Determination of the half-life of the ground state of ^{229}Th by using ^{232}U and ^{233}U decay series

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The half-life of the ground state of ^{229}Th (^{229}Th^g) has become an important factor in nuclear technology, for example, in the geological disposal of nuclear spent fuel. However, the values reported in two previous studies are not in agreement. This study reevaluates the half-life of ^{229}Th^g by using a simple and reliable method. The ^{232}U/^{233}U activity ratio of a ^{232,233}U sample was measured by high-resolution α-particle spectrometry. Next, the ^{228}Th/^{229}Th^g activity ratio of the Th sample, which was grown from the ^{232,233}U sample, was also measured. The half-life of ^{229}Th^g was calculated from these activity ratios, the growth time, and the half-lives of ^{232}U, ^{233}U, and ^{228}Th. From the results of these five measurements, the half-life of ^{229}Th^g is determined to be 7932 $\pm$ 55 yr at a confidence level of 2σ.

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I. INTRODUCTION

The ground state of ^{229}Th (^{229}Th^g) is an α-decay nuclide of the neptunium series, and the ^{229}Th^g half-life is an important property for various fields. In spent nuclear fuel, ^{237}Np and ^{233}U, which are produced in neutron capture reactions, yield ^{229}Th^g, which becomes a major α emitter after millions of years [1]. The intensity and peak time of the ^{229}Th^g activity depend on its half-life. Meanwhile, ^{229}Th^g does not exist naturally and can be detected with good sensitivity both by an ion-counting method, such as mass spectrometry, and by α-particle spectrometry because of its half-life of thousands of years. Therefore, it can be used as a good tracer and spike for isotope dilution mass spectrometry to determine the ^{232}Th and ^{230}Th concentrations in environmental samples [2]. In this case, the value of the half-life is important as it can be used to calculate the number of atoms of ^{229}Th^g by measuring the radioactivity.

In addition, ^{229}Th has a nuclear-excited state (^{229}Th^m) with an excitation energy of several electron volts [3–6], which is much lower than that of other nuclides, and is expected to be utilized for a very precise nuclear clock [7]. Direct observation of ultraviolet photons from ^{229}Th^m is a desirable method to precisely determine the excitation energy of ^{229}Th^m. Several different groups attempted to detect the direct photons from ^{229}Th^m [8,9] but were not successful due to radiation-induced fluorescence from the materials around the radioactive ^{233}U source [10,11]. We have also attempted to detect the direct photons by using a pure ^{229}Th source [12]. However, the most recent value of the excitation energy, 7.6 $\pm$ 0.5 eV [6], suggests that decay via the internal conversion process is allowed, which implies that emission of ultraviolet photons may become a minor process. Information about the exact half-life of ^{229}Th^g enables the estimation of the fluorescence background caused by α particles from ^{229}Th^g.

There are two reported values of the half-life of ^{229}Th^g: 7340 $\pm$ 160 yr [13] and 7880 $\pm$ 120 yr [14] (summarized in Ref. [15]). Hagemann *et al.* [13] determined the ^{229}Th^g half-life by an indirect method. They produced ^{229}Th^g by decaying a known amount of freshly purified ^{233}U. A known amount of ^{234}Th was added as a chemical tracer, and then the thorium isotopes were isolated from ^{233}U. Activity of ^{229}Th^g grown from ^{233}U was calculated using α-particle spectrometry after corrections for chemical yields and ^{228}Th impurity. The half-life of ^{229}Th^g was calculated from the measured activity of ^{229}Th^g, the amount of ^{233}U, and the growth time. On the other hand, Goldstein *et al.* [14] measured the half-life of ^{229}Th^g by a mass-spectrometry technique. They added a known amount of ^{232}Th to ^{229}Th^g standard solutions for α-particle spectrometry and measured the isotopic ratio of the mixture by isotopic-dilution mass spectrometry. The half-life of ^{229}Th^g was calculated from the activity of the standard solution and the measured isotopic concentration of ^{229}Th^g. However, there is a difference of approximately 7% between these results. About 2% of the difference is explained by the ^{233}U half-life used in Ref. [13], which is greater than the presently accepted half-life of ^{233}U. The source of the remaining difference is unclear, although there is speculation that the difference is caused by the underestimation of the effect of impurities such as ^{228}Th [14].

In this study, the half-life of ^{229}Th^g is reevaluated using a simple and reliable method described below. Generally, a ^{233}U sample contains ^{232}U produced by nuclear reactions as an impurity. A thorium sample grown from a purified ^{232,233}U sample contains ^{228}Th and ^{229}Th^g with a rate depending on the growth time of Th isotopes. The ^{232}U/^{233}U and ^{228}Th/^{229}Th^g activity ratios are comparatively easily determined by α-particle spectrometry because the energy difference of α particles emitted from these isotopes is larger than approximately 300 keV. The half-life of ^{229}Th^g can be calculated from these activity ratios, the half-lives of ^{232}U, ^{233}U, and

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^{228}Th, and the growth time of Th isotopes from U isotopes (details are given in Results and Discussion). Note that this method does not require absolute values of radioactivity and addition of tracer isotopes to determine the number of atoms of ^{229}Th^{g}. Thus, this method is little affected by experimental errors such as those in detection efficiency and operation. The half-lives of ^{232}U, ^{233}U, and ^{228}Th are determined to be 68.9 $\pm$ 0.4 yr [16], (1.592 $\pm$ 0.002) $\times$ 10^5 yr [16], and 1.9116 $\pm$ 0.0016 yr [16], respectively; these values are determined with satisfactory accuracy to determine the half-life of ^{229}Th^{g}.

II. EXPERIMENTAL PROCEDURES

For the determination of the ^{232}U/^{233}U activity ratio, a ^{232,233}U sample was purified by anion-exchange procedures and subjected to α-particle spectrometry. The $UO_2(NO_3)_2{\cdot}6H_2O$ sample containing 4.7 mg of ^{233}U was dissolved in 1 ml of 9 M HCl. The solution was passed through an anion-exchange column [Muromac(R) 1 $\times$ 8, 200–400 mesh, 8 mmϕ $\times$ 50 mm] to adsorb uranium. The resin with adsorbed uranium was washed with 12.5 ml of 9 M HCl to eliminate thorium and its daughters. The uranium was eluted from the column with 15 ml of 0.5 M HCl, and the solution was evaporated to dryness. This purification was repeated two times. About 2 μg of the purified uranium was dissolved in 1 ml of 9 M HCl. The solution was passed through an anion-exchange column [Muromac(R) 1 $\times$ 8, 200–400 mesh, 5 mmϕ $\times$ 10 mm]. The resin with adsorbed uranium was washed with 3 ml of 9 M HCl and then eluted from the column with 4 ml of 0.5 M HCl. The uranium isotopes were coprecipitated with samarium hydroxide by adding 10 μg of samarium and 15 M NH_4OH in that order. The precipitate was collected on an 18-mm-diameter alumina filter (Whatman, ANODISC membrane, 0.02-μm pore size) to prepare a counting source [17]. The filter was fixed on a stainless-steel supporting ring and dried on a hot plate at 150°C. α-particle spectrometry was performed using a Canberra model 7401 α-particle spectrometer and a 2048-channel pulse-height analyzer system assisted by a personal computer. The α-particle spectrometer was equipped with an ion-implanted planar silicon detector (Canberra, A450-18AM). The accumulation of an α-particle spectrum for 1 h was successively repeated more than 16 times. The cycle of purification and α-particle spectrometry with 2 μg of the uranium was separately performed three times.

To estimate the interference on the determination of the ^{232}U/^{233}U ratio from other uranium isotopes, isotope analysis using thermal-ionization mass spectrometry (TIMS) was conducted. A Finnigan MAT-261 magnetic sector mass spectrometer with a double-filament (Re-Re) ion source and a Faraday cup detector was used. About 10 μg of the purified ^{233}U sample in nitrate form was loaded on a sample filament and evaporated by applying a filament current of 2.1–2.4 A. An ionization filament that parallels the sample filament was operated at 5.1–5.3 A. The uranium ions were extracted on an analyzing magnet by applying an extraction voltage of 10 kV. The ratios of the five uranium isotopes, namely, ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U, were calculated as the average of ten measurements.

The ratios of ^{228}Th and ^{229}Th^{g} produced by ^{232}U and ^{233}U α-particle decay, respectively, were determined as described below. The purified ^{232,233}U sample was dissolved in 2 ml of 9 M HCl. The solution was passed through an anion-exchange column [Muromac(R) 1 $\times$ 8, 200–400 mesh, 8 mmϕ $\times$ 50 mm], which adsorbed uranium. The resin with adsorbed uranium was washed with 10 ml of 9 M HCl to eliminate thorium. The uranium was eluted from the column with 10 ml of 0.5 M HCl, and the solution was concentrated to near dryness. This purification was repeated two times to eliminate thorium completely. The purified ^{232,233}U sample was left to stand for 0.8–289 d to allow the growth of ^{228}Th and ^{229}Th^{g}. The ^{232,233}U sample that included fresh thorium isotopes was dissolved in 2 ml of 9 M HCl. The solution was passed through an anion-exchange column [Muromac(R) 1 $\times$ 8, 200–400 mesh, 8 mmϕ $\times$ 50 mm] to adsorb uranium. The thorium isotopes were eluted from the column with 5 ml of 9 M HCl. To eliminate the remaining uranium in the thorium fraction, the eluate was passed through an anion-exchange column [Muromac(R) 1 $\times$ 8, 200–400 mesh, 5 mmϕ $\times$ 40 mm]. The elimination procedure for ^{232,233}U was repeated two to five times. The thorium fraction was heated to dryness, and the residue was dissolved in 8 M HNO_3. The solution was passed through an anion-exchange column [Muromac(R) 1 $\times$ 8, 200–400 mesh, 5 mmϕ $\times$ 40 mm], which adsorbed thorium. The resin with adsorbed thorium was washed with 7 ml of 8 M HNO_3 to eliminate radium. The thorium was eluted from the column with 5 ml of 2 M HCl. The thorium isotopes were prepared for α counting by using a samarium hydroxide coprecipitation method [17], as described above. The accumulation of an α-particle spectrum for 1 h was successively repeated 100 times. A counting source was placed at a distance of 13–41 mm from the detector and measured with a 10–20 mm collimator in order to adjust the count rate for each sample. The measurements for the ^{228}Th/^{229}Th^{g} ratio were separately conducted six times with various growth times of thorium isotopes and the number of elimination procedures for ^{232,233}U.

III. RESULTS AND DISCUSSION

An example of the α-particle spectra of the ^{232,233}U samples measured for 35 h is shown in Fig. 1. The ^{233}U, ^{232}U, and slight ^{228}Th peaks are seen in the spectrum. The ^{233}U peak at 4824 keV has a full width at half maximum (FWHM) value of less than 20 keV in all measurements, and the ^{232}U and ^{233}U peaks are clearly separated from each other. The α events in the regions of 4627–4860 and 5122–5355 keV are considered to be from ^{233}U and ^{232}U, respectively. The background counts in these regions are assumed to be linear functions. The ^{228}Th peak at 5340 keV is overlapped with the ^{232}U peak at 5320 keV, which is corrected, although the correction is less than 0.1%. From TIMS results, the atomic ratios are determined to be 99.5287% $\pm$ 0.0008% for ^{233}U, 0.1858% $\pm$ 0.0004% for ^{234}U, 0.0628% $\pm$ 0.0002% for ^{235}U, 0.0143% $\pm$ 0.0004% for ^{236}U, and 0.2084% $\pm$ 0.0002% for ^{238}U at a confidence level of 2σ. The peaks of ^{234}U are overlapped with the peaks of ^{233}U, which is also corrected, although the correction is about 0.2%. From

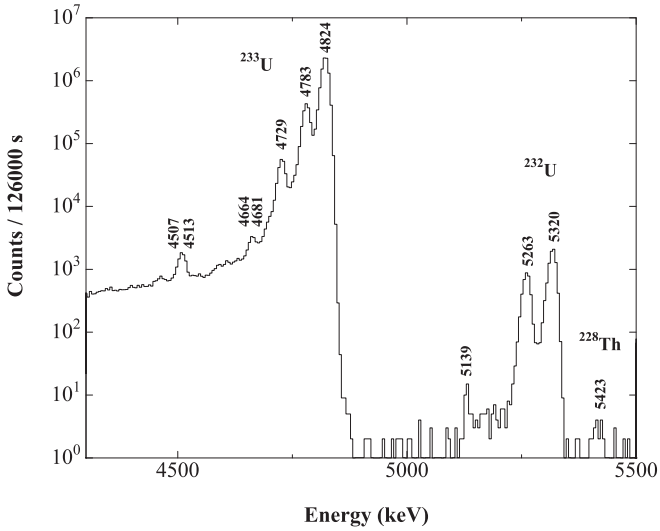

FIG. 1. An example of the α-particle spectra of ^{232,233}U samples.

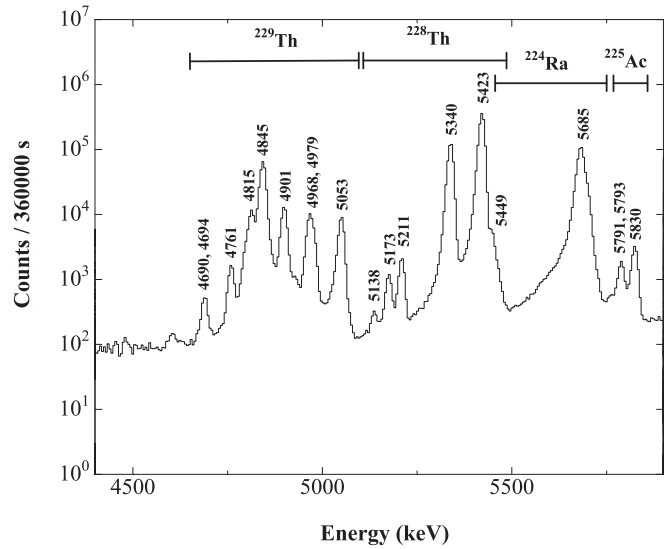

FIG. 2. An example of the α-particle spectra of ^{228,229}Th samples.

the results, the ^{232}U/^{233}U counts ratio and atomic ratio of the ^{232,233}U sample used in this study are determined to be (1.060 $\pm$ 0.005) $\times$ 10^{-3} and (4.590 $\pm$ 0.026) $\times$ 10^{-7}, respectively.

An example of the α-particle spectra of the ^{228,229}Th samples measured for 100 h is shown in Fig. 2. The ^{229}Th^{g}, ^{228}Th, and their daughters are seen in the spectrum. The ^{228}Th peak at 5423 keV has a FWHM of less than 18 keV in all measurements. The α events in the regions of 4650–5100 and 5110–5490 keV are considered to be from ^{228}Th and ^{229}Th^{g}, respectively. The background counts in these regions are assumed in the same manner as in the measurement for the ^{232,233}U sample. The component in the high-energy side of the ^{228}Th peak at 5423 keV is due to the ^{224}Ra peak at 5449 keV, which has an α branch of 5.06% $\pm$ 0.04% [16]. The α counts of this component are estimated from the ^{224}Ra peaks at 5685 keV, which has an α branch of 94.92% $\pm$ 0.04% [16], and subtracted from the α counts of ^{228}Th.

The half-life of ^{229}Th^{g} is calculated as described below. The activities of ^{228}Th and ^{229}Th^{g} at the end of the growth time are given by the following equations:

$$A_{228} = \frac{\lambda_{228}\lambda_{232}}{\lambda_{228} - \lambda_{232}} N_{232}(e^{-\lambda_{232}T} - e^{-\lambda_{228}T}), \quad (1)$$

$$A_{229} = \frac{\lambda_{229}\lambda_{233}}{\lambda_{229} - \lambda_{233}} N_{233}(e^{-\lambda_{233}T} - e^{-\lambda_{229}T}), \quad (2)$$

where A_{228} and A_{229} are the activities of ^{228}Th and ^{229}Th^{g}, respectively; N_{232} and N_{233} are the numbers of atoms of ^{232}U and ^{233}U, respectively; λ_{228}, λ_{229}, λ_{232}, and λ_{233} are the decay constants of ^{228}Th, ^{229}Th^{g}, ^{232}U, and ^{233}U, respectively; and T is the growth time of thorium. Assuming that the counting efficiencies of ^{228}Th and ^{229}Th^{g} are equal, the ratio of the α events from ^{228}Th and ^{229}Th^{g} is given by the following equation:

$$\frac{C_{228}}{C_{229}} = \frac{\int_{t_1}^{t_1+\Delta t} A_{228} e^{-\lambda_{228}t} dt}{\int_{t_1}^{t_1+\Delta t} A_{229} e^{-\lambda_{229}t} dt}, \quad (3)$$

where C_{228} and C_{229} are counts of ^{228}Th and ^{229}Th^{g}, respectively, t_1 is the elapsed time from the end of the growth time to the start time of the measurement, and Δt is the measurement time. Here, assuming that the numbers of atoms of ^{233}U and ^{229}Th^{g} do not decrease during the growth time of thorium and the number of atoms of ^{229}Th^{g} does not decrease during the measurement time, Eqs. (2) and (3) are represented by

$$A_{229} = \lambda_{229}\lambda_{233} N_{233} T \quad (4)$$

and

$$\frac{C_{228}}{C_{229}} = \frac{A_{228}}{A_{229}} \frac{\int_{t_1}^{t_1+\Delta t} e^{-\lambda_{228}t} dt}{\Delta t}, \quad (5)$$

TABLE I. Obtained half-lives of ^{229}Th^{g} and the experimental conditions. The ^{232,233}U elimination shows the number of times the ^{232,233}U elimination procedure was performed (see text). The first term of the $T_{1/2}$ error is the statistical uncertainty, and the second is systematic uncertainty.

Sample	T (d)	t_1 (s)	^{232,233}U elimination	C_{229}/C_{228}	$T_{1/2}$ (yr)
1	0.823	10410	2	0.2377 $\pm$ 0.0023	7493 $\pm$ 77 $\pm$12
2	28.9	18000	3	0.2296 $\pm$ 0.0004	7970 $\pm$ 37 $\pm$13
3	289	16500	4	0.2612 $\pm$ 0.0005	7994 $\pm$ 36 $\pm$12
4	45.9	17040	4	0.2326 $\pm$ 0.0004	7944 $\pm$ 35 $\pm$12
5	253	21854	5	0.2599 $\pm$ 0.0005	7887 $\pm$ 37 $\pm$12
6	32.9	18093	5	0.2339 $\pm$ 0.0004	7866 $\pm$ 36 $\pm$12

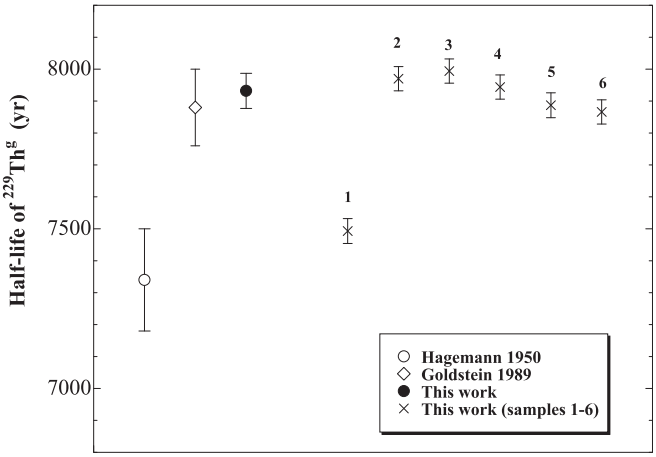

FIG. 3. The half-life values of ^{229}Th^{g}. Our results are compared with the literature values (Hagemann 1950: [13]; Goldstein 1989: [14]). The values in Table I are also plotted with 1σ confidence level (samples 1–6).

respectively. Therefore, assuming that the counting efficiencies of ^{232}U and ^{233}U are equal, the decay constant of ^{229}Th^{g} is given by the following equation:

$$\lambda_{229} = \frac{C_{232}}{C_{233}}\frac{C_{229}}{C_{228}}\frac{(e^{-\lambda_{232}T} - e^{-\lambda_{228}T})}{(\lambda_{228} - \lambda_{232})T}\frac{e^{-\lambda_{228}t_1} - e^{-\lambda_{228}(t_1+\Delta t)}}{\Delta t}, \quad (6)$$

where C_{232} and C_{233} are counts of ^{232}U and ^{233}U, respectively. The values of the ^{229}Th^{g} half-life calculated by Eq. (6) are tabulated in Table I with the experimental conditions. The errors of the ^{229}Th^{g} half-life have been separated into two parts: one is statistical uncertainty, and the other is systematic uncertainty derived from the uncertainty in the branching ratio of ^{224}Ra and in the half-lives of ^{228}Th and ^{232}U. The statistical uncertainty mainly derives from the counts of ^{232}U (approximately 0.85% per one measurement). The values of the ^{229}Th^{g} half-life are not dependent on the growth time. Note that the value of the ^{229}Th^{g} half-life obtained by conducting the ^{232,233}U elimination procedure two times is smaller than other values. This suggests that the counting source included the uranium isotopes that passed through the anion-exchange columns (the α peaks of ^{233}U and ^{229}Th^{g} overlap). Considering that the other values of the ^{229}Th^{g} half-life are comparable regardless of the number of times the ^{232,233}U elimination procedure was conducted, it may be expected that the ^{233}U contaminant is negligible after conducting the ^{232,233}U elimination procedure more than three times. From the results, except for the value of sample 1, the half-life of ^{229}Th^{g} is determined to be 7932 $\pm$ 34 yr at a confidence level of 2σ.

However, the deviation in the values of ^{229}Th^{g} half-life in Table I is larger than the statistical error of each data point. The reduced chi-square value of the half-lives obtained is 2.3, which means that the half-lives contain not only the statistical error estimated above but also other random errors. Therefore, we have estimated the statistical uncertainty from the scatter of the five half-lives obtained. As a result, the statistical uncertainty containing random errors is determined to be $\pm$49 yr at a confidence level of 2σ. The half-life of ^{229}Th^{g} is determined to be 7932 $\pm$ 55 yr at a confidence level of 2σ by the square root of the sum of squares of the statistical and systematic uncertainties.

The current results and the previous results [13,14] are shown in Fig. 3. The half-life of 7932 $\pm$ 55 yr is in agreement with the value 7880 $\pm$ 120 yr [14] and not 7340 $\pm$ 160 yr [13]. Goldstein *et al.* [14] conjecture that 5% of the difference between the ^{229}Th^{g} half-life of Hagemann *et al.* [13] is due to underestimation of the effect of impurities such as ^{228}Th. However, it seems that the effect of the ^{228}Th impurity on the net counts of ^{229}Th^{g} was less than 1%, considering the energy spectrum of ^{228}Th and ^{229}Th^{g} in Ref. [13], although we do not have sufficient information on the correction for the ^{228}Th impurity applied by Hagemann *et al.* [13]. In contrast to Goldstein *et al.* [14], we suggest that the difference was caused by the impurities derived from the inadequate separation of ^{233}U, as in sample 1 of our experiment.

In conclusion, we measured the half-life of ^{229}Th^{g} by using ^{232}U and ^{233}U decay series. From the results, the half-life of ^{229}Th^{g} is determined to be 7932 $\pm$ 55 yr at a confidence level of 2σ. This value is consistent with 7880 $\pm$ 120 yr [14] and has fewer uncertainties than the previous experimental value. Thus, our results have experimentally determined the half-life of ^{229}Th^{g} and improved the reliability of the value of the half-life of ^{229}Th^{g}.

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