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(U–Th)/He geochronology of single zircon grains of known Tertiary eruption age

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Abstract

We performed a systematic study of (U–Th)/He ages of volcanic zircons of known eruption age to establish a reliable protocol for zircon He dating and to validate the resulting ages. Using laser He extraction and dissolution by lithium borate flux melting we analyzed many aliquots of single zircon grains separated from four rapidly cooled rocks: Fish Canyon Tuff (accepted age 27.8 ± 0.7 Ma), Buluk Tuff (16.3 ± 0.2 Ma), Tardree Rhyolite (58.4 ± 0.7 Ma) and Utaosa Rhyolite (2.52 ± 0.02 Ma). He ages of Fish Canyon Tuff, Buluk Tuff and Utaosa Rhyolite zircons are in good agreement with their reference ages: mean α emission-corrected ages were 28.6 ± 1.4 (1σ), 16.1 ± 0.8 and 2.61 ± 0.18 Ma, respectively. However, the zircon He ages of Tardree Rhyolite are irreproducible and consistently too old, with a mean He age of 78.8 ± 7.0 Ma. Spontaneous fission track densities of Tardree Rhyolite zircons indicate that about 80% of these zircons are strongly zoned in U, with high track density (i.e., high U content) in the core and low density on the rim. This causes an overestimation of the α ejection correction that likely explains the erratic and excessively high He ages from these zircons. Assessment of the degree and style of U zonation within a zircon population is thus prudent before application of the (U–Th)/He method. Step-heating experiments indicate that for most zircons He extraction is >99% complete after ~1 h at 1300°C. However, for as yet unknown reasons occasional grains seem to retain substantial amounts of He under these conditions.

Keywords: zircon; helium; geochronology; standard; laser heating

1. Introduction

Recent studies have demonstrated the applicability of (U–Th)/He dating to a variety of geologic problems [1–13]. The technique has been most successfully applied to apatite, leading to a

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wide range of studies of the upper crust that take advantage of the low He closure temperature in this mineral [14–19]. Ultimately the validity of apatite He ages is supported by their agreement with independent constraints on quickly cooled apatites [12]. Zircons, which are very common and are rich in U and Th, are also an attractive target for (U–Th)/He geochronometry and thermochronometry. However, early applications of the method to zircons yielded anomalously young ages, ostensibly because of radiation damage-assisted He loss [20,21]. The degree of damage required for He loss has not yet been established, and at least some of the anomalous ages might be related to diffusive He loss in slowly cooled rocks [10]. A small number of diffusion experiments indicate a minimum closure temperature of about 180°C for He release from zircon [10], and (U–Th)/He age–paleodepth relationships in a rapidly and very deeply exhumed crustal block roughly support this closure temperature (Stockli et al., in preparation).

Although of potential value for a variety of problems, we are aware of no data that demonstrate that He ages of quickly cooled zircons reliably yield the expected ages, with the exception of a few multi-grain aliquots of Fish Canyon Tuff zircons [10]. Such a demonstration is important not only to assess whether any complications exist for zircon He geochronometry, but also to establish the reliability of a particular analytical method. Indeed zircons present analytical challenges distinct from those associated with the now routine apatite method. For example, while He can be extracted from apatite at ~1000°C, much higher temperatures are required for He extraction from zircon. Similarly, weak nitric acid is sufficient to dissolve apatite, but traditional dissolution techniques for zircon use hydrofluoric acid and high temperature bombs. Farley et al. [22] outlined an alternative approach for analyzing zircons: laser heating followed by flux melting in lithium metaborate. Here we report results of a systematic study of this method, applied to single-grain (U–Th)/He dating of known age zircons using Nd-YAG laser extraction. We used four zircons of different ages to see how the system works for dating Cenozoic zircons. This complements previous work [22] which consisted of dating a single sample of unknown but extremely young eruption age (< 400 kyr). In such a young sample the effects of U-series disequilibrium on He ages can be very large, possibly masking methodological complications.

2. Samples

We used zircon samples separated from four rapidly cooled rocks of known ages: Fish Canyon Tuff (FCT), Buluk Tuff (BT), Tardree Rhyolite (TR) and Utaosa Rhyolite (UR). The FCT erupted in the San Juan Mountains of Colorado at 27.8 ± 0.7 Ma [23–27], and zircons from this tuff have been used widely as an age standard for fission track dating (FC3 zircon [28,29]). The BT is a pantelleritic tuff occurring in the upper part of the Buluk Member of the Bakate Formation in northern Kenya [30]. It yields reproducible zircon fission track ages of 16.2 ± 0.6 Ma [31], consistent with a more precise weighted mean K–Ar age of 16.3 ± 0.2 Ma for high temperature alkali-feldspar crystals [32]. Here we adopt the latter as the time of eruption of BT and thus as a reference age of the zircon analyzed (FTBM4 zircon). The TR forms part of the interbasaltic formation of the lower Tertiary Antrim Lava group in Northern Ireland [33]. Two step heating $^{40}Ar/^{39}Ar$ analyses of sanidine provided total degassing ages of 59.1 and 60.2 Ma with good plateaus, concordant with a mean K–Ar sanidine age of 58.7 ± 1.1 Ma (Hurford and Hammerschmidt, personal communication). A U–Pb age of 58.4 ± 0.7 Ma was determined for Tardree zircons using the sensitive high resolution ion microprobe [34], in agreement with the K–Ar and $^{40}Ar/^{39}Ar$ ages. This value is adopted here as the reference age. The UR occurs in the lower part of the Pliocene Teragi Group, distributed in eastern San'in district, southwest Japan [35]. A weighted mean K–Ar age of 2.48 ± 0.02 Ma for TRG04 biotite using the peak height comparison method [36] is consistent with a weighted mean $^{40}Ar/^{39}Ar$ age of 2.52 ± 0.02 Ma derived from eight laser total fusion analyses of the biotite [37]. The latter is used here as a reference value.

3. Methods

3.1. Grain selection and measurement

Zircons for analysis were selected to be glassy and free of adhering volcanic glass fragments. Most zircons from these four samples had dark inclusions within them. Fission track U mapping suggests that these inclusions are not highly enriched in U, so we did not attempt to select inclusion-free grains for analysis. The grains were chosen to be euhedral, equant, and large to minimize errors associated with the α ejection correction [3]. The physical dimensions of the selected grains were measured and the grains placed in disposable Pt foil micro-crucibles [38].

3.2. Helium analysis

Helium was extracted and measured using a laser procedure slightly modified from that reported earlier [38]. The Pt micro-crucible containing each zircon grain was outgassed at 1300°C for 30 min, following procedures established for degassing of Gold Butte zircons using furnace heating [10]. The validity of this degassing protocol was investigated in the present study. The evolved helium was spiked with ^{3}He, cryogenically concentrated and purified, and analyzed by quadrupole mass spectrometry. After the initial extraction, each packet was heated a second time to ensure quantitative extraction. Blank corrections, established by lasing an empty micro-crucible, were $(5\pm5)\times10^{-17}$ mol and did not exceed 0.1% of sample. The estimated accuracy and precision of He measurements of the size obtained from the zircons is better than ~1% (1σ).

3.3. U–Th analysis

After He extraction, the Pt micro-crucibles were removed from the vacuum chamber and placed in individual ~1 cm deep×5 mm wide Pt fluxing crucibles. About 7 mg of ultrapure Li metaborate flux was placed on top of the micro-crucible, and the fluxing crucible was heated to 1200°C for 2 h. These conditions are apparently sufficient for the flux to penetrate into the micro-crucible and completely melt the zircon. After cooling, the fluxing crucible was placed in a beaker of 250 μl of concentrated HNO_3, spiked with ^{235}U and ^{230}Th, and placed in an ultrasonic bath for 15 min. Then the beaker was heated for 30 min in an oven at 90°C, diluted with 2 ml water, and again heated for 10 h in an oven at 90°C. The resulting solution was analyzed on a double focusing inductively coupled plasma mass spectrometer (Finnigan Element). Blanks were $(3\pm1)\times10^{-13}$ mol for U and $(1\pm1)\times10^{-13}$ mol for Th and constituted a significant portion of signal in a few small and U,Th-poor grains. Excluding samples with large blank corrections, the estimated precision and accuracy of the U and Th measurements is ~0.5% (1σ).

3.4. Alpha ejection correction

To correct for the effects of α ejection [3] we used the tetragonal prism geometric model and stopping distances appropriate for uranium in zircon [12]. This model relates the fraction of αs retained (F_T) to the surface/volume ratio (β) of the zircon prism:

$$F_T = 1-4.31\beta + 4.92\beta^2$$

To the greatest extent possible we analyzed zircons with square cross-section, such that $\beta=(4L+2W)/(LW)$ where L is the length and W is the width of the prism. For those grains with varying widths on the two axes perpendicular to the c-axis (W_1, W_2), we used $\beta=(2LW_1+2LW_2+2W_1W_2)/(LW_1W_2)$. Both widths were measured for all analyzed zircons by rolling them under a binocular microscope. For FCT, BT and UR, F_T values were fairly high: means of 0.81, 0.83 and 0.79, respectively, with ranges from 0.75 to 0.90. TR was generally smaller with F_T of 0.68–0.76.

4. Results and discussion

Initially helium was outgassed from zircons using a routine re-extraction procedure in which the sample was outgassed at 1300°C, then heated to the same temperature a second time. The second extraction yielded a few percent or less of total

Table 1
(U–Th/He) analytical data for single grains of zircon

Sample	Length	Width		Mass	U	Th	^{4}He	RE	F_T	Age		Number of steps
	(μm)	(μm)		(μg)	(ppm)	(ppm)	(ncc/mg)	(%)		(Ma)		
										Raw	Corrected	
Fish Canyon Tuff												
Routine re-extraction at 1300°C												
FCTZr-1	291	126,	126	21.7	223	186	818	0.09	0.84	25.2	30.0	
FCTZr-2	263	120,	96	14.2	260	113	827	0.67	0.82	23.6	29.0	
FCTZr-3	251	91,	91	9.9	245	102	755	0.85	0.79	23.0	29.1	
FCTZr-4	417	137,	137	36.9	242	85	454	2.90	0.86	14.2[b]	16.6[b]	
FCTZr-5	343	103,	103	17.1	302	118	1012	1.29	0.82	25.2	30.8	
FCTZr-6	251	103,	94	11.4	243	81	759	0.06	0.80	23.8	29.7	
FCTZr-7	314	120,	115	20.4	213	68	703	2.69	0.83	25.1	30.1	
FCTZr-8	229	86,	76	7.0	232	77	603	1.42	0.76	19.7	25.8	
FCTZr-9	286	126,	101	17.0	243	91	754	0.04	0.82	23.4	28.4	
FCTZr-10	263	91,	91	10.3	210	84	586	1.80	0.79	20.9	26.4	
FCTZr-11	229	97,	92	9.6	240	65	699	1.39	0.79	22.4	28.3	
FCTZr-12	240	91,	81	8.4	213	64	598	2.15	0.78	21.5	27.6	
FCTZr-13	194	80,	75	5.5	313	128	901	0.40	0.75	21.5	28.6	
Average	275	106,	98	14.6	245	97	729	1.21	0.80	22.9	28.6	
1σ	56	17,	18	8.1	30	32	141	0.94	0.03	1.7	1.4	
Repeated extraction at 1300°C with 30 min steps												
FCTZr-S1[a]	274	109,	94	13.1	230	88	776	1.97	0.81	25.4	31.4	7
FCTZr-S2[a]	560	149,	149	58.1	109	56	334	1.15	0.87	22.4	25.7	3
FCTZr-S3[a]	320	114,	109	18.8	166	48	608	1.26	0.83	28.1	34.0	3
FCTZr-S4[a]	200	103,	98	9.5	189	43	648	1.35	0.80	26.6	33.4	4
FCTZr-S5[a]	377	137,	132	32.2	167	79	708	2.23	0.86	31.2	36.5	4
Average	346	122,	116	26.3	172	63	615	1.59	0.83	26.8	32.2	
1σ	122	18,	21	17.7	39	18	151	0.43	0.03	2.9	3.6	
Repeated isothermal extraction at 1200–1350°C for 1–20 min intervals												
FCTZr1200°C	423	103,	93	18.9	112	77	425	–	0.81	26.9	33.1	
FCTZr1250°C	469	137,	119	35.9	145	37	498	–	0.85	26.6	31.3	
FCTZr1300°C	697	143,	143	66.9	198	31	308	–	0.87	12.3[b]	14.1[b]	
FCTZr1350°C-1	217	109,	99	10.9	168	84	529	–	0.80	23.1	28.7	
FCTZr1350°C-2	251	114,	114	15.4	111	56	369	–	0.82	24.3	29.5	
FCTZr1350°C-3	320	126,	116	21.9	202	130	692	–	0.84	24.4	29.1	
Average	411	121,	113	29.6	147	57	426	–	0.83	25.1	30.3	
1σ	172	16,	18	20.5	33	21	81	–	0.03	1.5	1.6	
Buluk Tuff												
Routine re-extraction at 1300°C												
BTZr-1	229	109,	93	10.9	39.5	25.0	72.1	1.12	0.80	13.0	16.2	
BTZr-2	206	97,	78	7.3	32.2	25.6	48.5	0.54	0.77	10.4	13.5	
BTZr-3	246	114,	99	13.1	25.2	10.0	35.3	0.73	0.81	10.5	13.0	
BTZr-4	194	103,	87	8.2	73.8	53.3	146.1	0.01	0.79	13.9	17.6	
BTZr-5	229	103,	82	9.1	62.4	27.0	111.0	0.37	0.79	13.2	16.8	
BTZr-6	251	91,	91	9.9	30.3	8.5	59.7	2.51	0.79	15.2	19.2	
Average	226	103,	89	9.7	43.9	24.9	78.8	0.88	0.79	12.7	16.1	
1σ	20	7,	7	1.9	17.9	14.7	38.3	0.80	0.01	1.7	2.2	
Repeated extraction at 1300°C with 30 min steps												
BTZr-S1[a]	526	240,	154	91.1	34.2	16.6	64.5	1.88	0.89	13.9	15.5	4
BTZr-S2[a]	354	171,	162	46.2	73.4	32.6	147.2	1.37	0.88	14.9	17.0	3
BTZr-S3[a]	400	131,	121	30.0	31.6	12.3	55.1	0.89	0.85	13.1	15.4	2
BTZr-S4[a]	594	217,	161	97.4	33.5	16.9	63.5	0.72	0.90	13.9	15.5	2
BTZr-S5[a]	400	177,	177	59.0	64.2	63.2	145.8	0.31	0.88	15.1	17.1	2

Table 1 (*Continued*).

Sample	Length (μm)	Width (μm)		Mass (μg)	U (ppm)	Th (ppm)	^{4}He (ncc/mg)	RE (%)	F_T	Age (Ma)		Number of steps
										Raw	Corrected	
Average	455	187,	155	64.7	47.4	28.3	95.2	1.04	0.88	14.2	16.1	
1σ	90	38,	18	25.9	17.7	18.8	42.0	0.54	0.02	0.7	0.8	
Tardree Rhyolite												
Routine re-extraction at 1300°C												
TRZr-1	154	80,	70	4.1	193	81	1505	0.00	0.74	58.0	78.9	
TRZr-2	183	69,	49	2.9	210	121	1779	0.01	0.68	61.0	89.3	
TRZr-3	263	86,	67	7.1	235	62	1955	0.00	0.76	64.0	84.7	
TRZr-4	189	69,	54	3.3	231	90	1653	0.02	0.70	53.5	76.7	
TRZr-5	149	80,	60	3.4	158	89	1054	0.05	0.72	48.1	67.2	
TRZr-6	246	57,	57	3.8	387	159	2727	0.23	0.69	52.5	75.8	
Average	197	73,	59	4.1	236	100	1779	0.05	0.71	56.2	78.8	
1σ	43	10,	7	1.4	72	31	508	0.08	0.03	5.4	7.0	
Utaosa Rhyolite												
Routine re-extraction at 1300°C												
TRG04-1	263	103,	84	10.7	199	122	54.9	4.70	0.79	1.98	2.49	
TRG04-2	337	97,	97	15.0	119	68	32.0	1.38	0.81	1.95	2.41	
TRG04-3	200	97,	87	8.0	180	84	48.0	0.42	0.78	1.98	2.52	
Average	267	99,	90	11.2	166	92	45.0	2.17	0.80	1.97	2.48	
1σ	56	3,	6	2.9	34	23	9.6	1.83	0.01	0.01	0.05	
Repeated extraction at 1300°C with 30 min steps												
TRG04-S1[a]	229	131,	86	12.1	124	81	34.8	0.64	0.81	1.99	2.47	2
TRG04-S2[a]	240	91,	81	8.4	214	196	68.9	1.96	0.78	2.18	2.80	4
TRG04-S3[a]	194	103,	93	8.7	110	69	35.2	0.52	0.79	2.28	2.88	2
TRG04-S4[a]	189	86,	76	5.8	216	161	65.6	0.00	0.76	2.12	2.80	2
TRG04-S5[a]	320	91,	81	11.2	164	85	43.4	0.33	0.79	1.94	2.47	2
Average	234	101,	83	9.2	166	119	49.6	0.69	0.78	2.10	2.68	
1σ	47	16,	6	2.2	44	51	14.8	0.67	0.02	0.12	0.18	

RE is a volume of re-extracted ^{4}He normalized to total ^{4}He. Width was measured in two directions for each zircon having tetragonal morphology: the left number in the column shows longer width for each.

[a] Samples for repeated laser heating and ^{4}He measurement, for which RE represents second extraction.

[b] Not included in calculating the average.

helium (see 'RE' column in Table 1). This indicates that outgassing was approximately complete for most zircons but possibly incomplete for others using the heating conditions proposed earlier (1300°C, 30 min [38]). Therefore calculated ages are lower limits (this issue is examined in more detail below).

As shown in Fig. 1, (U–Th)/He ages of FCT, BT and UR are in reasonable agreement with their reference ages, excluding a young outlier for FCT. Mean α ejection-corrected He ages are 28.6 ± 1.4 (1σ), 16.1 ± 2.2 and 2.48 ± 0.05 Ma, respectively. These data suggest that (U–Th)/He dating using Nd-YAG laser extraction is basically applicable for zircon single grains. However, the He ages of TR are consistently too old and with far more scatter, with a mean age of 78.8 ± 7.0 Ma. This old age cannot be attributed to inheritance of He from some earlier generation of zircons because He is extremely rapidly lost at magmatic temperatures.

We inspected spontaneous and induced fission track densities of TR zircons previously analyzed for zeta calibration [39] and found that about 80% of these zircons are strongly zoned, with high track density (i.e., high U content) in the core and low density on the rim (see Fig. 2). This type of zonation causes overestimation of α ejec-

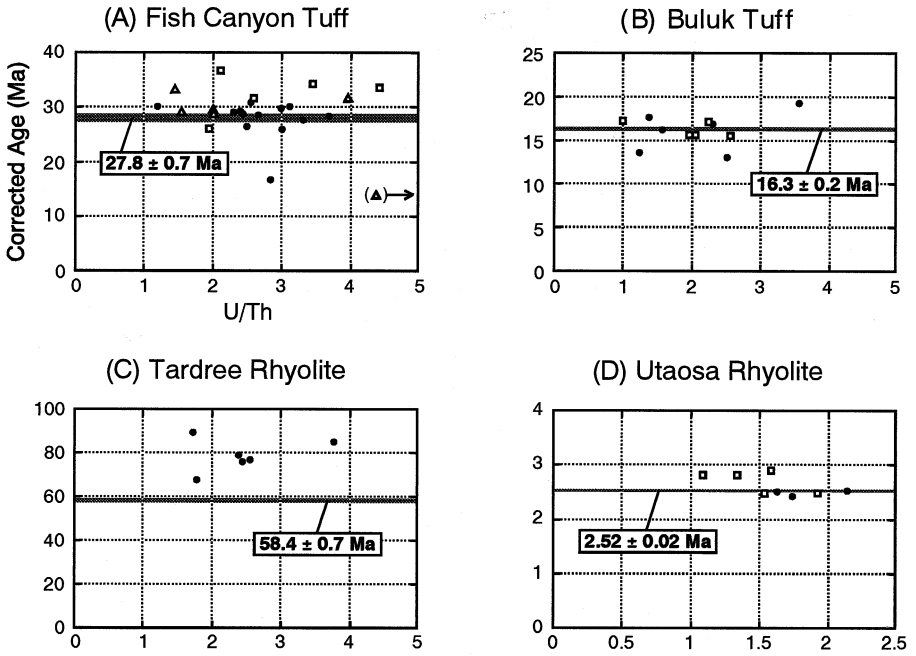

Fig. 1. (U–Th)/He age versus Th/U of zircons from (A) Fish Canyon Tuff, (B) Buluk Tuff, (C) Tardree Rhyolite and (D) Utaosa Rhyolite. Solid circles represent single-grain ages measured using a routine re-extraction at 1300°C; open boxes using a 30 min repeated extraction at 1300°C; and open triangles using an isothermal heating at 1200–1350°C for increasing time intervals of 1–20 min. Analytical precision is about 2% (1σ) throughout, smaller than the size of symbol. Shaded zones show reference ages.

tion losses that may account for the overestimation of He ages for TR zircons. In the extreme case of all U and Th located more than ~25 μm from the grain edges, no α ejection correction would be required, so the raw He age provides a minimum estimate of the age of the TR zircons: 56.2 ± 5.4 Ma. This is not far from the reference age of 58.4 ± 0.7 Ma. To more quantitatively assess this phenomenon we estimated the ejection losses for the degree of zonation suggested by the fission track mapping as shown in Fig. 2. The grain was assumed to be a 70×70×200 μm tetragonal prism with two homogeneous zones: a 17 μm cross-section inner zone an order of magnitude higher in U than the outer zone. We used a Monte Carlo simulation for α ejection [3] to estimate a revised fraction of αs retained (F_T) of 0.872, significantly higher than the homogeneous case, $F_T = 0.73$ (a value which well represents the average of six TR zircon grains, 0.71; Table 1). Thus if this calculation is representative then our reported ages are overcorrected for ejection by ~20% and the zonation-corrected mean age of six TR zircons would be 64.4 ± 6.2 (1σ) Ma, which is closer to but still somewhat higher than the reference age. Since every grain is probably zoned differently this calculation only approximates the magnitude of the induced error. These observations indicate that a careful check of the U (and Th) distribution is needed for reliable (U–Th)/He dating of zircons. Inspection of track densities indicates that such strong zonation of U is not common for other samples that we dated, i.e., FCT, BT and UR zircons.

To assess the possibility of under-extraction of He as indicated by He release in the re-extraction step and the anomalously young age on sample FCTZr-4 (Table 1), we performed additional stepped outgassing experiments involving several 30 min steps at 1300°C on five zircon grains for each of FCT, BT and UR samples (Fig. 3; see also Table 1). To assess the effects of grain size on He outgassing some especially large grains of BT and FCT were selected for this experiment.

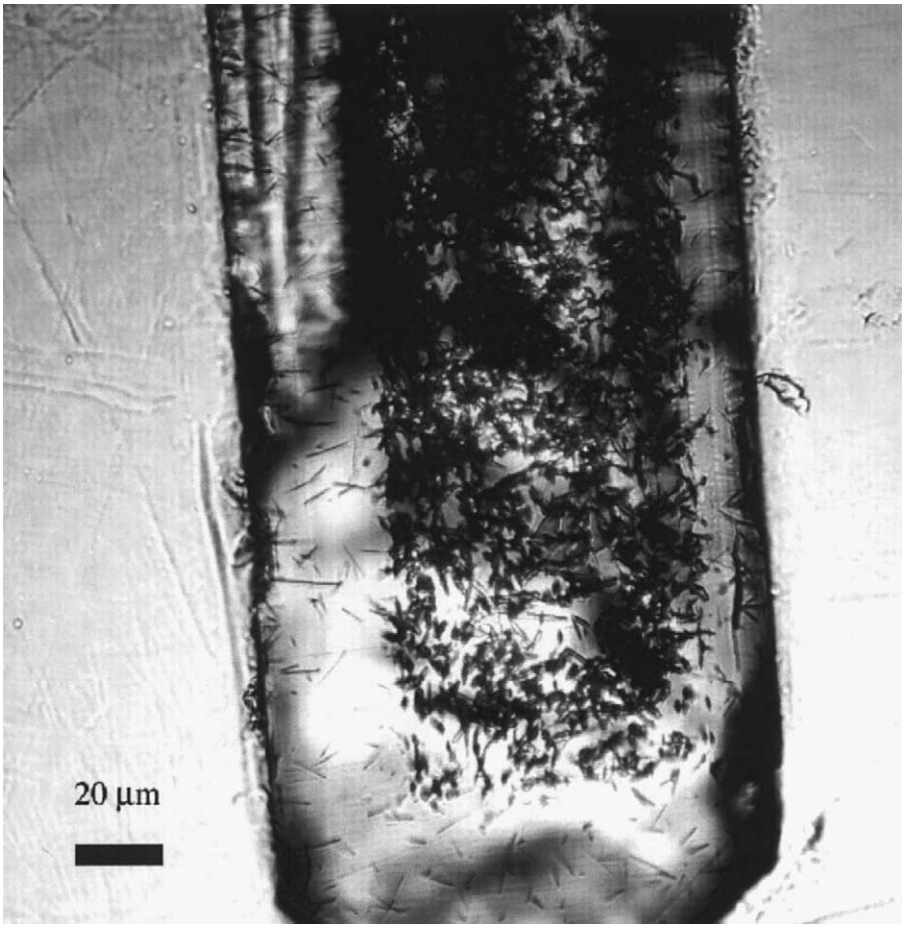

Fig. 2. A photograph of etched spontaneous fission tracks in a Tardree Rhyolite zircon, showing a typical zonation with high track density (i.e., high U content) at the core and low density at the rim. No spatial correlation is observed between the zone of high track density and inclusions contained. Note that a similar pattern of zonation is observed for induced tracks on muscovite external detector produced by neutron irradiation. This characteristic zonation causes an overestimation of the α ejection correction and explains the overestimation of He ages for the zircons.

The 30 min steps were repeated until the ^{4}He obtained dropped to $<1\%$ of the cumulative amount extracted. For four of the samples (FCTZr-S2, FCTZr-S3, BTZr-S2 and TRG04-S1), the analysis was repeated once more beyond this cutoff.

The amount of ^{4}He released at each step decreases steadily as the laser heating proceeds (Fig. 3). Eight of the 15 grains (five FCT, two BT and one UR) yielded $<1\%$ additional He by the second extraction. For all of the samples except FCTZr-S1, the $<1\%$ figure was achieved by the third or fourth step. In addition, further heating of these samples resulted in the extraction of a negligible additional amount of He ($<0.4\%$). These lines of evidence suggest that the residual ^{4}He retained after the routine single step re-extraction protocol represents less than a few percent of the total ^{4}He in the grain. Sample FCTZr-S1, however, yielded a prolonged ^{4}He degassing pattern for seven steps, or 3.5 h of heating (Fig. 3). We have no explanation for this unexpected behavior. Such high retentivity would cause a substantial underestimation of the ^{4}He in this sample if multiple re-extraction steps were not performed. Because the first series of analyses

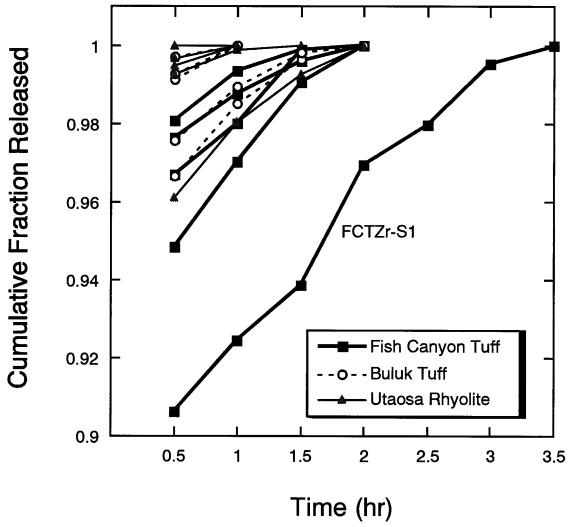

Fig. 3. Sum of degassed ^{4}He volumes normalized to total ^{4}He versus total time of laser heating for zircon single grains. The 30 min laser heating at 1300°C and ^{4}He measurement were repeated on five grains for each of Fish Canyon Tuff, Buluk Tuff and Utaosa Rhyolite. The analysis was repeated until the extracted ^{4}He volume becomes less than 1% of that totally extracted. The ^{4}He volume released at each step shows, in general, a monotonic decrease as the laser heating and degassing proceeds.

were performed using just a single re-extraction step, this phenomenon may explain the underestimation of the He age of sample FCTZr-4. Consistent with this possibility, this grain yielded the highest re-extraction signal of the 13 FCT zircons (Table 1).

Overall, it is clear that while lasing at 1300°C for ~1 h is sufficient to extract essentially all He from most zircons we studied, for some rare grains complete extraction at this temperature may require an extremely long period.

U and Th contents were also measured on the 15 zircon grains used for the repeated degassing experiment. U and Th blank corrections were improved for the BT samples because larger grains were selectively employed for the experiment (Table 1; note the difference of average mass between the two groups) and the resulting ages (average 16.1 ± 0.8 Ma) are in better agreement with the reference age. Five UR zircons also show approximately consistent ages with the reference, averaging 2.68 ± 0.18 Ma. Along with the first series of data, the ages give a grand average of 2.61 ± 0.18 Ma for UR.

The five FCT zircons (FCTZr-S1 to -S5; Table 1), however, exhibit a large scatter of ages with an average of 32.2 ± 3.6 Ma, significantly older than the reference. He blanks are far too low to account for this discrepancy, so this overestimation of age probably reflects a systematic underestimation of U and Th contents for these repeatedly heated samples. In fact, the average U and Th contents are lower on average for these five FCT zircons than for those analyzed with just a single re-extraction step (Table 1). Three explanations may be considered for this observation: (a) U volatilization during lasing [9], (b) incomplete dissolution of zircons during fluxing, and (c) fragmentation and partial loss of zircons due to the repeated laser heating and subsequent cooling. In the case of (a), significant U or Th volatilization

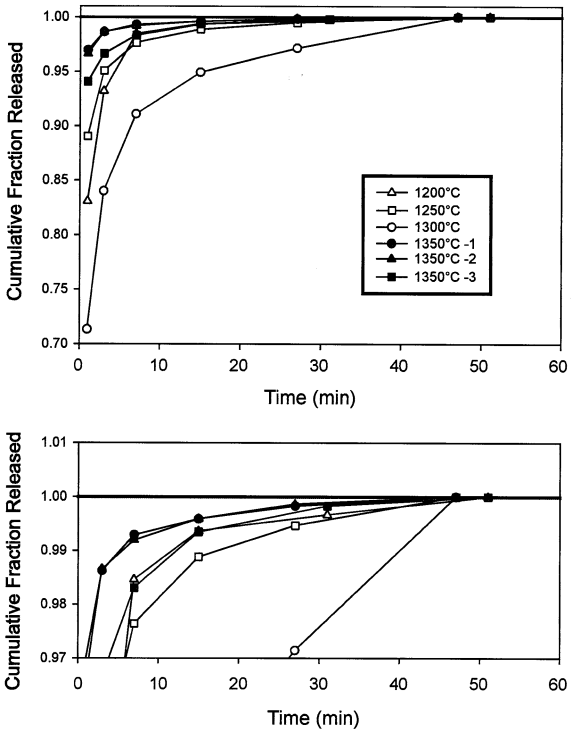

Fig. 4. Sum of degassed ^{4}He volumes normalized to total ^{4}He versus total time of laser heating for FCT zircon single grains. Isothermal laser heating was repeated for each grain at 1200–1350°C for increasing time intervals of 1–20 min, with a particular focus on the initial stage of ^{4}He degassing.

results in overestimated ages and an inverse correlation between U/Th and age (see fig. 6 of [9]), which is not observed in the present case (Fig. 1). The second case is also unlikely as these grains were melted in the same way as those analyzed earlier. Although some of the FCT grains subjected to long duration outgassing were unusually large and therefore may have been more difficult to flux melt, others (e.g., FCTZr-S3 and -S4) were smaller yet still gave systematically older ages (Table 1). Case (c) seems most likely because all five FCT zircons were lased at least four times during the repeated degassing experiment. These grains are subjected to extremely rapid heating (20°C to 1300°C in <60 s) and similarly fast cooling, suggesting the possibility of thermally induced fracturing. The Pt tubes which hold the grains are only loosely closed, so some fragments may be able to escape prior to dissolution. In any case, the present data provide an important precaution in handling/analyzing single-grain zircon samples using the laser heating procedure.

To identify a faster and more robust degassing procedure, we explored variable temperatures of laser heating: six FCT zircons were subjected to repeated isothermal lasing at 1200–1350°C for increasing time intervals of 1–20 min (Fig. 4). The six samples yield a consistent pattern of ^{4}He release, which first proceeds rapidly for a few minutes, with a monotonic decrease in the degassing rate in the following intervals. The present data, coupled with the repeated lasing experiment described above (Fig. 3), suggest that the amount of ^{4}He released decreases monotonically with total heating time for single zircon grains. Five samples were essentially completed degassed of He within 20 min. However, as seen earlier, a single grain (FCTZr1300°C), run at 1300°C, seems to have anomalously tightly retained helium. This sample yielded prolonged ^{4}He degassing with 2.9% of total gas released in the final step, i.e., between 27 and 47 min. In general this experiment implies that ^{4}He diffusivity increases with temperature, but the degassing rate must also be controlled by other as yet unidentified factors that vary within the FCT population (see also Fig. 3). The curves in Fig. 4 show that for reasonable lasing times (<30 min), a temperature of 1300–1350°C is sufficient for most but not all grains. Whether a higher temperature would have successfully extracted all of the He from the anomalous sample is unknown. Achieving substantially higher temperatures with our current technique is difficult because at temperatures >1400°C the Pt package is prone to failure.

To verify that the 1350°C lasing does not cause U–Th loss, U and Th contents were measured on the six zircon grains (Table 1). Except the 1300°C sample with high He retention, all samples yielded ages of 28.7–33.1 Ma, with an average of 30.3 ± 1.6 Ma. In particular, the three grains heated to 1350°C yield an average of 29.1 ± 0.3 Ma, approximately concordant with the mean age of 28.6 ± 1.4 Ma using the routine single re-extraction procedure (Table 1). Although perhaps coincidental, these results appear to be more accurate than those from grains subjected to a larger number of repeated extractions at a lower temperature. Along with faster ^{4}He release, this implies that the 1350°C lasing may be preferred, although further detailed investigations are strongly needed. The age of the anomalous 1300°C sample is just 14.1 Ma, probably as a result of (extremely) incomplete degassing. This again gives an important precaution that some of the FCT zircon grains are difficult to completely degas.

5. Conclusions

1. (U–Th)/He dating using Nd-YAG laser is basically applicable for single zircon grains. Measured (U–Th)/He ages are 28.6 ± 1.4 Ma for Fish Canyon Tuff, 16.1 ± 0.8 Ma for Buluk Tuff and 2.61 ± 0.18 Ma for Utaosa Rhyolite.
2. Tardree Rhyolite zircons yield He ages that are too old and much more variable than the other samples, an effect we attribute to U zonation observed in fission track maps. Because strongly zoned U concentrations can affect the α ejection correction, a careful check of U and Th distribution within a dated grain population is highly desirable for reliable dating. Populations with strong and probably variable zonation cannot in general yield accurate

or reproducible He ages. We improved the F_T modeling of Tardree Rhyolite zircons by incorporating the estimated U and Th zonation. An approximate ejection correction that incorporates zonation indicates a mean age of 64.4 ± 6.2 Ma, which is closer to the reference age than the conventional correction yields.

3. The repeated lasing and degassing experiments suggest that the amount of ^{4}He released decreases monotonically with total heating time for single zircon grains. For most samples heating to 1300–1350°C for 1 h is sufficient to extract >99% of He in the zircon. However, occasional samples of FCT retain He much more tightly. This observation suggests that a routine protocol for dating zircons should involve as many re-extraction steps as necessary to ensure He extraction, rather than the standard two steps we initially adopted in this study. Unfortunately multiple re-extraction steps may cause fragmentation and loss of zircon prior to U and Th analysis. Further work is needed to establish why some zircon grains are much more He retentive than others from the same population.

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