A simple method for in-situ U–Th–He dating

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Abstract

This paper presents a significantly simplified method for in-situ U–Th–He dating removing the need to know any absolute concentrations. This is done by calculating the normalised U, Th, and He concentrations of a conventionally dated calibration standard from its measured Th/U ratio and known U–Th–He age, and scaling these concentrations to the raw U, Th, and He signals of the sample. The Th/U ratio of the standard can be determined from its measured $^{208}Pb/^{206}Pb$ ratio, removing the need to use NIST glass as a reference material. We introduce an LA-ICP-MS-based method to correct for variable ablation depths between the standard and the unknown, using the strength of the ablated ^{29}Si signal. Finally, we propose a pseudo-depth profile method to assess the effects of compositional zoning on the accuracy of in-situ U–Th–He data. The effectiveness of the proposed method has been demonstrated on three samples of gem-quality Sri Lanka zircon, which yield ages that are in agreement with previously published conventional U–Th–He measurements.
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1. INTRODUCTION

U and Th decay to different isotopes of lead by α-emission. This radioactive decay forms the basis of the U–Th–Pb and U–Th–He methods of geochronology, each of which have different geological significance. The U–Th–Pb method is used to study igneous and metamorphic processes affecting U–Th-bearing minerals such as zircon and apatite, whereas the U–Th–He method is used to study low temperature processes occurring near the Earth's surface. Since its revival by Zeitler et al. (1987), the U–Th–He method has found a large number of applications in tectonics and geomorphology (Reiners and Shuster, 2009). A fundamental driving force behind these applications have been technological advances in mass spectrometry and micro-analytical technology, which have led to a steady reduction of sample size while increasing sample throughput at the same time. The technological evolution of the U–Th–He method can be broadly divided into three periods. From 1987 to 2000, helium was measured by bulk degassing of multi-grain aliquots in a resistance furnace, and measuring the U–Th content on either the same or a different aliquot by XRF or TIMS (Zeitler et al., 1987; Lippolt et al., 1994; Wolf et al., 1996). In 2000, a method was developed to degas individual mineral grains by means of laser-heating in Pt or Nb 'micro-furnaces', followed by acid dissolution and U–Th analysis by isotope dilution in an ICP-MS (House et al., 2000). This method is still the most widely used technique today. Finally, in 2006, Boyce et al. developed in-situ U–Th–He geochronology by laser ablation. So far, this method has been successfully applied to monazite (Boyce et al., 2006, 2009), zircon (van Soest et al., 2008; Tripathy et al., 2010), and apatite (van Soest et al., 2008).

In-situ U–Th–He geochronology by laser ablation potentially offers the following advantages over conventional U–Th–He dating by whole grain degassing and dissolution. First, it dramatically increases sample throughput. Measuring the U and Th content of zircon by isotope dilution requires dissolution in hydrofluoric acid at high temperature and pressure using a Parr bomb for up to 48 h. In contrast, measuring the U and Th content by

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LA-ICP-MS, SIMS, or EMPA can be done in a matter of minutes. Second, the process of in-situ measurements of U and Th content of grains yields U–Th–Pb ages as a by-product. Thus, in-situ dated zircon crystals are double-dated by default, opening up exciting new research opportunities in detrital geochronology (Reiners et al., 2005). Currently, in-situ U–Th–He geochronology involves the following analytical steps (Boyce et al., 2006):

1. Polish and mount the crystals in Indium, which is a malleable material that does not break down in ultrahigh vacuum, in contrast with most epoxy resins or teflon.
2. Ablate the sample with a short wavelength laser and measure the amount of helium released (in moles).
3. Measure the ablation pit volume with an interferometric microscope to calculate the helium concentration (in moles per cc).
4. Measure the U and Th concentration by ICP-MS, SIMS, or EMPA (in moles per cc).
5. Enter the U, Th, and He concentrations into the helium ingrowth equation to calculate an age.

The revised method presented in this paper greatly simplifies the second and fourth steps of the current method while potentially completely removing the third. Section 2 shows how this is achieved by using an independently dated U–Th–He age standard, precisely determining its Th/U ratio, and comparing its raw U, Th, and He signals with those of the unknown sample. Section 3 introduces a way to determine the Th/U ratio of the standard without the need for NIST glass as a reference material, by measuring the ^{208}Pb/^{206}Pb ratio and assuming concordance of the U–Th–Pb system in the age standard. Section 4 outlines a method to estimate relative differences in laser ablation rate without the need for absolute depth measurements, by tracking the signal strength of stoichiometric ^{29}Si. Section 5 discusses the complications arising from compositional zoning of zircons, and outlines a 'pseudo depth profiling' method to semi-quantitatively assess the extent to which a sample suffers from such problems. Finally, Section 7 applies the proposed method to three shards of gem-quality Sri Lanka zircons that had been previously dated with the conventional U–Th–He method.

2. METHOD

Because the U–Th–He age equation is scale invariant, it does not matter if a mineral's U, Th, and He contents are expressed as atomic abundances or concentrations. They can even be renormalised to unity and plotted on a ternary diagram (Vermeesch, 2010). To calculate a helium age, it is not necessary to know the absolute concentrations of U, Th, and He. It suffices that two elemental ratios are known, such as U/He and Th/He, or U/Th and U/He. This insight forms the basis of the simplified method, which does not require knowledge of any absolute abundances or concentrations, but instead uses the raw mass spectrometer measurements. In its simplest form, assuming identical laser ablation rates in the standard and the unknown, the method works as follows:

1. Polish and mount two sets of grains in Indium: a standard of known U–Th–He age, and the sample of interest, whose age is unknown.
2. Ablate the grains and measure the raw helium signal (in A, V, or Hz) of the sample along with helium measurements of the age standard.
3. Measure the U and Th signals of the standard and the sample by LA-ICP-MS (in Hz).
4. Obtain the U–Th–He age of the sample by scaling its U, Th, and He signals to those of the standard.

In practice, the standard and the unknown are combined on a pairwise basis. This is done by calculating the normalised U, Th, and He concentrations of the standard from its known age and measured Th/U ratio (Fig. 1a), and then using this normalised composition as a benchmark against which to compare the U, Th, and He signals of the unknown (Fig. 1b and c). To correct for instrument drift and plasma-induced fluctuations in the ICP-MS, the U and Th signals should be measured relative to stoichiometric ^{29}Si. Because any analytical uncertainty in the age standard propagates into the unknown age, the choice of standard is very important. In order to qualify as a good U–Th–He age standard, a sample must fulfil the following requirements. First, it should be a large gem-quality crystal, ensuring relatively uniform ablation behaviour, while saving the user the trouble of polishing and mounting large numbers of crystals in Indium. Second, it should lack major compositional zoning and have relatively uniform U and Th concentrations. Third, it must not show any significant core-to-rim depletion in helium content due to diffusive loss during cooling. Sri Lanka zircon fulfils all these requirements and will be used to illustrate the effectiveness of the proposed method at the end of this paper (Section 7).

3. TH/U RATIO MEASUREMENTS

One of the advantages of the simplified method is that it avoids the challenges of measuring U and Th concentrations by ICP-MS, which is generally done relative to a NIST glass (Pearce et al., 1997) under the assumption that the elemental fractionation of U and Th in glass is the same as in zircon. Instead of absolute concentrations, the revised method essentially hinges on correctly determining the Th/U ratio. This can be done without the need to use a separate reference material, if a U–Th–He age standard is used that is concordant in its ^{232}Th/^{208}Pb and ^{238}U/^{206}Pb ages. The Th/U ratio can then be determined from the ^{208}Pb/^{206}Pb-ratio and the U–Th–Pb concordia age t:

$$\frac{^{232}\text{Th}}{^{238}\text{U}} = \frac{^{208}\text{Pb}(e^{\lambda_{238}t} - 1)}{^{206}\text{Pb}(e^{\lambda_{232}t} - 1)} \tag{1}$$

It is important to note that the Th/U ratio only needs to be determined for the standard. In other words, the use of Eq. (1) does not require U–Th–Pb concordance of the sample.

4. AN ICP-MS-BASED DRILL RATE PROXY

The pairwise dating method outlined in Section 2 and summarised in Fig. 1 makes one assumption, namely that
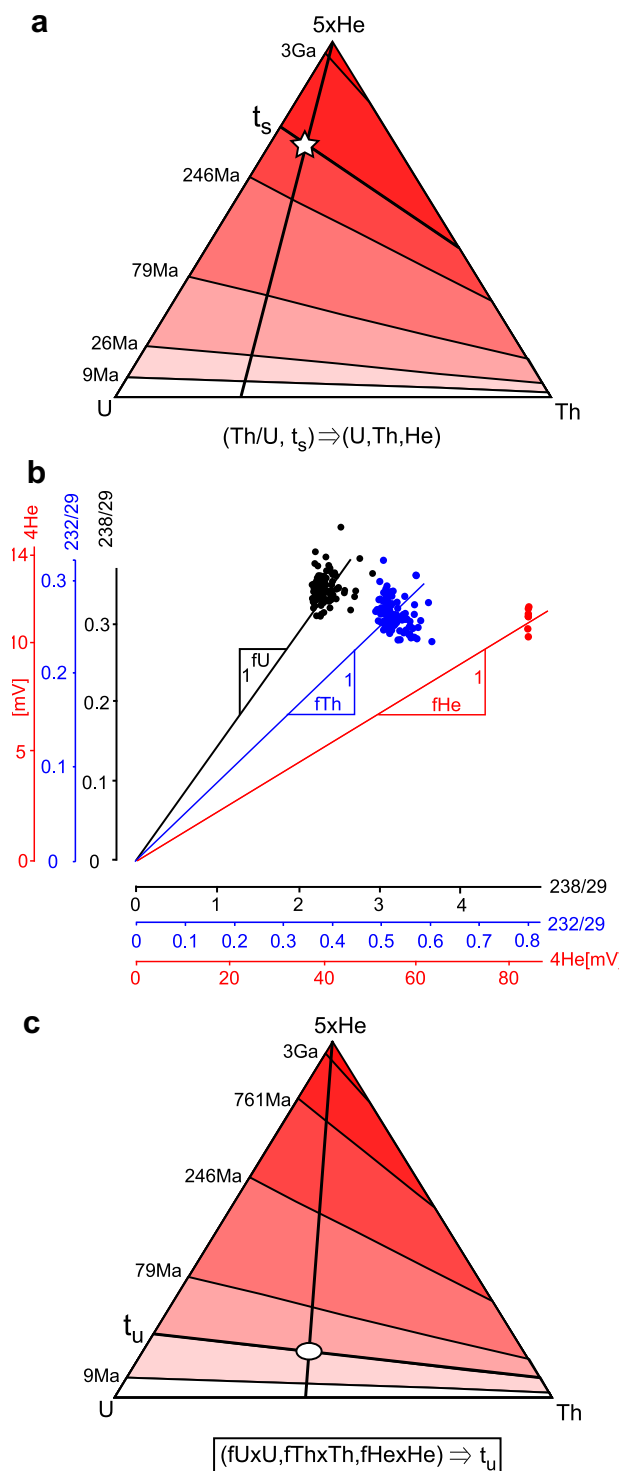
Fig. 1. Conceptual diagram of the pairwise dating method shown on ternary diagrams (Vermeesch, 2010). Age calculation involves the following steps: (a) Measure the Th/U-ratio of a standard of known U–Th–He age t_s, and calculate the corresponding normalised U, Th, and He abundances (star), where U + Th + He = 1. (b) Compare the raw mass spectrometer signals (relative to ^{29}Si for the ICP-MS measurements) of the standard with the corresponding signals of the unknown, to obtain three 'scaling factors' fU, fTh, and fHe. (c) Apply these scaling factors to the normalised U, Th, and He content of the standard and plug the resulting products (ellipse) in the U–Th–He age equation to obtain the U–Th–He age (t_u) of the unknown sample.

the ablation pit volume is the same for the U–Th–He age standard and the sample. Violation of this assumption may result in systematic errors. It is straightforward to correct these errors by defining a 'scaling factor' (fD, Table 1) for the ablation pit depth measured, for example, by interferometric microscopy (Boyce et al., 2006). At this point we should note that it is far easier to measure the depth of an ablation pit than it is to measure its volume. This is because the walls of pits produced by excimer lasers are often so steep that not enough light is available to produce an interferometric depth estimate of the ablation pit edges. Performing depth measurements adds another analytical step and partly defeats the purpose of the pairwise dating method. As a potential solution to this problem, we propose an LA-ICP-MS-based 'drill rate proxy' to be used instead of the interferometric microscope. The idea behind the drill rate proxy is that the beam intensity of a stoichiometric nuclide, such as ^{29}Si should increase proportionally with the rate of laser ablation. If this is correct, then the average ratio (fSi) of the time-resolved ^{29}Si spectrum of the unknown sample over that of the standard should equal the ratio of the ablation pit depths (fD). It then suffices to divide the normalised helium signal by fSi to account for the differential drill rates.

5. DEALING WITH COMPOSITIONAL ZONING

α-Particles are emitted with energies of several MeV and travel, on average, 15–20 μm in zircon before coming to rest (Farley et al., 1996; Hourigan et al., 2005). A significant fraction of the radiogenic ^{4}He produced by a typical ~100 μm grain is therefore ejected from the crystal. Corrections for this helium loss are on the order of 20% or more and represent the largest source of analytical uncertainty in conventional U–Th–He dating. The problem is that the α-ejection correction is made under the assumption of a uniform distribution of α-emitters, but that most naturally occurring crystals are zoned, resulting in incorrect α-retention factors. One of the advantages of in-situ dating is that, provided the ablation spot is located at least one α-stopping length away from the grain boundaries, no α-ejection correction is required. Unfortunately, this does not entirely free the method from the compositional zoning problem, because α-particles may be ejected from U–Th–enriched to U–Th–depleted zones, resulting in spatially variable U–Th–He ages.

These problems are not any easier to solve with the in-situ dating method than they are with the conventional U–Th–He method. In-situ dating, however, does allow zoning effects to be detected and quantified in ways that are not possible by conventional whole grain degassing and dissolution. Lateral age variations can be measured by placing several laser spots on the same polished zircon surface, while vertical age variability can be directly assessed from the time resolved ICP-MS signal (Hourigan et al., 2005). Applying the pairwise dating method to every ICP-MS measurement yields depth profiles of apparent U–Th–He ages, which may be more appropriately called 'pseudo depth profiles' because He is measured separately (in static vacuum) and from shallower depths than U and Th (which

are measured in dynamic vacuum). These pseudo depth profiles are very useful for detecting compositional zoning. If a pseudo depth profile is not flat, then the best age is obtained from the shallow parts of the U–Th ablation pit, which are closest to where the He was measured from.

6. ANALYTICAL METHODS

The effectiveness of the pairwise dating method was demonstrated using a number of independently dated test samples. This section provides the analytical details of the instrumental setup used in this proof of concept study.

6.1. Samples

We used three shards of gem-quality Sri Lanka zircon (G168, B188, and RB140), which had been previously analysed by conventional U–Th–He dating by micro-furnace heating and acid dissolution (Nasdala et al., 2004). All three crystals had similar U–Pb ages (547–566 Ma) and U–Th–He ages (437–450 Ma), but very different U and Th concentrations, with 'effective uranium' concentrations (eU ≡ U + 0.235Th) ranging from 317 to 1560 ppm. The combi-

nation of large (cm-scale) grain size, which enables multiple laser spots to be placed on the same crystal, and inter-sample compositional variability makes the Sri Lanka zircons ideally suited to test the precision and accuracy of the simplified method. In this study, we have used sample G168 as a standard, and samples RB140 and B188 as unknowns. In addition, the in-situ dating method was also applied to zircons from the Fish Canyon Tuff (27.8 ± 0.7 Ma, Tagami et al., 2003) and Tardree Rhyolite (58.7 ± 0.7 Ma, Tagami et al., 2003). These compositionally zoned samples were used to illustrate the pseudo-depth profile technique proposed in Section 4.

6.2. Noble gas measurements

All three grains were first mounted in teflon and polished with 3 μm alumina. They were then extracted from the teflon and pressed into strips of Indium foil with the polished side facing upwards. Helium analyses were done at the Open University. Gas was released by laser ablation using a 193 nm excimer laser, with a 70 μm spot size, an estimated fluence of ∼2 J/cm^2, and a pulse rate of 10 Hz for a duration of 20 s. The extracted gas was cleaned for 3 min using three SAES AP-10 getters to remove active

Table 1

Summary table of in-situ U–Th–He dating results from two shards of Sri Lanka zircon (B188 and RB140) measured relative to an independently dated standard (G168) of similar age (Nasdala et al., 2004). '2/8 (std)' = average ^{232}Th/^{238}U-ratio of the standard, calculated from its measured ^{208}Pb/^{206}Pb-ratio using Eq. (1). 'fU', 'fTh', and 'fHe' = average ratio of the blank-corrected ^{238}U, ^{232}Th, and ^{4}He signals relative to those of the standard. 'fD' = ratio of the average ablation pit depths. 't1' = U–Th–He age calculated using 'fD' as a depth correction factor. 'fSi' = average ratio of the blank-corrected ^{29}Si-signal of the unknowns relative to the standard. 't2' = U–Th–He age calculated using 'fSi' as a 'depth proxy'. 2σ analytical uncertainties are shown in between brackets. Extended analytical data tables are provided in the Supplementary information.

#	2/8 (std)	fU	fTh	fHe	fD	t1	fSi	t2
B188.1	0.1716	0.3793	0.2346	0.3219	0.901	431	0.883	439
	(0.0020)	(0.0063)	(0.0042)	(0.0045)	(0.039)	(21)	(0.016)	(12)
B188.2	0.1700	0.3927	0.2359	0.3412	0.890	447	0.892	445
	(0.0019)	(0.0064)	(0.0042)	(0.0043)	(0.051)	(27)	(0.016)	(12)
B188.3	0.1694	0.3961	0.2368	0.3313	0.894	428	0.888	431
	(0.0019)	(0.0070)	(0.0040)	(0.0066)	(0.036)	(21)	(0.015)	(14)
B188.4	0.1713	0.3876	0.2351	0.3199	0.914	414	0.959	395
	(0.0023)	(0.0111)	(0.0070)	(0.0060)	(0.037)	(22)	(0.015)	(15)
B188.5	0.1703	0.3762	0.2217	0.3114	0.869	436	0.946	402
	(0.0019)	(0.0068)	(0.0037)	(0.0061)	(0.059)	(32)	(0.014)	(12)
B188.6	0.1724	0.3863	0.2317	0.3089	0.890	412	0.888	413
	(0.0020)	(0.0072)	(0.0042)	(0.0040)	(0.049)	(25)	(0.010)	(10)
B188.7	0.1690	0.3799	0.2346	0.3160	0.897	424	0.869	438
	(0.0026)	(0.0085)	(0.0049)	(0.0054)	(0.044)	(24)	(0.015)	(14)
RB140.1	0.1716	0.2102	0.5836	0.1846	0.925	403	0.920	405
	(0.0020)	(0.0040)	(0.0095)	(0.0017)	(0.030)	(15)	(0.012)	(10)
RB140.2	0.1700	0.2164	0.5784	0.1932	0.926	411	0.963	395
	(0.0019)	(0.0031)	(0.0077)	(0.0039)	(0.047)	(23)	(0.011)	(11)
RB140.3	0.1694	0.2159	0.5854	0.1934	0.929	410	0.946	403
	(0.0019)	(0.0033)	(0.0100)	(0.0017)	(0.039)	(19)	(0.018)	(11)
RB140.4	0.1713	0.2069	0.5853	0.2015	0.963	428	0.959	429
	(0.0023)	(0.0062)	(0.0185)	(0.0034)	(0.040)	(23)	(0.017)	(17)
RB140.5	0.1703	0.2034	0.5622	0.2028	0.939	449	0.946	446
	(0.0019)	(0.0034)	(0.0074)	(0.0025)	(0.056)	(29)	(0.014)	(11)
RB140.6	0.1724	0.2032	0.5659	0.1965	0.932	439	0.985	416
	(0.0020)	(0.0042)	(0.0087)	(0.0028)	(0.049)	(26)	(0.014)	(12)
RB140.7	0.1690	0.2048	0.5810	0.2021	0.950	439	0.990	422
	(0.0026)	(0.0040)	(0.0120)	(0.0043)	(0.047)	(25)	(0.021)	(15)

gases before analysing ^{4}He using a multiplier collector on a MAP 215-50 noble gas mass spectrometer.

6.3. ICP-MS analyses

Following the helium measurements, the samples were recovered from the laser pan and analysed by LA-ICP-MS using the Agilent 7500 system at Birkbeck College, which is equipped with a frequency-quintupled (213 nm wavelength) New Wave Nd-YAG laser. Masses 29 (10 ms dwell time), 206 (40 ms), 207 (30 ms), 208 (100 ms), 232 (10 ms), 235 (10 ms), and 238 (10 ms) were analysed using a 55 μm spot, operated for 30 s at 8 Hz with a fluence of ~2 J/cm^2. A mixed Ar–He flux of 1.14 l/min carried the aerosol to the ICP-MS. The relatively unstable first 5 s of the ablation signal were discarded (Košler, 2008) and the remaining 25 s worth of data were corrected for the blank, which was measured during laser warmup time for each analysis. Plešovice zircon (Sláma et al., 2008) was analysed at regular intervals to normalise the ^{206}Pb/^{238}U, ^{207}Pb/^{235}U, and ^{208}Pb/^{232}Th ratios of the samples and verify their U–Th–Pb age concordance. Data reduction was done by taking the average ratios of the raw signals (in counts per second), and analytical uncertainties are reported as the standard errors of those averages.

7. RESULTS

All the relevant measurements required to calculate seven replicate U–Th–He age estimates of the two test samples (B188 and RB140) are shown in Table 1. This section discusses the different columns of this table from left to right. Extended data files for all three Sri Lanka zircon shards, as well as a detailed description of the data reduction protocols are provided in the Supplementary information.

7.1. Th/U ratio measurements

The second column of Table 1 contains the ^{232}Th/^{238}U-ratios of the age standard (G168), determined from its ^{208}Pb/^{206}Pb-ratio. These values cluster tightly around a mean value of 0.1706 ± 0.0011 with an MSWD of 1.4, indicating that the observed scatter is well explained by the analytical uncertainties. This confirms that G168 does not exhibit significant compositional zoning, thus fulfiling an important requirement for its use as a U–Th–He age standard. Although Th/U ratios are only needed for the standard, the fact that all three Sri Lanka zircons yield concordant ^{238}U/^{206}Pb, ^{232}Th/^{208}Pb (and ^{235}U/^{207}Pb) ages, offers an opportunity to thoroughly test the effectiveness of the ^{208}Pb/^{206}Pb-based method. Fig. 2 shows that the NIST610 and ^{208}Pb/^{206}Pb-based methods yield mutually consistent results, of similar analytical precision, which are generally in good agreement with the published Th/U ratio determined by ion-probe (Nasdala et al., 2004). In all three samples, the ^{208}Pb/^{232}Th-based ratio estimate is slightly closer to the published values than the NIST-based measurements. Only RB140 shows a significant disagreement, possibly indicating the presence of compositional zoning between different shards of this crystal.

7.2. Depth measurements

The next three columns of Table 1 contain the 'scaling factors' of U, Th, and He, as defined in Fig. 1. All these values are significantly less than one reflecting the lower actinide concentrations of samples B188 and RB140 compared to G168. B188 is richer in U, poorer in Th, and richer in He than RB140. At this point, the He signal has not yet been corrected for possible variations in the laser drill rate. Precise depth measurements of the ablation pits with a Zygo NewView 200 white-light microscope-based interferometer at Imperial College London indicate small but significant variability of the laser drill rates between samples. The average pit depths in the three Sri Lanka zircons used in this study are 17.93 ± 0.20 μm for B188, 18.65 ± 0.38 μm for RB140, and 19.93 ± 0.25 μm for sample G168, yielding 'fD-factors' of 0.90 ± 0.01 for B188 and 0.94 ± 0.02 for RB140, shown in the sixth column of Table 1. It is interesting to note that the greatest pit depths are found in sample G168, which also has the highest U and Th content. The eighth column contains the drill rate proxy (fSi) which shows a reasonable linear correlation with fD for the three Sri Lanka zircons (Fig. 3). The individual values of the drill rate proxy are significantly more scattered than the pit depths, but their averages scale proportionally.

7.3. Ages

Two ages have been calculated for each measurement. The first, shown in the seventh column of Table 1, was calculated using the measured pit depths (i.e., fHe was divided by fD). The second, shown in the last column, was calculated using the drill rate proxy (fHe divided by fSi). The central ages (Vermeesch, 2010) resulting from both methods are 429 ± 9 and 426 ± 16 Ma for B188, and 423 ± 9 and 419 ± 14 Ma for RB140, respectively, indicating that the drill rate proxy is equally accurate, but less precise than
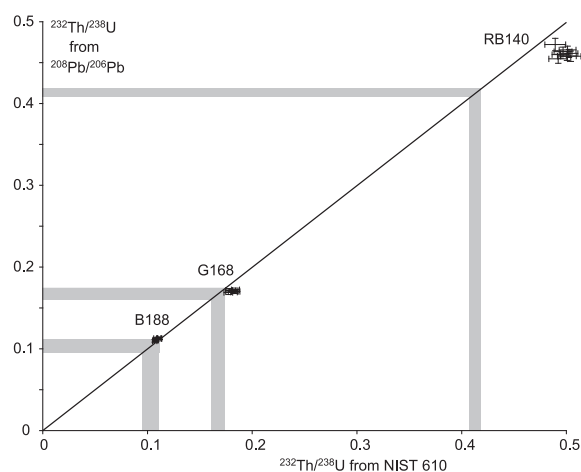

Fig. 2. Comparison of two ^{232}Th/^{238}U-ratio estimators. X-values were calculated relative to NIST SRM 610 glass (Pearce et al., 1997). Y-values were calculated from the measured ^{208}Pb/^{206}Pb-ratios using Eq. (1). Grey bands show the published Th/U ratios measured by SIMS (Nasdala et al., 2004). Black line shows the 1:1-ratio, error bars are 2σ.

the actual pit depth measurements. These central ages compare favourably with the published values of 438 ± 20 for B188 and 437 ± 20 Ma for RB140 (Nasdala et al., 2004), and are more tightly clustered than is commonly observed in conventional U–Th–He geochronology, with compositional MSWD values of 1.83 and 2.97, respectively (Fig. 4). This tight clustering confirms, first, the potential of in-situ U–Th–He geochronology to produce data that are just as precise as conventional whole-grain degassing and dissolution and, second, the suitability of Sri Lanka zircon as a well-behaved age standard.

7.4. Pseudo-depth profiles

The pseudo-depth profile method confirms that the Sri-Lanka zircons exhibit little or no compositional zoning (Fig. 5). The method was also tested on zircons from the Fish Canyon Tuff (FCT) and Tardree Rhyolite (TR), which are known to be strongly zoned (Tagami et al., 2003). Unfortunately, the relatively low sensitivity of the MAP-215 noble gas mass spectrometer used for the He measurements, combined with the young ages (27.8 ± 0.7 Ma for FCT and 58.7 ± 0.7 Ma for TR Tagami et al., 2003), and small grain size, which necessitated smaller 40 μm ablation spots, resulted in high (up to 20%) blank corrections of the He measurements limiting the precision of the U–Th–He ages. Therefore, the two depth-profiles shown in Fig. 5 are provided for illustrative purposes only. They confirm, however, that the analysed FCT and TR zircons are compositionally inhomogeneous, causing non-flat pseudo-depth profiles. The most reliable ages are obtained from the 'shallow' parts of these profiles.

8. DISCUSSION AND CONCLUSIONS

This paper introduced a simple method to measure U–Th–He ages in zircon by means of laser ablation. Instead
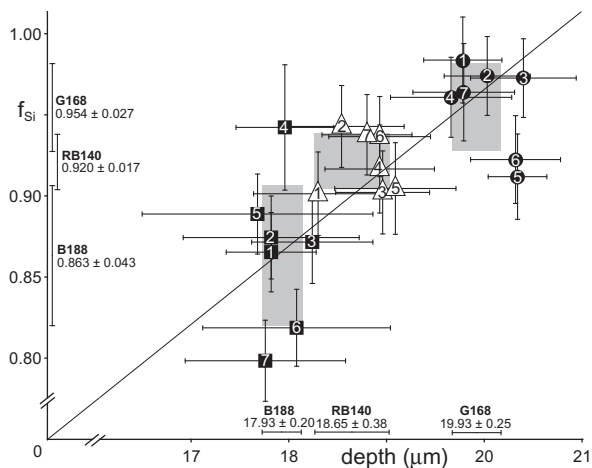
of measuring absolute concentrations of U, Th, and He, as is customary in conventional U–Th–He geochronology, the new method uses an independently dated age standard, against which the samples of interest are compared. Three shards of gem-quality Sri Lanka zircon were successfully dated, demonstrating the effectiveness of the pairwise dating method as a means of determining accurate and precise U–Th–He ages in just a fraction of the time required to perform a conventional U–Th–He age measurement. The use of independently dated calibration standards is not a new idea in thermochronology. Both the fission track and $^{40}Ar/^{39}Ar$ methods have benefited from similar approaches (Hurford and Green, 1983; McDougall and Harrison, 1999).

An important area of future progress is the further development of the drill rate proxy as a means of removing the need to measure pit depths by interferometric micros-
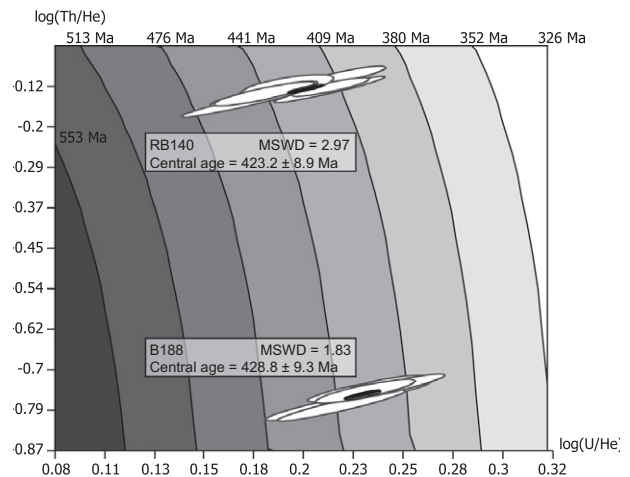

Fig. 4. Samples B188 and RB140 shown on a log-ratio plot (Vermeesch, 2010). White ellipses show the individual measurements and their analytical uncertainties (2σ). Black ellipses show the error-weighted geometric mean compositions. MSWD values refer to the compositions and not the ages.
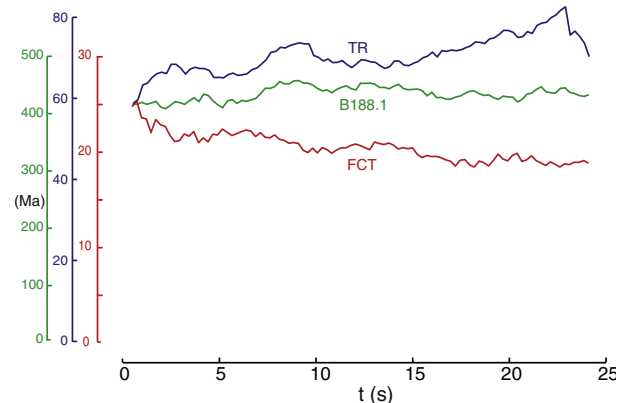

Fig. 5. U–Th–He 'pseudo depth profiles' of Sri Lanka zircon B188, Fish Canyon Tuff (FCT), and Tardree Rhyolite (TR). Horizontal axis shows ablation time, in seconds (preceding 5 s were discarded, Košler, 2008). Vertical axes show age (in Ma).

Fig. 3. Comparison of the ^{29}Si-based 'drill rate proxy' (y-axis), and the ablation pit depths measured by interferometric microscopy (x-axis) (black squares: B188, white triangles: RB140, black circles: G168). 'fSi' is the average ratio of time-resolved ^{29}Si beam intensity relative to Plešovice zircon (Sláma et al., 2008). Weighted mean values are shown as grey boxes. All error bars are 2σ.

copy. Preliminary experiments presented in this paper yield promising results but clearly more work needs to be done to make this a viable alternative to interferometric microscopy. First, this study employed two different types of laser, a 193 nm excimer laser for the helium measurements, and a 213 nm Nd-YAG laser for the U, Th, Pb and Si measurements. The accuracy of ^{29}Si beam intensity as a proxy for ablation rate is likely to improve if an excimer laser is used for both stages of the analysis. Second, it would be useful to quantify the efficiency of laser ablation in vacuum (in a noble gas mass spectrometer) versus ablation in a gas flux (in the ICP-MS). Third, some of the excess scatter of the drill rate proxy may be caused by plasma-induced variability of the ^{29}Si signal. One way to correct such drift in instrument sensitivity would be to use a desolvating nebuliser to aspirate a tracer solution into the plasma containing a nuclide absent from both the zircon and the carrier gas, and measure the ^{29}Si signal relative to this solution (Horstwood, 2008).

Further work is also needed to demonstrate the applicability of the proposed method to the small and young zircon crystals that are commonly found in real geological field settings, rather than the large and old samples used in the proof of concept study. Ongoing hardware upgrades in the noble gas laboratory at Birkbeck will allow us to move in this direction. In the meanwhile, we believe that the methodological developments outlined in this paper represent a significant step towards making in-situ (U–Th)/He geochronology a viable alternative to whole grain degassing and dissolution, with the potential to produce a quantum leap in sample throughput and resolution with significant benefits to the Earth surface geodynamics community.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.11.042.

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