

Geophysical determination of the ^{138}La β^- decay constant

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(Received 17 June 1999; revised manuscript received 23 February 2000; published 22 June 2000)

The ^{138}La β^- decay constant was determined geophysically. The isotopic growths of $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were examined from ancient igneous crystalline rocks. For the Ce isotope measurement, a newly developed dynamic multicollector technique was applied. The crystallization age of the rocks was calculated to be 2037 ± 13 Myr from the growth of ^{143}Nd . From the age and the growth of ^{138}Ce , λ_{β^-} of ^{138}La was estimated to be $(2.37 \pm 0.10) \times 10^{-12} \text{ yr}^{-1}$. This value is consistent with those of the latest two γ -ray counting data of lanthanum compounds within the analytical error.

PACS number(s): 23.40.-s, 91.35.Nm, 91.65.Dt

^{138}La is one of the long-lived radioactive nuclides, which decays to stable ^{138}Ce and ^{138}Ba through β^- decay and electron capture (EC) decay, respectively. The half-life of ^{138}La was reported by many investigators by counting the radioactivity of lanthanum compounds [1–11]. However, even after Ge(Li) detectors were introduced [6–9], the half-lives obtained before 1980 were scattered from 3.68×10^{11} to 4.7×10^{11} yr for the β^- decay and from 1.87×10^{11} to 2.34×10^{11} yr for the EC decay. In the 1980's, two mutually consistent results were obtained by Sato and Hirose [10] and Norman and Nelson [11] by paying attention to the problem of volatile impurities in the compounds. Their data seems most reliable, but this method has difficulty in determining precise and accurate efficiencies of the detector. Because of the long half-life of ^{138}La , a large volume of the compound is required to obtain precise data, which results in the difference of geometry between the samples and standard γ -ray sources. To avoid this, a potassium compound is mixed and relative half-lives are determined against the well-known ^{40}K half-life. The 1460.8-keV γ ray produced by the decay of ^{40}K is close to the 1435.9-keV EC decay γ ray, but far from the 788.7-keV β^- decay γ ray. Therefore, it is difficult to determine the precise and accurate partial half-life of the ^{138}La β^- decay.

The other method is the geophysical determination from ancient rocks. Cerium has four stable isotopes ^{136}Ce (0.19%), ^{138}Ce (0.25%), ^{140}Ce (88.45%), and ^{142}Ce (11.11%). The ^{138}La β^- decay constant can be estimated from the isotopic growth of ^{138}Ce , if the ages of the rocks are known. The age is usually obtained using the decay of ^{147}Sm to ^{143}Nd because of the similar chemical property of rare earth elements. The measurement of Ce isotope ratios and the comparison of the decay constants between the two methods were carried out by Tanaka and Masuda [12] first, but the uncertainty of Ce isotope ratios was quite large. This comparison was tried by several investigators. The value obtained by Dickin [13] from the whole rock analysis of six metamorphic rocks was consistent with those of Sato and Hirose [10] and Norman and Nelson [11]. That of Masuda

et al. [14] from three metamorphic rocks was more than twenty percent higher. Norman and Nelson [15] and Tanaka and Masuda [16] discussed the discrepancy between the two methods. The problems of the radioactivity measurement are the calibration of detector efficiencies and relative attenuation by self-absorption.

On the contrary, geophysical determination had a problem in measuring precise Ce isotope ratios. Ce isotope ratio is measured as oxide species (CeO^+) to obtain a stable and lasting ion beam and to reduce the isobaric interference of ^{138}Ba . The ion beam intensity of $^{140}\text{Ce}^{16}\text{O}$, which was usually more than 10^{-10} A, was ignored to obtain a more precise $^{138}\text{Ce}/^{142}\text{Ce}$ ratio, because such a large beam intensity was out of the detector (Faraday cup) linearity range. Thus, the mass fractionation of $^{138}\text{Ce}/^{142}\text{Ce}$ ratios during the measurement were normalized to $^{136}\text{Ce}/^{142}\text{Ce}$ after removing the interference of $n-2\text{Ce}^{18}\text{O}$ on the neighboring $n\text{Ce}^{16}\text{O}$. For the correction of ^{18}O , $^{18}\text{O}/^{16}\text{O}$ isotope ratio of Nier [17] or Wasserburg *et al.* [18] was used and considered as constant. The interference of $^{140}\text{Ce}^{18}\text{O}$ on $^{142}\text{Ce}^{16}\text{O}$ was estimated from a constant $^{140}\text{Ce}/^{142}\text{Ce}$ ratio without considering its mass fractionation.

Makishima and Nakamura [19] improved the precision of $^{138}\text{Ce}/^{142}\text{Ce}$ ratio using the static multicollector technique, which cancels out the fluctuation of ion beams. The mass-dependent fractionation was corrected to $^{136}\text{Ce}/^{142}\text{Ce} = 0.01688$. They measured $^{18}\text{O}/^{16}\text{O}$ ratio simultaneously and found a gradual change of $^{18}\text{O}/^{16}\text{O}$ ratio during the measurement. Thus, they pointed out the importance of *in situ* $^{18}\text{O}/^{16}\text{O}$ measurement to obtain a precise $^{138}\text{Ce}/^{142}\text{Ce}$ ratio. Although the precision of $^{138}\text{Ce}/^{142}\text{Ce}$ ratio was improved by this technique, it is difficult to obtain accurate data because of the change of the relative Faraday cup efficiencies and amplifier gains through time.

Recently, I developed the dynamic multicollector technique for Ce isotope ratio measurement with one order of magnitude smaller ion beam intensity compared with that of Makishima and Nakamura [19]. The dynamic multicollector technique is the most accurate technique among those used for the thermal ionization mass spectrometer (TIMS), because it cancels not only the fluctuation of ion beams but also the relative Faraday cup efficiencies and amplifier gains [20]. Since the ion beam intensity of $^{140}\text{Ce}^{16}\text{O}$ can be measured by

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applying this technique, the *in situ* interference of $^{140}\text{Ce}/^{18}\text{O}$ is correctly estimated. Also, the mass-dependent fractionation is corrected more appropriately with $^{140}\text{Ce}/^{142}\text{Ce}$ = 7.941, not the small $^{136}\text{Ce}/^{142}\text{Ce}$ ratio.

The growth of ^{138}Ce in a closed system is expressed by the following equation using the β^- decay constant (λ_β), the electron capture decay constant (λ_{EC}), present-day ^{138}Ce abundance ($^{138}\text{Ce}_p$), initial ^{138}Ce abundance ($^{138}\text{Ce}_i$), and the crystallization age T , which means elapsed time since the sample became a closed system:

$$^{138}\text{Ce}_p = ^{138}\text{Ce}_i + \left(\frac{\lambda_\beta}{\lambda_\beta + \lambda_{\text{EC}}} \right) \times ^{138}\text{La}_p \times (e^{(\lambda_\beta + \lambda_{\text{EC}})T} - 1). \quad (1)$$

If ^{142}Ce is used as a reference isotope, this equation is represented as

$$\left(\frac{^{138}\text{Ce}}{^{142}\text{Ce}} \right)_p = \left(\frac{^{138}\text{Ce}}{^{142}\text{Ce}} \right)_i + \left(\frac{\lambda_\beta}{\lambda_\beta + \lambda_{\text{EC}}} \right) \times \left(\frac{^{138}\text{La}}{^{142}\text{Ce}} \right)_p \times (e^{(\lambda_\beta + \lambda_{\text{EC}})T} - 1). \quad (2)$$

The decay from ^{147}Sm to ^{143}Nd is also written as follows using the decay constant of ^{147}Sm (λ_{Sm}):

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_p = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_i + \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}} \right)_p \times (e^{\lambda_{\text{Sm}}T} - 1). \quad (3)$$

By measuring these present ratios, the initial ratio and age T are calculated by the least square fitting from more than three data sets. By comparing these equations to the equation of a straight line in the slope-intercept form ($y = b + ax$), we see that the intercept on the y axis is

$$b = \left(\frac{^{138}\text{Ce}}{^{142}\text{Ce}} \right)_i \quad \text{or} \quad \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_i \quad (4)$$

and the slope is

$$a = \left(\frac{\lambda_\beta}{\lambda_\beta + \lambda_{\text{EC}}} \right) \times (e^{(\lambda_\beta + \lambda_{\text{EC}})T} - 1) \quad \text{or} \quad (e^{\lambda_{\text{Sm}}T} - 1). \quad (5)$$

Therefore, in some rock, coexisting minerals that have the same $(^{138}\text{Ce}/^{142}\text{Ce})_i$ or $(^{143}\text{Nd}/^{144}\text{Nd})_i$ and the same age are represented by points that define a straight line in coordinates of the measured $(^{138}\text{Ce}/^{142}\text{Ce})_p$ and $(^{138}\text{La}/^{142}\text{Ce})_p$ or $(^{143}\text{Nd}/^{144}\text{Nd})_p$ and $(^{147}\text{Sm}/^{144}\text{Nd})_p$. This straight line is called an ‘‘isochron’’ because all points on a given line have the same age. Equation (2) is called the La-Ce isochron and Eq. (3) is the Sm-Nd isochron.

The experimental procedure is summarized briefly below. Two ancient rocks were selected from South Africa. These rocks are gabbros, which is a group of SiO_2 poor crystalline igneous rocks composed of plagioclase, pyroxene, and some

minor minerals. No alteration was recognized by the microscopic observation of thin sections. This means that the gabbros are in closed system after the crystallization. The Sm-Nd isochron and the La-Ce isochron of another gabbro in this area were investigated previously [12].

The gabbros were crushed and sieved. After the sieving, the grain size 40–100 μm and 100–180 μm were separated into pure minerals, plagioclase, and pyroxene using their different magnetism. Samples, weighing about 1 g, were decomposed by HF, HNO_3 , and HClO_4 . The obtained solutions were split into two aliquots; one was used for the measurement of $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and the other one for the determination of concentrations of La, Ce, Nd, and Sm by the isotope dilution mass spectrometry. Each element was refined by cation exchange column separation using HCl and 2-methylacetic acid as eluents. $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were measured with a TIMS, VG Sector 54-30. Details of the Ce isotope measurement will be described elsewhere.

The obtained isotope ratios are shown in Table I and the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are plotted in Fig. 1(a). From Fig. 1(a) and Eq. (3), the age T was calculated to be 2037 ± 13 Myr (all errors in this text mean one standard error except as noted) with the initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50964 ± 0.00001 using $\lambda_{\text{Sm}} = 6.54 \times 10^{-12} \text{ yr}^{-1}$ [21,22].

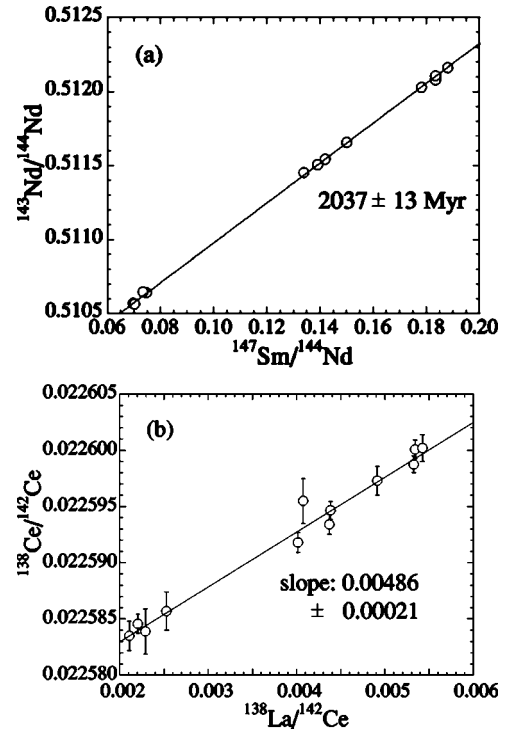


FIG. 1. (a) $^{147}\text{Sm}/^{144}\text{Nd}$ vs $^{143}\text{Nd}/^{144}\text{Nd}$ plot of the minerals and whole rocks of the gabbros. The age T was calculated from the Sm-Nd isochron to be 2037 ± 13 Myr with the initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50964 ± 0.00001 from Eq. (3) using $\lambda_{\text{Sm}} = 6.54 \times 10^{-12} \text{ yr}^{-1}$ [21,22]. (b) $^{138}\text{La}/^{142}\text{Ce}$ vs $^{138}\text{Ce}/^{142}\text{Ce}$ plot of the minerals and whole rocks of the gabbros. The slope and $^{138}\text{Ce}/^{142}\text{Ce}$ initial ratio were calculated to be 0.00486 ± 0.00021 and 0.0225733 ± 0.000009 from Eq. (2), respectively.

TABLE I. Isotope ratios of $^{138}\text{La}/^{142}\text{Ce}$, $^{138}\text{Ce}/^{142}\text{Ce}$, $^{147}\text{Sm}/^{144}\text{Nd}$, and $^{143}\text{Nd}/^{144}\text{Nd}$ in mineral separates and whole rocks from the gabbros. The errors of $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are statistical errors which have 95% confidence interval. The $^{138}\text{La}/^{142}\text{Ce}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios were calculated from the concentration of La, Ce, Nd, and Sm using the isotopic abundances and atomic weights estimated by IUPAC [26,27]. The uncertainty of $^{138}\text{La}/^{142}\text{Ce}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ is $\pm 0.5\%$ without including the uncertainties of the isotopic abundances and atomic weights.

Sample	$^{138}\text{La}/^{142}\text{Ce}$	$^{138}\text{Ce}/^{142}\text{Ce}$	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$
plagioclase rich gabbro				
whole rock	0.00408	0.0225955 ± 20	0.142	0.511543 ± 8
plagioclase (100–180 μm)	0.00534	0.0226001 ± 8	0.0698	0.510570 ± 6
pyroxene (100–180 μm)	0.00211	0.0225835 ± 13	0.184	0.512077 ± 7
plagioclase (40–100 μm)	0.00533	0.0225988 ± 7	0.0747	0.510641 ± 6
pyroxene (40–100 μm)	0.00229	0.0225839 ± 20	0.178	0.512027 ± 7
fine fraction (<40 μm)	0.00438	0.0225947 ± 8	0.134	0.511453 ± 7
pyroxene rich gabbro				
whole rock	0.00402	0.0225918 ± 9	0.150	0.511656 ± 7
plagioclase (100–180 μm)	0.00491	0.0225973 ± 13	0.0703	0.510564 ± 8
pyroxene (100–180 μm)	0.00221	0.0225846 ± 9	0.184	0.512107 ± 6
plagioclase (40–100 μm)	0.00542	0.0226002 ± 12	0.0735	0.510647 ± 8
pyroxene (40–100 μm)	0.00253	0.0225857 ± 17	0.188	0.512162 ± 7
fine fraction (<40 μm)	0.00437	0.0225934 ± 9	0.139	0.511507 ± 6

A program made by Ludwig [23] and named ISOPLOT, which is a plotting and regression program for radiogenic isotope data based on York's algorithm [24], was used for the calculation of least square fitting throughout this study. The age T obtained here agrees well with that of Tanaka and Masuda [12]. This age is also consistent with the age calculated from another long-lived radioactive nuclide ^{87}Rb [25]. The good agreement of ages calculated from different nuclides which

TABLE II. ^{138}La β^- decay constants reported after 1980 and in this study. Those of the geophysical determination were modified with the latest IUPAC report [26,27] and recalculated by a regression program ISOPLOT [23] by comparing the slopes of the La-Ce isochrons with the ages obtained from the Sm-Nd isochrons. The Sm-Nd isochron age of Tanaka and Masuda [12] was recalculated and 2051 ± 45 Myr was used. Also, 2631 ± 89 Myr and 2602 ± 149 Myr were used for Makishima *et al.* [29]. The error of all recalculated values is 1σ . The uncertainty of $^{138}\text{La}/^{142}\text{Ce}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ were assumed to be $\pm 0.5\%$. Those of the radioactivity measurement were also modified by the latest reports. The error size of Sato and Hirose [10] was modified according to the discussion of Norman and Nelson [15].

Year	Reported value (10^{-12} yr^{-1})	Recalculated value (10^{-12} yr^{-1})
1981 [10]	$2.30 \pm 0.03(1\sigma)$	2.27 ± 0.15
1982 [12]		2.97 ± 0.51
1983 [11]	$2.17 \pm 0.15(1\sigma)$	2.15 ± 0.15
1987 [13]		2.24 ± 0.14
1988 [14]	$2.77 \pm 0.21(2\sigma)$	2.86 ± 0.11
1991 [29]	$2.33 \pm 0.24(2\sigma)$	2.41 ± 0.14
This study		2.37 ± 0.10

have different chemical properties means that the gabbros in this area has been in closed system since its crystallization.

The isotope ratios of $^{138}\text{La}/^{142}\text{Ce}$ and $^{138}\text{Ce}/^{142}\text{Ce}$ are plotted in Fig. 1(b). The slope and initial ratio were calculated from Eq. (2) to be 0.00486 ± 0.00021 and 0.0225733 ± 0.000009 , respectively. From the slope, the ^{138}La β^- decay constant was calculated on the assumption that the age T of the La-Ce isochron should agree with that of the Sm-Nd isochron, while $\lambda_{\text{EC}} = 4.39 \times 10^{-12} \text{ yr}^{-1}$ was applied from the weighted average of the latest two γ -ray counting data [10,11]. Even if λ_{EC} changes 10%, λ_{β} changes less than 0.1%. Therefore, λ_{EC} can be treated as constant. As the result, λ_{β} was calculated to be $(2.37 \pm 0.10) \times 10^{-12} \text{ yr}^{-1}$ from Eq. (5).

The geophysically determined ^{138}La β^- decay constant values are summarized in Table II. These values were recal-

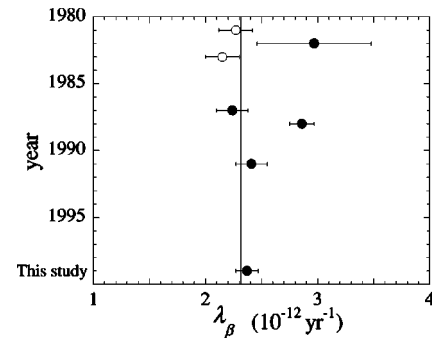


FIG. 2. Comparison of recalculated ^{138}La β^- decay constants reported after 1980. Solid circles represent the geophysical determinations. Open circles represent the radioactivity determinations. The solid line means a weighted average values of λ_{β} which were determined from the three data [10,11,29] and this study, equivalent to $(2.32 \pm 0.06) \times 10^{-12} \text{ yr}^{-1}$.

culated with ISOPLOT by comparing their slopes of their La-Ce isochrons with the ages obtained from their Sm-Nd isochrons. The Sm-Nd isochrons were also recalculated by this program, when data were available. Isotope abundances and atomic weights of the elements were modified with the latest reports of IUPAC [26,27]. The results are shown in Table II and Fig. 2 together with the latest two γ -ray counting data [10,11]. The size of error is comparable except Tanaka and Masuda [12]. The result of Masuda *et al.* [14] is apparently different from the other data. Their isochrons consist of only three points. A regression line calculated from three points may be unreliable fundamentally. In this respect, their original estimation of uncertainty which should have 95% confidence interval is too small. The result of Dickin

[13] is consistent with those of the radioactivity measurement, but he pointed out in his book [28] that some rocks became open system after the crystallization.

Based on these assessments, only the geophysical determinations of the ^{138}La β^- decay constant done by Makishima *et al.* [29] and this study should be reliable, as these values were calculated through appropriate sample selections and adequate number of data sets. These two values are consistent with the latest two γ -ray counting data [10,11] within the error. The weighted average value of these four data is $(2.32 \pm 0.06) \times 10^{-12} \text{ yr}^{-1}$.

I am very thankful to Professor T. Tanaka for advising this work. This research was supported in part by the Japan Society for the Promotion of Science for Young Scientists.

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