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Simultaneous U–Pb and U–Th Dating Using LA-ICP-MS for Young (<0.4 Ma) Minerals: A Reappraisal of the Double Dating Approach

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Abstract: Simultaneous U–Pb and U–Th dating using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) was performed on the ca. 0.1 Ma Toya tephra and the ca. 0.08 Ma SS14-28 U–Th zircon reference material. In U–Pb dating, both Th/U and Pa/U partitioning between magma and minerals were considered. In U–Th dating, both abundance sensitivity and molecular interferences on ^{230}Th were reevaluated. As a result, the Toya tephra yielded an accurate weighted mean U–Pb age of 0.103 ± 0.029 Ma (2σ) using zircon and monazite. Conversely, the SS14-28 zircon yielded an inaccurate U–Pb age (0.25 ± 0.10 Ma), which was attributed to low ^{206}Pb signal intensity. Both the Toya tephra zircon and the SS14-28 zircon yielded accurate U–Th model ages of 0.108 ± 0.014 Ma and 0.078 ± 0.007 Ma, respectively. The agreement of U–Pb and U–Th ages for Toya indicates that simultaneous U–Pb and U–Th dating is possible and viable. The inappropriate age of SS14-28 U–Pb age and appropriate U–Th model age also indicates it is preferable to apply both U–Pb and U–Th dating simultaneously for young (<0.4 Ma) zircons to check internal consistency. The proposed double dating approach may be especially useful for small grains when it otherwise would be impossible to obtain multiple ages from a single grain. By adopting simultaneous U–Pb and U–Th dating using LA-ICP-MS, zircon crystallization ages as old as 4.5 Ga to as young as 0.1 Ma (or even younger) can be obtained in a quick and cost-effective manner with a reasonable (~5% at 1σ) uncertainty.

Keywords: U–Pb dating; U–Th dating; LA-ICP-MS; zircon; monazite; Toya tephra

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Citation: Ito, H. Simultaneous U–Pb and U–Th Dating Using LA-ICP-MS for Young (<0.4 Ma) Minerals: A Reappraisal of the Double Dating Approach. *Minerals* **2024**, *14*, 436. https://doi.org/10.3390/min14040436

Academic Editor: Jim Lee

Received: 28 March 2024
Revised: 19 April 2024
Accepted: 20 April 2024
Published: 22 April 2024

1. Introduction

U–Pb and U–Th dating methods using zircon have greatly contributed to revealing the Earth's history. The zircon U–Pb method has a wide datable range of 4.5 Ga to 0.1 Ma (e.g., [1–3]), whereas zircon U–Th dating has a significantly narrower range of <0.4 Ma because it relies on the disequilibrium of ^{230}Th with a ca. 75 ka half-life. Up until now, it has been a common practice to date zircon >ca. 0.4 Ma by U–Pb and <ca. 0.4 Ma by U–Th to obtain accurate and precise ages (e.g., [4–7]).

For dating of Quaternary rocks, it is advantageous if both U–Pb and U–Th dating results are acquired simultaneously, because they can be cross-checked internally, in a manner similar to the U–Pb method, where ^{238}U–^{206}Pb and ^{235}U–^{207}Pb dates are used for verification of each other.

To this end, Ito [1] analyzed ca. 0.1 Ma Toya tephra, Hokkaido, Japan, and demonstrated that simultaneous U–Pb and U–Th dating is possible using LA-ICP-MS, which seemed to have established a method to date Quaternary igneous rocks with which these ages can be cross-checked in a quick and cost-effective manner. However, Guillong et al. [8] showed that Ito [1]'s approach lacked rigorous treatments on U–Th data, which raised questions regarding Ito [1]'s U–Th dating result. Specifically, Guillong et al. [8] pointed out two caveats of Ito [1]'s U–Th dating: lack of evaluation of (1) tailing on ^{230}Th from much abundant ^{232}Th and (2) molecular (zirconium oxides) interferences on ^{230}Th, and suggested that if these corrections are applied, then the (^{230}Th/^{238}U) or ^{230}Th/^{238}U activity ratio of reference zircons expected to be in secular equilibrium (i.e., >0.4 Ma) should become unity. In fact, as shown in Figure 1, it is evident that tailing on ^{230}Th occurs in thorium-rich minerals, such as monazite. Apart from the effort to date zircon U–Pb and U–Th simultaneously, recent progress of zircon U–Th dating methodology using LA-ICP-MS is summarized in [9].

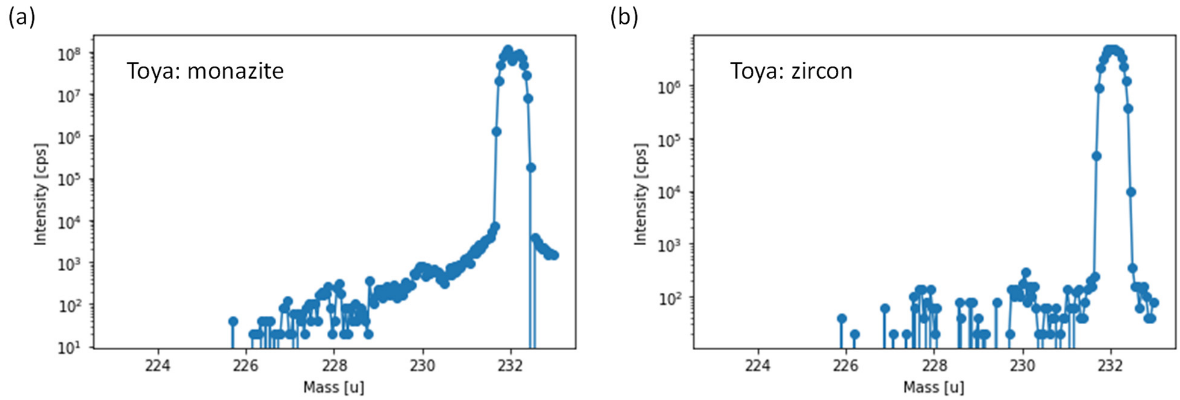

Figure 1. The effect of tailing on ^{230}Th from ^{232}Th. (**a**) Monazite from Toya tephra. (**b**) Zircon from Toya tephra. Contrary to zircon, a gentle slope (tailing) is observed from mass 232 to mass 230 in monazite. Data were obtained with the same ablation conditions shown in Section 2.2.

In this paper, we follow Guillong et al. [8]'s advice for U–Th disequilibrium dating and report simultaneous U–Pb and U–Th ages of Toya and SS14-28, a recently proposed U–Th zircon reference material [10], and demonstrate once again that simultaneous U–Pb and U–Th dating using LA-ICP-MS is viable and useful, although its precision is not so high as dating by U–Th solely (e.g., [9–12]).

2. Materials and Methods

2.1. Materials

A large (>10 kg) pumice block of Toya tephra from a quarry adjacent to Loc. 6 in [13] was collected. It belongs to the category Unit 2c of [13], which is a thick (~30 m) pumiceous pyroclastic flow deposit. The Toya tephra was erupted from the Toya caldera at 106–112 ka based on oxygen isotope stratigraphy [14,15]. Ito [1] reported zircon U–Pb age of 0.11 $\pm$ 0.01 Ma (error shown as 95% confidence level, which is nearly equivalent to 2σ and therefore we treat this as 2σ hereafter; also, age errors are shown as 2σ hereafter in the text unless specified) and zircon U–Th age of 0.11 $\pm$ 0.02 Ma. The collected Toya tephra of [1] was composed of large amounts of pumice and small amounts of lithic fragments (mostly andesite), and significant amounts of zircon (24 grains out of 42) showed xenocrystic U–Pb ages of >1 Ma. Since the newly collected tephra in this study is a single large pumice block, we expected fewer xenocrysts from this sample.

Zircons were separated using standard heavy liquid and magnetic techniques. To purify zircons, separated minerals were immersed in HF (~46%) and then in HCl (~10%) both for a few days at room temperature. Small amounts of zircon (~50 grains per kilogram) and monazite (~10 grains) were obtained as a residue. Typical zircon and monazite photos are shown in Figure 2. They were handpicked and embedded in a PFA Teflon sheet. No polishing was performed. Two sheet samples (sample name: Toya4-BP and Toya4-BP2) were prepared.

The SS14-28 is a trachyte sample outcropping in the Hallasan UNESCO World Heritage site on Jeju Island, South Korea [10]. Zircon SS14-28 was previously analyzed using two analytical approaches (SIMS and LA-ICP-MS) and four instruments: CAMECA IMS 1280, ASI SHRIMP II, sector field high-resolution LA-ICP-MS and multi-collector LA-ICP-MS, yielding a proposed age of 82 $\pm$ 6 ka [10]. Zircon SS14-28 (Figure 3) was embedded in a

PFA Teflon sheet without polishing, using the same method as sheet samples Toya4-BP and Toya4-BP2.

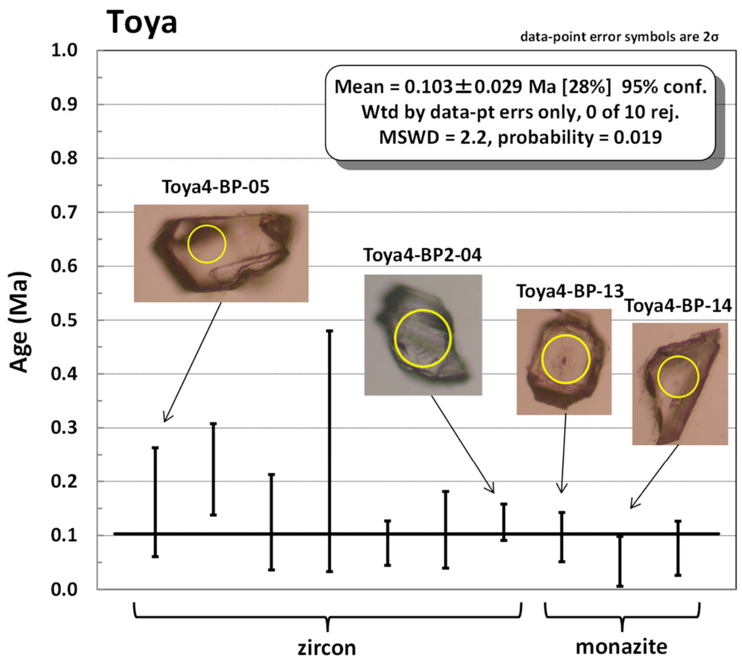

Figure 2. Individual U–Pb (^{238}U–^{206}Pb) ages for the Toya tephra minerals (zircon and monazite). Photos of some analyzed minerals are also shown. Yellow circles are 40 µm in diameter and denote the area where the laser beam was targeted.

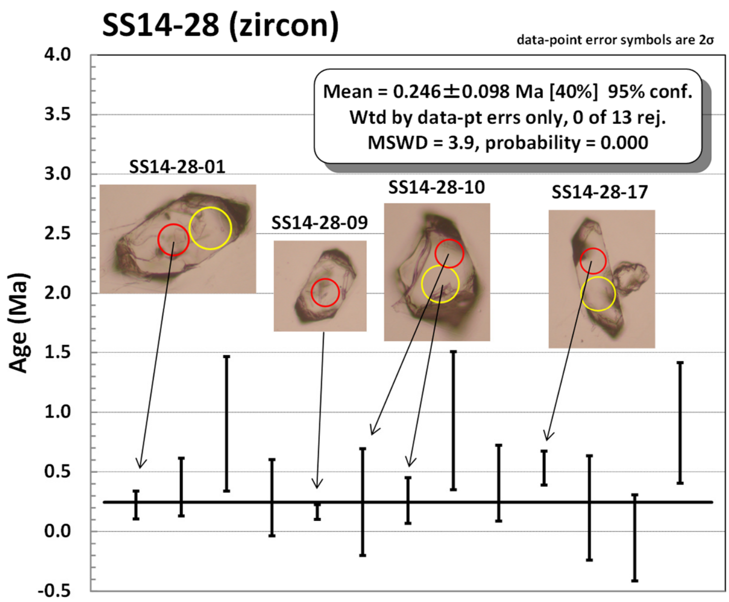

Figure 3. Individual U–Pb (^{238}U–^{206}Pb) ages for the SS14-28 zircon. Photos of some analyzed zircons are also shown. Red and yellow circles are 30 and 40 µm in diameter, respectively, and denote the area where the laser beam was targeted.

2.2. U–Pb Dating

LA-ICP-MS U–Pb dating was performed at the Central Research Institute of Electric Power Industry (CRIEPI), Abiko, Japan, using a Thermo Fisher Scientific ELEMENT XR magnetic sector-field ICP-MS (SF-ICP-MS) coupled to a New Wave Research UP-213 Nd-YAG laser. Data were acquired using instrumental parameters as shown in Table S1. Key features are as follows: In order to acquire U–Pb and U–Th ages simultaneously, the normal dating procedure for U–Pb was changed in that ^{230}Th was measured instead of ^{235}U. N_2 gas was added to increase signal intensity. The instrument was tuned daily to obtain ^{232}Th signal intensity of >500,000 cps (counts per second) and ThO/Th ratio of <0.8% using NIST SRM 613 with a 30 µm beam diameter, 10 Hz repetition, and ~9 J/cm^2 laser fluence at a 5 µm/s scanning speed. Samples were ablated in helium gas by pulses at a 10 Hz repetition rate with 7–8 J/cm^2 laser fluence and a 30 or 40 µm beam diameter. The focus of the laser beam was fixed at the sample surface throughout the data acquisition. Data were acquired in electrostatic scanning (E-scan) mode over 1080 mass scans over a 30 s background measurement, followed by 30 s sample ablation and then a 45 s background measurement. A typical U–Th–Pb raw data plot for Toya tephra is shown in Figure 4.

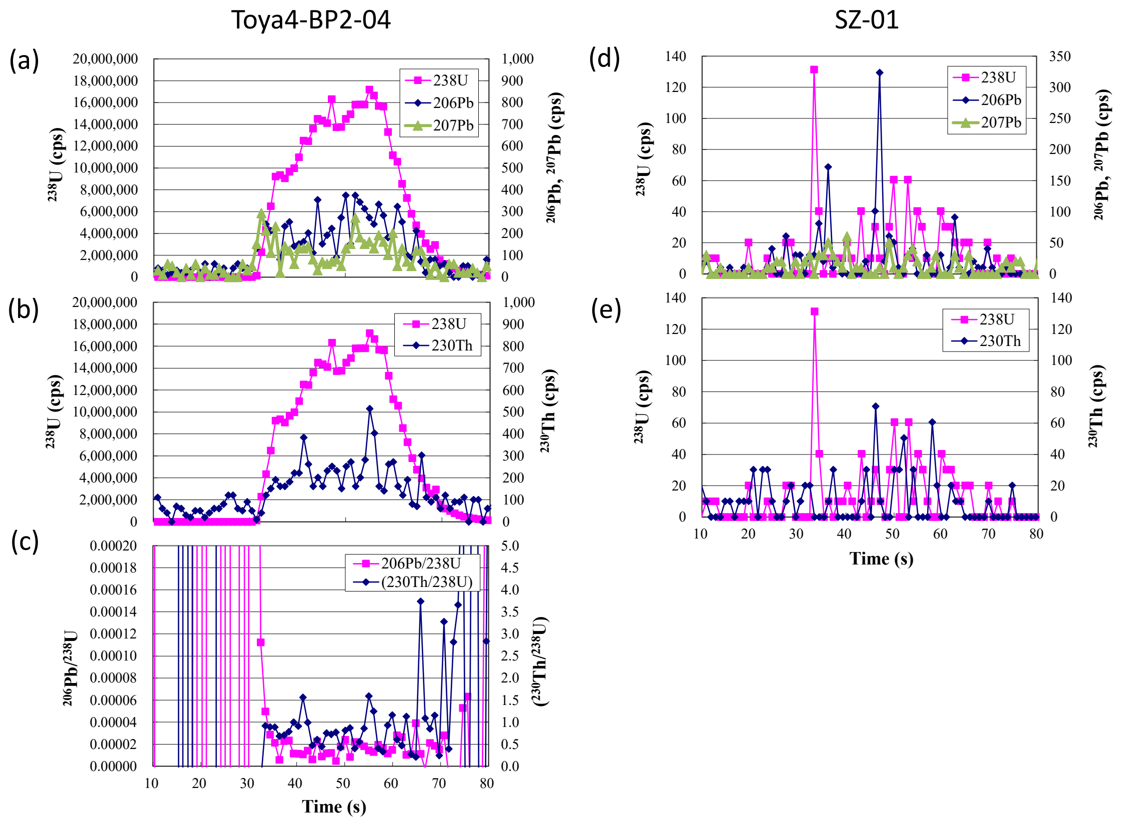

Figure 4. Raw U–Th–Pb data for Toya zircon 'Toya4-BP2-04' (**a**–**c**) and synthetic zircon 'SZ-01' (**d**,**e**). Toya4-BP2-04 yielded a U–Pb age of 0.124 ± 0.034 Ma from 40 s to 50 s data and a U–Th model age of 0.113 ± 0.049 Ma from 40 s to 60 s data. A photo of this zircon is shown in Figure 2. In (**c**), parentheses indicate activity ratios.

Data for the first 10 s of ablation were neglected to avoid surface Pb contamination and signal instability, and the 10–20 s laser ablation data and the 20–30 s data were adopted as shallow and deep section data, respectively. Sections approximately 24 µm in depth were drilled during the 30 s laser ablation (Table S2), and therefore the shallow section age is derived from material ablated to between ~8 and 16 µm and ~16 to 24 µm for the deep section.

Individual U–Pb ages were corrected for common Pb using a modified ^{207}Pb-based method [3] adopting the common ^{207}Pb/^{206}Pb ratio of 0.8357 from the Pb isotope evolution model [16] and measured ^{207}Pb/^{206}Pb. The modified ^{207}Pb method employs both Th/U and Pa/U partitioning ($f_{Th/U}$ and $f_{Pa/U}$, respectively) for correcting initial ^{230}Th and ^{231}Pa disequilibrium in the mineral–magma system. The $f_{Th/U}$ was calculated assuming the Th/U of magma or $(Th/U)_{magma}$ was 4.0 ± 2.0 and employing individually measured Th/U of mineral. The reason to choose $(Th/U)_{magma}$ of 4.0 ± 2.0 is because it covers most silicic magma Th/U [17], including $(Th/U)_{magma}$ of 2.96 that was employed for Toya in [1]. The measured $f_{Th/U}$ with a 50% uncertainty and an assumed $f_{Pa/U}$ of 3.36 ± 0.40 [3] were used for all age calculations. Data with a high common Pb contamination ($f_{206\%}$) of >75% were excluded for further analyses [1], and the mean square weighted deviation (MSWD) [18] is used as a statistical test of validity of weighted mean ages. The 91,500 zircon (1062 ± 15 Ma; [19]) was used as a primary reference material with zircons of Plešovice (337.13 ± 0.37 Ma; [20]), Bishop Tuff (0.767 ± 0.001 Ma; [21]) and Fish Canyon Tuff (28.402 ± 0.023 Ma; [22]) used as secondary reference materials.

Uranium and Th concentrations were quantified by comparing counts of ^{238}U and ^{232}Th for the sample relative to the 91,500 zircon reference material, which is assumed to have homogeneous U and Th concentrations of 80 and 30 ppm respectively [19], followed by a drift correction relative to NIST SRM 610 glass reference material. No down-hole isotopic (Pb/U, Th/U) fractionation correction was performed because data from the same depth range (or time span) were used for reference materials and unknowns in each analysis. In fact, it was ascertained that all zircons in this study were drilled to a depth of ~23–25 μm regardless of zircon age and laser diameter (30 μm and 40 μm) using a KEYENCE VK-X 1000 laser scanning confocal microscope (Table S2), although the pit's bottom created by 40 μm laser was inclined (e.g., sample BST-67 in Table S2).

The Toya tephra sample (zircon and monazite) was analyzed using a 40 μm laser beam on two occasions, and the SS14-28 zircon were analyzed twice using a 30 μm laser beam on the first occasion and 40 μm laser beam on the second occasion. Some SS14-28 grains were analyzed twice on the same grain (e.g., SS14-28-01 in Figure 3).

2.3. U–Th Dating

U–Th ages were obtained as follows. Firstly, (^{230}Th/^{238}U) activity ratios were measured for all reference zircons expected to be in secular equilibrium (i.e., 91,500, Plešovice, Bishop Tuff and Fish Canyon Tuff, which are all >0.4 Ma). Data with low ^{230}Th counts (i.e., ^{230}Th < 30 cps) were omitted to reduce the effect of molecular interferences on ^{230}Th (See Section 3.2.1). The weighted mean of (^{230}Th/^{238}U) for all the reference zircons was calculated as a correction factor and then the (^{230}Th/^{238}U) for unknown sample was calculated using this correction factor ([1,12,23].

Zircon isochron and model ages were obtained using IsoplotR v.5.5 [24]. The model ages were calculated assuming Th/U of magma to be 4.0 for Toya and 7.8 for SS14-28 [10]. Data with a high (>100% at 2σ) uncertainty were excluded for weighted mean age calculation.

3. Results

3.1. U–Pb Age

Tables S3 and S4 show the U–Pb dating results for shallow and deep sections, respectively. They include both unknowns (Toya, SS14-28) and zircon U–Pb secondary reference materials (Plešovice, Bishop Tuff, Fish Canyon Tuff). All U–Pb ages for the secondary reference materials in this study are in accordance with or slightly older than their respective reference ages both for shallow and deep sections. In Table 1, U–Pb ages that pass the common Pb criteria and the age with smaller absolute uncertainty between shallow and deep sections were listed for the unknown samples. As a result, the Toya zircon and monazite yielded a weighted mean age of 0.12 ± 0.04 Ma (n = 7; MSWD = 1.8) and 0.08 ± 0.03 Ma (n = 3; MSWD = 1.0), respectively. Combined, the Toya zircon and monazite yielded a U–Pb age of 0.103 ± 0.029 Ma (n = 10; MSWD = 2.2) (Figure 2).

The SS14-28 zircon yielded a U–Pb age of 0.25 ± 0.10 Ma (n = 13; MSWD = 3.9) (Table 1; Figure 3). Note that the SS14-28-19 (2) shows ^{206}Pb of −3 cps, yielding a negative age of −0.05 ± 0.36 Ma (Table 1).

Table 1. LA-ICP-MS U-Pb analytical results. U-Pb ages that pass the common Pb criteria of $f_{206\%}$ < 75% and the age with smaller uncertainty between shallow and deep sections were listed.

Sample Name	Th	U	Th/U	^{206}Pb	$f_{Th/U}$ [a]	f_{206}% [b]	Total [c]							Age [Ma] [d]		MSWD [e]	Memo [f]
	[ppm]	[ppm]					^{207}Pb/^{206}Pb	2σ	^{207}Pb/^{235}U	2σ	^{206}Pb/^{238}U	2σ		^{206}Pb/^{238}U	2σ		
Toya: zircon																	
Toya4-BP-05	978	1940	0.50	214	0.13	38.5	0.34857	0.39182	0.00094	0.00045	0.00002	0.00001		0.16	0.10		221,201 d: 40 µm
Toya4-BP-07(2)	515	1165	0.44	142	0.11	58.4	0.50482	0.57045	0.00150	0.00047	0.00002	0.00001		0.22	0.09		221,201 d: 40 µm
Toya4-BP-11	444	954	0.47	140	0.12	69.9	0.59561	0.21904	0.00205	0.00086	0.00003	0.00001		0.12	0.09		221,201 d: 40 µm
Toya4-BP-16	561	945	0.59	482	0.15	71.9	0.61122	0.21562	0.00742	0.00189	0.00009	0.00004		0.26	0.22		221,201 d: 40 µm
Toya4-BP2-01	5094	1413	3.61	854	0.90	66.9	0.57212	0.08818	0.00271	0.00092	0.00003	0.00001		0.09	0.04		230,323 d: 40 µm
Toya4-BP2-02(2)	304	776	0.39	230	0.10	64.5	0.55293	0.24966	0.00127	0.00044	0.00002	0.00000		0.11	0.07		230,323 d: 40 µm
Toya4-BP2-04	412	878	0.47	181	0.12	38.0	0.34466	0.18541	0.00058	0.00025	0.00001	0.00000		0.12	0.03		230,323 s: 40 µm
													Weighted mean (n = 7)	0.12	0.04	1.8	
Toya: monazite																	
Toya4-BP-13	50,237	254	198.15	1783	49.54	53.6	0.46742	0.03767	0.07237	0.00580	0.00112	0.00007		0.10	0.05		221,201 s: 40 µm
Toya4-BP-14	47,010	252	186.90	1556	46.73	67.9	0.57991	0.19217	0.07833	0.01784	0.00098	0.00009		0.05	0.05		221,201 s: 40 µm
Toya4-BP-18(2)	51,339	307	167.26	1757	41.82	61.7	0.53126	0.11879	0.07168	0.02097	0.00098	0.00017		0.08	0.05		221,201 d: 40 µm
													Weighted mean (n = 3)	0.08	0.03	1.0	
SS14-28: zircon																	
SS14-28-01	847	945	0.90	476	0.22	74.2	0.62886	0.13616	0.00710	0.00108	0.00008	0.00002		0.22	0.12		220,915 s: 30 µm
SS14-28-02	91	115	0.79	32	0.20	19.7	0.20073	9.58752	0.00124	0.00321	0.00004	0.00003		0.37	0.24		220,915 d: 30 µm
SS14-28-03	111	122	0.91	95	0.23	60.2	0.51888	0.81711	0.00908	0.00432	0.00013	0.00009		0.90	0.56		220915 s: 30 µm
SS14-28-06	163	192	0.85	38	0.21	30.8	−0.19583	2.42063	−0.00086	0.00185	0.00003	0.00004		0.28	0.32		220,915 d: 30 µm
SS14-28-09	828	795	1.04	76	0.26	42.3	0.37829	0.90885	0.00082	0.00081	0.00002	0.00001		0.16	0.06		220,915 s: 30 µm
SS14-28-10	88	100	0.88	17	0.22	−62.6	−0.44607	1.19473	−0.00163	0.00318	0.00003	0.00003		0.25	0.45		220,915 d: 30 µm
SS14-28-10-2	68	111	0.62	51	0.15	73.8	0.62610	7.48864	0.00238	0.00120	0.00003	0.00002		0.26	0.19		230,329 d: 40 µm
SS14-28-11	133	149	0.90	97	0.22	74.2	0.62944	0.77382	0.01137	0.00753	0.00013	0.00009		0.93	0.58		220,915 s: 30 µm
SS14-28-16(2)	54	77	0.69	23	0.17	−56.9	−0.40146	1.91933	−0.00274	0.00386	0.00005	0.00004		0.41	0.32		220,915 d: 30 µm
SS14-28-17	207	283	0.73	101	0.18	73.6	0.62440	1.08847	0.00593	0.00309	0.00007	0.00002		0.53	0.14		220,915 s: 30 µm
SS14-28-18(2)	106	120	0.88	14	0.22	62.2	0.53529	0.64666	0.00145	0.00331	0.00002	0.00003		0.20	0.44		220,915 d: 30 µm
SS14-28-19(2)	54	89	0.60	−3	0.15	−814.7	−6.35652	1.67859	0.00469	0.00307	−0.00001	0.00003		−0.05	0.36		220,915 d: 30 µm
SS14-28-20	21	35	0.61	26	0.15	53.4	0.46599	6.30158	0.00815	0.01708	0.00013	0.00008		0.91	0.50		220,915 d: 30 µm
													Weighted mean (n = 13)	0.25	0.10	3.9	

[a] $f_{Th/U} = (Th/U)_{mineral}/(Th/U)_{magma}$. $(Th/U)_{magma}$ of 4.0 ± 2.0 was used. [b] f_{206}% denotes the percentage of ^{206}Pb that is common Pb and is calculated as follows: $f_{206}\% = 100 \times (x-0.0461)/(0.832-0.0461)$, where x is a measured ^{207}Pb/^{206}Pb ratio [25]. [c] Measured isotope ratio, that is, before corrections of initial ^{230}Th and ^{231}Pa disequilibrium and common Pb. [d] Individual U-Pb (^{238}U-^{206}Pb) ages were determined using the modified ^{207}Pb method [3]. Error of weighted mean is shown as 95% confidence level. [e] MSWD: mean square weighted deviation. [f] Shown are analyzed date, section (s: shallow; d: deep), and laser diameter.

3.2. U–Th Dating

3.2.1. Molecular Interferences on ^{230}Th

Guillong et al. [8] pointed out that zirconium sesquioxide ions ($Zr_2O_3^+$) are produced, which would cause erroneous ^{230}Th counts when using low resolution mode of SF-ICP-MS. Guillong et al. [8] evaluated this by using synthetic zircon nearly free of U and Th. Here, we used the same synthetic zircon nearly free of U and Th used in [9] and measured ^{230}Th in various conditions (Table 2). The ^{230}Th counts are 2 ± 1 cps (1 SE, or 1 standard error), which indicates that molecular interferences are negligible under various conditions applied. Therefore, if ^{230}Th counts of zircon are >100 cps, the errors caused by molecular interreferences are normally <2%. However, because counts of ^{230}Th as large as 8 cps were observed ('SZ-01' in Table 2), a spurious ^{230}Th counts of ~10 cps may have happened. Judging from the raw data of SZ-01 (Figure 4e), we found it is difficult to omit this level of spurious counts. From this regard, to reduce erroneous ^{230}Th effect on U–Th ages caused by molecular interferences, we used U–Th data in which >30 cps on ^{230}Th was obtained.

Table 2. LA-ICP-MS analytical results for synthetic zircon using various conditions.

	^{206}Pb	^{230}Th	^{232}Th	^{238}U	Fluence	
	[cps]	[cps]	[cps]	[cps]	[J/cm^2]	Memo [a]
SZ-01	27	8	62	15	7.1	221,201 w: 40 µm, 1500 W, N_2
SZ-02	6	−3	60	17	7.1	221,201 w: 40 µm, 1500 W, N_2
SZ-03	6	−3	10	−2	7.1	221,201 w: 40 µm, 1500 W
SZ-04	−10	3	11	4	7.3	221,201 w: 40 µm, 1500 W
SZ-05	0	0	27	1	7.6	221,201 w: 30 µm, 1500 W, N_2
SZ-06	6	0	17	6	7.5	221,201 w: 30 µm, 1500 W, N_2
SZ-07	−1	0	7	1	7.4	221,201 w: 30 µm, 1500 W
SZ-08	−4	4	−2	4	7.7	221,201 w: 30 µm, 1500 W
SZ-09	5	1	16	3	18.2	221,201 w: 40 µm, 1200 W
SZ-10	5	5	17	7	15.3	221,201 w: 40 µm, 1200 W
SZ-11	−5	2	13	5	5.5	221,201 w: 65 µm, 1200 W
SZ-12	7	6	27	8	5.5	221,201 w: 65 µm, 1200 W
SZ-13	36	0	19	5	5.3	221,201 w: 65 µm, 1200 W
Mean	**6**	**2**	**22**	**6**		
1SE	**3**	**1**	**5**	**1**		

[a] Shown are analyzed date, section (w: whole), laser diameter, RF power, and N_2 gas addition (if denoted).

Molecular interferences on ^{230}Th were further checked by analyzing masses 223–233 for gas blank (Figure 5a), Plešovice zircon with N_2 gas (Figure 5b) and without N_2 gas (Figure 5c) during laser ablation. Guillong et al. [8] corrected ^{230}Th by analyzing mass 228 while Bernal et al. [11] mentioned that complex polyatomic species were barely detectable when ThO/Th was <1%. As shown in Figure 5, the intensity of mass ~228 or masses 227.5–228.2 was 63, 57, 24 cps for gas blank, Plešovice zircon with and without N_2 gas, respectively, which also indicates that no molecular interferences correction is needed. Note that adding N_2 gas increases intensity of mass 232 (^{232}Th) (Figure 5b) by eight times compared with that without N_2 gas (Figure 5c).

3.2.2. Abundance Sensitivity on ^{230}Th

Guillong et al. [8] pointed out that erroneous ^{230}Th counts result from abundance sensitivity for mass 232, denoted as ^{232}Th′, which is defined as mass 230 counts derived from tail of the major ^{232}Th peak. To evaluate ^{232}Th′, Guillong et al. [8] used monazite as a material with high Th/U to determine abundance sensitivity for mass 232.

Figure 6 shows ^{232}Th vs. mass 230 correlation of Toya monazite in this study and monazite in [12]. The system in this study corresponds to an abundance sensitivity (^{232}Th′) of 1/207,420 or 4.8 ppm while that of [12] corresponds to 3.5 ppm, both of which indicate a several-ppm correction is necessary as follows: $^{230}Th_c = {}^{230}Th_m - f \times {}^{232}Th_m$, where subscripts c and m denote corrected and measured, respectively, and f is a correction factor (ppm).

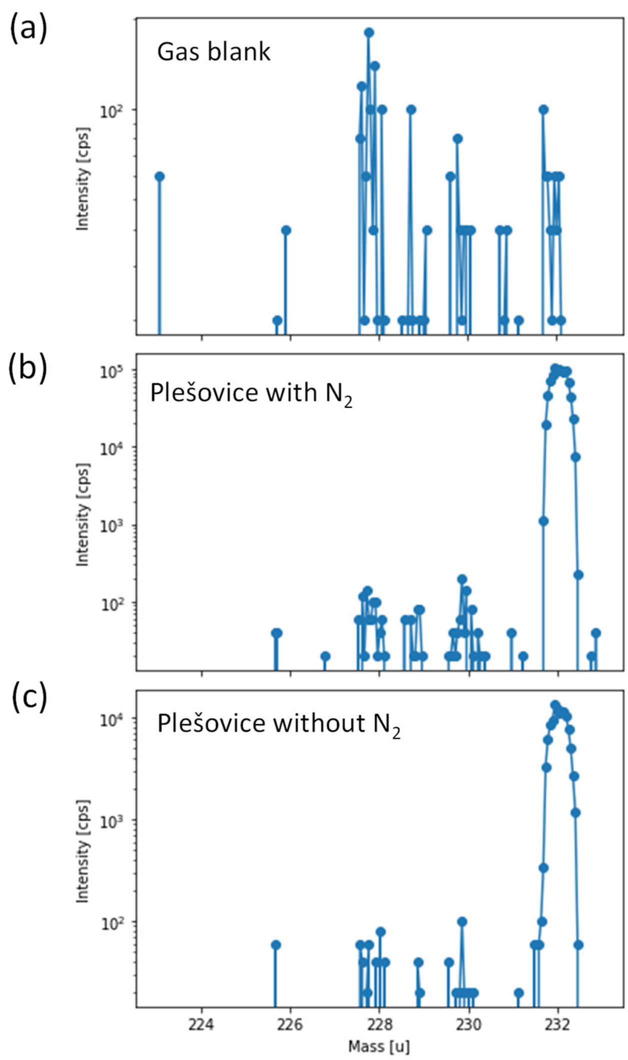

Figure 5. Low resolution mass scan for masses 223–233 during gas blank (**a**) and laser ablation of Plešovice zircon (30 µm crater, 10 Hz, 7 J/cm^2) with N_2 (**b**) and without N_2 (**c**).

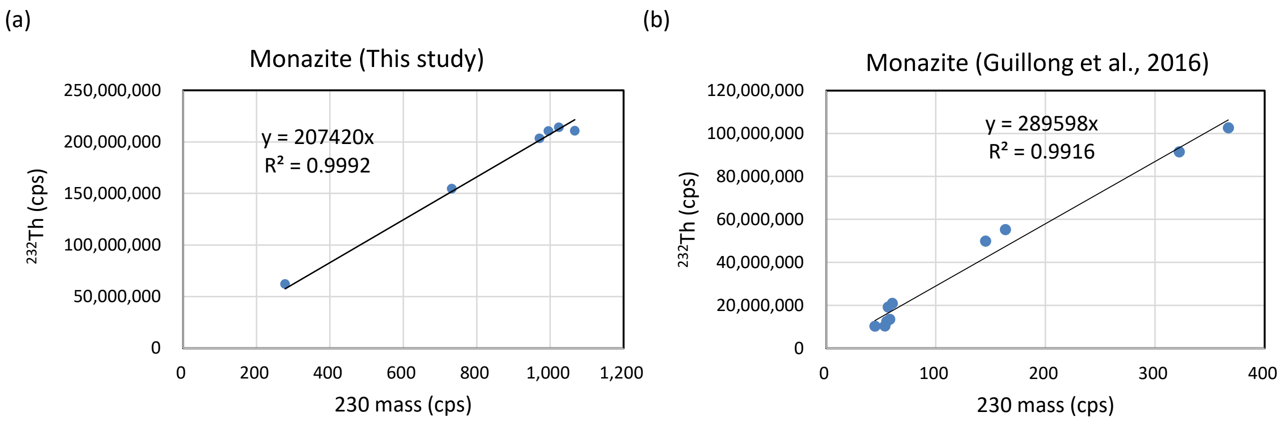

Figure 6. ^{232}Th vs. mass 230 correlation of Toya monazite in this study (**a**) and monazite in [12] (**b**). Toya monazite data were obtained on 1 December 2022 and 23 March 2023 and are shown in Table S6.

In order to evaluate the effects of abundance sensitivity on the reference zircons expected to be in secular equilibrium (i.e., 91,500, Plešovice, Bishop Tuff, Fish Canyon Tuff), we calculated (^{230}Th/^{238}U) of these >0.4 Ma reference zircons for five different abundance sensitivity cases of 1/150,000 (6.7 ppm), 1/200,000 (5.0 ppm), 1/300,000 (3.3 ppm), 1/400,000 (2.5 ppm) and 0 ppm (Table 3 and Table S5; Figure 7). The (^{230}Th/^{238}U) varies both among each correction factor and among each experiment from ~0.9 to ~1.1. Overall, the 5 ppm correction seems to be the best correction because its (^{230}Th/^{238}U) of >0.4 Ma reference zircons is closest to unity, i.e., secular equilibrium.

Table 3. (^{230}Th/^{238}U) for reference zircons (91,500, Plešovice, Bishop Tuff, Fish Canyon Tuff) after various (6.7, 5, 3.3, 2.5, 0 ppm) ^{232}Th' correction.

Memo [a]	6.7 ppm	95% conf.	5 ppm	95% conf.	3.3 ppm	95% conf.	2.5 ppm	95% conf.	0 ppm	95% conf.
220,915 w: 30 µm	0.929	0.055	0.972	0.055	1.014	0.055	1.036	0.055	1.100	0.055
221,201 w: 40 µm	0.883	0.036	0.928	0.036	0.974	0.046	0.986	0.043	1.050	0.059
230,323 w: 40 µm	0.980	0.025	1.011	0.026	1.046	0.026	1.064	0.027	1.114	0.033
230,329 w: 40 µm	1.010	0.058	1.041	0.055	1.077	0.055	1.095	0.055	1.150	0.060
Mean	**0.951**		**0.988**		**1.028**		**1.045**		**1.104**	
1SE	**0.020**		**0.017**		**0.016**		**0.016**		**0.015**	

[a] Shown are analyzed date, section (w: whole), and laser beam diameter.

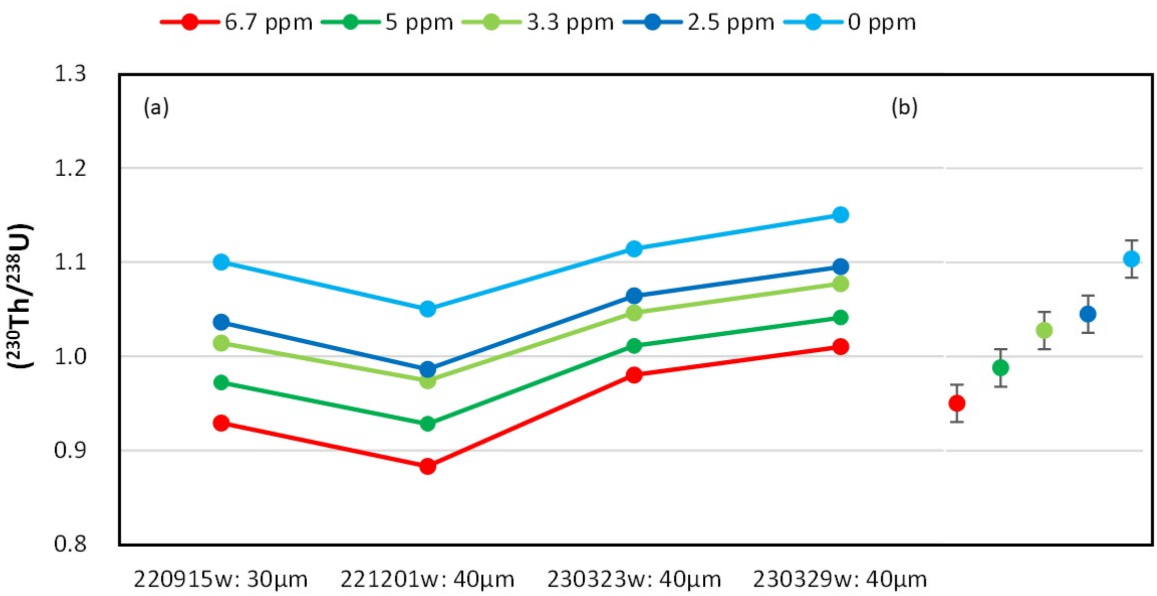

Figure 7. (^{230}Th/^{238}U) for reference zircons (91,500, Plešovice, Bishop Tuff, Fish Canyon Tuff) calculated using different ^{232}Th' correction values for each experiment (**a**) and average (**b**). Errors are 1 SE. See Table 3 for more explanation.

3.2.3. U–Th Age

Table 4 and Table S6 show zircon U–Th model age results of Toya and SS14-28 calculated using these five different correction factors. Among these corrections, the 2.5 ppm correction seems to yield the best ages because it yields 108 ± 14 ka for Toya and 78 ± 7 ka for SS14-28, which are in accordance with reference ages of 106–112 ka for Toya [15] and 82 ± 6 ka for SS14-28 [10]. Table 5 shows zircon U–Th isochron ages. Here again, the 2.5 ppm correction yields the best (or nearly the best) ages of 118 ± 23 ka for Toya and 82 ± 32 ka for SS14-28.

Table 4. Summary of zircon U-Th model age results. The 2.5 ppm correction was accepted and shown in bold.

	6.7 ppm Correction				5 ppm Correction				3.3 ppm Correction				2.5 ppm Correction				0 ppm Correction			
	U-Th Age [ka]	95% Conf.	n	MSWD [a]	U-Th Age [ka]	95% Conf.	n	MSWD	U-Th Age [ka]	95% Conf.	n	MSWD	U-Th Age [ka]	95% Conf.	n	MSWD	U-Th Age [ka]	95% Conf.	n	MSWD
Toya	95	15	13	1.2	81	21	15	2.4	102	13	15	1	**108**	**14**	**15**	**1**	114	15	14	0.9
SS14-28	47.7	6.1	15	0.9	57.1	6.1	17	1.1	71.2	6.8	17	0.7	**78.2**	**7.2**	**17**	**0.7**	98.3	8.3	18	0.8

[a] MSWD: mean square weighted deviation. Model ages were calculated assuming Th/U of magma to be 4.0 for Toya and 7.8 for SS14-28 [10].

Table 5. Summary of zircon U-Th isochron age results. The 2.5 ppm correction was accepted and shown in bold.

	6.7 ppm Correction				5 ppm Correction				3.3 ppm Correction				2.5 ppm Correction				0 ppm Correction			
	U-Th age [ka]	2σ	n	MSWD [a]	U-Th Age [ka]	2σ	n	MSWD	U-Th Age [ka]	2σ	n	MSWD	U-Th Age [ka]	2σ	n	MSWD	U-Th Age [ka]	2σ	n	MSWD
Toya	>350	NA	13	0.8	130.8	27.2	15	0.9	121.1	23.9	15	0.9	**118.4**	**23**	**15**	**0.9**	115.9	28.4	14	0.8
SS14-28	94.8	130.1	15	0.8	88.9	35.9	17	0.7	84.5	33.3	17	0.7	**82.4**	**32.1**	**17**	**0.7**	84.3	29.9	18	1.1

[a] MSWD: mean square weighted deviation. NA: not available.

4. Discussion

4.1. U–Pb Age of Toya

The U–Pb zircon age of Toya in this study (0.12 ± 0.04 Ma) (Table 1) is comparable with the U–Pb zircon age of [1] (0.11 ± 0.01 Ma), although the precision in this study is lower than [1]. We speculate that the lower precision in this study may simply be due to quality of zircons selected.

The 'zircon' in [1] with Th/U of >100 was later confirmed to be monazite. None of the monazite with the U–Pb age studied in [1] yielded ca. 0.1 Ma, whereas in this study monazite U–Pb age of 0.08 ± 0.03 Ma was obtained (Table 1). We speculate that this is because we employed the modified ^{207}Pb method of [3], which better corrects 'common Pb' and 'disequilibrium in the mineral–magma system' than that in [1]. In fact, monazite of 'Toya4-BP-13' yielded a U–Pb age of 0.10 ± 0.05 Ma in this study (Table 1), whereas it yielded an age of 1.15 ± 0.48 Ma using the calculation method in [1]. We used the partitioning factors ($f_{\mathrm{Th/U}}$ and $f_{\mathrm{Pa/U}}$) for zircon and monazite in the same way, although these factors for monazite are not well established [3]. The partitioning factors for monazite in this study were 40–50 for $f_{\mathrm{Th/U}}$ (Table 1) and 3.36 ± 0.40 for $f_{\mathrm{Pa/U}}$. Although the obtained monazite age of ca. 0.1 Ma may be even more inaccurate because no monazite reference materials [26] were used for age calculation, it agrees with the stratigraphy and zircon U–Pb age. This may support the conclusion that the partitioning factors used for monazite and age calculation applied were appropriate.

We found no >1 Ma zircon from the Toya pumice sample (although the analyzed zircons were only 23 grains), which is in stark difference with [1] (24 out of 42 grains showed >1 Ma). This may indicate that the Toya magma contained no inherited or xenocrystic zircons, and the old (>1 Ma) zircons in [1] from Toya pyroclastic deposits were incorporated during its caldera-forming eruption and deposition. Niki et al. [9] also reported no xenocrystic (i.e., >0.4 Ma in U–Th dating) zircons in their Toya pumice, which also supports this interpretation.

4.2. U–Pb Age of SS14-28

The U–Pb age of SS14-28 (0.25 ± 0.10 Ma) (Table 1) is older than the reference age of 0.082 ± 0.006 Ma [10]. The age changes insignificantly to 0.26 ± 0.10 Ma using (Th/U) of magma at 8.0 ± 4.0, which encompasses the proposed value of 7.8 [10]. The three ca. 1 Ma zircons show a large uncertainty of ca. 0.5 million years (Figure 3) and therefore may not be problematic. The 'SS14-28-17' zircon yields a rather confined age of 0.53 ± 0.14 Ma using 30 μm laser beam, which is apparently older than the reference age. This grain has a large proportion of common Pb at ~74%, which barely passed the common Pb criteria of <75%. Although the U–Th age of this grain using 30 μm laser beam was omitted because ^{230}Th intensity was too low (6 cps) to pass the criteria of 30 cps, it yields a U–Th model age of 0.069 ± 0.018 Ma using 40 μm laser beam by the 2.5 ppm correction ('SS14-28-17-2' in Table S6), which agrees with the reference age within uncertainty. Therefore, we assume the U–Pb age of this grain may be an outlier. Without these four >0.5 Ma zircons, a weighted mean age of 0.19 ± 0.05 Ma (n = 8, MSWD = 0.87) is obtained. This age is still significantly older than the reference age of ca. 0.08 Ma and the U–Th model age of ca. 0.08 Ma in this study.

We assume that the inaccurate U–Pb age of SS14-28 is due to low signal intensity of ^{206}Pb (Table 1). The ^{206}Pb intensity for Toya zircon were all >100 cps, whereas those for SS14-28 were mostly <100 cps. Judging from ^{206}Pb intensity of synthetic zircon (e.g., 27 cps for 'SZ-01' in Table 2; See also Figure 4d), a U–Pb age calculated from data with low ^{206}Pb intensity (e.g., <100 cps) will be severely compromised. Only two SS14-28 zircons ('SS14-28-01' and 'SS14-28-17') showed ^{206}Pb intensity of >100 cps, while they showed a high (~74%) common Pb contamination, and thus their U–Pb ages are also of poor quality.

4.3. U–Th Age

As mentioned previously, (^{230}Th/^{238}U) of >0.4 Ma reference zircons varies from ~0.9 to ~1.1 (Figure 7) using different ^{232}Th' correction factors. Assuming the 'best' correction factor is a factor that corrects the (^{230}Th/^{238}U) as close as possible to unity, then the 3.3 ppm correction is the best for Sept. 15, 2022 experiment. Likewise, choosing the 'best' correction factor in each experiment yields a U–Th model age of 83 ± 22 ka for Toya and 49 ± 8 ka for SS14-28 (Table S6), which are significantly younger than their reference ages. This indicates that simply choosing the 'best' correction factor is not suitable. Overall, the 5 ppm correction brings the (^{230}Th/^{238}U) of >0.4 Ma reference zircons closest to unity (Figure 7b), while its model ages of Toya (81 ± 21 ka) and SS14-28 (57 ± 6 ka) (Table 4) are significantly younger than their reference ages, indicating that this correction factor is too large. Although it is not certain why the 5 ppm correction yields the 'best' correction for >0.4 Ma zircons, in the present system the 2.5 ppm correction seems the most appropriate correction, which yields accurate ages of 108 ± 14 ka for Toya and 78 ± 7 ka for SS14-28. Figure 8 shows (^{230}Th)/(^{232}Th) vs. (^{238}U)/(^{232}Th) for >0.4 Ma reference zircons both using 5 ppm and 2.5 ppm corrections, which indicates that both corrections plot >0.4 Ma zircons nearly along the equiline, while the (^{230}Th/^{238}U) for 2.5 ppm correction is slightly above unity.

The U–Th ages with the 0 ppm correction (Table 4) are ages calculated without the two corrections pointed out by [8]. Without these corrections, the Toya yields an appropriate U–Th model age of 114 ± 15 ka while SS14-28 gives an older model age of 98 ± 8 ka than the reference age of 82 ± 6 ka [10]. Therefore, although Guillong et al. [8]'s suggestion is important, the effect of neglecting these corrections on U–Th ages may not be so large.

For U–Th dating of the Toya tephra, Niki et al. [9] reported a U–Th zircon model age of 110 ± 7 ka, a U–Th zircon isochron age of 111 ± 22 ka, and a U–Th isochron age of 114 ± 5 ka using zircon and monazite. Using the 2.5 ppm correction, we obtained a U–Th zircon model age of 108 ± 14 ka and a U–Th zircon isochron age of 118 ± 23 ka, which are comparable to those of [9]. Assuming the uncertainty (1σ) of (^{238}U/^{232}Th) for monazite is 0.001, the IsoplotR v.5.5 [24] yields a U–Th isochron age of 110 ± 14 ka using zircon and monazite (Figure 9), which is also comparable to that of [9].

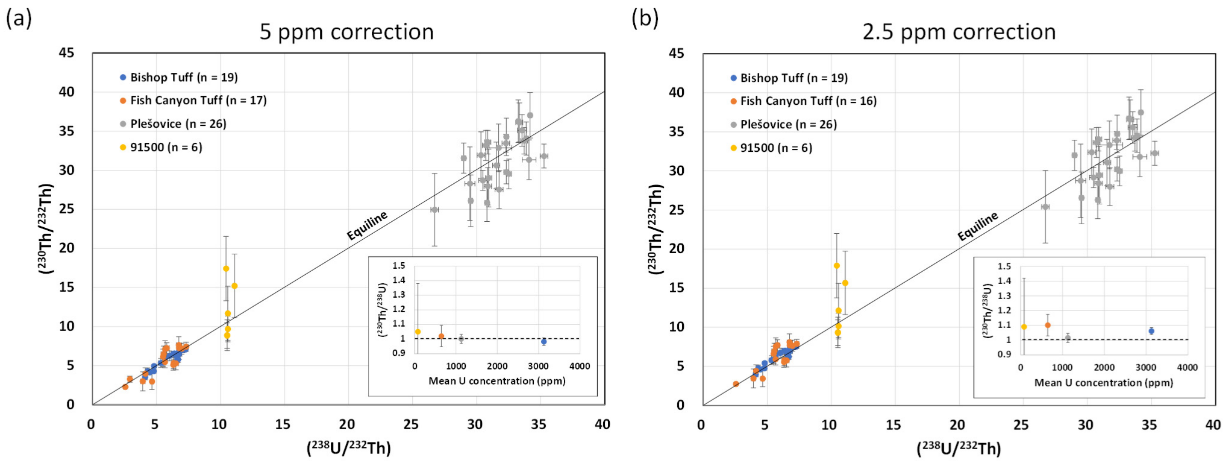

Figure 8. (^{230}Th/^{232}Th) vs. (^{238}U/^{232}Th) activity ratios for reference zircons expected to be in secular equilibrium, measured by LA-ICP-MS and corrected for abundance sensitivity of ^{232}Th on ^{230}Th at 5 ppm (**a**) and 2.5 ppm (**b**). Note that nearly all reference zircons demonstrate secular equilibrium and plot along the equiline. Uncertainty is given as 1σ. Inset: (^{230}Th/^{238}U) vs. U concentration for the same reference zircons. Dashed line ((^{230}Th/^{238}U) = 1) demonstrates secular equilibrium. Uncertainty is given as 95% confidence level.

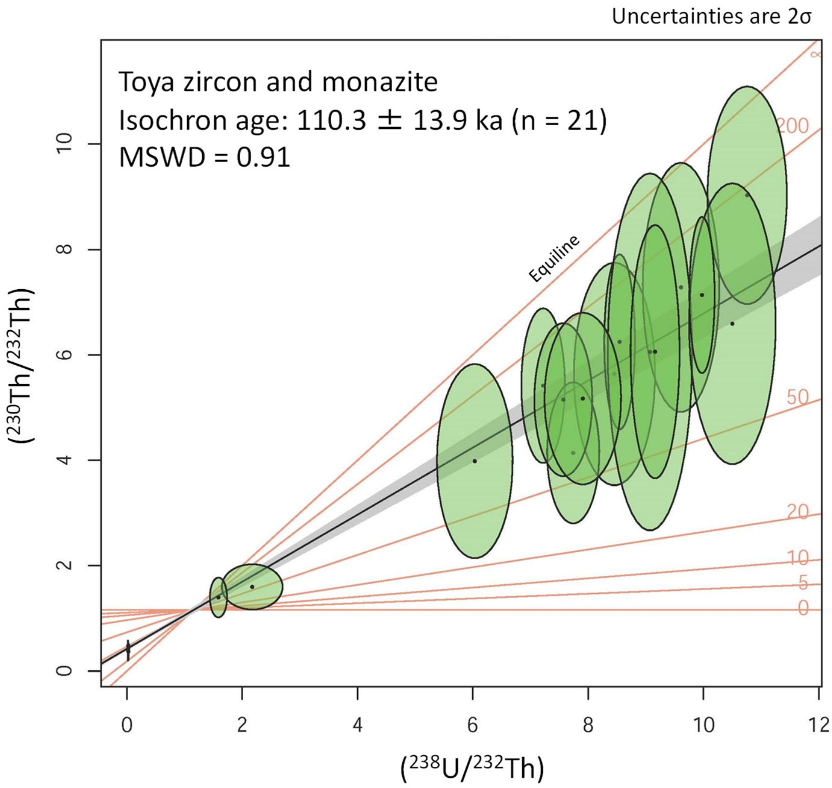

Figure 9. U–Th activity ratio diagram for Toya zircon and monazite. The 2.5 ppm correction data were plotted.

4.4. Pros and Cons of Simultaneous U–Pb and U–Th Dating

To begin this section, some issues of the present techniques are discussed. Marsden et al. [10] reported a U–Th weighted mean age of SS-14-28 at 85.0 ± 4.0 Ma (n = 47; MSWD = 0.50) by a sector field high-resolution LA-ICP-MS following the method of [12], whereas in this study 78.2 ± 7.2 Ma (n = 17; MSWD = 0.7) was obtained using 2.5 ppm correction. Both laboratories used the same ICP-MS, while the former yielded better precision. This may be because the former used a 193 nm Resonetics Resolution excimer laser as opposed to the New Wave Research UP-213 Nd-YAG laser used in this study. One possible reason why a less precise age was obtained and also why the 'best' correction did not yield the 'best' age in this study is that using a laser wavelength of 213 nm might produce different and less favorable size particles than using 193 nm laser, causing more elemental fractionation [27] and more scatter of individual age. Some small zircons, especially Toya and SS14-28 zircons, were occasionally chipped during laser ablation (e.g., 'SS14-28-17' in Table S2), which may have altered the particle size distribution, causing further elemental fractionation [27].

Another issue in this study may be that data with ^{230}Th < 30 cps were omitted to avoid influence of molecular interferences on ^{230}Th, which will limit the capability to date young (e.g., <50 ka) zircons.

Despite these issues, all Toya zircon grains that yielded both a U–Th model age with a small (<100% at 2σ) uncertainty and a U–Pb age that passed the common Pb criteria yielded internally consistent U–Th and U–Pb ages within 2σ uncertainty (Table 6). For example, zircon Toya4-BP2-04 yielded a U–Th model age of 113 ± 48 ka and a U–Pb age of 124 ± 34 ka. This grain (Figure 2) is small (~50 μm in diameter), and therefore it may be difficult to obtain U–Pb and U–Th ages on different analytical sessions, especially using LA-ICP-MS. In this regard, it is useful to date U–Pb and U–Th simultaneously.

Table 6. LA-ICP-MS U-Th analytical results. U-Th model age with a high (>100% at 2σ) uncertainty was omitted. U-Pb age is also included for comparison.

Sample Name	Mineral	230Th [a] [cps]	($^{238}U/^{232}Th$)	σ	($^{230}Th/^{232}Th$)	σ	U-Th Age [ka] [b] $^{230}Th/^{238}U$	1σ	MSWD [c]	U-Pb Age [ka] $^{206}Pb/^{238}U$	1σ	MSWD [c]	Memo for U-Pb [d]
2.5 ppm correction													
Toya													
Toya4-BP-05	zircon	93	8.455	0.283	5.637	0.850	109	31		162	51		221,201 d: 40 µm
Toya4-BP-16	zircon	67	7.218	0.152	5.416	0.591	139	32		257	112		221,201 d: 40 µm
Toya4-BP-07(2)	zircon	66	9.608	0.267	7.282	0.952	145	42		223	43		221,201 d: 40 µm
Toya4-BP-11	zircon	55	9.159	0.171	6.061	0.968	108	31		124	44		221,201 d: 40 µm
Toya4-BP2-02(2)	zircon	162	9.973	0.088	7.136	0.597	128	21		110	35		230,323 d: 40 µm
Toya4-BP2-04	zircon	189	7.568	0.202	5.150	0.585	113	24		124	17		230,323 s: 40 µm
						Weighted mean (n = 6)	122	23	0.2	136	39	1.3	

[a] ^{230}Th < 30 cps were omitted. [b] Ages were calculated assuming Th/U of magma to be 4.0 for Toya. Error of weighted mean is shown as 95% confidence level. [c] MSWD: mean square weighted deviation. [d] Shown are analyzed date, section (s: shallow; d: deep), and laser diameter.

As shown in the obtained U–Pb age of the SS14-28, zircon U–Pb dating as young as ca. 0.1 Ma is challenging and may yield an inaccurate age. In this sense also, it is preferable to apply both U–Pb and U–Th dating simultaneously for young (<0.4 Ma) zircons to check internal consistency. By adopting simultaneous U–Pb and U–Th dating using LA-ICP-MS, zircon crystallization ages as old as 4.5 Ga to as young as 0.1 Ma (or even younger) can be obtained in a quick and cost-effective manner with a reasonable (~5% at 1σ) uncertainty.

5. Conclusions

Simultaneous U–Pb and U–Th dating using LA-ICP-MS was reexamined using ca. 0.1 Ma Toya tephra and ca. 0.08 Ma SS14-28 U–Th zircon age reference material, especially by taking account of ^{230}Th correction. It was found that molecular interferences in ^{230}Th are insignificant. After correction of abundance sensitivity on ^{230}Th, the ^{230}Th/^{238}U activity ratio became close to unity for old (>0.4 Ma) reference zircons. Zircon and monazite of Toya yielded U–Pb age of ca. 0.10 Ma and zircon U–Th model age of ca. 0.10 Ma in accordance with stratigraphy. The SS14-28 zircon yielded ca. 0.08 Ma U–Th model age in accordance with the reference age, whereas its U–Pb age (0.25 $\pm$ 0.10 Ma) was apparently older due to low (<100 cps) ^{206}Pb intensity. In conclusion, simultaneous U–Pb and U–Th dating using LA-ICP-MS is possible and useful to check internal consistency and especially useful for small grains that cannot apply both methods independently.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14040436/s1, Table S1. LA-ICP-MS operating conditions at the Central Research Institute of Electric Power Industry (CRIEPI); Table S2. Results of laser ablated pits measurements using a KEYENCE VK-X 1000 laser scanning confocal microscope; Table S3. LA-ICP-MS U-Pb analytical results for shallow section. Data in italics (>75% common Pb contamination) are excluded for further U-Pb analyses; Table S4. LA-ICP-MS U-Pb analytical results for deep section. Data in italics (>75% common Pb contamination) are excluded for further U-Pb analyses; Table S5. LA-ICP-MS U-Th analytical results for reference zircons.Error of weighted mean is shown as 95% confidence level; Table S6. LA-ICP-MS U-Th analytical results. U-Th age with >50% uncertaity are shown in italics. U-Pb age is also included for comparison. For U-Pb data, common Pb contamination (f_{206}%) of >75% are shown in italics.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article.

Acknowledgments: I thank Y. Adachi for her help with LA-ICP-MS analyses and N. Hasebe and R. Marsden for the Toya tephra sampling. I also thank H. Iwano who lent me a synthetic zircon. R. Marsden is also thanked for providing me with the SS14-28 zircon and English assistance. Two anonymous reviewers are thanked for their comments that improved the manuscript.

Conflicts of Interest: The author declares no conflicts of interest.

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