ± 8	0.099722 ± 2	0.676840 ± 8	0.715826 ± 6	1.135861 ± 8

The data are normalized to $^{156}\text{Gd}/^{160}\text{Gd}=0.9361$.

Table 4. Dy isotopic compositions.

	$^{156}\text{Dy}/^{163}\text{Dy}$	$^{158}\text{Dy}/^{163}\text{Dy}$	$^{160}\text{Dy}/^{163}\text{Dy}$	$^{161}\text{Dy}/^{163}\text{Dy}$	$^{162}\text{Dy}/^{163}\text{Dy}$	$^{164}\text{Dy}/^{163}\text{Dy}$
IUPAC (1989)	0.00241 ± 40	0.0040 ± 40	0.0940 ± 25	0.7590 ± 101	1.0241 ± 115	1.1325 ± 121
HOLLIGER and DEVILLERS (1981)	0.00225 ± 4	0.00386 ± 81	0.09398 ± 84	0.7594 ± 29	1.0245 ± 40	1.1321 ± 45
This work*	0.002150 ± 1	0.003783 ± 1	0.093568 ± 13	$\equiv 0.75904$	1.023598 ± 34	1.135146 ± 99

*The data are normalized to $^{161}\text{Dy}/^{163}\text{Dy}=0.75904$.

Table 5. Er isotopic compositions.

	$^{162}\text{Er}/^{166}\text{Er}$	$^{164}\text{Er}/^{166}\text{Er}$	$^{167}\text{Er}/^{166}\text{Er}$	$^{168}\text{Er}/^{166}\text{Er}$	$^{170}\text{Er}/^{166}\text{Er}$
IUPAC (1989)	0.00417 ± 30	0.04792 ± 66	0.6830 ± 60	0.7976 ± 76	0.4435 ± 65
HOLLIGER and DEVILLERS (1981)	0.00408 ± 3	0.04787 ± 18	0.6822 ± 21	0.7971 ± 27	0.44421 ± 175
This work*	0.004134 ± 1	0.048291 ± 1	0.679136 ± 11	≡ 0.79708	0.436247 ± 15

The data are normalized to $^{168}\text{Er}/^{166}\text{Er}=0.79708$.

Table 6. Yb isotopic compositions.

	$^{168}\text{Yb}/^{174}\text{Yb}$	$^{170}\text{Yb}/^{174}\text{Yb}$	$^{171}\text{Yb}/^{174}\text{Yb}$	$^{172}\text{Yb}/^{174}\text{Yb}$	$^{173}\text{Yb}/^{174}\text{Yb}$	$^{176}\text{Yb}/^{174}\text{Yb}$
IUPAC (1989)	0.00409 ± 32	0.0959 ± 22	0.4497 ± 85	0.6887 ± 128	0.5069 ± 61	0.3994 ± 59
HOLLIGER and DEVILLERS (1981)	0.00399 ± 7	0.09551 ± 76	0.4486 ± 32	0.6858 ± 44	0.5068 ± 31	0.4009 ± 24
McCULLOCH et al.* (1977)	0.00429 ± 5	0.0964 ± 1	≡ 0.4512	0.6887 ± 4	0.5075 ± 3	0.3997 ± 2
This work*	0.004048 ± 1	0.096319 ± 1	≡ 0.4512	0.688597 ± 28	0.506994 ± 12	0.399164 ± 12

*The data are normalized to $^{171}\text{Yb}/^{174}\text{Yb}=0.4512$

have tried to determine a precise isotopic composition of oxygen by use of the oxide ion beam of a mono-isotope element. As shown in Fig. 1, our preliminary data from PrO, $^{18}\text{O}/^{16}\text{O}=0.002136\pm0.000008(2\sigma)$, are significantly different from those by NIER ($^{18}\text{O}/^{16}\text{O}=0.002045$; NIER, 1950) and WASSERBURG ($^{18}\text{O}/^{16}\text{O}=0.00211$; WASSERBURG *et al.*, 1981), while these are close to that of MAKISHIMA's ($^{18}\text{O}/^{16}\text{O}=0.002129\pm0.000010$; MAKISHIMA *et al.*, 1987). Further investigation of how to utilize an appropriate oxygen isotopic composition, and to determine an accurate isotopic composition of La recalculated from the data of oxide ion are in progress.

As shown in Tables 2 to 6, multi-static mode can offer excellent reproducibilities

Table 7. Lu isotopic compositions.

	$^{176}\text{Lu}/^{175}\text{Lu}$
McCULLOCH et al. (1976)	0.02665 ± 0.00001
HOLLIGER and DEVILLERS (1981)	0.02659 ± 0.00002
This work	0.026510 ± 0.000001

The correction for mass fractionation is not made.

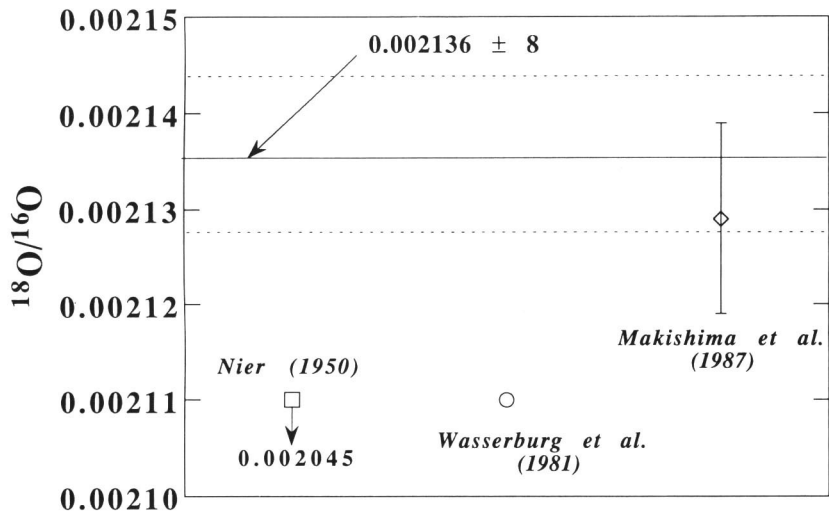


Figure 1. Comparison of isotopic data for $^{18}\text{O}/^{16}\text{O}$. Our data were obtained from the isotopic measurements of PrO^+ by thermal ionization mass spectrometry (TIMS). Other data were from O^+ measurement by electron bombardment mass spectrometry (NIER, 1950), NdO^+ by TIMS (WASSERBURG *et al.*, 1981), and PrO^+ by TIMS (MAKISHIMA *et al.*, 1987).

for isotopic measurements. Because the measurements with single collector require more time to collect the complete data than those with multi collectors, the analytical reproducibilities largely depend upon a stability of ion beam. The use of static analyses with seven collectors is sufficient for the isotopic measurements of many REE. Data acquisition by multi collector can offer quick and precise measurement. In this study, major isotopic ratios for Sm, Gd, Dy, Er and Yb can be quantified within 0.005% precision at the 95% of confidential level. Even the minor ratios such as $^{152}\text{Gd}/^{160}\text{Gd}$, $^{156}\text{Dy}/^{163}\text{Dy}$, $^{158}\text{Dy}/^{163}\text{Dy}$ and $^{162}\text{Er}/^{166}\text{Er}$ and $^{162}\text{Er}/^{166}\text{Er}$ can be more precisely measured

than those in previous studies. Our method will be applied to search for isotopic deviations derived from cosmo- and geochemical events, as well as to determine the accurate isotopic abundance and atomic weight of each element which have been widely used in the scientific field.

Acknowledgments

This work was partly supported by a Grant-in-Aid for Scientific Research of Ministry of Education, Science and Culture, Japan (No. 05217214 to M.S., 06640637 to H.H. and 05453012 to M.E.).

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