LGC-1: a zircon reference material for *in-situ* (U-Th)/He dating

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Abstract

A pairwise *in-situ* (U-Th)/He dating method has been proposed for mitigating matrix-related bias in U and Th measurements using synthetic reference materials. This method requires a natural zircon reference material whose (U-Th)/He age should be homogeneous on the scale (~10-100 µm) to be used in such dating experiments. A newly characterised zircon LGC-1 megacryst fulfils this requirement. This pale-yellowish, flawless Sri Lanka gem specimen is about 1.2\*0.8\*0.8 cm in size. Optical microscopy, cathodoluminescence-imaging, X-ray elemental mapping, and Raman spectroscopy on a large number of random shards did not reveal any detectable textural and compositional heterogeneity. Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) analyses on a large number of randomly selected fragments yield 266 measurements of U, Th and Pb concentrations, which are within the corresponding experimental uncertainties. The weighted mean U, Th and Pb concentrations are 357.7 ± 1.8 ppm, 740.9 ± 5.0 ppm, and 39.06 ± 0.18 ppm, respectively, with a weighted mean Th/U ratio of 2.07 ± 0.01, indistinguishable from Isotope Dilution ICP-MS (ID-ICP-MS) and Thermal Ionization Mass Spectrometry (ID-TIMS) results. ID-TIMS U/Pb ages are concordant within uncertainties of decay constants, with a concordia age of 541.70 ± 0.70 Ma. Conventional (U-Th)/He dating on 28 random shards from the crystal in different laboratories gives a central age of 476.4 ± 5.7 Ma. Six *in-situ* (U-Th)/He analyses yield consistent 4He concentrations and ages with weighted mean values of 1248 ± 46 nmol/g and 462 ± 21 Ma, respectively. Fractions of this zircon have been shared with several laboratories in the Australia, China, UK and US, and are expected to serve as a reference for both *in-situ* and conventional (U-Th)/He analyses. The combination of analytical methods used to characterize LGC-1 zircon may be used as a template for future age reference calibration.

**Highlights:**

No texture and compositional zoning in zircon LGC-1

A zircon reference material for *in-situ* (U-Th)/He dating

Suggestions for future age reference calibration

**Keywords**: Zircon LGC-1, Reference material, *In-situ* (U-Th)/He dating, Geochronology.

1. Introduction

Zircon is an extremely durable mineral, which is commonly found in siliciclastic rocks and is rich in U and Th. These properties make zircon uniquely well suited for sedimentary provenance studies. Using micro-analytical methods such as laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) or secondary ion mass spectrometry (SIMS), it has become routine practice to determine the probability distribution of ~100 detrital zircon U/Pb ages as a characteristic fingerprint to trace the flow of sand through modern and ancient sediment routing systems. Dozens of papers employing this method are published each year. The power of such provenance studies would greatly increase if it were possible to routinely double-date detrital zircons with the *in-situ* U/Pb and (U-Th)/He methods (Evans et al., 2015; Horne et al., 2016; Rahl et al., 2003; Reiners et al., 2005).

Several research groups around the world are currently pursuing this goal using a variety of approaches. While the *in-situ* U/Pb method has been well-established, the *in-situ* (U-Th)/He method is still under development. Boyce et al. (2006), Tripathy-Lang et al. (2013) and Horne et al. (2016) used a 'first principles' approach, in which the absolute concentrations (e.g., in units of ppm or fmol/µm3) of U, Th and 4He are measured by laser ablation. Vermeesch et al.(2012) proposed an alternative approach, in which the raw mass spectrometric measurements are normalised to a standard of known 206Pb/238U, 208Pb/232Th and 206Pb/238U, 208Pb/232Th and 208Pb/206Pb and (U-Th)/He ages. A recent study by Evans et al. presented a modified version of a ‘pairwise’ dating method proposed by Vermeesch et al.(2012). The modified method uses a ‘Kappa’ calibration constant derived from multiple standard analyses for age calculation of unknown samples. The method is similar to the zeta calibration factor for fission-track (Hurford and Green, 1983) or the J-factor for 40Ar/39Ar dating (Mitchell, 1968).

The pairwise dating method crucially depends on the availability of a well behaved age reference material that is spatially homogeneous in its U, Th and He content. This condition in turn requires large, unzoned crystals with a simple thermal history. Previous in-situ dating studies by Vermeesch et al. (2012) and Evans et al. (2015) employing the pairwise dating methods have used Sri Lanka zircon crystals (RB140 and B188) from Nasdala et al. (2004) as age references. These cm-sized gem-quality zircons are an attractive option for three reasons. First, they are old (> 400 Ma) and rich in actinides. This is important because the analytical uncertainty of the reference’s U, Th and He measurements is propagated into the sample’s age uncertainty. By being very rich in the three elements of interest, this error component is kept very small. Second, Sri Lanka zircons are often of centimeter-size, so that a single crystal can supply enough material to last several laboratories for many years. Third and finally, although all Sri Lanka zircons are found as pebbles in alluvial sediments, their ultimate source is likely to be found in pegmatitic rocks that have undergone a simple cooling history. Being tectonically inactive, Sri Lanka is characterised by extremely low erosion rates that have kept the zircons near the Earth’s surface for hundreds of millions of years (Von Blanckenburg, 2004). As a result, the gem quality zircons lack the helium depleted rims that characterise most natural zircons. Furthermore, by virtue of having been transported and abraded during transport and deposition, Sri Lanka zircons have generally lost any diffusively depleted rim that might have existed.

Motivated by the above background information, we examined a number of commercially sourced gem-quality Sri Lanka zircon megacrysts, from which we selected five grains with different, but uniform colours for further detailed compositional analyses using a combination of methods, including optical microscopy, Cathodoluminescence-imaging, Raman Spectrometry, wavelength dispersive X-ray spectroscopy, Electron-probe Microanalysis (EPMA), LA-ICP-MS, Isotopic Dilution Thermal Ionization Mass Spectrometry (ID-TIMS) U/Pb dating,conventional (U-Th)/He dating, and *in-situ* (U-Th)/He dating. Results determined from a large number of randomly selected chips of LGC-1 grain did not reveal any remarkable textural zoning or compositional heterogeneity. The consistent (U-Th)/He ages fulfil the requirements for a high-quality age reference materia for the pairwise *in-situ* (U-Th)/He dating methods of Vermeesch et al. (2012) and Evans et al. (2015).

2. Requirements for age references of the pairwise method

Similar to requirements for age references of other *in-situ* geochronological methods, an *in-situ* (U-Th)/He age reference needs to be homogenous in its (U-Th)/He age. An *in-situ* (U-Th)/He age analysis involves two ~10-50-µm laser ablation spots, one for 4He analyses in an ultra-high vacuum noble-gas system, and the other for U-Th analyses using LA-ICP-MS, or SIMS. These two spots are positioned either spatially close, or one reoccupying (or inside of) the other (e.g., Evans et al., 2015; Vermeesch et al., 2012). To produce a consistent age, the 4He and U-Th measurements from the two spots should be representative of each other; it is thus required to have uniform 4He and U-Th distributions at least at a scale of tens of micrometers. Otherwise, incomparable 4He and U-Th results would be obtained, due to 4He redistribution by alpha recoil (Farley et al., 1996).

Also, zircon samples that have experienced a complex thermal history may not be suitable as an *in-situ* dating reference material. This is because helium diffusion at elevated temperatures may produce a 4He gradient from the grain margin to the core. To summarize, an *in-situ* (U-Th)/He age reference material should fulfil the following criteria. (1) The grain should be of a relatively considerable size to allow for sharing among laboratories. (2) No significant U and Th zoning and impurities (such as mineral or fluid inclusions) should be present in the grain. (3) The sample’s thermal history should be relatively simple.

3. General physical properties, sample preparation and analytical methods

Zircon LGC-1 is one of five samples studied. It is of uniform pale-yellowish colour, with a size of about 1.2 × 0.8 × 0.8 cm (Fig. 1a). The grain is moderately rounded; no original crystalline facets are preserved, suggesting long-distance fluvial transport. The removal of the grain’s crust has thus probably eroded away any marginal helium gradient zone formed by 4He redistribution through alpha-ejection and 4He diffusion prior to fluvial rounding. 4He is likely depleted in the rim due to post rounding 4He redistribution. To distinguish the rim from interior, the shell of this grain was painted using dark permanent ink before crushing into small fragments. All analyses performed in this study were carried out using inkless shards from its interior.

Sub-mm-sized fragments were used for compositional and conventional (U-Th)/He studies, and mm-sized ones for *in-situ* (U-Th)/He analyses. To ensure thorough characterization of the studied zircon, the chemical and isotopic analyses were conducted using a range of different techniques. Where possible and necessary, the measurements were reproduced by similar techniques in different laboratories, as detailed below.

3.1. Fission-track mapping and dating

Fission tracks in zircon, formed by spontaneous fission events of 238U, are visible under optical microscopes after being enlarged by chemical etching. Any density zoning of fission-tracks thus indicate U inhomogeneity. The most appealing advantage of optical fission-track mapping is that it enables quick examination of evident U zoning in large and numerous grains without incurring any significant financial cost. For this reason, we firstly studied the fission-track distribution in the zircon sample.

Zircon shards were mounted in Teflon sheet, ground and polished to an optical finish to expose internal grain surfaces. Polished mounts were etched in a eutectic KOH-NaOH melt at ~235 oC for ~10 hours. Spontaneous track distributions were analyzed using a Zeiss Axioplan microscope, coupled with a projection tube and a digitizing tablet. The microscope eyepiece graticule was precisely calibrated using a stage micrometer.

Zircon fission-track dating used a modified version of the LA-ICP-MS dating method of Hasebe et al. (2004). After point-counting of fission-track density, the zircon mount was transferred to LA-ICP-MS for U concentration determination (for the experiment method, see section 3.4). Age calculation used the following equation:

where *t* is fission-track age (in yr), *λD* and *λf* are 238U total decay constant (1.55125 × 10-10 yr-1) (Jaffey et al., 1971) and spontaneous fission decay constant (8.45 × 10-17 year-1) (Holden and Hoffman, 2000), *ρs* is the spontaneous fission track density (in N/cm-2), *M*238isthe molar mass of the parent isotope (in g/mol), *cU* is the present U concentration (in ppm), *NA* is Avogadro's number (in mol-1), *d* is the zircon density (4.65 g/cm3), *Rsp* (5.51 × 10-4 cm) is a half of the mean etchable spontaneous fission-track length in unannealed zircon (Yamada et al., 1995), *k* (set as 1) is an experimental factor that may vary with etching and observation conditions.

3.2. Cathodoluminescence (CL)-imaging, Electronprobe microanalysis (EPMA) and X-ray elemental mapping

To provide electric conductivity, carbon coating was applied to the zircon fission-track mounts and new ones mounted in epoxy resin on glass slides. CL-imaging, EPMA and X-ray elemental mapping was performed using a Jeol JXA8100 Super­probe equipped with wavelength dispersive spectrometers (WDS) and an Oxford Instruments INCA energy dispersive system (EDS) at UCL/Birkbeck. CL-imaging was performed using 15 kV accelerating voltage and 1.0 × 10-8 A beam current.

EPMA major element analyses were carried out using an accelerating voltage of 15 kV, current of 2.5 × 10-8 A, and a beam diameter of ~1 μm. The counting times were 20 s on the peak and 10 s each on the high and low backgrounds. Analyses were calibrated against standards of natural silicates, oxides and Spec-pure metals with data corrected using a ZAF program.

X-ray U and Th elemental distribution maps were obtained using an accelerating voltage of 15 kV with an acquisition time of 20 s and a beam current of 1 × 10-8 A with a diameter of ~1 μm.

3.3. Raman Spectrometry

A ~1.5-mm-size fragment was mounted with cyanoacrylic glue on glass and polished to an optical finish to expose internal grain surfaces. By dissolving away the glue in acetone, the polished grain was retrieved for Raman Spectrometry. Raman spectra were obtained using a Renishaw spectrograph system 1000 grating spectrometer, based on use of Kayser™ notch filters with a sensitive CCD (charge-coupled device) detector, coupled to a Leica microscope equipped with a ×50 ultra-long working distance objective. The spatial resolution at the sample surface is approximately 2 μm. Spectra were excited with a near-infrared (785 nm) laser. The spectral resolution is ~2.5 cm-1. The wavenumber is calibrated to an accuracy of ±1 cm-1 by reference to the emission lines of a Ne lamp. Band wave numbers and peak areas were determined by fitting a single Lorentzian curve to the appropriate data range after conducting a local baseline correction. Real band full width at half band maximum (FWHM) values were calculated by correcting measured FWHMs according to the function (Irmer, 1985)

where *b* is the real (i.e. corrected) FWHM, *bs* is the measured FWHM, and *s* is the spectral resolution of the Raman system (2.5 cm−1).

3.4. LA-ICP-MS (U and Th measurements and U/Pb dating)

About 50 grains on the zircon mounts used for CL-imaging and FT-mapping were analysed using a LA-ICP-MS system for determining their U and Th concentrations and U/Pb ages. The LA-ICP-MS system includes a New Wave NWR193 excimer laser ablation system and an Agilent 7700x quadrupole mass spectrometer. The laser was set to produce ~2.5 J/cm2 energy density at 8 Hz repetition rate for 25 seconds. The spot diameter was set to 25 µm for all batches of analyses except for one batch, which used a 15 µm spot. Repeated measurements of internal U/Pb age standard Plešovice [TIMS reference age of 337.13 ± 0.37 Ma (Sláma et al., 2008)] and NIST-610 silicate glass (Jochum et al., 2011) were used to correct for instrumental mass bias and laser-pit-depth-dependent isotopic fractionation. GJ-1 (Jackson et al., 2004) and 91500 zircon (Wiedenbeck et al., 2004) were used as external standard to provide additional check of the analytical accuracy. Data reduction was processed using the GLITTER® software package (Griffin et al., 2008).

3.5. ID-TIMS analysis

Several randomly selected sub-mm-sized shards were used for ID-TIMS U/Pb dating at NERC Isotope Geosciences Laboratory (NIGL). A modified version of the chemical-abrasion (CA) technique (Mattinson, 2005) was applied to the shards. Zircons were heated in a muffle furnace at 900 ± 20 °C for ~60 hours in quartz beakers before being transferred to 3 ml Hex Savillex beakers, which were in turn placed in a Parr vessel, and leached in a ~5:1 mix of 29M HF + 30% HNO3 for 12 hours at ~180 °C. The acid solution was evaporated; grains rinsed in ultrapure H2O, fluxed on a hotplate at ~80 °C for 1 hr in 6 M HCl, ultrasonically cleaned for ~1 hr, and then placed back on the hotplate for an additional 30 min. The HCl solution was removed and the grains were selected and again rinsed (in ultrapure acetone) prior to being transferred to 300 µl Teflon PFA microcapsules and spiked with the mixed EARTHTIME 233U-235U-205Pb tracer (Condon et al., 2015; McLean et al., 2015). The zircon fragments were dissolved in ~120 µl of 29 M HF with a trace amount of 30% HNO3 at ~220 °C for 48 hours, with the microcapsules housed within Parr vessels. The zircon digests were subsequently dried to fluorides and then converted to chlorides in 3M HCl at ~180 °C overnight. U and Pb were separated using standard HCl-based anion-exchange chromatographic procedures on 0.05 ml PTFE columns manufactured in-house (Corfu and Noble, 1992).

Isotope ratios were measured using NIGL’s Thermo-Electron Triton TIMS dedicated to low-blank U/Pb geochronology (Triton 2). Pb and U were loaded together on a single Re filament in a silica-gel/phosphoric acid mixture (Gerstenberger and Haase, 1997). Pb isotopes were measured by peak-hopping on a single SEM detector. U isotope measurements were made in static Faraday mode. Age calculations and uncertainty estimation (including U/Th disequilibrium) were based upon the algorithms of Schmitz and Schoene (2007). All acids were prepared by sub-boiling distillation: HCl and HNO3 were double-distilled in quartz and HF was double-distilled in Teflon. Ultrapure water with a resistance of 18 MΩ was prepared with a Milli-Q system. All reagents were blank-checked prior to use.

206Pb/238U dates are calculated using the 238U and 235U decay constants of Jaffey et al. (1971) and corrected for initial U/Th disequilibrium using an assumed magma Th/U ratio of 4, typical for magmatic systems. A value of 238U/235Uzircon = 137.818 ± 0.045 (Hiess et al., 2012) was used in the data reduction calculations. Compared to calculations using the old ‘consensus’ value (238U/235U = 137.88) this has the effect of reducing 207Pb/206Pb dates by ca. 0.98 Myr at the age range of interest (ca. 540 Ma) and reduces the 206Pb/238U dates by <5 kyr.

3.6. Conventional (U-Th)/He dating

Conventional (U-Th)/He dating was performed at three laboratories at the University of Melbourne (UoM), Institute of Geology, Chinese Academy of Geological Sciences (IGCAGS), and Univerisity College London (UCL), respectively. Zircon shards were randomly selected under a binocular microscope. Protocols for He analysis in all laboratories followed an established routine for laser He extraction (House et al., 2000). Zircon samples were loaded into platinum (at UoM) or niobium capsules (at IGCAGS and UCL), and outgassed at ~1300 oC for 10 minutes, using a fibre-optically coupled near infrared diode laser. 4He abundances were determined by isotope dilution using a pure 3He spike. Standard calibration runs are performed two – three times a day using a standard 4He tank, which is periodically calibrated against a second 4He depletion rank. After degassing, the packages were transferred out of the laser-heating chamber for U and Th analyses, using Isotopic Dilution ICP-MS (ID-ICP-MS) method. The zircon packages have been processed differently in the three laboratories. (1) For grains packed and degassed in platinum tubes at UoM, the package is firstly pried open to retrieve the grain for zircon digestion. (2) For grains packed and degassed in niobium tubes at IGCAGS and UCL, the entire package was digested. The same zircon digestion procedures were used in all laboratories. The retrieved zircon grain or Nb-grain package was transferred to 350 µl Teflon PFA microcapsules and spiked with 235U and 230Th tracer. The zircon fragments were dissolved in ~300 µl of ultrapure 29 M HF with 50-100 µl 30% ultrapure HNO3 at ~220 °C for 48 hours, with the microcapsules housed within Parr bombs. Samples are then heated until dry and rebombed in HCl for 12-24 hours at 200°C to ensure dissolution of fluoride salts. After a final partial evaporation, the sample is diluted in 2% HNO3 with a trace amount of HF at MoU and UCL, or in Milli-Q water at IGCAGS for analysis on a Varian quadrupole ICP-MS (Agilent #7700x at UoM and UCL and Agilent 7500CS at IGCAGS). Fish Canyon Tuff zircon grains were run as an external standard with samples analysed to provide an additional check on analytical accuracy.

3.7. *In-situ* (U-Th)/He dating

*In-situ* (U-Th)/He dating was conducted at Curtin University on the RESOchron instrument and the methods loosely followed the protocols of Evans et al. (2015). Zircon shards were mounted onto Teflon ground and polished to an optical finish to expose internal grain surfaces. Helium extraction used a Compex 102 excimer laser at consistent laser conditions (50 μm diameter beam size, 1-2 J/cm2 energy and 5 Hz repetition rate for 6 seconds). Gas from the ablated sample was purified using hot and cold Ti-Zr getters, spiked with 3He, and expanded to a Pfeiffer PrismaPlus™ quadrupole mass spectrometer. Sample 4He was determined by isotope-dilution using 3He spike and 4He gas standards of known volume, analyzed throughout the run. The volume of each laser pit for helium extraction was extracted directly from topography images captured using the Atomic Force Microscopy (AFM) using a Bruker Dimension Icon SPM system operated in ScanAsyst Mode using a ScanAsyst-Air probe. Then, the zircon mount was transferred to the Laurin Technics S-155 flow-through cell for a second ablation to determine U and Th contents (in addition to a range of trace elements, if desired) using a CompexPro 102 excimer laser and an Agilent 7700x ICP-MS. The laser ablation spot was placed over the previously ablated 4He pit. Samples and standards were ablated using the same laser settings (a 75 μm diameter beam, laser energy of 2.5 J/cm−2, 30 s at a 7 Hz repetition rate). International glass standard NIST 610 was used as the primary standard to calculate elemental concentrations (using 29Si as the internal standard element) and to correct for instrument drift.

4. Results and discussion

4.1. Textural study by CL-imaging and Raman Spectroscopy

CL-imaging was performed to check textural heterogeneity of the LGC-1 and to guide other analyses. CL-imaging of two zircon mounts including some 150 shards of LGC-1 did not show any visible internal texture variations (Fig. 1b). Since the zircon shards appear to be uniform in CL, other analyses, presented below were performed on randomly selected grains.

Raman band broadening has been calibrated as an index for characterizing radiation damage of zircon crystal lattice by alpha-decay events of U and Th, and their unstable daughter nuclei (Nasdala et al., 2004; Nasdala et al., 2001). Heterogeneous radiation damage is thus expected if the U and Th distribution is zoned. Following Nasdala et al. (2001), the FWHM of the ν3(SiO4) Raman band (internal antisymmetric stretching of SiO4 tetrahedrons; B1g mode) is determined. A total of 14 analyses suggest that the ν3(SiO4) band is located at a Raman shift of ~1003 cm−1, irrespective of the variations in the incident laser energy (Fig. 2). Both the raw and corrected FWHMs of the 14 analyses vary narrowly between 8.2 cm−1 and 9.7 cm−1. The weighted mean of corrected FWHMs is 8.6 ± 0.3 (1sd) cm−1. The consistent values of the Raman shift and FWHMs indicate little, if any, heterogeneity in radiation damage exist. Further, these Raman shift values are evidently lower than most zircon standards, such as Plešovice zircon (Sláma et al., 2008) with the corresponding FWHMs of 10-30 cm−1, M257 (Nasdala et al., 2008) of ~11 cm−1, suggesting a low to moderate radiation-damaged state of LGC-1.

To evaluate the degree of radiation damage healing, the Raman data is compared to the alpha-fluence *Dα*, the number of α-decay events per gram (α/g), calculated from

where *cU* and *cTh* are the present U and Th concentrations (in ppm), *NA* is Avogadro's number (mol-1), *M238, M235*, and *M232* are the molecular masses of the parent isotopes (g/mol), *λ238, λ235*, and *λ232* are the respective decay constants of 1.55125 × 10-10 yr-1, 9.8485 × 10-10 yr-1, and 4.9475 × 10-11 yr-1 (Holden and Hoffman, 2000), and *t* is the integration time (yr), assumed to be U/Pb age of the zircon. Using the LA-ICP-MS determinations of U and Th concentrations and U/Pb age, presented in the section 4.4, the fluence is calculated as ~1.08 × 1018 α/g. The Raman data and the effective alpha-fluence, which is suggested to be 0.55 times the total alpha-fluence (1.08 × 1018) for Sri Lanka zircon (Nasdala et al., 2004), fits well with the empirical relationship calibrated in Nasdala et al. (2001), suggesting partial healing of radiation damage in the LGC-1 (Fig. 3). This is consistent with partial annealing of fission-tracks and partial retention of 4He in the grain, as indicated by the relatively younger fission-track and (U-Th)/He ages (~210 and 476.4 Ma, respectively) than the crystallisation age (~541 Ma) (see section 4.5 for details).

4.2. Major element composition and elemental mapping

Major element composition (Table 1) derived from 43 EPMA point analyses on five shards show little variation. Average SiO2, ZrO2 and HfO2 contents of 32.94 ± 0.38, 66.15 ± 0.46, and 1.545 ± 0.088 (wt%), respectively. P and U trace element measurements are significantly variable, with mean of 0.018 ± 0.016 and 0.199 ± 0.139 (wt%), respectively. The high dispersion probably reflects the low precision of the EPMA in quantifying the concentrations of these trace elements, considering that U measurements using LA-ICP-MS is highly consistent (see sections 4.4).

High-resolution (1 μm) X-ray elemental mapping were performed on a randomly selected grain to check potential U and Th variations at a μm-scale. As shown in figure 4, no visible zoning in these elements was revealed. These results are consistent with the uniform CL and LA-ICP-MS measurements (see sections 4.4).

4.3. Qualitative U and Th distribution by fission-track

Spontaneous fission-track mapping was performed on two mounts including ~150 random shards. Detailed fission-track counting was only done for a few shards, because visual checking of track distribution pattern is enough to detect any evident density difference. No sharp change or visible gradient in fission-track density was observed on any examined shards, as shown by the representative grain in figures 1c-d.

Detailed fission-track counting was performed on 12 regions of 6 shards. The resulting density values ranges from 36.9 to 45.5 tracks per square millimeter, as determined from areas ranging from 2.77 × 10-6 to 9.70 × 10-6 cm-2 (Table 2). U concentrations determined directly from the counted areas using the LA-ICP-MS method range narrowly from 356.5 ± 12.6 ppm to 381.9 ± 13.8 ppm. Therefore, the variation in the counted track density reflects the Poisson distribution of fission track frequency, rather than U inhomogeneity. Twelve fission-track ages were derived from the track density and U concentration measurements using the age equation presented in the section 3.3. The calculated ages range from 180.7 ± 19.0 (1σ) Ma to 224.3 ± 14.9 (1σ) Ma, thus agreeing with the analytical uncertainty. The central age is 198.9 ± 4.0 Ma, calculated using RadialPlotter (Vermeesch, 2009) (Fig. 5).

4.4. LA-ICP-MS measurements U, Th and Pb

LA-ICP-MS measurements of U, Th and Pb concentrations were carried out using the following two strategies: (1) a general survey on 23 random grains to check compositional homogeneity among shards, and (2) compositional mapping by multiple spot analyses along 14 transects in six grains, resulting in a further 160 measurements. In the general U survey, two to five spot analyses were performed on each grain depending on grain size, resulting in ~100 measurements.

Figure 6 compiles all the results (n = 266) derived from both strategies. It is shown that all U, Th, and Pb concentrations are overlapping at 2σ uncertainty levels. For this reason, the data derived from the two strategies are not differentiated. U, Th and Pb concentrations cluster at 320-388 ppm, 659-849 ppm and 36-41 ppm, respectively, with weighted means of 354.5 ± 1.9 ppm, 732.6 ± 5.3 ppm, and 38.9 ± 0.2 ppm, respectively (Figs. 3a-c). The Th/U ratios, ranging between 1.82 and 2.28, are also overlapping with a weighted mean of 2.07 ± 0.02 (Fig. 3d).

Figure 7 shows a representative detailed mapping on one shard consisting of 44 determinations using two different types of laser spot sizes (~25 µm and ~15 µm). The U, Th, and Pb concentrations derived from the relatively smaller laser spots are associated with relatively larger uncertainties of 6-8%; whereas those from larger spots are associated with smaller uncertainties of 3-5% (Supplementary data). These U and Th determinations are overlapping at 2σ uncertainty levels, with weighted means of 345.2 ± 4.3 ppm and 707.2 ± 8.5 ppm, respectively (Figs. 7b-c). These values are undifferentiable from those of the entire dataset (Fig. 6) at 2σ uncertainty levels.

4.5. U/Pb age by LA-ICP-MS and ID-TIMS

A total of 225 U/Pb age by-products were derived as quantifying the element concentrations using LA-ICP-MS method. The disconcordance between the 206Pb/238U and 207Pb/235U ages varies from -8.6% to 4.4%, evidently lower than the commonly adopted disconcordance threshold (±10%) for LA-ICP-MS U/Pb data. Visualizing the age data in the Wetherill concordia diagram (Wetherill, 1956) shows that the variations in 206Pb/238U and 207Pb/235U ages prevent concordia age calculation from the entire data dataset (Fig. 8). The preferred 206Pb/238U ages range from 515.8 ± 5.8 (1σ) Ma to 577.9 ± 7.1 (1σ) Ma, with a weighted mean of 536.3 ± 1.4 Ma (Fig. 6e).

Four ID-TIMS U/Pb age determinations yield 206Pb/238U and 207Pb/206Pb ages of 541-542 Ma and 542-543 Ma, respectively (Fig. 9). Taking into account the decay constant uncertainties (Ludwig, 2000), those two types of ages are concordant. The calculated concordia age (541.70 ± 0.70 Ma) is consistent with the weighted mean 206Pb/238U age (541.54 ± 0.47 Ma). Th/U ratios determined by ID-TIMS method range between 2.103 and 2.113 (Table 3).

4.5. Conventional (U-Th)/He age

Conventional (U-Th)/He age analyses were carried out on 28 fragments in three laboratories (Table 4). Fourteen determinations were derived in the IGCAGS thermochronology laboratory; these ages range from 446.6 ± 16.0 Ma to 488.0 ± 17.5 Ma. The Th/U ratios cluster at 2.11-2.18. Six (U-Th)/He age determinations at the UoM thermochronology laboratory range from 443.7 ± 13.8 Ma to 511.1 ± 15.8 Ma with Th/U ratios between 1.87 and 2.07. Eight (U-Th)/He analyses at UCL thermochronology laboratory range from 457.6 ± 19.2 to 479.7 ± 16.5 Ma. Th/U ratios are between 2.01 and 2.12.

All ages determined at the three laboratories are concordant at 2σ uncertainty levels (Fig. 10). The central and geometric mean ages of all dates are 476.4 ± 5.7 Ma and 475.9 ± 3.1 Ma, respectively (Fig. 10), as calculated using the HelioCalc program of Vermeesch (2010).

4.6. *In-situ* (U-Th)/He age

Six *in-situ* (U-Th)/He ages were obtained using the first principle method (Table 5). The ages are concordant, ranging from 439.2 ± 15.3 Ma to 495.4 ± 17.2 Ma. The calculated weighted mean is 462 ± 21 Ma (Fig. 11), indistinguishable from those determined using the conventional method.

The 4He concentrations yielded by these analyses range from 1206.7 ± 35.0 nmol/g to 1322.7 ± 38.4 nmol/g, with a weighted mean of 1248 ± 46 nmol/g. The consistent 4He concentration and *in-situ* ages are in line with the uniform distribution of U and Th, shown by the data presented above.

5. Discussion

5.1. Compositional and age homogeneity of LGC-1

The textural and compositional homogeneity of LGC-1 zircon is supported by various data. A summary of compositional and geochronological values and the corresponding analytical methods are compiled in Table 6. Qualitative U mapping of a large number of random shards using fission-track and X-ray elemental mapping methods did not reveal any significant spatial heterogeneity, consistent with uniform texture shown by CL-imaging and Raman spectroscopy. This is further supported by 266 quantitative LA-ICP-MS analyses of U, Th and Pb concentrations, which are within experimental uncertainties. The weighted mean U, Th and Pb concentrations are 355 ± 4 ppm, 735 ± 4 ppm, and 38.5 ± 1.0 ppm, respectively, with a Th/U ratio of ~2.1. The different matrix between the zircon and reference material NIST610 may introduce an unknown and small systematic error to these concentration measurements. This error is expected to be reduced by the pairwise *in-situ* dating methods, which use the U/Si or U/Zr ratios between the reference material and unknown zircon samples for age calculation (Evans et al., 2015; Vermeesch et al., 2012).

LA-ICP-MS and ID-TIMS analyses of LGC-1 suggest U/Pb ages of ~536.3 ± 1.2 Ma and 541.54 ± 0.47 Ma, respectively. The slightly younger mean LA-ICP-MS age and associated variations (12%) might result from the ‘matrix effect’, as pointed out in previous studies (e.g. Allen and Campbell, 2012; Black et al., 2004; Marillo-Sialer et al., 2014). Those studies suggest that matrix-dependent ionisation of U and Pb isotopes and the ablation rate could induce different isotopic fractionation among different unknown grains and the age standards. A variance of ±6% in 206Pb/238U ages has been explained by such an effect (e.g. Allen and Campbell, 2012; Black et al., 2004; Marillo-Sialer et al., 2014). The ‘matrix’ difference is probably a function to several factors, including the degree of radiation damage (Allen and Campbell, 2012), trace element concentration (Black et al., 2004), and crystalline oritentation (Marillo-Sialer et al., 2014). As to this study, the Plešovice zircon has a higher degree of radiation damage than the LGC-1, as indicated by its wider FWHM of the ν3(SiO4) Raman band of 10-30 cm-1 (Sláma et al., 2008), comparing to that of the LGC-1 (8-10 cm-1). Zircon with a higher degree of radiation damage has lower density and hardness (Murakami et al., 1991). Therefore, it is expected to have a faster rate of laser penetration and a higher degree of isotopic fractionation in the Plešovice zircon standard than in the LGC-1. Such a radiation damage dependant isotopic fractionation may explain the offset between the LA-ICP-MS and ID-TIMS U/Pb age determinations, as also found in previous studies (e.g. Allen and Campbell, 2012).

Multi-laboratory conventional (U-Th)/He dating suggest consistent weighted mean results of 476.4 ± 5.7 Ma. The 28 conventional (U-Th)/He age analyses provide constraints not only to the age, but also to the 4He homogeneity, because, with uniform distributions of U and Th, any dispersion in (U-Th)/He ages, if present, could only be explained by 4He heterogeneity. Such an explanation is supported by six *in-situ* (U-Th)/He analyses, which yield consistent 4He concentrations and ages with weighted mean values of 1248 ± 46 nmol/g and 462 ± 21 Ma, respectively.

Th/U ratios obtained using different analytical methods in different laboratories are indistinguishable. The weighted mean Th/U ratio analysed using LA-ICP-MS, ID-ICP-MS, and ID-TIMS analyses is 2.07 (n=265), 2.1 (n=265), and 2.08 (n=265), respectively. Such consistent Th/U ratio makes the LGC-1 zircon also suitable as a reference material for checking and calibrating zircon compositional analyses, involved in conventional (U-Th)/He dating, LA-ICP-MS experiments, etc.

The zircon fission-track age of the LGC-1 zircon is 198.9 ± 4.0 (1σ) Ma, as calculated from 12 single shard analyses. This age is significantly younger than the (U-Th)/He age, as also reported in Garver (2002) for other Sri Lanka zircon megacrysts. This observation indicates a higher closure temperature for the He system than the ZFT system in LGC-1. As shown in the closure temperature plots for different models, the radiation damage model of Guenthner et al. (2013) predicts (U-Th)/He closure temperatures in LGC-1 zircon that are significantly higher than those of alpha-damaged ZFT at a cooling rate less than 5 °C/Ma (Fig. 12), consistent with the observations. Other zircon fission-track models, calibrated using zircon grains with zero or very low degree of radiation damage (Rahn et al., 2004; Yamada et al., 2007), predict evidently higher closure temperatures.

The concordant (U-Th)/He ages of LGC-1 results partly from its relatively simple thermal history. The thermal history of the Sri Lankan Highland, where the detrital Sri Lanka zircon megacrysts originate (Nasdala et al., 2004), include a fast cooling stage from the time of crystallization to Early Ordovician time, as constrained by multi-geochronological dates (Fig. 13a). Post-early Ordovician thermal history has not been well constrained. The zircon fission-track age of the LGC-1 suggests the grain probably has exhumed to a temperature lower than the fission-track closure temperature (<240 °C at cooling rates less than 100 °C/Ma) of natural alpha-damaged zircon since the early Jurassic (Fig. 12). On the basis of the He diffusion model of Guenthner et al. (2013), the simplified thermal history model shown in figure 13a predicts a uniform He distribution and a (U-Th)/He age of ~476 Ma in the grain interior (Fig. 13b). These predictions are consistent with the reproducible 28 conventional and six *in-situ* (U-Th)/He ages of random shards (Figs. 10 and 11).

5.2. Suggestions for future zircon calibration

Fractions of the LGC-1 zircon have been shared with several laboratories in the UK, US, Australia, and China. Plenty of material is still available for distribution to other laboratories. It is expected that this zircon will serve as a reference material for both *in-situ* and conventional (U-Th)/He for about ten years. Therefore, more similar zircon reference materials will need to be developed. The experience of this study offers the following suggestions for future similar zircon calibration studies. (1) If calibrating Sri Lanka zircon megacrysts as age references, it is worth checking whether or not they have been annealed or irradiated. Some commercially available Sri Lanka zircon gems have been treated to form appealing colours. (2) The appearance, especially the colour of zircon grains is an important index of zircon textural and compositional zoning. Compositional homogenous grains are often uniform in colour. (3) Visual fission-track mapping is a convenient and affordable way to detect the existence of U zoning. A large number of zircon grains can be quickly examined using optical microscopy. From this perspective, the method is time-saving, comparing to other methods, such as CL-imaging, or X-ray elemental mapping. Worth noting is that fission-track mapping method may not work for zircons with a high degree of radiation damage, because this kind of grains tend to be dissolved in the etchant (KOH-NaOH melt). (4) When performing LA-ICP-MS U/Pb dating, using age standards with a similar degree of radiation damage to the zircon of interest would help mitigate the matrix-induced differential laser ablation rate and downhole isotopic fractionation. The FWHM of the ν3(SiO4) Raman band can be used as an index of radiation damage (Nasdala et al., 2001).

6. Conclusions

Pairwise *in-situ* zircon (U-Th)/He dating has been proposed to reduce the so-called ‘matrix effect’ - the influence of mismatched matrix between synthetic standard material and natural unknown samples on ablation rates and isotopic fractionation. Such a method requires an age reference material to have a consistent (U-Th)/He and homogenous U, Th and He distributions over 10s of micrometers.

The variety of data reported here make LGC-1 one of the most comprehensively characterized zircon samples. No internal variations in optical properties, luminescence emissions, micro-Raman parameters and fission-track distribution have been detected. Variations in U, Th and Pb compositions as determined by LA-ICP-MS analyses did not exceed analytical uncertainties. Conventional (U-Th)/He dating (n=28) at three thermochonological laboratories yield consistent ages of 476.4 ± 5.7 Ma. ID-TIMS 206Pb/238U and 207Pb/206Pb analyses yield a concordia age at 541.70 ±0.70 Ma, when considering the decay constant uncertainties. Therefore, it is concluded that the U, Th and He distributions in the zircon LGC-1 megacryst are remarkably homogeneous; therefore, the grain is suitable as a future reference material for *in-situ* (U-Th)/He dating.

Th/U ratios, determined by LA-ICP-MS, ID-ICP-MS and ID-TIMS, are highly consistent at ~2.1. Such consistent Th/U ratio makes the LGC-1 zircon also suitable as an external reference material for checking the zircon compositional analyses, involved in conventional (U-Th)/He dating, LA-ICP-MS studies, etc.

Zircon megacrysts with a high-degree of homogeneity in texture and composition can be potentially calibrated as reference material for various *in-situ* analyses. Because of the limited size of the LGC-1 zircon, we restrict its use for *in-situ* and conventional (U-Th)/He dating only. Fractions of LGC-1 have been distributed to several thermochronological laboratories. There are still some fractions available; and it is expected that this zircon will serve for ten years. Therefore, more similar zircon reference materials will need to be developed, and this study offers suggestions for future zircon calibration studies.

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Tables:

Table 1. Results of electron microprobe analyses.

Table 2. Fission-track analyses results.

Table 3. Results of U/Pb dating using ID-TIMS method

Table 4. Results of conventional (U-Th)/He dating

Table 5. Results of *in-situ* (U-Th)/He dating

Table 6. A summary of compositional and geochronological values of LGC-1.

**Appendix A. Supplementary data**

Supplementary data to this article can be found online at xxx.

Figures captions:

Figure 1. (a) Appearance of LGC-1. (b) Representative CL images of two random shards showing textural homogeneity of LGC-1 zircon. (c) A representative spontaneous fission-track map of a randomly selected shard indicating the uniform distribution of 238U, spontaneous fission of which formed the observed fission-tracks. (d) A close-up view of the upper portion of panel (c).

Figure 2. Raman spectra obtained from Sri Lanka zircon crystal LGC-1, showing the range of 942-1043 cm-1. Spectra, induced by different laser energy, are stacked for clarity. To characterize the radiation damage, FWHM (8.7 ± 0.3 cm–1) and Raman Shift (~1003 cm–1) of the ν3(SiO4) Raman band are estimated.

Figure 3. Plot of the effective alpha-dose of Sri Lanka zircon, equivalent to 0.55 times the alpha-fluence (~1.08 × 1018), versus the corrected FWHM (a) and Raman Shift (b) of the main ν3(SiO4) band.

Figure 4. X-ray elemental (U, Th) distribution maps of a random shard of LGC-1 zircon, revealing spatial homogeneity in U and Th. The inserted colour bar denotes the relative U and Th concentration levels.

Figure 5. Radial plot of fission-track ages derived from 12 regions of 6 single shards, yielding a central age of 198.9 ± 4.0 Ma.

Figure 6. Relative probability density (cyan) and individual date (arranged in an increasing order) (blue and red vertical lines) plots of LA-ICP-MS determinations of U (a), Th (b) and Pb (c) concentrations, Th/U ratios (d), and 206Pb/238U ages (e). Statistics inserted in each panel are calculated using Isoplot 4.15 (Ludwig, 2012) from the dates marked in blue. Rejected values, as identified using 2σ error outlier rejection method (Ludwig, 2012), are marked in red. The horizontal green lines denote the calculated weighted mean values. Data for plotting these figures are available in tabular form as the attached supplementary file.

Figure 7. (a) Map showing results of 44 spot U and Th analyses on a randomly selected shard. Blue and red texts denote measurements with laser spot sizes of ~25 µm and ~15 µm, respectively. The upper and lower number of each text combination marks the U and Th concentrations (in ppm), respectively. (b and c) Statistics of the U and Th concentrations. Blue and red lines in panels b and c depict data from derived from ~25 µm and ~15 µm laser pits, respectively. Data for plotting these figures are available in tabular form as the attached supplementary file.

Figure 8. Concordia plot of LA-ICP-MS U/Pb dates of LGC-1 zircon using IsoplotR (https://pvermees.shinyapps.io/IsoplotR/). Uncertainties are 95% confidence level. Data for plotting this figure are available in tabular form as the attached supplementary file.

Figure 9. ID-TIMS U/Pb dates of LGC-1 zircon. (a) Concordia plot with decay constant uncertainties (Ludwig, 2000), and (b) weighted mean of 206Pb/238U dates. Uncertainties are 2σ.

Figure 10. Logratio plot of conventional (U-Th)/He data using the Helioplot program of Vermeesch (2010). Green ellipses denote analyses at IGCAGS, and purple ones at UCL. The white ellipse marks the geometric mean composition of the entire dataset.

Figure 11. Weighted mean plot of in-situ (U-Th)/He ages (a) and He concentration (b).

Figure 12. Closure temperatures of different zircon (U-Th)/He and fission-track models. The red line, (U-Th)/He model of LGC-1, is calculated using the radiation damage model of Guenthner et al. (2013). At cooling rate lower than 5 °C/Ma, the closure temperature of LGC-1 (U-Th)/He model is significantly higher than that of alpha-damaged ZFT (solid blue line).

Figure 13. (a) Simplified thermal history (solid line) of the Sri Lanka highland, as constrained by different geo- and thermochronological data denoted by ellipses. The Sm-Nd internal isochron data are from Sajeev et al. (2007), whereas garnet Sm-Nd and biotite Ar/Ar from Nasdala et al. (2004) and references therein. (b) Predicted normalized concentration of 4He (solid line) and (U-Th)/He age profile (dash line) in LGC-1 by the thermal history shown in (a). The modelling is performed using the QTQt program (Gallagher, 2012) and the helium diffusion model of Guenthner et al. (2013). The grain size is set as 1 cm, whereas the U and Th contents as those of LGC-1 (Figs. 6a-b). The thermal history model (solid line in panel a) predicts (1) a (U-Th)/He age of ~476 Ma in the grain interior, (2) a uniform He distribution until 0.9 cm from the grain centre.