Here, we document a detailed characterisation of two zircon gemstones, GZ7 and GZ8. Both stones had the same mass at 19.2 carats (3.84 g) each; both came from placer deposits in the Ratnapura district, Sri Lanka. The U-Pb data are in both cases concordant within the uncertainties of decay constants and yield weighted mean $^{206}$Pb/$^{238}$U ages (95% confidence uncertainty) of 530.26 Ma ± 0.05 Ma (GZ7) and 543.92 Ma ± 0.06 Ma (GZ8). Neither GZ7 nor GZ8 have been subjected to any gem enhancement by heating. Structure-related parameters correspond well with the calculated alpha doses of $1.48 \times 10^{18}$ g$^{-1}$ (GZ7) and $2.53 \times 10^{18}$ g$^{-1}$ (GZ8), respectively, and the (U-Th)/He ages of 438 Ma ± 3 Ma (2σ) for GZ7 and 426 Ma ± 9 Ma (2σ) for GZ8 are typical of unheated zircon from Sri Lanka. The mean U mass fractions are 680 μg g$^{-1}$ (GZ7) and 1305 μg g$^{-1}$ (GZ8). The two zircon samples are proposed as reference materials for SIMS (secondary ion mass spectrometry) U-Pb geochronology. In addition, GZ7 (Ti mass fractions 25.08 μg g$^{-1}$ ± 0.18 μg g$^{-1}$; 95% confidence uncertainty) may prove useful as reference material for Ti-in-zircon geothermometry.

Keywords: zircon, reference material, SIMS, U-Pb geochronology, Ti-in-zircon geothermometry.
In situ microprobe geochronology by means of SIMS (secondary ion mass spectrometry; Compston et al. 1984, Williams 1998) is a comparative method. That is, results of analyses of unknowns need to be calibrated against equivalent analyses of a well-characterised reference material. Such materials need to be exceptionally homogeneous in isotopic composition, on a scale smaller than the size of SIMS analysis pits (typically comprising ~1 ng of material).

For zircon (ZrSiO$_4$; tetragonal space group $I4_1/amd$) U-Pb geochronology, however, suitable synthetic reference materials that meet the above requirement are currently not available. To the best of our knowledge, no homogeneous Pb-doped ZrSiO$_4$ crystal has been synthesised thus far. This is explained by the broadly incompatible behaviour of Pb in zircon (Watson et al. 1997). Homogeneous Pb-doped ZrSiO$_4$ glass can be synthesised with relative ease, but it is unsuitable as SIMS reference material because the sputtering of a glass under the O$_2^-$ beam differs appreciably from that of the unknown zircon crystals (Stem and Amelin 2003).

For the above reasons, reference materials for SIMS zircon U-Th-Pb geochronology are currently limited to well-characterised natural zircon. Apart from exceptional isotopic homogeneity, a suitable natural reference material should have a (close to) concordant U-Pb system and negligible mass fractions of non-radiogenic Pb (Pidgeon 1997, Kennedy 2000, Kennedy et al. 2014, Nasdala et al. 2015, Schaltegger et al. 2015). Furthermore, the reference material’s structural state should be homogeneous and sufficiently similar to that of the unknowns. The latter requirement needs to be checked carefully before a natural zircon sample can be proposed as a new reference material. On the one hand, a SIMS reference material should contain sufficiently high mass fractions of radiogenic Pb. This is advantageous insofar as higher mass fractions result in better counting statistics, which minimise analytical uncertainties and may even allow one to decrease the size of the analysis spots and/or the counting times without losing measurement precision. On the other hand, the emplacement of radiogenic Pb nuclei in the zircon lattice is a destructive process (note that alpha recoils are short-distance implantations; Weber 1990, Weber et al. 1994, Devanathan et al. 2006, Valley et al. 2015). Therefore, higher mass fractions of radiogenic Pb are typically associated with higher degrees of accumulated self-irradiation damage, provided no structural reconstitution through thermal annealing has occurred (compare Nasdala et al. 2001). Radiation damage will not necessarily affect the material’s U-Th-Pb isotopic system: even though elevated levels of structural damage enhance the susceptibility of zircon to secondary loss of radiogenic Pb (Krogh and Davis 1975, Nasdala et al. 1998, Davis and Krogh 2001, Horie et al. 2006), it is well known that radiation damage alone does not cause any Pb loss (note that amorphised but nevertheless concordant zircon has been described by Nasdala et al. 2002, 2014, Kostrovitsky et al. 2016). However, the potential problem caused by too high levels of radiation damage in the reference material is that significantly different structural states of unknowns and reference material may result in ‘matrix effects’, that is, different ionisation yields and/or U and Pb fractionation during SIMS analysis. Finding a suitable reference material may therefore be a balancing act, as the material should contain enough radiogenic Pb, but still should not have too much radiation damage.

In addition, a suitable SIMS reference material should not have internal fractures, cracks and inclusions, a prerequisite met by highest quality zircon gemstones. SIMS has a comparably low demand of reference material (typically a 100 µm chip will suffice for a 1-day measurement session); on the other hand, unknowns and the reference material always need to be placed in the same sample mount, which increases the consumption. The intended distribution of multitudes of tiny reference chips to several SIMS laboratories is possible only if a sufficient quantity of material is available. In view of the above, and given the high analytical effort for characterising thoroughly a potential reference material, gemstones to be considered should be sufficiently large. Here, we present measurement results characterising two large zircon gemstones from Sri Lanka, GZ7 and GZ8.

### Samples and preparation

#### General description

Zircon samples GZ7 and GZ8 were purchased in 2014 and 2015 from gem traders as cut and faceted gemstone specimens. In our experience, this approach is most expedient. The polished faces of a gem are perfect windows that allow one to examine the specimen’s interior, whereas a rough stone cannot be checked in sufficient detail. For reasons elucidated above, our search was focused on large (>15 ct/>3 g) gemstones only. Stones to be purchased were first placed in an immersion liquid and carefully inspected with a 10× magnifying lens. Only specimens without visible zoning and seemingly free of inclusions were considered. The shortlisted stones were then subjected to rough mass density measurement and analysis of the degree of broadening of Raman bands. For the semiquantitative evaluation of results that were obtained with a rather basic Raman system in a gem-testing laboratory in Colombo, whose apparatus function (i.e., instrumental band broadening) was unknown, well-characterised reference
samples were analysed with the same system. Moderately decreased mass densities (ca. 4.65–4.50 g cm\(^{-3}\)) and moderately broadened Raman bands were taken as evidence for significant, but not too high, radiation damage. This, in turn, may indicate the presence of suitably high levels of U and Pb and allows one to exclude thermal gem enhancement.

Based on promising preliminary tests, two gemstones (GZ7 and GZ8) were purchased. Both originated from placer deposits in the Ratnapura district, Sri Lanka (Dahanayake and Ranasinghe 1985, Zoysa 2014). The presumed source area belongs to the Highland Complex (Cooray 1994, Króner et al. 1994, Mathavan and Fernando 2001), which is dominated by Proterozoic rocks that have experienced high-grade (partially ultrahigh-temperature) metamorphism during the Pan-African event at ca. 550 Ma (Sjeev et al. 2010, Dharmaprya et al. 2017, and references therein). The primary source rocks of the gem zircon specimens, however, remain unknown to date.

The two specimens GZ7 and GZ8 had oval cut, maximum dimensions of 16.8 and 15.9 mm, respectively, and exactly the same mass of 19.2 ct (3.84 g) each (Table 1). Both stones appeared unzoned and flawless, that is, clear and free of inclusions. GZ7 was light brown to dark yellow, with orange hue; GZ8 was yellowish green (Figure 1a). According to the traders, these colours were natural and no heat treatment for colour enhancement had ever been applied.

**Sample preparation**

The two stones were cut into ~2.8-mm-thick slices using a Struers AWS1 abrasive wire saw, with a 0.17-mm-diameter high-grade steel wire coated with 20 μm diamond grains (Well Diamantdrahtsägen GmbH, Mannheim). The slicing was done perpendicular to the longest dimension of the gemstone (Figure 1b) to minimise mass loss, that is, the crystallographic orientation was not considered. After washing in pure ethanol and ultrasonic cleaning, the materials. After finishing the analyses, slices were detached from their glass slides and, after removal of remnant carbon by mechanical polishing, were subjected to ethanol washing and ultrasonic cleaning.

To estimate the degree of radiation damage and associated parameter changes, small chips of GZ7 and GZ8 were subjected to dry heating in air at 1400 °C for 96 h for structural reconstitution. Samples were placed in a Pt crucible (note that annealing zircon in an alumina crucible may, as an analytical artefact, result in surficial decomposition into oxides; Vácz et al. 2009) and heated at a rate of 30 °C min\(^{-1}\) to the designated temperature. After 4 days, the furnace was shut off and samples cooled slowly. Slow heating and cooling were preferred to avoid the possible build-up of strain during shock heating or quenching.

**Analytical techniques**

**Electron probe microanalysis imaging and major-element analysis**

A JEOL 8900 RL EPMA (Universität Göttingen) was used for obtaining BSE (back-scattered electrons) and CL (cathodoluminescence) images and for determining mass fractions of major elements by means of wavelength-dispersive X-ray analysis. Imaging was done by scanning the fully focused beam at 20 kV accelerating voltage and 50 nA beam current. For point analyses, the system was operated at 20 kV accelerating voltage and 80 nA beam current, with the electron beam focused to a 10 μm spot. For each sample, 84 point analyses were done along two 13 and 8 mm traverses (that were oriented perpendicularly to each other) across the large polished slice. The measured element-specific lines (with synthetic or natural calibrant materials and peak/background counting times quoted in brackets) included Al-K\(_a\) (Al\(_2\)O\(_3\); 120 s, 120 s), Si-K\(_a\) (ZrSiO\(_4\); 15 s, 10 s), P-K\(_a\) (ScPO\(_4\); 300 s, 300 s), Ca-K\(_a\) (CaSiO\(_3\); 120 s, 120 s), Fe-K\(_a\) (FeSiO\(_3\)); 120 s, 120 s), Mg-K\(_a\) (MgO; 300 s, 300 s), and Ti-K\(_a\) (TiO\(_2\); 300 s, 300 s). Data were reduced using the CITZAF routine in the JEOL software, which is based on the \(\Phi(p)\) method (Armstrong 1991, 1995). For element mapping (660 x 450 analyses of GZ7, 650 x 600 analyses of GZ8), the system was operated at 20 kV and 300 nA. The beam diameter was 10 μm, the step width was 20 μm, and the dwell time was 100 ms.
Table 1. General characterisation of zircon specimens GZ7 and GZ8 (Universität Wien) and comparison with well-crystalline zircon

| Parameter | Zircon GZ7 Natural | Zircon GZ7 Annealed | Zircon GZ8 Natural | Zircon GZ8 Annealed | Reference: Ratanakiri a | Reference: Synthetic ZrSiO₄ b |
|-----------|------------------|-------------------|------------------|-------------------|-------------------|-------------------|
| Weight (ct mg⁻¹) | 19.238/3847.6 | 19.238/3847.6 | 15.9/13.4/7.8 | 4.668/4.668 | – | – |
| Mass density (g cm⁻³) | 4.658 ± 0.005 | 4.537 ± 0.005 | 4.656 ± 0.005 | 4.657 ± 0.005 | 4.674 ± 0.005 | 4.668 ± 0.001 |
| Alpha dose (x 10¹⁸ g⁻¹ A⁻¹) | 2.14 ± 0.11 | 2.37 ± 0.11 | 2.09 ± 0.11 | 2.09 ± 0.11 | 2.09 ± 0.11 | 2.09 ± 0.11 |
| Unit-cell dimension a₀ (Å) | 6.625 ± 0.002 | 6.625 ± 0.002 | 6.625 ± 0.002 | 6.625 ± 0.002 | 6.625 ± 0.002 | 6.625 ± 0.002 |
| Unit-cell volume (Å³) | 264.12 ± 0.22 | 264.12 ± 0.22 | 260.82 ± 0.08 | 260.82 ± 0.08 | 270.26 ± 0.02 | 270.26 ± 0.02 |
| Raman shift (cm⁻¹) | 38 ± 2 | 40 ± 2 | 40 ± 2 | 40 ± 2 | – | – |
| PL (Dy³⁺) FWHM (cm⁻¹) | 14.1 ± 1.0 | 14.1 ± 1.0 | 14.1 ± 1.0 | 14.1 ± 1.0 | – | – |
| PL (Nd³⁺) FWHM (cm⁻¹) | 21.1 ± 1.8 | 21.1 ± 1.8 | 21.1 ± 1.8 | 21.1 ± 1.8 | – | – |

Quoted uncertainties are 2σ.

a Mass density, alpha dose and unit-cell parameters for the well-crystallised Ratanakiri, Cambodica, zircon are from Zieg et al. (2018). PL FWHM values are from Lenz and Nasdala (2015).
b Unit-cell parameters for pure, undoped ZrSiO₄ are from van Westrenen et al. (2004). Unit-cell parameters were converted to a theoretical X-ray density, which is quoted as reference value for the mass density.
c Calculated according to Murakami et al. (1991) from the present U and Th mass fractions and the U-Pb age.
d Raman spectral parameters are quoted for the 4H13/2 emission of Dy³⁺ and the -1 sublevel of m = 7/2 of Nd³⁺, respectively.

Titanium determination (GZ7 only)

This sample was subjected to precise Ti analysis by ID-MS at the Institute of Geochemistry and Petrology, ETH Zürich. Eleven aliquots of 1 mg mass were dissolved in concentrated HF in a pressure vessel, followed by drying and redissolving in HF and HCl and subsequently dissolved in concentrated HNO₃ and HCl. The aliquots were loaded into a 1.2 mg flow cell. Intensities were recorded for 70 s, which included 30 s gas blank and 40 s sample signal. The NIST SRM 610 glass was used as primary reference material. At ETH, LA-ICP-MS trace element determination by ID-MS was carried out in three laboratories: By NIST SRM 610 (Jochum et al. 2003), 612 (Jochum et al. 2002) and 613 (Jochum et al. 2001) were used as secondary reference materials. At ETH, only GZ7 was analysed. Analyses consisted of 60 s background of 30 s and 40 s Ti analysis, followed by 120 s of ablation. The ablation spot size was 30 μm. The measurement conditions included 50 μm beam size, 5 Hz pulse rate and 200 W laser power. The ablation was performed with an Agilent 7700x ICP-MS. The method has been described by Hagemann et al. (2004). The ablation conditions were done by means of an Agilent 7500a ICP-MS. Analyses were done by means of an Agilent 7700x ICP-MS at the Geochemical Analysis Unit, CCFS/GEMOC, Macquarie University, Sydney. Analyses were done by means of an Agilent 7700x ICP-MS at the Geochemical Analysis Unit, CCFS/GEMOC, Macquarie University, Sydney. Analyses were done by means of an Agilent 7700x ICP-MS at the Geochemical Analysis Unit, CCFS/GEMOC, Macquarie University, Sydney.
evaporated to dryness. The dry residues were then dissolved in HNO₃ with a trace of HF, and the resulting solutions were analysed using a Thermo Element XR single-collector ICP-MS. Details of the analyses including blank and interference corrections are described elsewhere (Szymanowski et al. 2018).

Mass density determination

Mass densities were determined prior to sample preparation, by repeated weighing of the gemstones in distilled water and in air. A minute amount of detergent was added to the distilled water to decrease surface tension.

Single-crystal X-ray diffraction

Unit-cell parameters were obtained at Universität Wien by single-crystal X-ray diffraction analysis of small zircon chips (150–300 μm). To check for structural effects of radiation damage, chips of the natural and annealed samples were analysed. Measurements were done by means of a Huber 5042 four-circle diffractometer, using MoKα₁₂ radiation (λ ~ 0.71 Å) from a conventional fine-focus sealed tube (50 kV, 30 mA). The sample-to-detector distance was 420 mm. A scintillation counter with variable Soller slit was used to measure about 10–20 nonequivalent Bragg peaks for eight-position centring according to the method of Hamilton (1974). The software SINGLE (Angel and Finger 2011) was used for diffractometer control and for calculation of lattice parameters by applying refinements with symmetry-constraint vector least squares. The diffractometer was checked and corrected for systematic errors using the NIST SRM 1990 ruby-sphere standard (Wong-Ng et al. 2001).

Spectroscopy

Raman and laser-induced PL (photoluminescence) spectra were obtained at Universität Wien using a dispersive Horiba LabRAM HR Evolution system equipped with an Olympus BX41 optical microscope, a grating with 1800 grooves per mm and a Si-based, Peltier-cooled charge-coupled device (CCD) detector. Point measurements were done on natural and annealed samples, to check for structural effects of radiation damage. As reference analyses, PL measurements were also done on REE³⁺-doped ZrSiO₄ crystals grown using a Li-Mo flux technique (for details see Lenz et al. 2015, and references therein). Line scanning across the large slices was done using a software-controlled Märzhäuser SCAN x-y stage. Raman spectra were excited using the 632.8 nm emission of a He-Ne laser (8 mW at the sample surface). The PL spectra were excited using the 473 nm emission of a diode-pumped solid-state laser (5 mW at the sample surface) or a frequency-doubled Nd:YAG laser (532 nm; 10 mW at the sample surface). The Olympus 100× objective (numerical aperture 0.9) was used. With the spectrometer system operated in full confocal mode, the lateral resolution was ~ 1 μm, and the spectral resolution was between ~ 1.5 cm⁻¹ in the blue and 0.7 cm⁻¹ in the NIR (near infrared) range of the electromagnetic spectrum. Wavenumber calibration was done using the Rayleigh line and Kr-lamp emissions, resulting in a wavenumber accuracy of better than 0.5 cm⁻¹. Background-corrected spectra were fitted assuming Lorentzian–Gaussian band and line shapes. For FWHM (full width at half-maximum) correction, the empirical formula (Vácz 2014).

\[
\text{FWHM} \approx \text{FWHM}_{\text{meas.}} - \text{IPF}^2 / (0.9 \times \text{FWHM}_{\text{meas.}} + 0.1 \times \text{IPF})
\]

(1)

has been applied, where FWHM_{meas.} = measured (i.e., fitted) FWHM of the spectroscopic signal obtained, and IPF = FWHM of the instrumental profile function.

Unpolarised optical absorption spectra were obtained from the large slices of GZ7 and GZ8. Note again that slicing of the stones was done independent from the
crystallographic orientation, and subjecting large fragments of the samples to the preparation of oriented slabs, for obtaining polarised spectra, would have consumed too much material. Reference measurements were done on U\textsuperscript{6+}-doped ZrSiO\textsubscript{4} (for details see Chase and Osmer 1966) and U\textsuperscript{5+}-containing zircon, produced by oxidised heating of crystals from Ratanakiri, Cambodia (Zeug et al. 2018). Spectra were measured at room temperature in transmission geometry, by means of a BrukerIFS66v/S FTIR spectrometer equipped with a mirror-optics IR-scope II microscope. Circular areas of 200 \( \mu \)m diameter were analysed. The following combinations of light sources, beam splitters and detectors were used: Xe lamp, quartz beam splitter and Ge detector for the range 28000–19400 cm\(^{-1}\) (1024 scans; 40 cm\(^{-1}\) spectral resolution); W lamp, quartz beam splitter and Si detector for the range 19400–10000 cm\(^{-1}\) (1024 scans; 20 cm\(^{-1}\) spectral resolution); W lamp, quartz beam splitter and Ge detector for the range 10000–5250 cm\(^{-1}\) (512 scans; 10 cm\(^{-1}\) spectral resolution). Each final optical absorption spectrum hence consists of a combination of three subspectra, which were aligned to match in absorbance if necessary.

**Oxygen isotope determination**

Six chips of GZ7 and seven chips of GZ8, with masses in the range 1.77–3.05 mg, were analysed for oxygen isotope ratios by laser fluorination gas source spectrometry, at the University of Wisconsin, Madison. These analyses were done in three separate sessions. All data presented in Table 3 are for chips that were analysed without any HF-etching pretreatment (compare discussion in Valley et al. 2005, 2015, Nasdala et al. 2016). Zircon chips were heated by an infrared laser (\( \lambda = 10.6 \) \( \mu \)m) in the presence of Bf\textsubscript{5}. The evolved O\textsubscript{2} gas was cryogenically purified, passed over hot Hg, converted to CO\textsubscript{2} and analysed by means of a dual-inlet gas source mass spectrometer that has been described elsewhere (Valley et al. 1994, 1995). Measured \( \delta^{18} \)O values were normalised to the recommended value of 5.80 VSMOW (Vienna Standard Mean Ocean Water) for the garnet reference material UWG-2 (Valley et al. 1995), which was analysed six or seven times before, and two times after, analyses of GZ7 and GZ8 in each analysis session (Table 3).

**Hafnium isotope determination**

Hafnium mass fractions, and \( ^{176} \)Hf/\( ^{177} \)Hf and \( ^{176} \)Lu/\( ^{173} \)Yb ratios, were measured by solution isotope dilution analysis of two chips each of GZ7 and GZ8 at IGG-CAS, Beijing. After being weighed, chips were dissolved in HF-HNO\textsubscript{3} in high-pressure bombs at 210 \( ^{\circ} \)C for 1 week, then dried down and dissolved again in 3 mol l\(^{-1}\) HCl. Sample solutions were then split. About 80% of each initial sample solution was used to determine the Hf isotopic composition. The remaining about 20% per solution was spiked with a mixed \( ^{176} \)Lu and \( ^{180} \)Hf tracer for determining the Lu and Hf mass fractions. The spike solution used was calibrated beforehand against a standard solution made from pure metals (Yang et al. 2010) that was tested on several calibrant materials, including BCR-2 and W-2 (Münker et al. 2001). The chemical purification procedure of Nebel-Jacobsen et al. (2005) and Morel et al. (2008) was applied. Isotope measurements were performed on a Thermo Scientific Fisher Neptune MC-ICP-MS system; details of the procedure have been published elsewhere (Yang et al. 2010). Instrumental mass bias was corrected offline using the exponential law and assuming \( ^{179} \)Hf/\( ^{177} \)Hf = 0.7325. Possible interferences of \( ^{176} \)Yb and \( ^{176} \)Lu on \( ^{176} \)Hf were corrected based on the measured \( ^{173} \)Yb and \( ^{176} \)Lu values, applying \( ^{176} \)Lu/\( ^{173} \)Yb = 0.02655 and \( ^{176} \)Yb/\( ^{173} \)Yb = 0.79631 (Vervoort et al. 2004). Measured \( ^{176} \)Hf/\( ^{177} \)Hf ratios were normalised to the recommended value of 0.282160 for the Johnson Matthews Company Hf standard JMC 475 (Novell et al. 1998), which was analysed in the same measurement session.

**(U-Th)/He geochronology**

(U-Th)/He analyses were done at the University of Arizona at Tucson, to evaluate the retention of radiogenic He. Details of the experimental procedure are described elsewhere (Nasdala et al. 2004, Reiners 2005, Guenthner et al. 2016). Because the analysed aliquots were internal fragments of much larger grains, no alpha ejection correction was applied.

**U-Pb geochronology by ID-TIMS**

The U-Pb isotopic ratios and ages were determined by ID-TIMS (isotope dilution–thermal ionisation mass spectrometry) in five laboratories, including NIGL (NERC Isotope Geosciences Laboratory, Keyworth, UK), University of Oslo, University of Geneva, Boise State University and Princeton University. For each of the zircon samples GZ7 and GZ8, small chips were separated from three slabs. Aliquots consisting of 5–7 fragments (with at least one fragment from each of the three slabs per sample), with total masses per aliquot in the range 2.01–2.48 mg, were given to the five ID-TIMS laboratories for U-Pb analysis. All laboratories were asked not to subject zircon grains to the CA (chemical abrasion) method (Mattinson 2005), in order to analyse the present U-Pb isotope ratios and to quantify any possible postgrowth Pb loss associated with the material. Also, all
laboratories were asked to report the isotopic ratios as
measured, that is, without any correction for initial disequi-
librium in $^{230}$Th/$^{238}$U (Schärer 1984).

At each laboratory, the received fragments were broken
into smaller fragments of the desired size. Zircon fragments
were rinsed with some combination of distilled acetone, 6 N
HCl, pure (Milli-Q) H$_2$O and 3 N HNO$_3$, which varied
slightly depending on the laboratory. Fragments were
placed in a Teflon capsule $\sim$ 200 $\mu$l in size prior to spiking
with either the EARTHTIME ETS35 203$^{\text{Pb}}$/238$^{\text{U}}$, 233$^{\text{U}}$/235$^{\text{U}}$, 205$^{\text{Pb}}$/233$^{\text{U}}$,
235$^{\text{U}}$/233$^{\text{U}}$, or the ET2535 201$^{\text{Pb}}$/203$^{\text{Pb}}$–
235$^{\text{U}}$/233$^{\text{U}}$ tracer (NIGU) (Lindgren et al. 2015, McLean
et al. 2015) or a laboratory-specific tracer (Oslo; see
below). Zircon was dissolved in 29 mol l$^{-1}$ HF + 3 mol l$^{-1}$
HNO$_3$ in pressure vessels for 60–80 h at 210–220 $^0$C.
Dissolved zircon solutions were subsequently dried down,
redissolved in 6 N HCl and converted to chlorides at
185 $^0$C overnight. U and Pb were isolated by anion
exchange column chromatography AG–1 X8 resin (either
Eichrom or Bio-Rad (Krogh 1973)). Following ion exchange
chemistry, the U–Pb aliquots was dried down with dilute
(0.02 mol l$^{-1}$) H$_3$PO$_4$ loaded in a silica gel emitter
(Gersenberger and Haase 1997) onto an outgassed,
zone-refined Re filament for isotopic analysis. Specifics of
the instrumental conditions have been described elsewhere
(Kennedy and de Laeter 1994, de Laeter and
Stock 1995). The decay constants of $^{235}$U and $^{238}$U were
determined, that is, without any correction for initial disequi-
librium in $^{230}$Th/$^{238}$U (Schärer 1984).

SIMS U–Pb analysis

The homogeneity of the U–Pb isotopic system of zircon
samples GZ7 and GZ8, and their SIMS analysis perfor-
ance (with particular attention at potential matrix effects;
White and Ireland 2012), was checked by multiple analyses
using the SHRIMP II (Sensitive High-mass Resolution Ion
MicroProbe) of the John de Laeter Centre for Isotopic
Research, Perth. Measurements were done in two sessions,
comprising 35/33/30 and 49/26/32 (GZ7/GZ8/M257)
individual analyses, respectively, that were placed on a
multitude of small chips embedded in an epoxy mount.
Details of the instrumental conditions have been described
elsewhere (Kennedy and de Laeter 1994, de Laeter and
Kennedy 1998, Kennedy et al. 2010). The primary, mass-
filtered O$_2$ beam ($\sim$ 2 nA) was focused to a $\sim$ 15 $\mu$m
elliptical spot. Data for each spot were collected through the
mass range of 196$^{\text{Zr}}$O$_7^+$, 206$^{\text{Pb}}^+$, 207$^{\text{Pb}}^+$, 208$^{\text{Pb}}^+$, 238$^{\text{U}}^+$, 248$^{\text{Th}}$O$^+$ and 254$^{\text{U}}$O$^+$. Analyses consisted of seven cycles through these nine
masses. The mass resolution, M/ΔM, was better than
5000. Results were calibrated against reference zircon
M257 with an assumed 206$^{\text{Pb}}$/238$^{\text{U}}$ age of 561.3 Ma
(Nasdala et al. 2008).

The 206$^{\text{Pb}}$ method was used for common Pb correction
(Compston et al. 1984, see also Ireland and Williams
2003), based on the relevant common Pb compositions from
the model curve of Stacey and Kramers (1975). The high Th/
U of GZ7 prevented use of the 208$^{\text{Pb}}$ common Pb correction
method (Compston et al. 1984). The correction for instru-
mental Pb/U fractionation was done based on the formula
of Claoué-Long et al. (1995).

\[
206^{\text{Pb}}/238^{\text{U}} = a(238^{\text{U}}^{16}O^+/238^{\text{U}}^{18}O^+) \tag{2}
\]

using the parameter values (a, b) of Black et al. (2003). Data
reduction and processing were done with the Excel macro
Squid 2 (Ludwig 2009). For conversion of U–Pb isotopic
ratios into ages and preparation of Wetherill Concordia
diagrams (Wetherill 1956), the U decay constants of Jaffey
et al. (1971) and a Th/U of GZ7 prevented use of the 208$^{\text{Pb}}$
common Pb correction method (Compston et al. 1984). The correction for instru-
mental Pb/U fractionation was done based on the formula
of Claoué-Long et al. (1995).

Results and discussion

Chemical composition

The element distribution within GZ7 and GZ8 appeared
widely homogeneous. The BSE and CL images (not shown)
and element maps (Figure 2) obtained in the EPMA did not
reveal any growth zoning or other features of internal
heterogeneity. Also, multiple trace element analyses in three
samples (GZ7; n = 56) and two laboratories (GZ8; n = 28),
respectively, did not show significant differences across and among
the slabs and chips analysed. However, counting statistics in
the EPMA element distribution maps is poor and faint
differences in the trace element mass fractions are obscured
by the signal noise. Quantitative EPMA line profiles across
the large sample slabs (see Appendices S2 and S3)
reveal slight systematic differences in U (both samples),
Th (especially GZ7) and Hf (especially GZ8) mass fractions
at the outer rims of the slabs. Although some systematic trend
is observable, it has to be pointed out that the 2 s errors
(single point errors calculated by counting statistics) do
overlap for most EPMA analysis points at each slab (see
Appendix S3).
The EPMA and LA-ICP-MS Results are listed in Table 2. In general, both samples contain low levels of nonformula elements, with Hf being the only constituent with a mass fraction higher than 1%. The different Ti mass fractions (Table 2) suggest different formation temperatures for the two samples (ca. 830 °C for GZ7 and ca. 720 °C for GZ8; based on the Ti-in-zircon thermometer of Watson et al. 2006), which in turn suggests that the two samples were derived from different host rocks. The U mass fractions (GZ7, 680 µg g⁻¹ ± 31 µg g⁻¹; GZ8, 1305 µg g⁻¹ ± 57 µg g⁻¹) correspond to those of other Sri Lankan gem zircon, which typically have U mass fractions in the (0.0x–0.x)% range (Murakami et al. 1991, Nasdala et al. 2004, 2008, 2016). The U mass fraction of GZ8, however, is higher than in any other SIMS U-Pb reference zircon. The Th/U mass fraction ratios (GZ7, 0.90; GZ8, 0.18) are significantly different, which also may indicate that the two specimens came from different source rocks. The REE (rare earth element) patterns of the two samples, in contrast, are fairly similar (Figure 3). There is a general increase in C1-normalised mass fractions towards the heavy REE, with positive Ce anomalies and negative Eu anomalies. The slightly higher positive Ce anomaly of GZ7 (Ce/Ce* = 13.3) compared to GZ8 (Ce/Ce* = 5.86) seems to correspond well with the slightly weaker Eu anomaly of GZ7 (Eu/Eu* = 0.20) compared to GZ8 (Eu/Eu* = 0.05), both indicating somewhat more oxidising conditions in the formation of GZ7.

The ID-ICP-MS analyses of GZ7 yielded uniform Ti mass fractions of 25.08 µg g⁻¹ ± 0.18 µg g⁻¹ (Figure 4). The Ti homogeneity in GZ7 was further supported by results of 64 LA-ICP-MS analyses placed at seven chips of GZ7, whose mean ⁴⁹Ti/⁴⁰Si ratio had a 1 s deviation of only 1.1%. Based on these results, zircon GZ7 was proposed by Szymanowski et al. (2018) as reference material for analyses of Ti in zircon for the purpose of Ti-in-zircon geothermometry (Watson et al. 2006, Ferry and Watson 2007).

**Structural state**

The mass densities (Table 1) were determined at 4.658 ± 0.005 g cm⁻³ (GZ7) and 4.537 ± 0.005 g cm⁻³ (GZ8), respectively. Both values coincide well with published mass densities for Sri Lankan zircon (Figure 5a), which scatter between 4.68 and 4.72 g cm⁻³ for well-crystallised and below 4 g cm⁻³ for metamict zircon (cf. Holland and Gottfried 1955, Vaz and Seltile 1971, Murakami et al. 1991, Ellsworth et al. 1994, Nasdala et al. 2002, 2008, 2016).

Results of single-crystal X-ray diffraction analyses are quoted in Table 1. The unit cell of GZ7 (264.12 Å³ ± 0.22 Å³) shows moderate volume expansion and the unit cell of GZ8 (270.13 Å³ ± 0.20 Å³) shows significant volume expansion, compared to mildly radiation-damaged zircon from Sri Lanka (~ 261 Å³; Holland and Gottfried 1955).
1955, Robinson et al. 1971, see Figure 3b). The unit-cell expansions are consistent with the decreases in mass density. For both zircon samples, unit-cell parameters $a_0$ and $c_0$ correlate with each other. This allows us to exclude any heat treatment of the gemstones, because partial annealing at comparably low temperatures would be associated with an $a_0 - c_0$ mismatch (Nasdala et al. 2004, Chanmuang et al. 2017) that is explained by preferential recovery of irradiation-induced volume swelling perpendicular to the crystallographic $c$ axis (Weber 1990, 1993).

The FWHM of the $v_3$(SiO$_4$) Raman band (internal $B_{1g}$ mode: antisymmetric stretching of SiO$_4$ tetrahedra; Dawson et al. 1971) was determined at $10.9$ cm$^{-1} \pm 0.6$ cm$^{-1}$ (GZ7) and $21.1$ cm$^{-1} \pm 1.8$ cm$^{-1}$ (GZ8), indicating moderate and significant radiation damage, respectively (Nasdala et al. 1995, 2001). Multiple analyses across the large slices and of additional small chips did not yield FWHM values outside the above error ranges, indicating homogeneous structural states of both samples.

Emission spectra (Figure 6a) do not show the yellow broadband, defect-induced emission that typically dominates the PL of mildly radiation-damaged zircon (Gaft et al. 2000, Nasdala et al. 2003, 2011). This indicates the presence of at least moderate defect densities, at which the yellow broadband emission is quenched already (Nasdala et al. 2011). The PL spectra show groups of narrow lines that are assigned to crystal-field-split electronic transitions of REE$^{3+}$ (for the assignment see, e.g., Carnall et al. 1968, Gaft et al. 2000, 2015, Lenz and Nasdala 2015). The REE-related emission intensities of GZ7 exceed in general those

Table 2.
Chemical compositions of zircon samples GZ7 and GZ8 (EPMA, Universität Göttingen; LA-ICP-MS, Chinese Academy of Sciences Beijing, Macquarie University Sydney and ETH Zürich)

| Oxide/element | EPMA mass fractions (%) | Isotope measured | Zircon GZ7 | Zircon GZ8 |
|---------------|-------------------------|------------------|------------|------------|
| $\text{SiO}_2$ | $-32.85 \pm 0.08$      |                 | $32.53 \pm 0.17$ |
| $\text{P}_2\text{O}_5$ | $-0.052 \pm 0.004$ | | $0.022 \pm 0.003$ |
| $\text{Y}_2\text{O}_3$ | $0.078 \pm 0.005$ | | $0.059 \pm 0.005$ |
| $\text{ZrO}_2$ | $-66.40 \pm 0.15$ | | $66.48 \pm 0.16$ |
| $\gamma\text{Y}_2\text{O}_3$ | $-0.017 \pm 0.005$ | | $0.012 \pm 0.003$ |
| $\text{HfO}_2$ | $1.25 \pm 0.01$ | | $1.39 \pm 0.02$ |
| $\text{ThO}_2$ | $-0.069 \pm 0.005$ | | $0.027 \pm 0.003$ |
| $\text{UO}_2$ | $-0.076 \pm 0.004$ | | $0.151 \pm 0.006$ |
| Total | $100.80 \pm 0.18$ | | $100.67 \pm 0.29$ |

LA-ICP-MS results ($\mu g \ g^{-1}$)

| Element | (n = 56) | (n = 28) |
|---------|---------|---------|
| $P$ | $31 \pm 17$ | $82.9 \pm 12.0$ |
| $Ti$ | $49 \pm 1.2$ | $8.16 \pm 1.06$ |
| $Y$ | $89 \pm 3$ | $436 \pm 3$ |
| $Nb$ | $93 \pm 0.7$ | $8.03 \pm 0.48$ |
| $La$ | $139 \pm 0.006$ | $8.08 \pm 0.003$ |
| $Ce$ | $140 \pm 3.9$ | $14.3 \pm 0.9$ |
| $Pr$ | $141 \pm 0.0032$ | $0.057 \pm 0.011$ |
| $Nd$ | $146 \pm 0.37$ | $1.14 \pm 0.11$ |
| $Sm$ | $147 \pm 0.40$ | $1.90 \pm 0.18$ |
| $Eu$ | $151 \pm 0.0067$ | $0.061 \pm 0.010$ |
| $Gd$ | $157 \pm 0.9$ | $8.96 \pm 0.48$ |
| $Tb$ | $159 \pm 0.19$ | $3.27 \pm 0.09$ |
| $Dy$ | $163 \pm 2.3$ | $37.5 \pm 0.8$ |
| $Ho$ | $165 \pm 0.7$ | $13.1 \pm 0.3$ |
| $Er$ | $166 \pm 2.8$ | $54.4 \pm 1.0$ |
| $Tm$ | $169 \pm 0.4$ | $11.1 \pm 0.2$ |
| $Yb$ | $173 \pm 12$ | $104.2 \pm 4.2$ |
| $Lu$ | $175 \pm 14.0$ | $15.5 \pm 0.9$ |
| $Hf$ | $178 \pm 0.006$ | $116.0 \pm 240$ |
| $Th$ | $181 \pm 0.22$ | $5.73 \pm 0.38$ |
| $U$ | $204/206/207/208$ | $240 \pm 6$ |
| $Pb$ | $232 \pm 33$ | $240 \pm 6$ |
| $U$ | $238 \pm 31$ | $1305 \pm 57$ |

Quoted uncertainties are 2$s$.

$^*_A\text{I}_{2}\text{O}_3$, CaO and FeO were not detected or average mass fractions were below 0.005%.
of GZ8 by about one-third (Figure 6a), which corresponds to the REE mass fraction ratios of the two samples (Table 2). The fact that, in both samples, Dy\(^{3+}\) shows particularly high intensity whereas Er\(^{3+}\) and Ho\(^{3+}\) are virtually not detected, even though the mass fractions of these elements are on a similar order, is due to the different wavelength-dependent excitation sensitivities of REE-related emissions (Gaft et al. 2000, Friis et al. 2010, Lenz et al. 2015), which in turn are controlled by the particular electronic structure of each REE ion (Dieke and Crosswhite 1963, Reisfeld and Jørgensen 1977). Following Lenz and Nasdala (2015), the FWHMs of the \(~17210\) cm\(^{-1}\) sublevel of the \(^{4}F_{9/2} \rightarrow ^{4}I_{13/2}\) emission of Dy\(^{3+}\) and the \(~11360\) cm\(^{-1}\) sublevel of the \(^{4}F_{3/2} \rightarrow ^{4}I_{9/2}\) emission of Nd\(^{3+}\) (Figure 6b) were used to estimate the degree of radiation damage. These PL FWHMs are moderately (GZ7) and significantly broadened (GZ8) when compared with FWHMs of crystalline zircon (Table 1); the degrees of broadening correlate with the alpha doses (Lenz and Nasdala 2015, Figure 5d).

After reconstitution of the crystalline state through annealing at 1400 °C, the unit-cell volumes had decreased to \(<261\ \text{Å}^3\) for both samples. Also, the annealed chips of GZ7 and GZ8 yielded narrow Raman bands and narrow Dy\(^{3+}\) and Nd\(^{3+}\) emission lines whose FWHMs are identical within errors to FWHMs of Raman bands and PL lines of crystalline zircon (Table 1). As references for crystalline zircon, we use the Ratanakiri, Cambodia, zircon \(^{206}\text{Pb}/^{238}\text{U}\) age \(0.92 \pm 0.07\ \text{Ma}\) (95% confidence uncertainty); calculated alpha dose \(0.0004 \times 10^{18}\ \text{g}^{-1}\); Zeug et al. 2018) and synthetic undoped \(\text{ZrSiO}_4\) (van Westrenen et al. 2004). Unit-cell expansion and Raman band and PL line broadening of GZ7 and GZ8 are predominantly assigned to the accumulated radiation damage, whereas effects of minor amounts of nonformula elements on unit-cell parameters and spectroscopic signals appear insignificant.

### Optical absorption

Optical absorption spectra are presented in Figure 7. In spite of their noticeably different colours, GZ7 and GZ8 yield similar principal absorption characteristics. First, an intense absorption edge that extends from the ultraviolet into the visible range and down towards the NIR region causes enhanced absorption especially of the blue fraction of the visible light. Second, there is a multitude of narrow absorption features, with the most intense at \(~15290\) cm\(^{-1}\). These are assigned to U\(^{4+}\) (Richman et al. 1967, Mackey et al. 1975) and cause absorption preferentially in the red range. The two absorption features bracket a ‘window of enhanced transmission’ in the green to yellow range that causes the yellowish green colour of GZ8. In contrast, the U\(^{4+}\) absorption of GZ7 in the red range is much less intense, which, along with a slightly different shape of the absorption edge, results in brownish colour. Both samples also are yield a fairly intense U\(^{5+}\) absorption band at \(~6660\) cm\(^{-1}\) (for assignment, see Vance and Mackey 1974), whereas the group of overlapping absorption features near \(~8970\) cm\(^{-1}\) is assigned to a combination of U\(^{4+}\) and U\(^{5+}\). The two latter, however, do not contribute to sample colouration as these absorptions are in the NIR.

The U\(^{4+}\) and U\(^{5+}\) absorption lines are significantly broadened compared to reference spectra. The effect is
again assigned to radiation damage in GZ7 and GZ8. The intensity ratio of the absorption lines at $\sim 15290 \text{ cm}^{-1}$ ($\text{U}^{4+}$) and $\sim 6660 \text{ cm}^{-1}$ ($\text{U}^{5+}$) is notably lower for GZ7, when compared to GZ8. Although interpretations are somewhat limited, as unpolarised spectra are compared, this may indicate that GZ7 has higher $\text{U}^{5+}/\text{U}^{4+}$, which in turn seems to agree well with more oxidising conditions in the formation of GZ7 as concluded from the REE patterns.

Further characterisation: O isotopes, Hf isotopes and (U-Th)/He dating

Results of oxygen isotope analyses are presented in Table 3. These data yield mean $\delta^{18}\text{O}$ values of $6.88^{\pm}0.05\% \text{ VSMOW}$ (2$s$) for GZ7 and $8.88^{\pm}0.10\% \text{ VSMOW}$ (2$s$) for GZ8. The significant difference of the two means strongly indicates that GZ7 and GZ8 must be derived from different host rocks. This is consistent with the different Th/U ratios and the difference in Ti mass fractions (Table 1). However, the $\delta^{18}\text{O}$ values obtained for GZ7 and GZ8 do not provide independent evidence on the type of formation environment. Even though they fall well within the range of typical oxygen isotope compositions of igneous zircon (Valley et al. 2005), $\delta^{18}\text{O}$ values of $6.88\%$ and $8.88\%$ VSMOW are not conclusive for igneous growth. Note that, for some homogeneous Sri Lankan reference zircon, exceptionally high $\delta^{18}\text{O}$ values are reported (13.9% VSMOW for M257 (Nasdala et al. 2008); 15.4% VSMOW for CZ3 (Cavosie et al. 2011)), which rather suggest a metamorphic origin of zircon, perhaps by the metasomatic formation of skarns or similar Ca-rich, acidic rocks from marble-like precursors (Cavosie et al. 2011). This, however, does not pertain to the $\delta^{18}\text{O}$ values of $6.88\%$ and $8.88\%$ VSMOW obtained here; there is no evidence for a
Figure 6. Laser-induced PL spectroscopy. (a) Emission spectra (473 nm excitation) of GZ7 and GZ8 in comparison with reference spectra of REE-doped ZrSiO₄. GZ7 and GZ8 show widely similar REE-emission patterns; the higher emission intensities of GZ7 are due to slightly higher REE mass fractions. (b) Enlargements of the ⁴F₃/₂ → ⁴I₃/₂ emission of Nd³⁺ in the near infrared range (532 nm excitation) and the ⁴F₉/₂ → ⁴H₁₃/₂ emission of Dy³⁺ in the green range (473 nm excitation). Spectra of untreated samples (solid) are compared with spectra obtained after structural reconstitution through annealing at 1400 °C (dotted; intensity × 0.5). Lines whose FWHMs are quoted in Table 1 are marked with asterisks.
measured Lu-Hf isotopic ratios, based on a decay constant of 1.865 × 10^{-11} \text{ a}^{-1} for $^{176}$Lu (Scherer et al. 2001) and the CHUR (chondritic uniform reservoir) ratios of $^{176}$Hf/$^{177}$Hf of 0.282772 and $^{176}$Lu/$^{177}$Hf of 0.0332 (Blichert-Toft and Albarède 1997). Low $^{176}$Hf/$^{177}$Hf ratios and hence low εHf(t) values of -27.7 (GZ7) and -27.4 (GZ8) indicate that both of the two zircons samples presumably have formed from reworked ancient (probably Archaean) protolith material (compare Kinny et al. 1991, Santosh et al. 2014). There is, however, no independent evidence for the formation environment. On the one hand, low εHf(t) values may imply metamorphic formation as reworking product of ancient crust (as discussed by Kinny et al. 1991). On the other hand, in rare cases igneous zircon may also yield similarly low εHf values (e.g., Yang et al. 2007, Wotzlaw et al. 2015).

Results of (U-Th)/He analyses are summarised in Table 5. The mean He ages (2σ uncertainties) of 438 Ma ± 3 Ma (GZ7) and 426 Ma ± 9 Ma (GZ8) fall well within the range of He ages of unheated Sri Lankan zircon (Hurley 1954, Nasdala et al. 2004). The He ages hence indicate that both zircon specimens have not experienced any unusual thermal history, which in turn supports that the gemstones have never been subjected to any colour enhancement through thermal treatment. The fact that He ages postdate typical U-Pb ages of Sri Lankan gem zircon by ~ 100 Ma is explained by a prolonged cooling history of the Sri Lankan Highland Complex: After closure of the zircon U-Pb system in the Cambrian, rocks of the Highland Complex underwent slow cooling at elevated $T$ that was followed by exhumation and cooling to temperatures lower than roughly 200 °C in the Ordovician (Hölzl et al. 1991).

U-Pb geochronology results (ID-TIMS)

U-Pb isotopic ratios and ages are listed in Tables 6 and 7. They are reported with internal errors only, including counting statistics, uncertainties in correcting for mass discrimination and the uncertainty in the common (blank) Pb composition. Wetherill Concordia plots are presented in Figure 8. Here, errors for calculated weighted mean ages quoted are of the form $x/y/z$, where $x$ is solely analytical uncertainty, $y$ is the combined analytical and tracer uncertainty, and $z$ is the combined analytical, tracer and U decay constant uncertainty. The uncertainties in tracer calibration (0.03%; Condon et al. 2015, McLean et al. 2015) and U decay constants (0.108%; Jaffe et al. 1971, see also Schoene et al. 2006, Mattinson 2010, Boehnke and Harrison 2014) were added to the ‘internal error’ in quadrature.

A total of thirty-one ID-TIMS analyses without prior CA treatment were done for each of the two zircon samples GZ7 and GZ8. The recommended mean $^{206}$Pb/$^{238}$U values are 0.085735 ± 0.000009 (2σ) for GZ7 and 0.088037 ± 0.00010 (2σ) for GZ8. The weighted mean $^{206}$Pb/$^{238}$U ages (uncertainties quoted at the 95% confidence level) are 530.26 Ma ± 0.05 Ma (MSWD 3.1) for GZ7 and 543.92 Ma ± 0.06 Ma (MSWD 6.0) for GZ8. Both of these ages are concordant within the uncertainties of decay constants. It should be noted that at NIGL, three additional ID-TIMS analyses of each zircon sample were done that were preceded by CA treatment according to Mattinson (2005). The results are included in Tables 6 and 7; however, they were disregarded in the calculation of mean isotopic ratios and ages. Systematic deviations of the results (isotopic ratios and degrees of U-Pb discordance) from those of analyses without CA were not observed.

The ~ 14 Ma difference between the two U-Pb dates is not unusual for gem zircon from the Sri Lankan Highland Complex. Published ages scatter in the approximate range 575–520 Ma (Pidgeon et al. 1994, Colomé-Long et al. 1995, Kennedy 2000, Stern 2001, Nasdala et al. 2004, 2008, 2016). However, the age difference supports again that GZ7 and GZ8 were derived from different source rocks.
SIMS U-Pb analysis

Results of SIMS analyses are presented in Figure 9 and given in Appendix S4 (which contains data, additional Concordia diagrams and plots of Th/U for GZ7 and GZ8). Zircon GZ8 exhibits somewhat variable Th/U, with a single chip having Th/U = 0.1872 ± 0.0004 (n = 13), which is significantly higher than all other chips, which have Th/U = 0.1816 ± 0.0002 (n = 46). There is no correlation between Th/U and the U-Pb isotopic ratios obtained. Based on the EPMA line scans, we may speculate that this chip originated from a rim area of the initial stone (see Appendix S3).

Table 3.
Results of oxygen isotope analyses by laser fluorination (University of Wisconsin at Madison)

| Analysis number | Sample/reference name | Material analysed | Mass (mg) | δ18O Raw | (‰ VSMOW) a |
|-----------------|-----------------------|-------------------|-----------|----------|--------------|
| 1               | UWG-2                 | Garnet reference  | 4.40      | 5.54     |              |
| 2               | UWG-2                 | Garnet reference  | 2.28      | 5.82     |              |
| 3               | UWG-2                 | Garnet reference  | 2.32      | 5.60     |              |
| 4               | UWG-2                 | Garnet reference  | 1.64      | 5.59     |              |
| 5               | UWG-2                 | Garnet reference  | 1.67      | 5.72     |              |
| 6               | UWG-2                 | Garnet reference  | 1.92      | 5.71     |              |
| 7               | UWG-2                 | Garnet reference  | 2.30      | 5.72     |              |
| 8               | GZ8                   | Zircon            | 3.05      | 8.71     | 8.82         |
| 9               | GZ8                   | Zircon            | 2.16      | 8.82     | 8.93         |
| 10              | GZ8                   | Zircon            | 1.77      | 8.81     | 8.92         |
| 11              | GZ7                   | Zircon            | 2.86      | 6.73     | 6.84         |
| 12              | GZ7                   | Zircon            | 2.30      | 6.76     | 6.87         |
| 13              | GZ7                   | Zircon            | 2.53      | 6.78     | 6.89         |
| 14              | UWG-2                 | Garnet reference  | 2.71      | 5.65     |              |
| 15              | UWG-2                 | Garnet reference  | 3.14      | 5.74     |              |
| 1               | UWG-2                 | Garnet reference  | 3.27      | 5.58     |              |
| 2               | UWG-2                 | Garnet reference  | 2.58      | 5.50     |              |
| 3               | UWG-2                 | Garnet reference  | 2.17      | 5.70     |              |
| 4               | UWG-2                 | Garnet reference  | 2.88      | 5.61     |              |
| 5               | UWG-2                 | Garnet reference  | 2.44      | 5.75     |              |
| 6               | UWG-2                 | Garnet reference  | 2.08      | 5.61     |              |
| 7               | GZ7                   | Zircon            | 2.24      | 6.67     | 6.81         |
| 8               | GZ8                   | Zircon            | 2.77      | 8.79     | 8.93         |
| 9               | GZ8                   | Zircon            | 2.88      | 8.88     | 9.02         |
| 10              | GZ7                   | Zircon            | 2.45      | 5.60     |              |
| 11              | GZ7                   | Zircon            | 2.39      | 5.70     |              |
| 1               | UWG-2                 | Garnet reference  | 3.19      | 5.45     |              |
| 2               | UWG-2                 | Garnet reference  | 2.86      | 5.47     |              |
| 3               | UWG-2                 | Garnet reference  | 2.30      | 5.42     |              |
| 4               | UWG-2                 | Garnet reference  | 1.72      | 5.39     |              |
| 5               | UWG-2                 | Garnet reference  | 1.50      | 5.45     |              |
| 6               | UWG-2                 | Garnet reference  | 1.74      | 5.44     |              |
| 7               | UWG-2                 | Garnet reference  | 1.54      | 5.46     |              |
| 8               | GZ7                   | Zircon            | 2.56      | 6.65     | 6.97         |
| 9               | GZ7                   | Zircon            | 2.55      | 6.56     | 6.88         |
| 10              | GZ8                   | Zircon            | 2.27      | 8.38     | 8.70         |
| 11              | GZ8                   | Zircon            | 1.95      | 8.53     | 8.85         |
| 12              | UWG-2                 | Garnet reference  | 2.19      | 5.60     |              |
| 13              | UWG-2                 | Garnet reference  | 2.29      | 5.49     |              |

Summary Zircon GZ7 (six individual analyses); Mean δ18O = 6.88‰ ± 0.05‰ VSMOW (2s)
Zircon GZ8 (seven individual analyses); Mean δ18O = 8.88‰ ± 0.10‰ VSMOW (2s)

a GZ7 and GZ8 data are corrected to the respective UWG-2 reference analyses.
The calculated mean Concordia ages (Ludwig 1998) given in Figure 9 coincide within errors with the ID-TIMS results, even though they seem to be slightly (ca. 2 Ma) younger. It may be speculated that the apparently systematic bias is caused by the particular data reduction calibration parameters. For instance, applying $^{208}$Pb correction to the same SIMS data for zircon GZ8 results in a mean Concordia age of 546.4 Ma $\pm$ 1.3 Ma (1s), which is 2.5 Ma older than the ID-TIMS result. However, the apparent age differences are below the reproducibility of SIMS results (typically ~ 1%). It nevertheless seems worthwhile that more SIMS laboratories check whether there is a systematic bias between SIMS and ID-TIMS results, prior to using GZ7 and GZ8 as reference materials.

Two important observations can be made from the SIMS results. First, both zircon samples did not reveal any detectable heterogeneity of the U-Pb isotopic ratios within and between the sessions. Second, even though zircon GZ8 is significantly more radiation-damaged than M257 and any other SIMS reference, there were no noticeable matrix effects under the O$_2^-$ beam. Too high levels of radiation damage can effectuate systematically enhanced emission of Pb$^+$ relative to U and U oxide species, which would result in reversely discordant U-Pb isotopic ratios (White and Ireland 2012). This has not been observed, suggesting that the sputter behaviour under the O$_2^-$ beam of both GZ7 and GZ8 does not cause systematically different ion yields to that of unknowns, which in turn is most promising in terms of the performance as reference materials.

**Concluding remarks**

Zircon samples GZ7 and GZ8 constitute suitable reference materials for the U-Pb analysis of unknown zircon samples by means of SIMS. Both reference materials are isotopically homogeneous and have a concordant U-Pb system, low levels of non-radiogenic Pb and comparably high U and Pb mass fraction. The latter are expected to result in high count rates and good Poisson statistics during analysis. Both reference materials did not show noticeable matrix effects (that is, preferred sputtering of Pb isotopes

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Table 4.

Results of Hf isotope determinations by ID-ICP-MS (Chinese Academy of Sciences Beijing)

| Sample name | Lu (µg g$^{-1}$) | Hf (µg g$^{-1}$) | $^{176}$Lu/$^{177}$Hf | $^{176}$Hf/$^{177}$Hf | $^{176}$Hf/$^{177}$Hf(a) | $\varepsilon_{Hf}(t)$ b |
|-------------|-----------------|-----------------|------------------|------------------|------------------|------------------|
| GZ7 #1      | 32.4            | 9323            | 0.00049          | 0.281666 ± 0.0000004 | 0.281661         | -27.7            |
| GZ7 #2      | 32.8            | 9351            | 0.00050          | 0.281666 ± 0.0000007 | 0.281661         | -27.7            |
| GZ8 #1      | 17.0            | 10259           | 0.00024          | 0.281662 ± 0.0000005 | 0.281660         | -27.4            |
| GZ8 #2      | 17.0            | 10226           | 0.00024          | 0.281661 ± 0.0000005 | 0.281659         | -27.4            |

Quoted uncertainties of measured $^{176}$Hf/$^{177}$Hf ratios are 2s.

a Age-corrected (i.e., initial) $^{176}$Hf/$^{177}$Hf ratios (GZ7, 530 Ma; GZ8, 544 Ma).

b $\varepsilon_{Hf}(t) = ([^{176}$Hf/$^{177}$Hf(calib) $^{176}$Hf/CHUR] - 1) $\times$ 104 (Faure and Mensing 2004, CHUR $^{176}$Hf/$^{177}$Hf ratio from Blichert-Toft and Albarède 1997).

Table 5.

(U-Th)/He ages of GZ7 and GZ8 (University of Arizona at Tucson)

| Sample name | $^4$He (pmol) | U (pg) | Th (pg) | Th/U | Age (Ma) |
|-------------|--------------|-------|---------|------|----------|
| Zircon GZ7  |              |       |         |      |          |
| 16A598      | 1.316 ± 0.034| 445 ± 6| 394 ± 6 | 0.908| 437 ± 13 |
| 16A599      | 0.366 ± 0.016| 122 ± 2| 106 ± 2 | 0.894| 442 ± 20 |
| 16A600      | 1.172 ± 0.050| 399 ± 6| 349 ± 5 | 0.897| 435 ± 20 |
| 16A602      | 0.799 ± 0.015| 271 ± 4| 238 ± 3 | 0.901| 437 ± 10 |
| Mean age of four analyses: 438 Ma ± 3 Ma (2s) | | | | | |

Zircon GZ8

| Sample name | $^4$He (pmol) | U (pg) | Th (pg) | Th/U | Age (Ma) |
|-------------|--------------|-------|---------|------|----------|
| 16A603      | 0.563 ± 0.011| 232 ± 3| 42.1 ± 0.6| 0.186| 415 ± 10 |
| 16A604      | 1.670 ± 0.032| 676 ± 10| 1198 ± 1.7| 0.182| 423 ± 10 |
| 16A605      | 0.758 ± 0.015| 295 ± 4| 52.1 ± 0.8| 0.181| 440 ± 11 |
| 16A606      | 0.655 ± 0.013| 261 ± 4| 47.5 ± 0.7| 0.187| 429 ± 10 |
| 16A607      | 1.235 ± 0.012| 502 ± 7| 88.7 ± 1.3| 0.181| 421 ± 7 |
| Mean age of five analyses: 426 Ma ± 9 Ma (2s) | | | | | |

Quoted uncertainties on individual ages are 1s measurement precision.
| Analysis | Compositional parameters | Isotopic ratios | Isotopic ages |
|----------|--------------------------|----------------|--------------|
|          | Th/U (pg) | Pb_{rad} (pg) | Pb_{com} (pg) | Pb_{rad} / Pb_{com} | 206Pb/204Pb | 207Pb/206Pb | 206Pb/235U | ρ (err. corr.) | 207Pb/206Pb age (Ma) | 207Pb/235U Age (Ma) | 206Pb/238U Age (Ma) | Disc. (%) |
| (a)      | (b) | (c) | (d) | (e) | (f) | (g) | (h) | (i) | (j) | (k) | (l) | (m) | (n) |
| z1 (CA)  | 0.893 | 4728 | 1.13 | 4203 | 228816 | 0.6860 ± 0.0007 | 0.08569 ± 0.000008 | 0.90 | 533.54 ± 0.104 | 530.65 ± 0.45 | 529.97 ± 0.48 | 0.67 |
| z2 (CA)  | 0.909 | 2243 | 0.45 | 4932 | 267503 | 0.6861 ± 0.0004 | 0.08571 ± 0.000004 | 0.82 | 531.74 ± 0.80 | 530.43 ± 0.26 | 530.13 ± 0.24 | 0.30 |
| z3 (CA)  | 0.890 | 1773 | 0.54 | 3259 | 177571 | 0.6856 ± 0.0007 | 0.08559 ± 0.000007 | 0.89 | 533.18 ± 1.09 | 530.14 ± 0.44 | 530.62 ± 0.70 | 0.70 |
| z5       | 0.888 | 3262 | 3.14 | 1039 | 566.44 | 0.6860 ± 0.0004 | 0.08567 ± 0.000004 | 0.78 | 532.58 ± 0.77 | 530.38 ± 0.07 | 530.97 ± 0.15 | 0.51 |
| z6       | 0.890 | 1503 | 0.50 | 2996 | 163211 | 0.6864 ± 0.0007 | 0.08573 ± 0.000007 | 0.86 | 532.34 ± 1.19 | 530.64 ± 0.04 | 530.24 ± 0.40 | 0.39 |
| z8       | 0.910 | 606  | 0.47 | 128  | 6941  | 0.6865 ± 0.0007 | 0.08571 ± 0.000007 | 0.86 | 533.35 ± 2.11 | 530.71 ± 0.17 | 530.10 ± 0.17 | 0.61 |
| z9       | 0.891 | 502  | 0.54 | 93   | 5064  | 0.6867 ± 0.0008 | 0.08572 ± 0.000003 | 0.31 | 533.67 ± 2.42 | 530.84 ± 0.48 | 530.19 ± 0.17 | 0.65 |
| z10      | 0.889 | 357  | 0.33 | 107  | 8524  | 0.6866 ± 0.0009 | 0.08573 ± 0.000004 | 0.47 | 533.03 ± 2.64 | 530.75 ± 0.55 | 530.22 ± 0.18 | 0.53 |

University of Oslo

464/15 | 0.881 | 40087 | 3.37 | 11890 | 259486 | 0.6847 ± 0.0019 | 0.08561 ± 0.000022 | 0.97 | 530.22 ± 1.42 | 529.64 ± 1.14 | 529.50 ± 1.28 | 0.14 |

464510 | 0.881 | 45378 | 3.13 | 14520 | 279916 | 0.6844 ± 0.0020 | 0.08555 ± 0.000023 | 0.98 | 530.41 ± 1.47 | 529.42 ± 1.23 | 529.19 ± 1.39 | 0.24 |

University of Geneva

GZ7/z3 | 0.882 | 107149 | 2.16 | 49694 | 179890 | 0.6841 ± 0.0017 | 0.08552 ± 0.000019 | 0.97 | 530.62 ± 1.35 | 529.27 ± 1.01 | 528.96 ± 1.12 | 0.33 |

Boise State University

z1 | 0.895 | 753 | 1.43 | 53 | 2866 | 0.6872 ± 0.0013 | 0.08576 ± 0.000007 | 0.78 | 534.08 ± 2.97 | 531.09 ± 0.78 | 530.39 ± 0.42 | 0.69 |

z2 | 0.898 | 2281 | 1.41 | 1617 | 87638 | 0.6874 ± 0.0009 | 0.08574 ± 0.000006 | 0.97 | 535.33 ± 1.29 | 531.26 ± 0.53 | 530.32 ± 0.38 | 0.94 |

z3 | 0.891 | 976 | 2.05 | 477 | 29928 | 0.6875 ± 0.0013 | 0.08584 ± 0.000014 | 0.95 | 532.91 ± 1.46 | 531.28 ± 0.81 | 530.90 ± 0.83 | 0.38 |

z4 | 0.898 | 2776 | 0.38 | 7316 | 396417 | 0.6870 ± 0.0011 | 0.08578 ± 0.000012 | 0.98 | 532.88 ± 0.79 | 530.99 ± 0.66 | 530.55 ± 0.73 | 0.44 |

z5 | 0.915 | 813 | 0.75 | 1085 | 58582 | 0.6870 ± 0.0007 | 0.08576 ± 0.000006 | 0.93 | 533.73 ± 0.96 | 531.02 ± 0.41 | 530.39 ± 0.35 | 0.63 |

z6 | 0.915 | 1128 | 0.30 | 3796 | 204903 | 0.6870 ± 0.0007 | 0.08576 ± 0.000007 | 0.95 | 533.60 ± 0.88 | 531.02 ± 0.45 | 530.42 ± 0.43 | 0.60 |

z7 | 0.892 | 437 | 0.25 | 1777 | 96454 | 0.6876 ± 0.0008 | 0.08583 ± 0.000006 | 0.98 | 533.68 ± 1.31 | 531.36 ± 0.51 | 530.82 ± 0.34 | 0.54 |

z8 | 0.914 | 407 | 0.33 | 1241 | 67017 | 0.6877 ± 0.0010 | 0.08581 ± 0.000008 | 0.98 | 534.47 ± 1.04 | 531.43 ± 0.58 | 530.72 ± 0.50 | 0.70 |
Table 6 (continued).
Results of U-Pb determinations (ID-TIMS) of zircon GZ7

| Analysis | Compositional parameters | Isotopic ratios | Isotopic ages |
|---------|--------------------------|----------------|--------------|
|         | Th/U | Pb$_{rad}$/Pb$_{com}$ | 206Pb/238U | 206Pb/204Pb | 207Pb/206Pb | 206Pb/235U | 207Pb/235U Age (Ma) | 207Pb/206Pb Age (Ma) | 206Pb/238U Age (Ma) | Discord. (%) |
|---------|-----|---------------------|-----------|-----------|-----------|-----------|------------------|------------------|------------------|------------|
| Princeton University |
| z1     | 0.897 | 842 | 0.50 | 1680 | 90671 | 0.00816 ± 0.00002 | 0.6873 ± 0.0006 | 0.08574 ± 0.00005 | 0.88 | 534.86 ± 1.17 | 531.15 ± 0.39 | 530.29 ± 0.27 | 0.85 |
| z2     | 0.898 | 596 | 0.38 | 1566 | 84504 | 0.00815 ± 0.00002 | 0.6873 ± 0.0007 | 0.08577 ± 0.00005 | 0.88 | 534.35 ± 1.17 | 531.18 ± 0.39 | 530.44 ± 0.28 | 0.73 |
| z3     | 0.897 | 546 | 0.36 | 1522 | 82125 | 0.00813 ± 0.00003 | 0.6868 ± 0.0007 | 0.08573 ± 0.00005 | 0.88 | 533.57 ± 1.19 | 530.86 ± 0.40 | 530.23 ± 0.27 | 0.63 |
| z4     | 0.897 | 1052 | 0.34 | 3130 | 168926 | 0.00814 ± 0.00002 | 0.6867 ± 0.0006 | 0.08571 ± 0.00004 | 0.90 | 533.93 ± 1.14 | 530.83 ± 0.38 | 530.11 ± 0.25 | 0.72 |
| z5     | 0.897 | 220 | 0.56 | 390 | 21070 | 0.00810 ± 0.00004 | 0.6864 ± 0.0008 | 0.08572 ± 0.00004 | 0.86 | 532.40 ± 1.63 | 530.61 ± 0.46 | 530.19 ± 0.25 | 0.42 |
| z6     | 0.897 | 419 | 0.47 | 885 | 47797 | 0.00809 ± 0.00003 | 0.6861 ± 0.0007 | 0.08570 ± 0.00006 | 0.87 | 532.31 ± 1.29 | 530.48 ± 0.44 | 530.05 ± 0.35 | 0.42 |
| z7     | 0.896 | 302 | 0.43 | 694 | 37506 | 0.00813 ± 0.00003 | 0.6869 ± 0.0007 | 0.08573 ± 0.00005 | 0.83 | 533.76 ± 1.14 | 530.91 ± 0.42 | 530.25 ± 0.29 | 0.66 |
| z9     | 0.897 | 623 | 1.06 | 590 | 31860 | 0.00811 ± 0.00003 | 0.6872 ± 0.0009 | 0.08580 ± 0.00009 | 0.89 | 533.08 ± 1.37 | 531.09 ± 0.55 | 530.62 ± 0.53 | 0.46 |
| z10    | 0.897 | 1105 | 0.22 | 4966 | 267986 | 0.00810 ± 0.00002 | 0.6869 ± 0.00010 | 0.08573 ± 0.00010 | 0.93 | 533.75 ± 1.17 | 530.91 ± 0.58 | 530.25 ± 0.60 | 0.65 |

Summary: Means of 31 individual analyses

Quoted uncertainties are 2s. a, Three analyses marked ‘(CA)’ were done after chemical abrasion following Mattinson (2005); these results were disregarded in the calculation of mean isotopic ratios and ages. The analysis marked ‘(a)’ was done on an aliquot of 464/15. b, Model Th/U ratios were calculated from the radiogenic 208Pb and the 230Th-corrected 206Pb/238U age. c, Pb$_{rad} =$ total mass of radiogenic Pb; Pb$_{com} =$ total mass of common Pb. d, Measured 206Pb/204Pb ratio corrected for fractionation and spike contribution only. e, Measured ratios corrected for fractionation, tracer and blank. f, Discordance = 100 - 100 × (207Pb/235U date)/(207Pb/206Pb date).
### Table 7.
Results of U-Pb determinations (ID-TIMS) of zircon GZ8

| Analysis | Compositional parameters | Isotopic ratios | Isotopic ages |
|----------|--------------------------|----------------|--------------|
|          | Th/U | Pb_206 (pg) | Pb_204 (pg) | Pb_206/Pb_204 | 207Pb/206Pb | 207Pb/235U | 206Pb/238U | p (err. corr.) | 207Pb/206Pb age (Ma) | 207Pb/235U Age (Ma) | 206Pb/238U Age (Ma) | Disc. (%) |
| (a)      | Th/U | Pb_206 (pg) | Pb_204 (pg) | Pb_206/Pb_204 | 207Pb/206Pb | 207Pb/235U | 206Pb/238U | p (err. corr.) | 207Pb/206Pb age (Ma) | 207Pb/235U Age (Ma) | 206Pb/238U Age (Ma) | Disc. (%) |
| z1 (CA)  | 0.189 | 4029 | 100 | 4040 | 263427 | 0.05846 ± 0.00000 | 0.7088 ± 0.0005 | 0.08798 ± 0.00006 | 0.92 | 545.96 ± 0.83 | 5440.4 ± 0.38 | 5435.8 ± 0.37 | 0.44 |
| z2 (CA)  | 0.189 | 6237 | 153 | 11774 | 767738 | 0.05844 ± 0.00000 | 0.7086 ± 0.0005 | 0.08798 ± 0.00006 | 0.92 | 545.29 ± 0.73 | 5438.9 ± 0.35 | 5435.6 ± 0.37 | 0.32 |
| z3 (CA)  | 0.188 | 2985 | 159 | 1878 | 122508 | 0.05846 ± 0.00000 | 0.7089 ± 0.0005 | 0.08800 ± 0.00004 | 0.87 | 546.18 ± 0.86 | 5440.6 ± 0.32 | 5455.5 ± 0.30 | 0.48 |
| z5       | 0.189 | 4369 | 107 | 5859 | 382041 | 0.05845 ± 0.00000 | 0.7089 ± 0.0005 | 0.08800 ± 0.00004 | 0.87 | 547.11 ± 0.72 | 5441.0 ± 0.28 | 5471 ± 0.25 | 0.37 |
| z6       | 0.185 | 3417 | 2.1 | 624 | 106018 | 0.05845 ± 0.00001 | 0.7084 ± 0.0004 | 0.08793 ± 0.00004 | 0.85 | 548.0 ± 0.71 | 5437.9 ± 0.26 | 5433.1 ± 0.24 | 0.46 |
| z8       | 0.188 | 149 | 0.3 | 495 | 32317 | 0.05845 ± 0.00003 | 0.7084 ± 0.0009 | 0.08793 ± 0.00004 | 0.68 | 547.9 ± 1.44 | 5437.8 ± 0.37 | 5430.0 ± 0.24 | 0.46 |
| z10      | 0.189 | 212 | 0.9 | 224 | 14640 | 0.05845 ± 0.00005 | 0.7098 ± 0.0006 | 0.08803 ± 0.00006 | 0.73 | 547.4 ± 1.90 | 5445.6 ± 0.52 | 5438.8 ± 0.35 | 0.65 |

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Table 7 (continued).
Results of U-Pb determinations (ID-TIMS) of zircon GZ8

| Analysis | Compositional parameters | Isotopic ratios | Isotopic ages |
|----------|--------------------------|----------------|--------------|
|          | Th/U Pb_rad (pg) | Pb_rad / Pb_com | 206Pb/204Pb | 207Pb/206Pb | 207Pb/235U | 206Pb/238U | 207Pb/206Pb age (Ma) | 207Pb/235U Age (Ma) | 206Pb/238U Age (Ma) | Discord. (%) |
| z1       | 0.188 | 574 | 0.43 | 1321 | 85485 | 0.05849 ± 0.00003 | 0.7102 ± 0.0007 | 0.08810 ± 0.00004 | 0.88 | 547.21 ± 1.21 | 544.86 ± 0.39 | 544.30 ± 0.25 | 0.53 |
| z2       | 0.188 | 352 | 0.39 | 913  | 59074 | 0.05850 ± 0.00003 | 0.7103 ± 0.0007 | 0.08810 ± 0.00004 | 0.90 | 547.55 ± 1.19 | 544.90 ± 0.39 | 544.27 ± 0.24 | 0.60 |
| z3       | 0.189 | 252 | 0.49 | 518  | 33525 | 0.05846 ± 0.00003 | 0.7092 ± 0.0007 | 0.08803 ± 0.00004 | 0.86 | 545.91 ± 1.33 | 544.26 ± 0.41 | 543.87 ± 0.25 | 0.37 |
| z4       | 0.188 | 456 | 0.52 | 870  | 56301 | 0.05846 ± 0.00003 | 0.7092 ± 0.0007 | 0.08802 ± 0.00005 | 0.89 | 546.16 ± 1.21 | 544.29 ± 0.41 | 543.84 ± 0.27 | 0.42 |
| z5       | 0.188 | 1134| 0.45 | 2543 | 164470| 0.05848 ± 0.00002 | 0.7098 ± 0.0007 | 0.08806 ± 0.00005 | 0.89 | 547.00 ± 1.14 | 544.63 ± 0.41 | 544.06 ± 0.31 | 0.54 |
| z6       | 0.188 | 706 | 0.36 | 1982 | 128214| 0.05847 ± 0.00002 | 0.7101 ± 0.0007 | 0.08812 ± 0.00005 | 0.92 | 546.41 ± 1.08 | 544.81 ± 0.40 | 544.43 ± 0.29 | 0.36 |
| z7       | 0.189 | 488 | 0.53 | 916  | 59261 | 0.05850 ± 0.00003 | 0.7103 ± 0.0007 | 0.08809 ± 0.00004 | 0.88 | 547.74 ± 1.21 | 544.90 ± 0.39 | 544.22 ± 0.25 | 0.64 |
| z8       | 0.188 | 309 | 0.56 | 1165 | 75402 | 0.05848 ± 0.00003 | 0.7097 ± 0.0007 | 0.08806 ± 0.00005 | 0.88 | 546.87 ± 1.19 | 544.57 ± 0.41 | 544.03 ± 0.29 | 0.52 |

Summary: Means of 31 individual analyses

Quoted uncertainties are 2σ. a. Three analyses marked ‘CA’ were done after chemical abrasion following Mattinson (2005); these results were disregarded in the calculation of mean isotopic ratios and ages. The two analyses marked ‘al’ were done on aliquots of 464/13 and 464/14, respectively. b. Model Th/U ratios were calculated from the radiogenic 208Pb and the 230Th-corrected 206Pb/238U age. c. Pb_rad = total mass of radiogenic Pb; Pb_com = total mass of common Pb. d. Measured 206Pb/204Pb ratio corrected for fractionation and spike contribution only. e. Measured ratios corrected for fractionation, tracer and blank. f. Discordance = 100 - (100 × (206Pb/238U date)/(207Pb/206Pb date)).
resulting in reverse discordance) under the O₂ beam. Features pointing to a postgrowth chemical alteration history have not been found, and our measurement results allow us to exclude any unusual thermal history. This also applies to the common practice of Sri Lankan gem miners and dealers to enhance colour and clarity of zircon specimens by heating them in an open fire, which can be excluded in the case of GZ7 and GZ8.

More than 3500 mg are still available for each of the samples GZ7 and GZ8. They will be distributed and made available for SIMS U-Pb analysis. A major fraction of the material will be used and distributed for SIMS analytical work in other laboratories, by the Beijing SHRIMP Centre, Institute of Geology, Chinese Academy of Geological Sciences (contact: liudunyi@bjshrimp.cn). However, it needs to be emphasised that samples will not be provided for LA-ICP-MS U-Pb geochronology. This explicit decision is made to reduce the consumption of the two reference materials to a minimum. We wish to ensure that the materials will be available for SIMS work for a long period.

Figure 8. Wetherill Concordia diagrams showing results of U-Pb isotope analyses (ID-TIMS) performed in five laboratories. Ellipses represent 2s. Three uncertainties for mean ages are quoted: analytical uncertainty (2σ) / combined analytical and tracer uncertainty / combined analytical, tracer and ²³⁸U decay constant uncertainty.

Figure 9. Wetherill Concordia diagrams showing results of U-Pb analyses (SIMS) performed at Curtin University, Perth. Error ellipses represent 1s uncertainties. Results were calibrated versus M257 with an assumed ²⁰⁶Pb/²³⁸U age of 561.3 Ma (Nasdala et al. 2008). Concordia ages are quoted at the 95% confidence level and include uncertainties of decay constants.
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Supporting information

The following supporting information may be found in the online version of this article:

Appendix S1. Details for ID-TIMS analytical procedures in the laboratories.

Appendix S2. Measurement results from EPMA (n = 84 for each of the two zircon samples) at Universität Göttingen, Germany.

Appendix S3. Documentation of locations of EPMA (Universität Göttingen, Germany) linescans, and plots and histograms of mass fractions of HfO₂, ThO₂ and UO₂.

Appendix S4. Measurement results from SHRIMP analyses (Curtin University, Perth, Australia) including additional Concordia plots and Th/U histograms.

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