Integrated Single Crystal Laser Ablation U/Pb and (U-Th)/He Dating of Detrital Accessory Minerals – Proof-of-Concept Studies of Titanites and Zircons from the Fish Canyon Tuff

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Abstract

Excimer laser technologies enable a rapid and effective approach to the simultaneous U/Pb geochronology and (U-Th)/He thermochronology of a wide range of detrital accessory minerals. Here we describe the ‘laser ablation double dating’ (LADD) method and demonstrate its viability by applying it to zircon and titanite crystals from the well-characterized Fish Canyon tuff. We found that LADD dates for Fish Canyon zircon ($^{206}\text{Pb}/^{238}\text{U} - 28.63 \pm 0.11$ Ma; (U-Th)/He – 28.38 ± 0.73 Ma) are statistically indistinguishable from those obtained through established, traditional methods of single-crystal dating. The same is true for Fish Canyon titanite LADD dates: $^{206}\text{Pb}/^{238}\text{U} - 28.08 \pm 0.90$ Ma; (U-Th)/He – 27.98 ± 0.86 Ma. As anticipated, given that LADD involves the analysis of smaller amounts of material than traditional methods, it yields dates with higher analytical uncertainty. However, this does not substantially reduce the utility of the results for most applications to detrital datasets. An important characteristic of LADD is that it encourages the chemical characterization of crystals by backscattered electron, cathodoluminescence, and/or Raman mapping prior to dating. In addition, by permitting the rapid and robust dating of crystals regardless of the degree of their abrasion during sedimentary transport, the method theoretically should yield dates that are more broadly representative of those of the entire population of detrital crystals in a natural sample.

1. INTRODUCTION

Coordinated geochronometry and thermochronometry of detrital accessory minerals in sedimentary rocks and sediments can provide important insights regarding both sediment provenance and the thermal evolution of source regions. In recent years, a number of studies of this kind have been conducted, with special emphasis on combining

U/Pb and either (U-Th)/He or fission-track methods, a procedure often referred to in the literature as ‘double dating’ (e.g. Rahl et al., 2003; Reiners et al., 2005; Bernet et al., 2006; Kirstein et al., 2010; Saylor et al., 2012; Painter et al., 2014; Tang et al., 2014; Wang et al., 2014). In some cases, all three techniques have been combined for ‘triple dating’ of detrital apatites (e.g., Carrapa et al., 2009; Zattin et al., 2012). Projects involving a combination of U/Pb geochronology and (U-Th)/He thermochronology typically have relied on ‘laser ablation, inductively coupled plasma-source mass spectrometry’ (LA-ICPMS) microanalytical techniques for U/Pb, and what might be called ‘conventional’ analytical techniques for (U-Th)/He, which yields cooling dates for entire single grains. In principle, the relatively recent development of laser ablation microanalytical methods for (U-Th)/He thermochronology (Boyce et al., 2006) presents the opportunity for a different approach: integrated laser ablation U/Pb and (U-Th)/He dating of individual accessory mineral crystals.

Several characteristics of laser ablation helium dating are particularly attractive for work on detrital samples (Tripathy-Lang et al., 2013). Conventional (U-Th)/He protocols require the application of an alpha ejection correction to calculated ‘raw’ dates (Farley et al., 1996). This calculation depends on knowledge of the shape and size of each dated crystal, both of which can be modified significantly during transport from a sediment’s source to the site of its deposition. In addition, U and Th zoning in accessory minerals can negatively affect the robustness of alpha ejection corrections if not properly taken into account. Conventional (U-Th)/He thermochronology procedures used in most laboratories offer no opportunity to characterize zoning in crystals prior to destructive analysis, or to use that information to make better informed alpha ejection corrections using methods outlined by several research groups (Reiners et al., 2004; Hourigan et al., 2005; Herman et al., 2007; Gautheron et al., 2012). The laser ablation method addresses both of these potential problems by eliminating the need for an alpha ejection correction. In addition, it does not require some of the most time-consuming steps of the conventional (U-Th)/He procedure (e.g., chemical digestion of each grain in preparation for parent element isotopic measurements), and thus increases the number of crystals that can be dated in a detrital sample over a particular time interval. Such improved analytical efficiency can be especially valuable for detrital studies. Although most double- and

72 triple-dating studies thus far have yielded no more than a few tens of paired dates per
73 sample, it has been suggested by some researchers that no fewer than a hundred
74 (Vermeesch, 2004), and perhaps a thousand or more (Pullen et al., 2014), analyses might
75 be needed to fully characterize complex detrital age populations. Microanalytical
76 methods based on laser ablation improve sample throughput to the point that producing
77 such massive detrital datasets can be a realistically envisioned.

78 Here we report the results of a proof-of-concept study designed to establish the
79 viability of integrated U/Pb and (U-Th)/He ‘laser ablation double dating’ (LADD) of
80 individual detrital titanite and zircon crystals by ultraviolet laser ablation and quadrupole
81 mass spectrometry. While examples of detrital titanite dating in the literature are less
82 common than examples of detrital zircon dating, titanite is a common accessory mineral
83 in many igneous and metamorphic rocks and is nearly as abrasion resistant as zircon, so it
84 can be a useful target for detrital thermochronometry, especially for samples in which
85 zircons are scarce.

86 2. STUDY STRATEGY

87 In an earlier research paper (Tripathy-Lang et al., 2013), our group demonstrated the
88 viability of laser ablation (U-Th)/He dating of zircon from a detrital sample and showed
89 that conventional and laser ablation techniques, as applied to detrital zircons from the
90 same sediment sample, can be expected to yield comparable spectra of detrital dates.
91 However, the results of that study did not unambiguously demonstrate that the
92 conventional and laser ablation techniques would yield the same results for a well-
93 characterized standard material with a well-constrained age. Our aim for the current study
94 was to test this hypothesis through a comparison of conventional and LADD titanite and
95 zircon results. While it would have been straightforward to conduct this work on large,
96 gem-quality, chemically homogeneous crystals, such crystals are extremely
97 uncharacteristic of most detrital accessory mineral suites. Instead, we wanted to explore
98 the reproducibility of LADD and conventional results for zircon and titanite from a
99 standard material with a well-established age and a reputation for containing accessory
100 minerals that are: 1) abundant; 2) approximately the sizes encountered in fine- to
101 medium-grained sand deposits; and 3) complexly zoned in ways commonly encountered

in detrital accessory minerals suites. With these desired characteristics in mind, we decided to focus our study on the ~ 28 Ma Fish Canyon tuff (FCT; Lipman et al., 1970).

The Fish Canyon ash-flow tuff is the most voluminous eruptive product of the La Garita caldera in the San Juan volcanic field of Colorado (Lipman, 1975; Bachmann et al., 2002). Because it contains a wide variety of minerals commonly used for $^{40}\text{Ar}/^{39}\text{Ar}$, (U-Th)/He, and fission-track dating, it has become a popular standard in many laboratories worldwide. In particular, Fish Canyon sanidine is among the most reliable and widely used irradiation monitors for $^{40}\text{Ar}/^{39}\text{Ar}$, and is frequently employed for cross-calibration of other monitors (e.g., Cebula et al., 1986; Renne et al., 1998; Gleadow et al., 2015). As a consequence of its widespread adoption as a standard, there are numerous published U/Pb and (U-Th)/He dating results from various laboratories for FCT zircon and titanite against which our new laser ablation data can be compared.

In order to ensure a valid comparison of the conventional and LADD techniques in a single laboratory environment, we present here the results of conventional (U-Th)/He analyses of Fish Canyon titanite and zircon obtained in the Group 18 Laboratories at Arizona State University over an eight-year period (2006-2014), as well as new LADD U/Pb and (U-Th)/He data for the same minerals. As a consequence, previously published conventional results, conventional results from our laboratories, and our new LADD datasets all can be compared. Our study confirms that the LADD method yields results consistent with those obtained using more familiar and well-established whole-crystal methods, albeit with larger analytical uncertainties, as is typically the case with microanalytical techniques.

2. 1 Notable Previous Applications of the U/Pb and (U-Th)/He Chronometers to FCT Titanite and Zircon

Understanding the U/Pb ages of Fish Canyon tuff zircon and titanite have become especially important in recent years in light of attempts to improve our understanding of ^{40}K branched decay constants and reconcile the U/Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ dating techniques in pursuit of high accuracy geochronology as part of the international Earthtime initiative. Published $^{206}\text{Pb}/^{238}\text{U}$ dates for zircon determined through isotope dilution, thermal ionization mass spectrometry (ID-TIMS) range from 28.33 ± 0.15 Ma to 28.61 ± 0.08 Ma

and imply a rather extended crystallization period of ≥ 300 ka (Schmitz and Bowring, 2001; Bachmann et al., 2007). (Throughout this paper, all uncertainties in apparent ages are cited at the 2σ , ca. 95% confidence level.) For Fish Canyon titanite, Schmitz and Bowring reported an ID-TIMS $^{206}\text{Pb}/^{238}\text{U}$ date of 28.53 ± 0.05 Ma, whereas Chew et al. (2014) reported a LA-ICPMS concordia date of 28.78 ± 0.41 Ma. All of these dates were obtained for minerals from samples collected at the ‘classic’ Fish Canyon tuff collection site near South Fork, Colorado. Sampling outcrops at the site lie near the base of a ≥ 600 m-thick ignimbrite sheet and beneath several other younger units, suggesting that the sampled tuff may have experienced a somewhat complex cooling history (Gleadow et al., 2015). Gleadow and co-workers obtained ion microprobe $^{206}\text{Pb}/^{238}\text{U}$ dates for rims and interiors of zircons from a newly collected sample from the classic South Fork site (their FCT-1) with inverse-variance weighted means of 29.5 ± 0.6 Ma and 29.0 ± 0.6 Ma, respectively. They also reported ion microprobe $^{206}\text{Pb}/^{238}\text{U}$ dates for zircons separated from a sample (AG10-02) collected at a second site southeast of Del Norte, Colorado. More distal from the inferred center of the La Garita caldera than the classic site, there the ignimbrite sheet is only approximately 40 m-thick and presumably experienced more rapid post-eruption cooling than the sheet at the classic site. The reported ion microprobe $^{206}\text{Pb}/^{238}\text{U}$ dates for AG10-02 rims and interiors were 28.5 ± 0.6 Ma and 29.0 ± 0.4 Ma, respectively.

The most thorough study of (U-Th)/He systematics in Fish Canyon zircon to date has been that of Dobson et al. (2008) using grains from the classic site. Following Schmitz and Bowring (2001), they noted that individual zircon from the ignimbrite exhibit extreme (orders of magnitude) U and Th zoning, the nature of which varies from crystal to crystal. This undoubtedly introduces non-systematic errors in alpha ejection corrections for conventional (U-Th)/He dates for Fish Canyon zircon. From a compilation of conventional FCT zircon results from several laboratories that make routine measurements of this material, Dobson et al. (2008) calculated a mean apparent age of 28.3 ± 3.1 Ma and attributed the observed 10.9% dispersion to uncertainties introduced by applying an alpha ejection correction schema that assumed uniform U + Th in all crystals. Gleadow et al. (2015) reported inverse-variance weighted mean (U-Th)/He zircon dates of 28.7 ± 0.8 Ma for the classic locality and 28.4 ± 2.0 Ma for the locality SE

of Del Norte. Within the limits of analytical uncertainty, there is no discernable difference between (U-Th)/He zircon dates from the two different localities. There has been no systematic study of Fish Canyon titanite (U-Th)/He, but House et al. (2000) reported a mean apparent age for seven crystals from the classic site of 27.9 ± 2.2 Ma. Notably, given the relatively large magnitude of the uncertainties for the (U-Th)/He thermochronometers and the rapidity of post-eruptive cooling, the (U-Th)/He dates for FCT zircon and titanite are indistinguishable from the U/Pb dates for the same minerals.

3. ANALYTICAL METHODS

The analytical protocols for conventional (U-Th)/He dating of single crystals are well established and similar in nearly all laboratories worldwide. Specific procedures for our laboratories are described in the first section of the Electronic Annex for this paper (EA 1). The LADD method is procedurally very different in that it integrates ‘laser ablation, gas-source mass spectrometry’ (LA-GMS) and LA-ICPMS analytical techniques. We briefly outline the LADD protocols used for our FCT titanite and zircon studies in the paragraphs below (see also Figure 1), and provide a much more detailed description of the method in the second section of the Electronic Annex for this paper (EA 2).

Zircon crystals (≥ 100 μm in diameter) and titanite crystals (≥ 125 μm in diameter) were first mounted in a ‘puck’ of *Torr Seal*, a low vapor-pressure epoxy. The puck was then polished to remove the outer 20-30 μm of the crystals, which both eliminates the need for alpha ejection corrections and ensures a smooth surface for analysis. Next, both cathodoluminescence (CL) and backscatter electron (BSE) images were acquired before the puck was re-polished to eliminate the carbon coat and any (minimal) amount of the crystal surface that could have been damaged during electron beam imaging (e.g., Flude et al., 2013).

The CL and BSE images aid with targeting specific areas within each crystal for analysis. Targeted locations were selected to be at least 20 μm away from both the crystal boundaries as well as any inclusions (Figure 2). For Cenozoic zircons and titanites, we typically used 25 μm and 65 μm diameter laser footprints, respectively, for the LA-GMS analyses and larger (typically 65 μm for zircon and 110 μm for titanite), concentric

192 footprints for the LA-ICPMS analyses. Larger laser footprints were used for titanite
193 analyses to account for their typically lower parent isotope concentrations. It is important
194 to note that zoning patterns exhibited in the CL or BSE images were used primarily to
195 assist in our interpretations of LADD data, and that complex zoning was not used as a
196 selection criterion for crystals that will be dated.

197 Once we had marked the targeted locations on the CL or BSE images, we conducted
198 *in vacuo* laser ablation of the innermost, smaller pits for ^4He measurements. All LADD
199 analyses were performed with a Photon Machines (now Teledyne CETAC) *Analyte G2*, a
200 193 nm Atlex 300 ArF excimer laser. We used operating conditions that were slightly
201 different for titanite and zircon. For the former, we applied a 5 mJ laser energy at 100%
202 output power and a pulse frequency of 5 Hz for a total of 60 s. For zircon, the pulse
203 frequency was increased to 10 Hz and the duration of the ablation experiment was
204 decreased to 15 s. These operating conditions produced ablation pits roughly as deep as
205 the radius of the laser footprint.

206 Following ablation and gas purification, we measured ^4He using a modified version
207 of the extraction subsystem supplied as part of our ASI *Alphachron* analytical system –
208 described in more detail in the Electronic Annex (EA 2) – and a Pfeiffer-Balzars *Prisma*
209 quadrupole mass spectrometer for helium isotopic analysis.

210 After ^4He analyses, the ablated pits were scanned with an ADE PhaseShift
211 *MicroXAM* interferometric microscope, which generates a high-resolution digital
212 elevation model of the ablated pit and surrounding crystal surface. By processing these
213 data with an in-house *Matlab* script, we calculated a best-fit volume for the ablated pit,
214 and thus ascertained the concentration of ^4He from previously measured ^4He abundances.

215 We next determined the concentrations of contributing parent isotopes by LA-
216 ICPMS, integrating the *Analyte G2* laser system with a Photon Machines (Teledyne
217 CETAC) *HelEx Active* two-volume ablation cell and a Thermo Scientific *iCAP Q*
218 quadrupole mass spectrometer. For this portion of the analysis, we centered the laser over
219 the same spots ablated for the ^4He analysis, but increased the laser footprint diameter by
220 $\sim 40\text{--}45\text{ }\mu\text{m}$ and increased the number of laser pulses to ablate pits $\geq 20\text{ }\mu\text{m}$ deeper than
221 the ^4He pits (Figure 2). By doing so, we ensured that the parent element analyses

averaged over any compositional zoning that may have contributed ^4He to the first ablation pit, since the nominal alpha recoil distances for ^4He produced by U, Th, and Sm in titanite and zircon range from $\sim 16\text{-}20\ \mu\text{m}$ (e.g., Ketcham et al., 2011). Lasing conditions for the second ablation experiment on the Fish Canyon samples were: 5 mJ laser energy, 100% output power, 4 Hz pulse frequency, 90 s duration for titanite; and 5 mJ laser energy, 75% output power, 10 Hz pulse frequency, 40 s duration for zircon. Once the second cycle of ablation experiments was complete, we returned to the interferometric microscope to measure the volume of the newly ablated pits, following the same protocol implemented previously when measuring the volumes of the ^4He pits.

Since the LADD technique requires knowledge of both isotopic ratios and concentrations, we must employ concentration standards as well as isotope-ratio standards as part of the procedure. For isotope-ratio standards, we used both Plešovice (Sláma et al., 2008; $337.13 \pm 0.37\ \text{Ma}$) and 94-35 (Klepeis et al., 1998; $55.5 \pm 1.5\ \text{Ma}$) for zircon, and BLR-1 for titanite (Aleinikoff et al., 2007; $1047.1 \pm 0.4\ \text{Ma}$). Our composition standard for the Fish Canyon titanite work was a gem-quality titanite from San Quintín, Mexico (SQT1). While SQT1 is our best available titanite concentration standard at present, we remain concerned that subtle zoning variations in its U, Th, and Sm concentrations may add to the analytical uncertainty in laser ablation (U-Th)/He titanite dates that, because they are unquantified, cannot be rigorously propagated through the age equation. For the Fish Canyon zircon work, we used ‘SynZircon’, a sintered, synthetic rock made from micromilled zircon powder so as to have a uniform parent element composition (Monteleone et al., 2009).

4. RESULTS

4.1 Conventional (U-Th)/He Results

A total of 165 conventional, alpha-ejection corrected, (U-Th)/He dates for Fish Canyon zircons ranged from $31.60 \pm 0.92\ \text{Ma}$ to $24.40 \pm 0.88\ \text{Ma}$, with a simple inverse-variance weighted mean of $28.158 \pm 0.068\ \text{Ma}$ (Table 1; Figure 2a). The dispersion of these data (taken here as equivalent to two inverse-variance weighted standard deviations of the sampled population, in contrast to two standard deviations of the inverse-variance

weighted mean) is 11.0 %, a value essentially the same as that obtained by Dobson et al. (2008) for their multi-laboratory analysis. As were their results, these data are over-dispersed, which is to say that the dispersion cannot be explained by analytical uncertainty alone. Following Hourigan et al. (2005) and Dobson et al. (2008), we regard it as probable that this is due to erroneous alpha ejection corrections due to variable parent element zoning. The degree of over-dispersion can be quantified using the mean squared weighted deviation (MSWD) of data relative to the weighted mean (Wendt and Carl, 1991). For $n = 165$, the MSWD has an expected value of 1.00 ± 0.22 , but the MSWD for our conventional zircon dataset is 12.62. In the geochronology community, an established way to present more realistic uncertainties for over-dispersed datasets is to multiply the calculated inverse-variance weighted mean by the square-root of the MSWD (e.g., Ludwig, 2003). Doing so in this instance results in our preferred estimate of the conventional (U-Th)/He age of FCT zircon for comparison with LADD results: 28.16 ± 0.24 Ma.

The range of dates obtained using the conventional method for 41 titanite crystals was between 30.3 ± 1.0 Ma and 26.29 ± 0.60 Ma, with an inverse-variance weighted mean of 28.12 ± 0.12 Ma (Table 2; Figure 2b). The dispersion about this population was considerably less than that for zircon (5.1%), which probably reflects the lesser degree of chemical zonation apparent in Fish Canyon titanites as compared to zircons (Schmitz and Bowring, 2001). Nevertheless, this dataset is still over-dispersed; the MSWD is 3.44, as compared to the expected value of 1.00 ± 0.45 for $n = 41$. The same error-magnification approach as was used for the zircon population results in our calculation of 28.12 ± 0.22 Ma as the best estimate of the conventional titanite (U-Th)/He age.

4.2 Laser Ablation Double Dating Results

Using the analytical protocols described in Section 3, we analyzed 45 titanites and 44 zircons from the Fish Canyon ignimbrite by the LADD method (Tables 3 and 4). These minerals were separated from a sample of the tuff collected by KVH at the same locality southeast of Del Norte, Colorado, as sample AG10-02 of Gleadow et al. (2015).

Laser ablation $^{206}\text{Pb}/^{238}\text{U}$ dates for zircon ranged from 30.3 ± 1.5 Ma to 27.86 ± 0.74 Ma (Figure 3a), with a dispersion of 2.8%, which is easily explained by analytical imprecision alone (MSWD = 1.31). The inverse-variance weighted mean of all 44 results is 28.63 ± 0.11 Ma. Laser ablation $^{206}\text{Pb}/^{238}\text{U}$ dates for titanite had considerably higher analytical uncertainty due to the need for substantial correction of the analyses for common Pb. As noted earlier, our common Pb corrections were performed using ^{204}Pb . The ^{204}Pb measurements for these analyses were very near operational blank levels, such that they carried relatively large uncertainties, which propagated into large apparent age uncertainties. For example, the calculated dates ranged from 33.2 ± 9.2 Ma to 24.1 ± 5.4 Ma (Figure 3b). Despite the data having a relatively large (16.5%) dispersion, the magnitudes of the uncertainties are such that they readily account for the scatter. Collectively, the 45 analyses yield an inverse-variance weighted mean of 28.08 ± 0.90 Ma (MSWD = 0.59).

Laser ablation (U-Th)/He dates from the same zircons and titanites for which $^{206}\text{Pb}/^{238}\text{U}$ dates were obtained are illustrated in Figure 2c and 2d. (For these, as for all laser ablation (U-Th)/He dates, no alpha-ejection corrections were necessary.) Zircon dates ranged from 33.6 ± 2.6 Ma to 23.2 ± 1.8 Ma, whereas titanite dates ranged from 33.8 ± 3.6 to 23.6 ± 1.2 Ma, with dispersions of 17.0 and 20.6%, respectively. Both datasets were over-dispersed (MSWDs of 4.58 for zircon and 15.53 for titanite) and we consequently multiplied the nominal 2σ uncertainty for the inverse-variance weighted means by the square root of the MSWD to arrive at more realistic uncertainties for the calculated means: 28.38 ± 0.73 Ma for zircon and 27.98 ± 0.86 for titanite.

5. DISCUSSION

LADD results for Fish Canyon tuff titanites and zircons compare well with previously published U/Pb and (U-Th)/He results, as well as conventional (U-Th)/He results from our laboratories. Our inverse-variance weighted mean laser ablation $^{206}\text{Pb}/^{238}\text{U}$ date for Fish Canyon zircon (28.63 ± 0.11 Ma) overlaps the high end of the published range of ID-TIMS dates for these materials from the classic site (Schmitz and Bowring, 2001; Bachmann et al., 2007), and is statistically indistinguishable from the ion microprobe $^{206}\text{Pb}/^{238}\text{U}$ zircon interior and rim dates reported by Gleadow et al. (2015) for their

sample from this locality. Our inverse-variance weighted mean laser ablation $^{206}\text{Pb}/^{238}\text{U}$ date for Fish Canyon titanite (28.08 ± 0.90 Ma) is also indistinguishable from published ID-TIMS and LA-ICPMS results (Schmitz and Bowring, 2001; Chew et al., 2014).

The inverse-variance weighted means for conventional (U-Th)/He dates determined for zircon (28.16 ± 0.24 Ma; $n = 165$) and titanite (28.12 ± 0.22 Ma; $n = 41$) from the classic site presented here are statistically the same as laser ablation dates for the two minerals from the site SE of Del Norte, Colorado. The same can be said for comparisons between our laser ablation (U-Th)/He dates and conventional dates reported by other researchers from both sampling sites (House et al., 2000; Dobson et al., 2008; Gleadow et al., 2015).

While our proof-of-concept study appears to confirm the *accuracy* of LADD results, at least for Fish Canyon titanite and zircon, the *precision* and *dispersion* of these results bear further scrutiny. It is not surprising that microanalytical methods yield lower precision than bulk methods such as ID-TIMS U/Pb or conventional (U-Th)/He. Comparing U/Pb results for Fish Canyon zircon, the LADD $^{206}\text{Pb}/^{238}\text{U}$ protocols described in Section 3 yield precisions slightly less than an order of magnitude worse than ID-TIMS dates. Due to the need for common Pb corrections, the fact that we used ^{204}Pb measurements for those corrections, and the reality that measured ^{204}Pb abundances were near blank levels, our individual $^{206}\text{Pb}/^{238}\text{U}$ dates for Fish Canyon titanites were about two orders of magnitude less precise than published ID-TIMS dates (Schmitz and Bowring, 2001).

The propagation of analytical uncertainties only – without regard to uncertainties in the alpha ejection correction – leads to an average 2σ uncertainty in our individual, conventional, zircon (U-Th)/He dates of roughly 3.1%. For comparison, uncertainties in our laser ablation (U-Th)/He dates for individual zircon crystals are almost six times larger, averaging 17.8%. Dispersion of the conventional and laser results are similar, however: two inverse-variance weighted standard deviations of the conventional and laser ablation data are 3.1 Ma and 4.8 Ma, respectively. We interpret this similarity, despite the significant difference in analytical precision, as a reflection of the fact that the laser ablation method reduces over-dispersion associated with parent-element zoning

(Hourigan et al., 2005; Dobson et al., 2008). Unfortunately, this improvement is masked to some extent by the larger uncertainties in the laser ablation data.

Both the average 2σ uncertainty in our individual, laser ablation, titanite (U-Th)/He dates (13.2%) and the dispersion of the dataset overall (5.8 Ma) are much higher than the equivalent parameters for conventional (U-Th)/He data (5.5% and 1.4 Ma). Similar to the uncertainties in the laser ablation (U-Th)/He zircon ages, the imprecision of the titanite ages derives primarily from uncertainty in ^4He measurements (Table 5). Other primary contributors to the uncertainty budget are measurements of the ablated pit volumes and uncertainties in the U, Th, and Sm concentrations of the SynZircon and SQT1 standards.

5.1 Improving Precision

The precision of both zircon and titanite LADD analyses could be improved in multiple ways. With regard to U/Pb analyses, installation of an effective mercury filter on the LA-ICPMS system would minimize propagated uncertainties related to the ^{204}Hg correction to ^{204}Pb and, thus, to common Pb corrections. In addition, using a magnetic sector mass spectrometer for the LA-ICPMS work instead of a quadrupole could yield higher precision measurements for U, Th, and Pb isotopes. However, doing so would limit analytical flexibility and reduce some opportunities for building on the technique, as discussed below.

With regard to laser ablation (U-Th)/He dating using the specific protocols described in Section EA 2, a sensitivity analysis shows that, by far, most of the final apparent age uncertainty (nearly 50%) can be attributed simply to uncertainties in the measurement of ^4He (Table 5). Thus, the shortest route to improved precision in the overall technique is through modified analytical protocols that employ a different mass spectrometry system for LA-GMS analyses that could permit higher precision ^4He measurements. For the proof-of-concept study reported here, it was our intention to show how the same kinds of small quadrupole mass spectrometers typically found in laboratories doing conventional (U-Th)/He thermochronology could also be used for laser ablation studies when an excimer laser microprobe is also available. However, in our laboratories, we more frequently use our Thermo Scientific *Helix SFT* magnetic sector mass spectrometer for

helium analyses in support of LADD work. Beyond the higher ^4He sensitivity of this instrument (and better constraints on that sensitivity), it permits more precise quantification of system blanks, which dramatically improves the precision of ^4He measurements. We have found that, on average, the precisions for individual laser ablation zircon (U-Th)/He dates obtained using the *Helix SFT* are two- to three-times better than those obtained using a small quadrupole for ^4He measurements (compare the results of Tripathy-Lang et al., 2013, to those presented here). We anticipate the same to be true for titanite.

To a lesser extent, the uncertainty of laser ablation (U-Th)/He dates is also affected by propagated uncertainties in U, Th, and Sm concentrations for matrix-matched standards. An important focus of our methods-development research at present is the identification and characterization of suitable natural and synthetic LADD standards. We have high expectations for the increased utility of synthetic materials such as the SynZircon used for the Fish Canyon zircon LADD results reported here, and are expanding our experiments with synthetic rocks produced from micromilled natural minerals to include apatite, rutile, and titanite.

A question we commonly encounter in the course of discussions about the LADD method is the extent to which uncertainties in ablated pit volume measurements propagate into uncertainties in the final laser ablation (U-Th)/He ages. As Table 5 shows, these uncertainties contributed roughly 21-27% of the total error. For the Fish Canyon zircon data, for example, a 50% increase or decrease in the uncertainties assumed for measured ablation pit volumes would increase age uncertainties by only about 9%.

Ultimately, the nature of a particular geochronologic problem dictates the level of analytical precision required to address it. For many – if not most – detrital studies, uncertainties of the magnitude we obtained for individual $^{206}\text{Pb}/^{238}\text{U}$ and (U-Th)/He dates in our Fish Canyon study would likely not significantly affect geological interpretations of the results.

5.2 Prospects

As explained in detail by Tripathy-Lang et al. (2013), there are both advantages and disadvantages associated with employing laser ablation methods for (U-Th)/He detrital mineral thermochronometry, and the same can also be said more generally for the LADD methods discussed here. LADD benefits (U-Th)/He detrital dating by obviating the need for alpha-ejection corrections, by minimizing the effects of alpha-redistribution from inclusions or alpha-injection from neighboring crystals, and by enabling the robust analysis of detrital crystals that are substantially rounded. However, the method is less well suited for detrital crystals derived from source regions that have experienced extremely slow cooling histories. Such a cooling history can lead to marked intracrystalline diffusive loss gradients in radiogenic helium that can hinder meaningful interpretations of laser ablation (U-Th)/He dates. Similarly, extremely rapid cooling (and/or source regions with very low relief) can lead to a low variation in (U-Th)/He dates in a detrital sample that might not be distinguishable given the lower precision of the laser ablation method as compared to the conventional method. Care also must be taken when analyzing detrital samples in which a large component of the available crystals are smaller than the minimum diameters required to reliably conduct LADD because this could bias inferences regarding the true spectrum of apparent ages in a detrital sample. However, we regard the advantages of LADD to outweigh the disadvantages for most studies.

Theoretically, the LADD technique is also applicable to minerals such as apatite, rutile, and the orthophosphates monazite and xenotime. High parent-element concentrations make LADD dating of monazite and xenotime straightforward, but lower concentrations and higher common Pb make apatite and rutile LADD more challenging. Preliminary work on rutile is promising, although relatively coarse crystals may be required to ensure that sufficiently large ablation pits can be used to obtain enough ^4He for relatively precise analysis. Unfortunately, we suspect that most detrital apatites are too low in U, Th, Sm, and ^4He for effective LADD dating.

5.3 Including Complimentary Analyses

Although the use of a quadrupole mass spectrometer for U, Th, Sm, and Pb isotopic measurements in support of LADD may require a sacrifice of analytical precision compared with the use of a magnetic sector instrument, the capacity of a quadrupole instrument to rapidly scan a range of elements presents additional opportunities for characterization of individual mineral grains. For example, we have recently started including the routine analysis of Zr in titanite and rutile, as well as Ti in zircon, to enable the application of a variety of element partitioning thermobarometers (Ferry and Watson, 2007; Hayden et al., 2008).

One of the more significant developments in (U-Th)/He thermochronology in recent years has been evidence that alpha radiation damage can substantially affect the diffusivity of ^4He in accessory minerals and thus the paleo-temperatures corresponding to measured (U-Th)/He ages (Shuster et al., 2006; Flowers et al., 2009; Gautheron et al., 2009; Guenthner et al., 2013; Guenthner et al., 2014). For zircon, it has been suggested that reasonable corrections for this effect can be made using effective alpha doses calculated from the effective uranium (eU) concentrations – where $eU = U + 0.235Th$ – and an independently determined zircon fission-track date for an estimate of the time since a crystal last cooled below the threshold temperature for long-term radiation damage annealing (Guenthner et al., 2013). This approach requires the assumption that effective alpha dose is a reasonable proxy for alpha radiation damage. The potential for a more direct approach derives from the observation that non-destructive Raman spectroscopy can be used to quantify the degree of alpha radiation damage in zircon (Nasdala et al., 1995; Nasdala et al., 2001; Nasdala et al., 2006). The LADD sample preparation strategy described here enables the addition of Raman spectroscopic mapping to the suite of pre-analytical sample characterization activities if so desired.

5.4 Other Variations of the Technique

Vermeesch et al. (2012) presented a different variation of laser ablation (U-Th)/He dating by employing LA-ICPMS coupled with further modifications of the methods used by Boyce et al. (2006; 2009). Their aim was to simplify and streamline laser ablation (U-

Th)/He dating by pairwise analysis of unknowns and standards for which the ‘correct’ (U-Th)/He age can be assumed. In their approach, (U-Th)/He dates of the unknowns could be determined by normalizing isotopic abundances and pit volumes to those obtained for standards analyzed during the same session. In theory, this approach eliminates the need for measuring ablation pit volumes. Evans et al. (2015) illustrated how the pairwise protocol could be modified and improved upon to include the LA-ICPMS measurement of Pb isotopes in addition to ^4He parent element isotopes in order to enable *in situ* (U-Th)/He and U/Pb double dating. Notably, the reliability of the pairwise approach to (U-Th)/He dating is strongly dependent on: 1) the availability of appropriate parent element concentration standards; and 2) either the assumption that ablation rates are identical in both the standards and the unknowns, or that differences can be adequately corrected for with an ablation-rate proxy. We have not adopted the pairwise approach because, in our experience, ablation rate is dependent on mineral chemistry, mineral structure, and the quality of surface polish, all of which can vary substantially across a single unknown or standard crystal. For example, in the course of measuring ablation pit volumes for the data reported here, we found that ablation rates in polished FCT titanites and zircons varied by a factor of two to three. Even so, both Vermeesch et al. (2012) and Evans et al. (2015) demonstrated the first-order viability of the pairwise approach by showing that it yielded dates comparable to conventional results for large crystals of Sri Lankan zircon (a standard material; Nasdala et al., 2004) and lamproite zircons from the Ellendale diamond mine in Western Australia (previously studied by Evans et al., 2012).

6. CONCLUSIONS

Laser ablation procedures simplify and accelerate the U/Pb and (U-Th)/He ‘double dating’ of detrital mineral suites, and may reduce or eliminate sampling biases related to selective picking of well-formed crystals for conventional (U-Th)/He analyses. In this contribution, we have outlined effective methods for laser ablation double dating of detrital titanite and zircon, building from previously well-established protocols for LA-ICPMS U/Pb geochronology. A proof-of-concept study using titanites and zircons separated from a sample of the Fish Canyon tuff confirms the viability of the method and

illustrates typical levels of analytical uncertainty that might be expected when a small quadrupole mass spectrometer – like that used for most conventional (U-Th)/He studies – is used for helium analyses. In general practice, the protocols described here result in analytical precisions for individual Cenozoic (U-Th)/He dates of between 10 and 20% at the ~ 95% confidence level, roughly three times worse than typical analytical uncertainties on conventional (U-Th)/He dates. However, these uncertainties can be reduced by up to two-thirds through the use of a magnetic sector instrument for LA-GMS measurements and through the development and careful characterization of better matrix-matched composition standards for U, Sm, and Th. Such protocols reduce the imprecision of laser ablation (U-Th)/He dating to nearly the level of conventional dating performed on quadrupole mass spectrometers.

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FIGURE CAPTIONS

- Figure 1.** Flow chart of the protocol implemented for LADD (as detailed in Section 3). Common flow chart symbology is employed. Hexagons indicate a preparation. Rectangles indicate a process. Parallelograms indicate intermediate data products. Ellipses indicate final data products. Workflow direction is indicated by arrowed lines.
- Figure 2.** $\frac{3}{4}$ plan view of a mounted crystal after analysis (left) and a cross sectional view of the ablated pits showing the rough dimensions of the U + Th + Sm pits (right). Dashed lines in the cross section indicate the location of the crystal surface, pre-ablation, as well as the location of the ^4He pit prior to ablation of the U + Th + Sm pit.

Figure 3. Conventional (U-Th)/He dates for Fish Canyon tuff zircon (**a**) and titanite (**b**) compared to those obtained with the LADD technique (**c** and **d**). Each dated grain is represented by a vertical black bar centered on the calculated apparent age. The heights of these bars indicate 2σ (ca. 95% confidence) analytical errors. Light grey horizontal bars indicate 2σ bounds for the inverse-variance weighted mean of the data set. The darker grey horizontal bars illustrate the dispersion of the data set calculated as $\pm 2\sigma$ of the sample population relative to the inverse-variance weighted mean.

Figure 4. LADD $^{206}\text{Pb}/^{238}\text{U}$ dates obtained for Fish Canyon tuff zircon (**a**) and titanite (**b**). Symbology is the same as in Figure 3.

TABLES

Table 1
Conventional (U-Th)/He dates of Fish Canyon tuff zircon.

Grain	⁴ He (pmole)	error (2σ)	²³⁸ U (pmole)	error (2σ)	²³² Th (pmole)	error (2σ)	(U-Th)/He Date _{RAW} ^a (Ma)	error (2σ)	R1 ^b (μm)	R2 ^b (μm)	L ^b (μm)	T1 ^b (μm)	T2 ^b (μm)	F _T ^c	(U-Th)/He Date ^d (Ma)	error (2σ)	²³² Th/ ²³⁸ U	eU ^e (ppm)
1	0.2279	0.0056	8.22	0.24	4.80	0.10	18.89	0.68	51.9	38.0	213.6	34.8	40.7	0.77	24.40	0.87	0.58	373
2	0.493	0.011	16.60	0.49	8.84	0.31	20.44	0.71	57.4	50.7	297.3	64.0	53.9	0.82	25.04	0.87	0.53	377
3	0.2319	0.0055	7.94	0.19	5.17	0.14	19.65	0.62	46.0	44.9	246.7	40.4	52.7	0.78	25.06	0.80	0.65	308
4	0.1501	0.0036	5.671	0.093	4.545	0.051	17.29	0.48	28.7	28.4	273.0	32.0	47.6	0.69	25.12	0.70	0.80	482
5	0.1662	0.0039	6.16	0.19	3.05	0.13	18.72	0.68	38.4	32.2	272.0	45.9	40.7	0.74	25.35	0.92	0.50	334
6	0.626	0.013	19.80	0.46	13.96	0.32	21.04	0.61	52.5	66.9	288.9	47.1	45.5	0.83	25.36	0.74	0.70	371
7	0.1720	0.0042	6.11	0.18	3.571	0.074	19.20	0.68	37.3	39.8	235.7	33.1	34.9	0.76	25.42	0.90	0.58	315
8	0.0977	0.0025	3.676	0.060	2.287	0.026	17.98	0.53	36.8	28.5	221.0	46.7	46.3	0.71	25.42	0.75	0.62	325
9	0.1099	0.0027	4.140	0.087	2.154	0.049	18.34	0.57	38.3	29.7	192.5	31.0	27.6	0.72	25.53	0.79	0.52	342
10	0.1685	0.0038	6.21	0.21	2.89	0.18	18.96	0.77	41.5	34.2	175.8	31.3	32.3	0.74	25.7	1.0	0.47	468
11	0.3487	0.0078	11.82	0.27	5.64	0.15	20.56	0.62	53.7	46.4	260.9	43.6	78.9	0.80	25.77	0.78	0.48	378
12	0.766	0.017	24.49	0.79	13.75	0.56	21.42	0.78	54.8	62.4	320.9	80.2	42.8	0.83	25.81	0.94	0.56	436
13	0.770	0.018	24.76	0.46	13.23	0.22	21.41	0.61	65.8	46.1	375.1	68.2	41.4	0.82	25.96	0.74	0.53	391
14	0.3188	0.0076	11.01	0.33	5.67	0.18	20.01	0.72	41.2	43.2	223.5	40.8	38.2	0.77	26.01	0.93	0.52	521
15	0.1545	0.0036	5.48	0.12	2.602	0.078	19.65	0.60	48.2	38.7	211.8	64.2	75.4	0.75	26.10	0.80	0.47	353
16	0.3236	0.0079	10.62	0.17	5.702	0.051	20.97	0.59	48.9	50.8	273.7	41.4	68.8	0.80	26.15	0.74	0.54	309
17	0.3028	0.0071	9.59	0.22	6.12	0.18	21.28	0.67	68.4	53.8	195.4	51.3	44.6	0.81	26.15	0.82	0.64	293
18	0.3904	0.0092	12.76	0.39	6.75	0.29	21.09	0.77	57.2	48.9	254.6	72.5	47.2	0.81	26.16	0.95	0.53	377
19	0.2793	0.0068	9.00	0.15	5.643	0.094	20.96	0.60	47.2	46.0	306.0	46.7	58.4	0.80	26.36	0.75	0.63	259
20	0.2046	0.0044	7.06	0.23	3.59	0.13	20.07	0.73	42.1	42.6	187.5	35.2	44.9	0.76	26.38	0.96	0.51	422
21	0.0987	0.0025	3.324	0.059	2.259	0.023	19.85	0.59	38.9	46.7	161.4	33.0	42.7	0.75	26.43	0.78	0.68	245
22	0.3480	0.0083	11.46	0.24	6.27	0.16	20.85	0.63	43.0	54.9	218.0	47.9	45.9	0.79	26.43	0.80	0.55	452
23	0.0424	0.0012	1.647	0.041	1.621	0.032	16.24	0.56	25.3	22.9	150.0	40.2	30.3	0.61	26.64	0.92	0.98	436
24	0.427	0.010	13.83	0.22	6.79	0.13	21.44	0.60	51.6	50.7	252.9	51.7	50.6	0.80	26.66	0.74	0.49	410
25	0.490	0.012	15.73	0.29	8.11	0.28	21.54	0.64	48.3	52.6	272.6	38.8	50.4	0.81	26.72	0.79	0.52	418
26	1.727	0.039	49.56	0.84	29.78	0.49	23.67	0.64	85.1	95.9	424.6	72.1	93.8	0.89	26.73	0.73	0.60	284
27	0.405	0.010	12.61	0.41	7.35	0.28	21.92	0.82	55.4	61.3	217.1	43.1	44.1	0.82	26.8	1.0	0.58	340
28	0.20	0.0047	6.75	0.21	4.30	0.12	20.33	0.72	40.1	40.6	200.2	34.8	36.1	0.76	26.87	0.95	0.64	400
29	0.714	0.016	22.29	0.61	11.44	0.31	22.14	0.74	54.9	54.8	329.4	49.8	61.0	0.82	26.89	0.90	0.51	418
30	0.619	0.013	18.75	0.42	12.61	0.30	22.09	0.64	52.4	61.6	263.8	60.0	44.9	0.82	26.94	0.78	0.67	445
31	0.490	0.012	14.76	0.40	10.10	0.27	22.19	0.74	52.7	60.7	291.4	50.0	56.6	0.82	26.95	0.90	0.68	312
32	0.1746	0.0041	6.06	0.15	2.95	0.10	20.04	0.65	52.6	32.2	181.5	54.2	45.7	0.74	27.05	0.87	0.49	445
33	0.1400	0.0033	4.58	0.13	3.204	0.093	20.38	0.69	33.6	44.6	243.9	41.1	39.2	0.75	27.06	0.92	0.70	239
34	0.1130	0.0027	4.07	0.12	2.32	0.11	18.98	0.69	34.3	30.6	158.1	28.3	28.4	0.70	27.08	0.98	0.57	469
35	0.1119	0.0027	3.90	0.12	2.291	0.058	19.55	0.72	33.7	39.4	147.1	29.5	29.6	0.72	27.1	1.0	0.59	399
36	0.2464	0.0060	8.09	0.13	4.203	0.036	21.03	0.59	46.1	41.4	212.0	38.1	33.9	0.77	27.17	0.76	0.52	373
37	0.0797	0.0019	2.833	0.086	1.817	0.063	18.96	0.68	35.7	30.5	143.4	31.6	27.4	0.70	27.20	0.97	0.64	369
38	0.0555	0.0014	2.085	0.035	1.271	0.017	18.06	0.53	27.1	33.2	117.6	23.8	24.1	0.66	27.24	0.80	0.61	397
39	0.4049	0.0092	12.58	0.28	7.19	0.18	21.99	0.66	60.1	45.6	251.1	42.6	47.7	0.81	27.25	0.82	0.57	350
40	0.3771	0.0088	11.97	0.27	6.53	0.14	21.65	0.67	47.4	45.4	273.1	38.9	35.2	0.79	27.27	0.84	0.55	360
41	0.538	0.012	16.66	0.33	9.00	0.20	22.20	0.65	51.5	52.4	304.9	47.8	46.5	0.81	27.27	0.80	0.54	370
42	0.1971	0.0048	6.05	0.10	4.765	0.040	21.33	0.59	45.4	44.0	259.8	38.7	62.5	0.78	27.29	0.76	0.79	239
43	0.583	0.014	18.12	0.33	8.66	0.16	22.39	0.64	63.3	48.1	297.8	55.2	50.1	0.82	27.30	0.78	0.48	374
44	0.628	0.015	19.70	0.41	9.47	0.20	22.20	0.68	52.7	52.4	274.6	45.1	47.1	0.81	27.31	0.84	0.48	478
45	0.609	0.013	18.82	0.55	10.15	0.37	22.25	0.77	49.4	57.9	266.4	43.0	55.9	0.81	27.38	0.94	0.54	475

Table 1 continued

Grain	^4He (pmole)	error (2 σ)	^{238}U (pmole)	error (2 σ)	^{232}Th (pmole)	error (2 σ)	(U-Th)/He Date _{RAW} ^a (Ma)	error (2 σ)	R1 ^b (μm)	R2 ^b (μm)	L ^b (μm)	T1 ^b (μm)	T2 ^b (μm)	F _T ^c	(U-Th)/He Date ^d (Ma)	error (2 σ)	$^{232}\text{Th}/^{238}\text{U}$	eU ^e (ppm)
46	0.831	0.015	24.88	0.55	15.99	0.35	22.50	0.61	52.5	56.9	310.6	50.9	48.4	0.82	27.39	0.74	0.64	503
47	0.1219	0.0030	4.269	0.073	2.059	0.027	19.87	0.58	39.2	35.8	149.7	34.9	34.3	0.73	27.40	0.80	0.48	419
48	0.1088	0.0027	3.781	0.063	2.812	0.036	19.01	0.54	30.7	32.2	164.3	29.7	33.8	0.69	27.41	0.78	0.74	473
49	0.1827	0.0048	6.44	0.11	2.979	0.026	19.84	0.61	35.3	33.9	192.4	41.1	33.5	0.72	27.43	0.85	0.46	537
50	0.2080	0.0049	6.48	0.20	4.17	0.15	21.61	0.77	56.8	44.2	212.0	48.0	63.2	0.79	27.44	0.98	0.64	277
51	0.2014	0.0047	6.38	0.18	3.27	0.11	21.85	0.75	45.8	56.8	216.6	46.3	52.7	0.80	27.46	0.94	0.51	234
52	0.2661	0.0058	8.68	0.20	4.64	0.19	21.12	0.65	41.0	46.2	202.3	41.9	46.0	0.77	27.50	0.84	0.54	461
53	0.754	0.018	22.99	0.48	11.96	0.32	22.63	0.68	53.5	57.4	307.1	59.0	46.9	0.82	27.50	0.83	0.52	456
54	0.1708	0.0038	5.69	0.15	3.78	0.10	20.15	0.66	34.3	37.3	189.3	25.1	25.1	0.73	27.52	0.90	0.67	423
55	0.3000	0.0073	9.54	0.18	5.03	0.10	21.69	0.65	45.3	48.7	233.7	52.9	39.0	0.79	27.52	0.82	0.53	362
56	0.478	0.011	14.71	0.39	9.67	0.28	21.81	0.71	43.7	47.8	296.2	52.8	34.2	0.79	27.53	0.90	0.66	437
57	0.1696	0.0041	5.70	0.12	3.354	0.079	20.27	0.63	38.5	37.6	170.5	32.6	38.3	0.74	27.54	0.85	0.59	468
58	0.592	0.012	18.36	0.48	9.90	0.39	22.19	0.74	60.3	43.2	308.6	65.6	79.8	0.80	27.60	0.92	0.54	481
59	0.656	0.015	19.89	0.35	10.54	0.29	22.72	0.64	54.4	55.6	312.2	46.7	65.3	0.82	27.65	0.78	0.53	400
60	0.696	0.015	21.55	0.38	11.67	0.25	22.19	0.60	46.3	46.1	393.9	36.3	44.6	0.80	27.66	0.75	0.54	430
61	0.2848	0.0064	9.18	0.25	4.91	0.14	21.37	0.72	47.1	40.0	214.9	38.8	37.4	0.77	27.66	0.93	0.53	429
62	0.1520	0.0038	5.21	0.10	2.671	0.033	20.17	0.62	35.7	39.0	155.1	34.6	34.2	0.73	27.75	0.85	0.51	494
63	0.2133	0.0055	6.83	0.11	4.377	0.039	21.04	0.61	40.0	40.8	196.5	30.5	32.6	0.76	27.80	0.81	0.64	401
64	0.2408	0.0058	7.90	0.14	4.671	0.044	20.75	0.60	37.1	36.8	222.8	31.2	26.5	0.75	27.83	0.80	0.59	459
65	0.477	0.011	13.89	0.32	10.76	0.30	22.54	0.69	50.0	57.1	248.7	50.2	47.4	0.81	27.85	0.85	0.77	402
66	0.730	0.016	21.18	0.47	14.76	0.35	22.98	0.67	55.5	59.3	299.6	46.6	72.6	0.82	27.85	0.81	0.70	437
67	0.1469	0.0036	5.16	0.10	3.111	0.044	19.32	0.58	35.6	27.6	170.3	34.8	30.1	0.69	27.86	0.84	0.60	606
68	0.3562	0.0089	11.06	0.23	8.11	0.16	21.30	0.65	48.2	38.1	207.0	44.5	45.0	0.76	27.88	0.85	0.73	615
69	0.0443	0.0011	1.470	0.041	0.967	0.037	20.22	0.70	36.2	36.8	163.8	36.8	34.0	0.73	27.89	0.97	0.66	140
70	0.3859	0.0093	11.88	0.26	6.85	0.16	22.17	0.69	54.9	44.6	242.4	46.7	62.8	0.79	27.91	0.87	0.58	417
71	0.487	0.011	15.07	0.29	7.57	0.17	22.40	0.66	46.3	52.1	281.6	49.5	52.3	0.80	27.94	0.82	0.50	420
72	0.1863	0.0045	5.84	0.11	3.677	0.061	21.53	0.63	47.6	44.0	179.4	41.3	45.4	0.77	27.99	0.82	0.63	338
73	0.1495	0.0035	5.22	0.12	2.696	0.082	19.79	0.61	30.8	31.4	214.2	26.4	32.2	0.71	28.01	0.87	0.52	444
74	0.1616	0.0040	5.362	0.089	3.055	0.040	20.60	0.59	37.4	35.2	190.3	33.7	28.5	0.73	28.04	0.81	0.57	398
75	0.1645	0.0042	4.936	0.086	2.533	0.031	20.17	0.61	37.8	32.0	178.0	36.9	36.9	0.72	28.06	0.85	0.51	457
76	0.3310	0.0078	10.20	0.31	5.94	0.28	22.13	0.80	61.9	39.3	238.7	64.1	61.2	0.79	28.1	1.0	0.58	395
77	0.463	0.010	13.75	0.37	8.58	0.19	22.78	0.75	51.0	52.7	278.4	50.3	53.3	0.81	28.14	0.92	0.62	360
78	0.3755	0.0087	11.71	0.29	6.03	0.19	22.16	0.71	45.6	44.2	268.1	43.6	41.0	0.79	28.16	0.91	0.51	395
79	0.1203	0.0031	4.159	0.080	2.099	0.028	20.04	0.62	34.2	35.7	173.2	52.5	42.9	0.71	28.18	0.87	0.50	446
80	0.1145	0.0029	4.123	0.076	3.048	0.065	18.36	0.55	33.6	21.7	199.2	42.6	41.6	0.65	28.18	0.85	0.74	596
81	0.3841	0.0093	12.03	0.19	6.113	0.049	22.10	0.62	46.0	41.7	291.2	56.8	40.0	0.78	28.19	0.79	0.51	398
82	0.1537	0.0039	5.290	0.086	2.824	0.029	20.02	0.58	34.1	28.7	223.9	26.5	25.8	0.71	28.23	0.82	0.53	413
83	0.3021	0.0052	9.22	0.25	5.64	0.17	22.20	0.66	47.2	45.3	230.3	41.7	41.2	0.79	28.24	0.84	0.61	361
84	0.1753	0.0040	5.87	0.16	2.97	0.15	20.69	0.74	39.5	31.9	201.4	30.3	27.1	0.73	28.3	1.0	0.51	411
85	0.580	0.014	17.31	0.42	8.42	0.20	23.32	0.75	64.2	51.2	275.7	46.8	49.5	0.82	28.30	0.91	0.49	357
86	0.525	0.012	16.06	0.36	7.53	0.23	22.82	0.75	53.3	51.2	284.2	63.3	82.0	0.81	28.31	0.93	0.47	449
87	0.3153	0.0076	10.19	0.17	4.975	0.066	21.50	0.61	37.0	39.3	330.9	39.9	72.0	0.76	28.32	0.80	0.49	391
88	0.520	0.012	15.70	0.48	9.25	0.30	22.53	0.81	42.6	58.8	240.1	53.3	54.7	0.79	28.3	1.0	0.59	545
89	1.213	0.028	35.26	0.75	18.14	0.50	23.79	0.71	71.3	49.5	420.1	54.0	73.0	0.84	28.40	0.85	0.51	429
90	0.1804	0.0043	5.118	0.094	4.280	0.055	20.00	0.57	32.0	33.1	173.8	35.6	28.2	0.70	28.41	0.81	0.84	564
91	0.2592	0.0061	8.44	0.21	4.05	0.12	21.38	0.70	36.9	42.7	200.8	30.8	45.7	0.75	28.41	0.93	0.48	512

Table 1 continued

Grain	^4He (pmole)	error (2 σ)	^{238}U (pmole)	error (2 σ)	^{232}Th (pmole)	error (2 σ)	(U-Th)/He Date _{RAW} ^a (Ma)	error (2 σ)	R1 ^b (μm)	R2 ^b (μm)	L ^b (μm)	T1 ^b (μm)	T2 ^b (μm)	F _T ^c	(U-Th)/He Date ^d (Ma)	error (2 σ)	$^{232}\text{Th}/^{238}\text{U}$	eU ^e (ppm)
92	0.0757	0.0019	2.694	0.046	1.441	0.020	19.36	0.57	30.4	29.7	162.4	33.4	38.4	0.68	28.47	0.84	0.53	377
93	0.1523	0.0037	5.122	0.084	2.812	0.030	20.41	0.58	38.7	33.2	169.3	40.8	48.2	0.72	28.47	0.81	0.55	525
94	0.1805	0.0044	5.78	0.11	3.014	0.051	21.54	0.64	39.4	42.4	201.6	47.1	41.8	0.76	28.49	0.84	0.52	351
95	0.1585	0.0040	5.23	0.10	2.664	0.033	20.96	0.64	41.7	33.5	186.2	39.2	42.2	0.73	28.53	0.87	0.51	409
96	0.3864	0.0093	10.90	0.18	8.152	0.081	23.38	0.66	57.3	55.9	263.4	34.4	68.1	0.82	28.55	0.80	0.75	263
97	0.490	0.012	14.66	0.25	7.694	0.081	23.07	0.66	47.9	54.4	286.9	56.4	51.6	0.81	28.55	0.82	0.52	378
98	0.3646	0.0087	11.35	0.28	5.92	0.18	22.18	0.73	45.8	41.3	228.2	35.1	32.9	0.78	28.55	0.94	0.52	473
99	0.1903	0.0043	6.31	0.13	3.176	0.078	20.91	0.61	34.1	35.0	223.8	34.8	29.6	0.73	28.59	0.84	0.50	420
100	0.821	0.019	24.20	0.62	12.74	0.30	23.39	0.76	50.1	55.0	351.7	51.4	68.7	0.82	28.60	0.93	0.53	466
101	0.2026	0.0049	6.36	0.12	3.257	0.042	22.05	0.65	46.1	40.4	211.9	44.3	32.3	0.77	28.61	0.84	0.51	305
102	0.2152	0.0051	6.98	0.14	4.239	0.094	20.91	0.61	38.1	33.6	186.3	35.4	29.9	0.73	28.66	0.84	0.61	560
103	0.2970	0.0069	9.51	0.22	4.46	0.16	21.80	0.72	39.4	42.3	205.9	38.2	36.8	0.76	28.67	0.94	0.47	522
104	0.540	0.012	15.94	0.35	7.88	0.26	23.49	0.70	61.1	50.8	275.2	61.9	55.6	0.82	28.71	0.85	0.49	374
105	0.707	0.016	20.67	0.45	10.76	0.26	23.60	0.71	58.6	51.6	315.6	57.3	57.6	0.82	28.72	0.86	0.52	412
106	0.2022	0.0049	6.06	0.10	4.786	0.043	21.82	0.62	47.6	37.8	188.0	41.1	34.4	0.76	28.72	0.82	0.79	372
107	0.568	0.013	16.60	0.42	8.97	0.27	23.52	0.76	57.3	52.9	272.5	46.2	49.8	0.82	28.73	0.93	0.54	380
108	1.204	0.028	31.34	0.66	33.02	0.77	23.90	0.71	57.0	69.5	251.0	48.9	53.1	0.83	28.78	0.85	1.05	691
109	0.2725	0.0064	8.13	0.18	7.22	0.20	21.52	0.64	37.5	42.1	180.4	37.8	30.3	0.75	28.80	0.86	0.89	591
110	0.596	0.014	17.54	0.28	10.26	0.19	23.15	0.65	49.0	48.9	293.0	45.1	46.9	0.80	28.81	0.81	0.58	462
111	0.2103	0.0049	6.77	0.15	3.54	0.10	21.43	0.66	37.0	38.0	211.7	37.6	49.4	0.74	28.87	0.89	0.52	452
112	0.543	0.013	15.94	0.26	8.744	0.087	23.40	0.67	54.7	50.6	260.4	64.1	46.1	0.81	28.95	0.83	0.55	447
113	0.2113	0.0050	6.84	0.22	3.55	0.10	21.34	0.80	39.9	36.4	191.6	54.3	43.5	0.74	29.0	1.1	0.52	536
114	0.560	0.013	16.69	0.54	8.56	0.30	23.19	0.87	43.6	55.5	257.1	42.2	32.3	0.80	29.0	1.1	0.51	479
115	0.1730	0.0042	5.63	0.16	2.801	0.059	21.30	0.76	36.6	36.6	187.2	34.3	36.9	0.73	29.0	1.0	0.50	431
116	0.0627	0.0017	2.311	0.040	1.420	0.021	18.38	0.57	29.8	24.3	143.2	35.7	45.7	0.63	29.03	0.90	0.61	527
117	0.2913	0.0069	8.45	0.22	5.60	0.14	23.12	0.76	47.3	51.6	220.6	44.7	40.7	0.79	29.12	0.96	0.66	314
118	0.1772	0.0044	5.532	0.088	2.904	0.029	22.09	0.63	38.8	40.6	217.8	36.5	30.9	0.76	29.14	0.84	0.52	293
119	0.1630	0.0040	5.296	0.088	3.106	0.033	20.97	0.61	39.0	31.2	170.1	32.1	28.7	0.72	29.16	0.84	0.59	491
120	0.392	0.020	11.63	0.18	5.79	0.10	23.4	1.2	54.7	47.8	229.9	46.7	39.6	0.80	29.2	1.6	0.50	371
121	0.483	0.012	14.34	0.22	8.452	0.079	22.93	0.65	47.6	41.4	272.2	38.9	38.2	0.79	29.19	0.82	0.59	482
122	0.1362	0.0033	4.23	0.12	2.981	0.062	21.42	0.75	33.1	34.1	298.4	39.1	38.6	0.73	29.3	1.0	0.70	227
123	0.2354	0.0053	7.36	0.21	3.61	0.11	22.21	0.77	41.5	42.6	186.2	45.1	35.7	0.76	29.3	1.0	0.49	450
124	0.4095	0.0095	12.63	0.31	7.55	0.27	22.04	0.74	43.5	35.5	210.6	33.4	40.5	0.75	29.29	0.98	0.60	743
125	0.2489	0.0061	7.81	0.13	3.581	0.035	22.30	0.64	41.3	39.7	219.3	37.0	42.1	0.76	29.30	0.84	0.46	407
126	0.519	0.011	15.39	0.34	7.52	0.17	23.42	0.70	48.8	49.4	234.6	42.0	35.8	0.80	29.37	0.88	0.49	500
127	0.970	0.023	25.94	0.62	23.22	0.72	23.97	0.75	57.6	52.7	271.8	41.1	64.2	0.82	29.37	0.92	0.90	658
128	0.1145	0.0028	3.667	0.060	2.211	0.024	21.20	0.60	37.6	33.4	164.5	27.3	34.5	0.72	29.40	0.83	0.60	347
129	0.2204	0.0052	7.18	0.25	3.57	0.14	21.31	0.85	35.6	33.6	192.4	30.1	38.7	0.72	29.4	1.2	0.50	587
130	0.1355	0.0033	4.352	0.067	2.446	0.029	21.31	0.60	36.8	35.9	157.4	32.1	32.2	0.72	29.43	0.83	0.56	417
131	0.624	0.013	17.45	0.40	12.35	0.28	23.79	0.70	46.9	55.0	297.8	65.2	37.9	0.81	29.47	0.86	0.71	442
132	0.2153	0.0053	6.53	0.10	3.257	0.036	22.87	0.64	40.5	46.5	211.2	24.8	35.2	0.77	29.56	0.83	0.50	291
133	0.0904	0.0021	2.855	0.086	2.260	0.073	20.72	0.72	32.6	36.2	138.6	31.6	33.3	0.70	29.6	1.0	0.79	387
134	0.972	0.022	27.07	0.46	12.67	0.21	25.07	0.68	73.6	58.8	320.8	57.8	75.1	0.84	29.68	0.81	0.47	384
135	0.1147	0.0028	3.863	0.063	2.182	0.028	20.32	0.58	30.5	28.7	169.7	28.6	28.0	0.68	29.73	0.84	0.56	486
136	0.439	0.011	12.99	0.20	6.470	0.065	23.43	0.65	45.7	44.7	268.5	41.3	46.0	0.79	29.73	0.83	0.50	434
137	0.558	0.013	15.47	0.43	14.89	0.49	22.85	0.76	34.9	53.0	269.3	68.2	48.2	0.77	29.74	0.99	0.96	685

Table 1 continued

Grain	⁴ He (pmole)	error (2σ)	²³⁸ U (pmole)	error (2σ)	²³² Th (pmole)	error (2σ)	(U-Th)/He Date _{RAW} ^a (Ma)	error (2σ)	R1 ^b (μm)	R2 ^b (μm)	L ^b (μm)	T1 ^b (μm)	T2 ^b (μm)	F _T ^c	(U-Th)/He Date ^d (Ma)	error (2σ)	²³² Th/ ²³⁸ U	eU ^e (ppm)
138	0.416	0.010	12.06	0.19	6.270	0.060	23.83	0.67	52.3	49.5	241.3	48.9	55.4	0.80	29.76	0.84	0.52	391
139	0.2574	0.0062	7.92	0.12	4.017	0.036	22.50	0.63	42.9	40.2	179.8	38.5	40.0	0.75	29.80	0.84	0.51	518
140	0.954	0.021	26.41	0.57	15.49	0.38	24.61	0.73	61.2	52.1	310.7	55.0	56.3	0.83	29.82	0.88	0.59	511
141	0.1561	0.0040	5.235	0.082	2.625	0.031	20.67	0.61	31.7	29.7	193.0	38.6	48.0	0.69	29.89	0.88	0.50	589
142	0.2238	0.0059	6.92	0.11	3.472	0.038	22.42	0.68	37.1	41.9	209.5	43.8	51.5	0.75	29.91	0.90	0.50	438
143	0.1648	0.0040	5.237	0.092	3.068	0.054	21.44	0.62	41.3	31.2	160.5	29.6	44.3	0.72	29.91	0.87	0.59	534
144	0.3819	0.0092	11.26	0.18	6.492	0.062	23.15	0.65	43.5	37.6	281.9	52.0	42.0	0.77	30.16	0.84	0.58	457
145	0.415	0.010	12.33	0.27	6.12	0.16	23.37	0.72	44.8	40.2	249.1	45.8	43.5	0.77	30.22	0.93	0.50	518
146	0.1863	0.0045	5.92	0.12	3.041	0.047	21.75	0.66	35.7	33.0	170.9	29.9	27.3	0.72	30.26	0.92	0.51	545
147	0.483	0.011	13.89	0.40	8.56	0.31	23.54	0.80	44.4	42.1	255.3	49.8	37.6	0.78	30.3	1.0	0.62	553
148	0.618	0.015	17.65	0.28	10.280	0.088	23.86	0.66	46.4	42.0	272.9	37.0	38.0	0.78	30.41	0.85	0.58	594
149	0.1684	0.0041	5.302	0.093	2.274	0.029	22.34	0.65	38.3	34.8	188.5	42.6	28.0	0.73	30.43	0.89	0.43	398
150	0.1027	0.0025	3.390	0.060	1.853	0.019	20.80	0.60	31.8	25.0	222.5	26.7	29.8	0.68	30.53	0.89	0.55	335
151	0.1027	0.0025	3.36	0.06	1.842	0.019	20.97	0.61	31.8	25.0	222.5	26.7	29.8	0.68	30.78	0.89	0.55	332
152	0.645	0.015	17.90	0.29	8.197	0.077	25.20	0.71	53.7	57.3	278.0	67.7	63.9	0.82	30.86	0.86	0.46	435
153	0.1871	0.0045	5.75	0.10	3.066	0.031	22.42	0.64	35.4	34.5	193.0	32.9	37.0	0.73	30.88	0.88	0.53	466
154	0.1998	0.0047	6.17	0.18	3.51	0.13	22.14	0.79	30.5	36.0	224.0	51.2	38.3	0.72	30.9	1.1	0.57	498
155	0.2647	0.0065	8.15	0.14	4.215	0.051	22.43	0.65	35.6	38.0	187.7	49.5	54.7	0.73	30.93	0.90	0.52	735
156	0.1136	0.0027	4.02	0.21	2.494	0.081	19.10	0.99	29.0	20.4	171.3	39.2	39.3	0.62	31.0	1.6	0.62	840
157	0.758	0.018	18.91	0.43	23.21	0.62	24.16	0.72	46.8	42.6	264.4	55.5	44.0	0.78	30.96	0.93	1.23	790
158	0.2034	0.0048	6.12	0.19	4.42	0.16	22.02	0.80	36.6	32.8	165.8	44.5	37.6	0.71	31.0	1.1	0.72	689
159	0.2378	0.0060	6.89	0.11	4.143	0.042	23.45	0.68	35.4	40.6	288.2	47.4	44.5	0.76	31.03	0.90	0.60	309
160	0.1296	0.0031	4.075	0.064	2.098	0.022	21.99	0.62	35.0	31.5	151.6	29.0	27.4	0.70	31.23	0.87	0.51	467
161	0.1754	0.0042	4.997	0.079	3.099	0.037	23.75	0.66	38.5	43.8	219.9	40.2	54.2	0.76	31.26	0.87	0.62	278
162	0.3158	0.0077	8.54	0.15	9.47	0.11	22.77	0.64	35.3	34.8	196.3	30.0	31.8	0.73	31.36	0.88	1.11	722
163	0.2229	0.0054	6.96	0.13	5.135	0.087	21.17	0.62	30.7	26.7	183.5	34.5	32.7	0.68	31.37	0.91	0.74	921
164	0.1683	0.0036	4.98	0.12	2.533	0.065	23.40	0.71	37.0	37.6	200.0	30.7	39.2	0.74	31.55	0.96	0.51	336
165	0.2367	0.0059	6.82	0.11	2.959	0.027	24.38	0.71	46.1	40.1	240.4	43.0	61.5	0.77	31.60	0.92	0.43	306
Inverse-Variance Weighted Mean ^f															28.16	± 0.24 2σ		
MSWD															12.62			
Dispersion															11.0%			

^a Date calculated without F_T correction.^b R1 and R2 describe the perpendicular half width of the zircon crystal. L describes the length along the c axis. T1 and T2 describe the height of the pyramidal terminations.^c The mean F_T correction calculated following Hourigan et al. (2005).^d Date re-calculated with the F_T correction applied.^e Effective uranium concentration.^f The inverse-variance weighted mean uncertainty has been expanded by multiplying by the square root of the MSWD.

Table 2

Conventional (U-Th)/He dates of Fish Canyon tuff titanite.

Grain	⁴ He (pmole)	error (2σ)	²³⁸ U (pmole)	error (2σ)	²³² Th (pmole)	error (2σ)	¹⁴⁷ Sm (pmole)	error (2σ)	(U-Th)/He Date (Ma)	error (2σ)	²³² Th/ ²³⁸ U
1	0.988	0.017	12.53	0.25	71.9	1.6	0	0	26.29	0.60	5.73
2	0.1308	0.0035	1.732	0.031	8.868	0.084	6.63	0.38	26.60	0.77	5.12
3	0.773	0.018	10.29	0.23	52.3	1.1	0	0	26.78	0.76	5.08
4	1.696	0.041	21.65	0.61	113.9	3.9	0	0	27.43	0.90	5.26
5	0.2446	0.0059	3.085	0.048	16.18	0.14	13.71	0.53	27.52	0.71	5.24
6	0.1055	0.0025	1.301	0.024	7.100	0.070	5.79	0.32	27.53	0.71	5.46
7	0.741	0.018	9.64	0.29	48.3	1.2	0	0	27.60	0.85	5.01
8	0.0845	0.0021	0.963	0.017	5.750	0.049	14.95	0.70	27.68	0.72	5.97
9	0.626	0.014	7.69	0.16	42.62	0.89	0	0	27.70	0.75	5.54
10	0.796	0.019	9.70	0.16	54.39	0.48	0	0	27.74	0.71	5.61
11	0.1127	0.0028	1.394	0.025	7.412	0.062	6.30	0.46	27.86	0.73	5.32
12	0.718	0.017	8.86	0.21	47.8	1.0	0	0	27.98	0.78	5.39
13	0.03611	0.00087	0.4440	0.0078	2.368	0.020	1.795	0.092	28.00	0.72	5.33
14	0.567	0.014	7.31	0.11	35.64	0.30	28.36	0.96	28.04	0.71	4.88
15	0.01785	0.00044	0.2111	0.0047	1.199	0.016	1.006	0.066	28.07	0.77	5.68
16	0.548	0.012	6.74	0.15	36.31	0.77	0	0	28.07	0.76	5.39
17	0.03511	0.00086	0.4289	0.0085	2.298	0.025	1.74	0.10	28.10	0.75	5.36
18	1.087	0.026	13.81	0.29	70.0	1.5	0	0	28.12	0.80	5.07
19	0.549	0.013	6.90	0.14	35.58	0.72	0	0	28.13	0.79	5.15
20	0.0680	0.0016	0.839	0.014	4.384	0.044	3.75	0.22	28.16	0.72	5.22
21	0.03335	0.00081	0.4052	0.0081	2.179	0.022	1.76	0.10	28.19	0.74	5.38
22	0.707	0.017	8.92	0.14	43.89	0.38	70.3	4.2	28.22	0.72	4.92
23	1.599	0.038	19.00	0.40	107.7	2.5	0	0	28.25	0.82	5.67
24	1.144	0.027	14.22	0.25	74.1	1.2	0	0	28.31	0.76	5.21
25	0.1696	0.0041	2.075	0.033	10.93	0.10	7.78	0.45	28.34	0.72	5.27
26	0.2974	0.0071	3.637	0.060	19.14	0.18	14.91	0.58	28.35	0.72	5.26
27	0.2726	0.0065	3.48	0.11	17.18	0.48	0	0	28.36	0.90	4.93
28	0.0431	0.0010	0.5335	0.0092	2.723	0.023	2.27	0.12	28.44	0.73	5.10
29	0.843	0.021	10.84	0.22	52.51	0.95	0	0	28.47	0.79	4.85
30	0.02588	0.00065	0.3054	0.0061	1.699	0.021	1.310	0.091	28.48	0.78	5.56
31	0.1953	0.0047	2.366	0.066	12.75	0.37	0	0	28.51	0.89	5.39
32	0.549	0.013	6.78	0.14	35.22	0.62	0	0	28.55	0.79	5.19
33	0.0815	0.0020	0.982	0.017	5.180	0.046	4.59	0.21	28.69	0.74	5.28
34	2.826	0.067	30.07	0.60	200.2	6.7	0	0	28.72	0.93	6.66
35	0.453	0.011	5.549	0.089	27.48	0.24	59.2	5.1	28.78	0.73	4.95
36	0.06	0.00	0.697	0.012	3.476	0.031	2.02	0.11	28.87	0.75	4.99
37	0.1712	0.0041	2.215	0.037	9.993	0.079	11.09	0.63	28.97	0.74	4.51
38	0.846	0.019	10.22	0.29	53.8	1.6	0	0	28.97	0.88	5.26
39	0.438	0.011	5.46	0.10	26.79	0.53	0	0	29.15	0.85	4.90
40	0.0407	0.0010	0.4844	0.0088	2.439	0.028	5.93	0.42	29.24	0.76	5.03
41	0.3143	0.0075	4.00	0.10	17.44	0.75	0	0	30.32	1.0	4.36
Inverse-Variance Weighted Mean ^a									28.12	± 0.22 2σ	
MSWD									3.44		
Dispersion									5.1%		

^a The inverse-variance weighted mean uncertainty has been expanded by multiplying by the square root of the MSWD.

Table 3

Table 3
(U-Th)/He and U/Pb dates by LADD of Fish Canyon tuff titanite.

Grain	⁴ He pit volume (μm ³)	error (2σ)	⁴ He (nmole/g)	error (2σ)	U-Th-Pb pit volume (μm ³) ^a	error (2σ)	²³⁸ U (nmole/g)	error (2σ)	²³² Th (nmole/g)	error (2σ)	¹⁶⁷ Sm (nmole/g)	error (2σ)	²³² Th/ ²³⁸ U	(U-Th)/He Date (Ma)	error (2σ)	²⁰⁶ Pb/ ²³⁸ U	error (2σ)	²³⁸ U/ ²⁰⁶ Pb Date (Ma)	error (2σ)
1	92000	1.2E+03	23.09	0.68	509174	7.7E+03	288	13	1667	65	1165	94	5.79	26.4	1.1	0.0045	1.7E-03	28.6	8.5
2	85336	1.2E+03	20.62	0.63	507320	6.2E+03	208.6	8.9	1328	50.	1765	1.4E+02	6.37	30.5	1.3	0.0044	1.0E-03	28.4	7.0
3	79099	1.1E+03	21.88	0.68	507012	7.0E+03	256	11	1326	50.	1173	95	5.18	29.8	1.3	0.0040	1.2E-03	25.9	6.9
4	70062	1.1E+03	23.83	0.79	517406	6.0E+03	245	10.	1293	46	935	74	5.29	33.7	1.4	0.0046	1.2E-03	29.6	4.4
5	76439	1.1E+03	22.91	0.72	495758	8.6E+03	331	14	1665	64	1462	1.2E+02	5.03	24.6	1.1	0.00378	5.6E-04	24.3	4.8
6	71466	1.1E+03	22.26	0.71	490364	7.6E+03	316	14	1680	63	1174	94	5.31	24.3	1.0	0.00444	6.0E-04	28.6	4.6
7	65559	8.7E+02	22.31	0.72	489825	6.1E+03	248	10.	1353	48	1097	87	5.45	30.6	1.3	0.00395	8.4E-04	25.4	7.0
8	63079	1.1E+03	21.43	0.75	482480	6.7E+03	264	11	1283	47	1135	91	4.86	29.3	1.3	0.00441	7.4E-04	28.3	6.3
9	60168	9.6E+02	12.14	0.57	474857	6.7E+03	146.8	6.2	853	31	2856	2.2E+02	5.81	26.3	1.4	0.0039	1.4E-03	24.8	8.1
10	60544	9.8E+02	20.36	0.63	481178	5.9E+03	230.2	9.4	1256	44	985	78	5.46	30.0	1.2	0.0041	1.5E-03	26.2	5.9
11	57038	8.3E+02	17.90	0.63	472128	8.6E+03	238	10.	1332	51	1625	1.3E+02	5.59	25.0	1.1	0.0049	1.4E-03	31.7	5.9
12	60797	8.2E+02	14.84	0.51	484477	8.8E+03	189.8	8.2	1064	40.	3003	2.4E+02	5.60	25.5	1.1	0.0050	1.0E-03	32.3	9.0
13	57625	9.1E+02	22.98	0.75	478984	8.8E+03	302	13	1572	60.	1172	95	5.20	26.5	1.1	0.0046	1.3E-03	29.8	5.0
14	50004	7.6E+02	16.04	0.74	487228	8.8E+03	145.5	6.3	908	34	2593	2.0E+02	6.24	33.8	1.8	0.0050	1.3E-03	32.1	8.8
15	38709	6.3E+02	23.45	0.85	476568	7.7E+03	249	10.	1263	46	2520	2.0E+02	5.06	32.8	1.5	0.0039	1.4E-03	25.0	8.1
16	50535	9.2E+02	22.37	0.76	469626	6.8E+03	305	13	1634	59	1173	94	5.36	25.2	1.1	0.00413	8.2E-04	26.5	3.5
17	48245	7.2E+02	21.74	0.76	478752	7.7E+03	274	12	1359	50.	1178	94	4.96	28.4	1.3	0.00402	7.2E-04	25.8	5.9
18	45177	6.8E+02	17.93	0.62	477827	8.1E+03	218.1	9.3	1360	51	1447	1.2E+02	6.24	25.8	1.1	0.0042	1.0E-03	26.7	7.6
19	49274	9.0E+02	23.01	0.79	479346	7.3E+03	350	15	1675	61	1321	1.1E+02	4.79	24.0	1.1	0.0039	1.5E-03	25.1	4.8
20	53416	8.3E+02	8.44	0.64	470561	8.7E+03	97.2	4.2	636	24	2797	2.3E+02	6.54	25.3	2.0	0.0043	1.7E-03	27.2	13
21	49750	8.0E+02	14.92	0.95	460291	5.8E+03	164.5	6.7	803	28	2315	1.8E+02	4.89	32.0	2.2	0.0052	1.3E-03	33.2	9.2
22	46925	7.5E+02	15.85	0.89	469056	6.7E+03	171	7.08	856	31	1799	1.4E+02	4.99	32.5	2.0	0.00445	9.2E-04	28.6	6.6
23	41866	6.6E+02	22.97	0.73	470120	8.4E+03	290	12.42	1484	56	1157	93	5.13	27.9	1.2	0.00461	7.0E-04	29.9	5.7
24	40856	6.9E+02	23.10	0.96	466833	6.6E+03	264	11	1273	45	998	79	4.81	31.8	1.6	0.00454	7.2E-04	29.2	6.2
25	41911	6.9E+02	22.78	0.85	472753	6.9E+03	249	10.	1342	48	863	69	5.39	31.4	1.4	0.00416	6.4E-04	26.7	6.0
26	37338	5.8E+02	22.23	0.91	468205	7.6E+03	259	11	1271	47	969	78	4.92	30.9	1.5	0.00445	6.8E-04	28.6	6.1
27	39288	6.2E+02	19.9	2.1	461448	7.8E+03	263	11	1351	50.	1130	91	5.15	26.6	2.9	0.00374	7.8E-04	24.1	5.3
28	38689	6.2E+02	22.5	1.3	461558	7.1E+03	242	10.	1323	48	848	68	5.46	31.5	2.0	0.00490	6.8E-04	31.5	5.0
29	38046	7.1E+02	21.4	1.5	464502	6.5E+03	226.1	9.3	1244	44	834	66	5.50	32.1	2.4	0.00424	7.2E-04	27.2	5.2
30	35307	5.9E+02	17.6	1.5	465715	5.9E+03	221.5	9.0	1241	43	1194	95	5.60	26.5	2.3	0.00417	8.6E-04	26.8	6.7
31	32755	5.1E+02	20.2	1.9	464518	8.5E+03	217.8	9.3	1087	41	819	66	4.99	33.1	3.2	0.00384	7.0E-04	24.7	5.4
32	33402	5.3E+02	16.0	1.6	460331	8.3E+03	226.0	9.9	1275	49	1406	1.1E+02	5.64	23.6	2.5	0.0039	1.9E-03	25.1	7.0
33	43459	6.2E+02	18.9	1.1	461435	7.9E+03	238	10.	1266	48	1409	1.1E+02	5.33	27.3	1.7	0.0047	1.1E-03	30.4	6.2
34	38928	6.2E+02	15.2	1.0	459125	8.3E+03	196.2	8.6	921	36	1270	1.0E+02	4.69	28.4	2.1	0.00469	8.4E-04	30.1	7.2
35	32282	4.9E+02	18.7	2.2	458312	6.9E+03	207.3	8.8	1088	40.	1089	87	5.25	31.2	3.7	0.0047	1.1E-03	30.6	5.6
36	29932	4.3E+02	18.8	2.0	463161	8.8E+03	201.7	8.8	978	37	757	61	4.85	33.8	3.6	0.00468	7.8E-04	30.1	6.4
37	29752	5.1E+02	21.5	2.3	459914	8.9E+03	261	11	1366	53	930	75	5.24	28.7	3.1	0.00426	6.0E-04	27.4	4.9
38	31912	5.2E+02	16.6	1.5	461583	9.4E+03	212.4	9.4	1040	41	1224	99	4.90	28.1	2.6	0.00467	7.8E-04	30.0	6.9
39	35512	6.1E+02	16.2	1.7	451025	8.6E+03	201.4	8.8	1044	40.	2714	2.2E+02	5.18	27.5	3.0	0.00453	9.8E-04	29.1	6.8
40	30527	4.7E+02	15.1	1.3	458100	7.8E+03	186.5	7.9	930	34	1972	1.6E+02	4.99	28.4	2.5	0.0043	1.6E-03	27.3	6.9
41	24619	3.4E+02	15.87	0.82	449250	9.3E+03	194.0	8.5	1030	40.	2497	2.0E+02	5.31	27.7	1.6	0.0050	1.0E-03	32.4	7.1
42	29177	4.3E+02	18.4	1.6	458239	7.9E+03	198.8	8.4	1002	37	896	72	5.04	32.8	3.1	0.00440	7.4E-04	28.3	6.0

Table 3 continued

Grain	⁴ He pit volume (μm ³)	error (2σ)	⁴ He (nmole/g)	error (2σ)	U-Th-Pb pit volume (μm ³) ^a	error (2σ)	²³⁸ U (nmole/g)	error (2σ)	²³² Th (nmole/g)	error (2σ)	¹⁶⁷ Sm (nmole/g)	error (2σ)	²³² Th/ ²³⁸ U	(U-Th)/He Date (Ma)	error (2σ)	²⁰⁶ Pb/ ²³⁸ U	error (2σ)	²³⁸ U/ ²⁰⁶ Pb Date (Ma)	error (2σ)
43	40149	6.5E+02	19.7	1.3	466095	8.8E+03	242	10.	1198	45	1088	88	4.95	29.2	2.1	0.00451	6.6E-04	29.0	5.3
44	36061	5.4E+02	22.4	1.1	462340	7.5E+03	271	11	1400	51	1098	88	5.17	28.9	1.6	0.00460	7.4E-04	29.6	6.6
45	37529	4.8E+02	21.22	0.94	462120	8.1E+03	270	12	1416	53	1234	99	5.24	27.3	1.4	0.00469	7.0E-04	30.2	5.8
Inverse-Variance Weighted Mean ^b														27.98	± 0.86 2σ			28.08	± 0.90 2σ
MSWD														15.53				0.59	
Dispersion														20.6%				16.5%	

^a When calculating parent isotope concentrations, we subtract the volume of the previously ablated ⁴He pit from the U-Th-Pb pit.

^b The (U-Th)/He inverse-variance weighted mean uncertainty has been expanded by multiplying by the square root of the MSWD.

Table 4

Table 4
(U-Th)/He and U/Pb dates by LADD of Fish Canyon tuff zircon.

Grain	⁴ He pit volume (μm ³)	error (2σ)	⁴ He (nmole/g)	error (2σ)	U-Th-Pb pit volume (μm ³) ^a	error (2σ)	²³⁸ U (nmole/g)	error (2σ)	²³² Th (nmole/g)	error (2σ)	²³² Th/ ²³⁸ U	(U-Th)/He Date (Ma)	error (2σ)	²⁰⁶ Pb/ ²³⁸ U	error (2σ)	²³⁸ U/ ²⁰⁶ Pb Date (Ma)	error (2σ)	
1	5398.3	3.7	84.2	5.8	125137	5.4E+02	1719	94	1570	1.5E+02	0.91	31.3	2.6	0.004419	5.8E-05	28.43	0.82	
2	5637.8	6.5	76.4	6.6	121047	5.7E+02	2165	1.2E+02	1135	1.1E+02	0.52	24.3	2.4	0.004331	3.8E-05	27.86	0.73	
3	5356.8	2.5	69.2	4.8	116389	4.8E+02	1659	91	648	64	0.39	29.6	2.6	0.004374	4.1E-05	28.13	0.75	
4	4863.4	4.6	86.3	7.3	114370	4.2E+02	1759	96	1627	1.6E+02	0.93	31.3	3.0	0.004344	3.7E-05	27.94	0.75	
5	4561.22	0.60	105.0	8.2	127931	4.2E+02	2294	1.3E+02	1334	1.3E+02	0.58	31.2	2.9	0.004356	5.1E-05	28.02	0.72	
6	4088.2	4.1	50.7	2.9	144624	4.6E+02	1089	59	861	84	0.79	30.4	2.3	0.004430	7.9E-05	28.49	0.80	
7	4339.6	5.9	79	16	118299	4.1E+02	2134	1.2E+02	1048	1.0E+02	0.49	25.9	5.5	0.004432	3.2E-05	28.51	0.76	
8	4494.9	6.8	96.6	9.0	115259	5.1E+02	2283	1.2E+02	1383	1.4E+02	0.61	28.7	3.0	0.004513	4.2E-05	29.03	0.79	
9	4361.7	4.5	117.7	6.9	120898	5.2E+02	2338	1.3E+02	1589	1.6E+02	0.68	33.6	2.6	0.004534	8.8E-05	29.16	0.81	
10	4613.2	4.9	105.5	7.8	120035	6.0E+02	2545	1.4E+02	1984	1.9E+02	0.78	27.2	2.4	0.004392	4.2E-05	28.25	0.82	
11	4721.9	7.8	57.1	4.3	119271	4.6E+02	1285	70	1607	1.6E+02	1.25	26.7	2.4	0.004473	3.9E-05	28.77	0.78	
12	4776.6	2.4	48.1	3.2	128497	5.1E+02	1006	55	1015	99	1.01	30.0	2.5	0.00471	2.4E-04	30.3	1.5	
13	4353.9	5.1	104.0	7.2	121527	5.4E+02	2288	1.2E+02	1106	1.1E+02	0.48	31.6	2.7	0.004561	3.8E-05	29.34	0.79	
14	4401.7	2.9	67.4	5.0	116449	4.4E+02	1893	1.0E+02	1056	1.0E+02	0.56	24.4	2.2	0.004526	5.2E-05	29.11	0.82	
15	3907.7	4.3	61.6	3.8	135118	4.5E+02	1363	74	1028	1.0E+02	0.75	29.8	2.3	0.004585	4.8E-05	29.49	0.87	
16	4185.4	4.2	69.5	5.8	114062	4.1E+02	1874	1.0E+02	1157	1.1E+02	0.62	25.1	2.4	0.004425	3.9E-05	28.46	0.77	
17	3639.4	2.7	67.4	4.6	122146	6.7E+02	1341	73	943	92	0.70	33.4	2.8	0.004411	5.1E-05	28.37	0.82	
18	3963.6	4.5	59.7	3.8	141161	4.9E+02	1456	79	1180	1.2E+02	0.81	26.7	2.2	0.00441	1.0E-04	28.36	0.91	
19	3789.0	6.8	43.1	3.0	126958	5.2E+02	969	53	515	50	0.53	30.6	2.6	0.00453	1.2E-04	29.1	1.1	
20	3744.5	3.4	51.5	3.2	138280	5.2E+02	1243	68	2064	2.0E+02	1.66	23.2	1.8	0.004465	9.8E-05	28.72	0.91	
21	3773.2	4.0	72.9	5.2	118568	4.6E+02	1951	1.1E+02	987	97	0.51	25.8	2.3	0.004406	3.7E-05	28.34	0.76	
22	3885.1	3.5	97.1	9.0	119178	5.5E+02	2354	1.3E+02	1466	1.4E+02	0.62	27.9	2.9	0.00440	4.1E-05	28.3	0.75	
23	3719.1	3.5	166.7	7.5	116682	4.1E+02	4036	2.2E+02	2421	2.4E+02	0.60	28.1	1.9	0.004338	4.6E-05	27.9	0.72	
24	2876.51	0.84	119	11	114590	3.0E+02	2766	1.5E+02	1518	1.5E+02	0.55	29.6	3.0	0.004383	3.0E-05	28.19	0.75	
25	3701.6	5.3	92.6	9.1	107745	4.3E+02	2656	1.4E+02	999	98	0.38	24.8	2.7	0.004466	5.3E-05	28.73	0.78	
26	3648.0	6.2	65.5	3.8	111686	2.7E+02	1380	75	599	59	0.43	31.8	2.5	0.004480	5.4E-05	28.81	0.82	
27	3445.9	3.6	122	10	120317	4.0E+02	2727	1.5E+02	1490	1.5E+02	0.55	30.6	3.0	0.004386	3.3E-05	28.22	0.74	
28	3568.4	3.4	50.2	3.5	113555	4.8E+02	1107	60	634	62	0.57	31.0	2.7	0.004517	8.3E-05	29.06	0.85	
29	3569.5	7.1	73.3	6.1	118546	3.9E+02	1481	81	943	92	0.64	33.3	3.2	0.004512	7.8E-05	29.02	0.82	
30	3419.78	0.40	78.7	5.8	116404	5.8E+02	1911	1.0E+02	916	90	0.48	28.7	2.6	0.004455	3.5E-05	28.65	0.77	
31	3253.6	3.0	52.7	3.0	115836	4.1E+02	1230	67	885	86	0.72	28.4	2.1	0.004511	9.7E-05	29.02	0.84	
32	3688.5	5.4	77.7	6.4	117092	3.0E+02	1835	1.0E+02	1069	1.0E+02	0.58	28.8	2.8	0.004388	3.2E-05	28.23	0.75	
33	3699.5	3.6	68.0	4.4	113370	3.2E+02	1581	86	966	95	0.61	28.9	2.4	0.004465	5.2E-05	28.72	0.79	
34	3931.3	1.1	95.8	8.2	107089	4.2E+02	2658	1.5E+02	1206	1.2E+02	0.45	25.2	2.5	0.004368	9.7E-05	28.09	0.95	
35	2965.4	3.0	96.4	8.3	113943	3.5E+02	2445	1.3E+02	1162	1.1E+02	0.48	27.5	2.7	0.004621	7.9E-05	29.72	0.83	
36	1500.76	0.62	228	20	70898	1.0E+02	4233	2.3E+02	5853	5.7E+02	1.38	31.6	3.2	0.004456	8.2E-05	28.66	0.53	
37	2021.0	2.4	46.7	4.2	69162	1.3E+02	1299	71	910	89	0.70	23.9	2.4	0.00442	1.0E-04	28.45	0.66	
38	1809.54	0.89	121.4	8.2	69331	8.4E+01	2653	1.4E+02	2123	2.1E+02	0.80	29.9	2.5	0.004443	6.4E-05	28.58	0.41	
39	1896.9	4.2	42.0	4.8	80334	1.1E+02	1073	58	636	62	0.59	26.7	3.3	0.00449	1.1E-04	28.87	0.71	
40	5468	59	76.18	0.84	87917	9.2E+02	1624	71	1815	79	1.12	28.8	1.3	0.004428	7.6E-05	28.48	0.49	
41	5413	57	89.8	1.0	96377	1.1E+03	2241	98	1092	1.0E+02	0.49	27.8	1.4	0.004477	8.0E-05	28.79	0.51	
42	6131	69	90.9	1.0	78878	8.7E+02	2322	1.0E+02	1054	97	0.45	27.4	1.4	0.004492	8.1E-05	28.89	0.52	
43	4540	47	54.19	0.71	90707	1.1E+03	1203	53	914	84	0.76	29.6	1.5	0.004491	9.9E-05	28.88	0.64	
44	2855	30	43.74	0.52	100379	1.2E+03	972	43	850	78	0.87	29.0	1.4	0.004473	5.7E-05	28.77	0.36	
Inverse-Variance Weighted Mean ^b												28.38	± 0.73 2σ			28.63	± 0.11 2σ	
MSWD												4.58				1.31		
Dispersion												17.0%				2.8%		

^a When calculating parent isotope concentrations, we subtract the volume of the previously ablated ⁴He pit from the U-Th-Pb pit.
^b The (U-Th)/He inverse-variance weighted mean uncertainty has been expanded by multiplying by the square root of the MSWD.
ital. ages: Indicate grains in which the U/Pb age is younger than the (U-Th)/He age *and* the discrepancy falls outside of the range of the analytical uncertainty.

Table 5

Table 5
Typical percent contributions of measurement uncertainties to Fish Canyon LADD dates.

	Zircon (U-Th)/He	Titanite (U-Th)/He
⁴ He	49%	46%
⁴ He pit	14%	12%
²³⁸ U	0.7%	1%
²³² Th	0.2%	2%
¹⁴⁷ Sm	-	0.02%
U-Th-Pb pit	16%	13%
²³⁸ U concentration in standard	12%	13%
²³² Th concentration in standard	9%	13%
¹⁴⁷ Sm concentration in standard	-	0.6%
Total	100%	100%

Figure 1

FIGURES

Figure 2

Figure 3

Figure 4