

DR. MICHAEL P EDDY (Orcid ID : 0000-0003-0907-5108)

DR. MATTHEW COBLE (Orcid ID : 0000-0002-7536-0559)

Article type : Original Article

## **GHR1 Zircon – A New Eocene Natural Reference Material for Microbeam U-Pb Geochronology and Hf Isotopic Analysis of Zircon**

Michael P. **Eddy** (1, 2)\*, Mauricio **Ibañez-Mejia** (1, 3)\*, Seth D. **Burgess** (4), Matthew A. **Coble** (5), Umberto G. **Cordani** (6), Joel **DesOrmeau** (7), George E. **Gehrels** (8), Xianhua **Li** (9), Scott **MacLennan** (2), Mark **Pecha** (8), Kei **Sato** (6), Blair **Schoene** (2), Victor A. **Valencia** (10), Jeffrey D. **Vervoort** (10) and Tiantian **Wang** (11)

(1) Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

(2) Department of Geosciences, Princeton University, Guyot Hall, Princeton, NJ 08544, USA

(3) Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627, USA

(4) U.S. Geological Survey, 345 Middlefield Road, Mail Stop 910, Menlo Park, CA 94025, USA

(5) Department of Geological Sciences, Stanford University, Stanford, CA 94305, USA

(6) Institute of Geosciences, University of São Paulo, Rua do Lago, 562, CEP 05508-080 São Paulo, Brazil

(7) Department of Geological Sciences, University of Nevada, Reno, NV 89557, USA

(8) Department of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, AZ 85721, USA

(9) State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

(10) School of the Environment, Washington State University, Pullman, WA 99164, USA

(11) State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, China

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/ggr.12246

This article is protected by copyright. All rights reserved.

\* Corresponding authors. e-mail: meddy@princeton.edu, ibanezm@rochester.edu

We present multi-technique U-Pb geochronology and Hf isotopic data from zircon separated from rapakivi biotite granite within the Eocene Golden Horn batholith in Washington, USA. A weighted mean of twenty-five Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  zircon dates produced at two independent laboratories using chemical abrasion-isotope dilution-thermal ionisation mass spectrometry (CA-ID-TIMS) is  $48.106 \pm 0.023$  Ma ( $2s$  analytical including tracer uncertainties, MSWD = 1.53) and is our recommended date for GHR1 zircon. Microbeam  $^{206}\text{Pb}/^{238}\text{U}$  dates from laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and secondary ion mass spectrometry (SIMS) laboratories are reproducible and in agreement with the CA-ID-TIMS date to within  $< 1.5\%$ . Solution multi-collector-ICP-MS (MC-ICP-MS) measurements of Hf isotopes from chemically purified aliquots of GHR1 yield a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.283050 \pm 17$  ( $2s$ ,  $n = 10$ ), corresponding to a  $\epsilon\text{Hf}_0$  of +9.3. Hafnium isotopic measurements from two LA-ICP-MS laboratories are in agreement with the solution MC-ICP-MS value. The reproducibility of  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios from GHR1 zircon across a variety of measurement techniques demonstrates their homogeneity in most grains. Additionally, the effectively limitless reserves of GHR1 material from an accessible exposure suggest that GHR1 can provide a useful reference material for U-Pb geochronology of Cenozoic zircon and Hf isotopic measurements of zircon with radiogenic  $^{176}\text{Hf}/^{177}\text{Hf}$ .

Keywords: U-Pb geochronology, zircon, reference material, Hf isotope ratios, ID-TIMS, LA-ICP-MS, SIMS, MC-ICP-MS.

**Received 23 May 18 – Accepted 16 Oct 18**

U-Pb zircon geochronology is a versatile and widely used technique to generate dates from the Hadean to the Pleistocene. Microbeam U-Pb zircon geochronology by LA-ICP-MS and SIMS has increasingly been used to address a variety of problems, including the provenance of sediments (e.g., Gehrels 2014 and references therein), the timescales of magmatic processes (e.g., Guillong *et al.* 2014, Padilla *et al.* 2016, Zimmerer *et al.* 2016), timing and rates of metamorphic processes (e.g., Vorhies *et al.* 2013, Viète *et al.* 2015), and, when combined with Hf-in-zircon isotopic measurements, crustal evolution (e.g., Dhuime *et al.* 2012, Roberts and Spencer 2015,

This article is protected by copyright. All rights reserved.

Bauer *et al.* 2017). Techniques for microbeam zircon geochronology and Hf isotopic measurements provide much faster analysis time, higher spatial resolution, and are less destructive than traditional bulk dissolution ( $\pm$  isotope dilution). However, microbeam methods require matrix-matched reference materials to correct measured U-Pb and Hf isotopic ratios for instrumental fractionation and to assess external reproducibility (e.g., Black *et al.* 2004, Jackson *et al.* 2004). Primary reference materials for calibration of U-Pb and Hf isotopic ratios are now widely available and are typically subsampled from large, homogenous zircon crystals (e.g., Wiedenbeck *et al.* 1995, Jackson *et al.* 2004, Gehrels *et al.* 2008, Kennedy *et al.* 2014). However, the availability of compositionally diverse secondary reference materials that span a variety of ages and Hf isotopic compositions remain limited. These materials are needed to evaluate external reproducibility and are particularly limited for Cenozoic zircon (Table 1). This limitation is due, in part, to the ability to distinguish subtle age heterogeneity in zircons of this age. Nevertheless, secondary reference materials of this age are needed as microbeam U-Pb geochronology of Cenozoic zircon becomes more common.

Ideal secondary zircon reference materials for microbeam analysis are homogenous with respect to U-Pb and Hf isotopic compositions, similar in age and Hf isotopic composition to the unknowns of interest, have variable composition to test matrix effects and isobaric interference corrections, and abundant and easily available. We present U-Pb and Hf isotopic data from a proposed natural zircon reference material of Eocene age, GHR1. The U-Pb and Hf isotopic data is reproducible across a variety of methods and we discuss the merits and limitations of this potential reference material below.

## Geological setting and sample description

The Golden Horn batholith is a large, Eocene-aged, epizonal intrusive complex exposed in the North Cascades, USA (Figure 1a). It is composed of several large sills that range in composition from peralkaline granite to calc-alkaline granite and granodiorite (Figure 1b: Stull 1969, Eddy *et al.* 2016). Al-in-hornblende barometry suggests that the batholith intruded at  $\sim 0.25$  GPa and U-Pb zircon data indicates rapid emplacement over  $739 \pm 34$  ka at  $\sim 48$  Ma (Eddy *et al.* 2016). The largest intrusive phase within the Golden Horn batholith is a  $> 424$  km<sup>3</sup> sill of biotite granite and granodiorite with a distinctive rapakivi texture (Stull 1969, 1978). Existing U-Pb zircon geochronology from this unit shows no resolvable dispersion in Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  dates within individual samples and no resolvable age dispersion between geographically disparate

samples (Eddy *et al.* 2016). Given this apparent homogeneity in U-Pb zircon dates, we have investigated the suitability of zircon from this unit as a natural reference material for microbeam U-Pb zircon geochronology. We have also investigated the homogeneity of the zircon Hf isotopic compositions from this granite and assessed its suitability as a reference material for microbeam Hf isotopic analyses of zircon.

The studied sample (GHR1) was collected from a road cut through biotite rapakivi granite located ~ 1.1 km west of the Lone Fir US Forest Service Campground along WA State Route 20 (Figure 1: 48.57308° N 120.63125° W), and corresponds to sample NC-MPE-086 in Eddy *et al.* (2016). Zircons from GHR1 are euhedral with aspect ratios 2:5 to 1:2 and lengths up to 250  $\mu\text{m}$ . Cathodoluminescence (CL) images of select GHR1 zircons were performed at the University of Nevada Reno on a JEOL 7100FT field emission scanning electron microscope using a 10.0 kV beam. The GHR1 grains exhibit oscillatory zoning typical of igneous zircon (Figure 2). Some zircons may have resorption features (Figures 2c and 2d) that are likely related to complex changes to physical conditions during crystal growth. However, we stress that there is no evidence in the current U-Pb zircon geochronological dataset for protracted zircon crystallisation and/or residence times in this unit that are in excess of the analytical uncertainties on individual CA-ID-TIMS analyses (30–90 ky; Eddy *et al.* 2016). Inclusions are common in GHR1 zircon. Energy dispersive X-ray spectroscopy shows that many of these inclusions are apatite, which may affect the common Pb ( $\text{Pb}_c$ ) and rare earth element (REE) contents derived from microbeam analyses. We further discuss the effects of this limitation below.

## Method and approach

The purpose of this study is to demonstrate the reproducibility of the U/Pb and Hf isotopic ratios in GHR1 zircon across a wide variety of analytical techniques and data reduction strategies. While standardisation of data acquisition, reduction, and reporting is an important step toward increasing reproducibility throughout the U-Pb zircon geochronology and Hf-in-zircon isotopic communities (i.e., Schmitz and Schoene 2007, McLean *et al.* 2011, Condon *et al.* 2015, Horstwood *et al.* 2016), it is not our goal to advocate for specific approaches in this study. Instead, our goal is to illustrate the utility of GHR1 zircon as reference material within the current state of the field. In the sections below we discuss the analytical conditions and data reduction procedures used within each participating laboratory. Participants include two

laboratories that produced U-Pb ID-TIMS data, one laboratory that produced Hf isotopic data using solution MC-ICP-MS, two laboratories that produced U-Pb and Hf isotopic data by LA-ICP-MS, and three laboratories that produced U-Pb SIMS data. All uncertainties are reported at  $2\sigma$  or  $2s$  and are explicitly noted as internal or external, where appropriate.

## U-Pb geochronology

### ID-TIMS (MIT and Princeton University)

A total of twenty-one CA-ID-TIMS analyses of single zircons were conducted at the Massachusetts Institute of Technology (MIT:  $n = 9$ ) and Princeton University ( $n = 12$ ) in addition to the 6 analyses previously published in Eddy *et al.* (2016). The methods used in each lab are slightly modified from Mattinson (2005) and are described in detail in Eddy *et al.* (2016) for MIT and Samperton *et al.* (2015) for Princeton University. Twenty-four of the grains were spiked with the EARTHTIME  $^{205}\text{Pb}$ - $^{233}\text{U}$ - $^{235}\text{U}$  (ET535) isotopic tracer, and three additional grains were spiked with the EARTHTIME  $^{202}\text{Pb}$ - $^{205}\text{Pb}$ - $^{233}\text{U}$ - $^{235}\text{U}$  (ET2535) isotopic tracer (Condon *et al.* 2015, McLean *et al.* 2015). Isotopic ratios were measured on a VG Sector 54 TIMS at MIT and on a IsotopX Phoenix TIMS at Princeton University.

Instrumental Pb fractionation ( $\alpha$ ; %  $\text{amu}^{-1}$ ) was calculated using a linear fractionation law from measurements of the  $^{202}\text{Pb}/^{205}\text{Pb}$  ratio in samples spiked with the EARTHTIME  $^{202}\text{Pb}$ - $^{205}\text{Pb}$ - $^{233}\text{U}$ - $^{235}\text{U}$  (ET2535) isotopic tracer in each laboratory. The resulting  $\alpha = 0.182 \pm 0.082$  ( $2s$ ,  $n = 287$ ) for the IsotopX Phoenix TIMS at Princeton is similar to the value ( $\alpha = 0.179 \pm 0.052$ ,  $2s$ ) calculated from repeat measurements of the NBS982 Pb isotopic reference material. However, the mean  $\alpha = 0.206 \pm 0.058$  ( $2s$ ,  $n = 53$ ) for the Sector 54 TIMS at MIT slightly differs from the value ( $\alpha = 0.25 \pm 0.04$ ,  $2s$ ) calculated from repeat measurements of the NBS-981 Pb isotopic reference material. For this study, we used the  $\alpha$  calculated using measurements of  $^{202}\text{Pb}/^{205}\text{Pb}$  in zircons spiked with the ET2535 isotopic tracer because they more closely match the running conditions of the unknown zircons. We have also applied this correction to the analyses reported in Eddy *et al.* (2016), which lowers the mean age of this sample by *ca.* 0.4%. For the three grains spiked with the ET2535 isotopic tracer at Princeton University, Pb fractionation was corrected point by point using the known  $^{202}\text{Pb}/^{205}\text{Pb}$  ratio. Instrumental fractionation of U was internally corrected using the known ratio of  $^{233}\text{U}/^{235}\text{U}$  in the EARTHTIME  $^{205}\text{Pb}$ - $^{233}\text{U}$ - $^{235}\text{U}$

(ET535) isotopic tracer and assuming a sample  $^{238}\text{U}/^{235}\text{U} = 137.818 \pm 0.0225$  from the zircon compositions reported by Hiess *et al.* (2012).

Contamination from  $\text{Pb}_c$  was corrected using laboratory blank isotopic compositions based on procedural blanks and by assuming all measured  $^{204}\text{Pb}$  is from laboratory contamination. We consider this assumption to be valid because the mass of  $\text{Pb}_c$  measured in procedural blanks is similar to that observed during the zircon measurements. A correction for initial secular disequilibrium in the  $^{238}\text{U}$ - $^{206}\text{Pb}$  decay chain due to preferential exclusion of  $^{230}\text{Th}$  during zircon crystallisation (e.g., Scharer 1984) was done using a fractionation factor ( $f_{\text{ThU}} = [\text{Th}/\text{U}]_{\text{Zircon}}/[\text{Th}/\text{U}]_{\text{Magma}}$ ) of  $f_{\text{ThU}} = 0.138$ , which is based on zircon and glass geochemical data from high-silica rhyolites from the Yellowstone magmatic system (Stelten *et al.* 2015). Corrected  $^{206}\text{Pb}/^{238}\text{U}$  dates for individual grains range between 90 and 94 ky older than the uncorrected dates, and the correction has a negligible effect on any potential inter-grain age dispersion within the sample. Regardless, we present both Th-corrected and uncorrected values in Tables S1 and S2.

All U-Pb isotopic data from the ID-TIMS analyses conducted at MIT and Princeton are presented in Tables 2, S1 and S2 and are shown as concordia plots and as a rank order plot of Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  dates in Figure 3. Uncertainties are reported as  $2\sigma$  in the format  $\pm A/B/C$ , where A represents analytical uncertainty only, B represents analytical uncertainty plus uncertainty in the composition of the ET(2)535 isotopic tracer and C includes propagation of uncertainty in the  $^{238}\text{U}$  decay constant. The analyses from MIT show no resolvable age dispersion and give a weighted mean Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  date of  $48.105 \pm 0.011/0.024/0.057$  Ma (MSWD = 1.52). Ten of the analyses from Princeton University show little age dispersion and give a weighted mean Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  date of  $48.0108 \pm 0.014/0.025/0.057$  Ma (MSWD = 1.70). However, two analyses are distinctly older, with dates of  $48.597 \pm 0.026$  Ma and  $50.451 \pm 0.098$  Ma ( $2\sigma$  analytical uncertainties). We discuss the significance of these grains in the Discussion section. Excluding these two grains, a weighted mean of twenty-five analyses from both Princeton University and MIT gives a Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  date of  $48.1063 \pm 0.0087/0.023/0.056$  Ma (MSWD = 1.53) and an uncorrected  $^{206}\text{Pb}/^{238}\text{U}$  date of  $48.0133 \pm 0.0086/0.023/0.056$  Ma (MSWD = 1.57). The weighted mean Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  date from the combined dataset is our recommended reference date for GHR1 zircon.

A second set of five zircons was analysed by ID-TIMS at Princeton University without using the chemical abrasion procedure to assess the possibility of Pb-loss in GHR1 zircon. All analytical methods follow those outlined above for Princeton University and the results are reported in Table S2 as both Th-corrected and uncorrected data. All of the Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  dates for these grains are younger than the reference date reported above (Figure 4), indicating the presence of either younger overgrowths or Pb-loss. We discuss the likelihood of these two possibilities in the Discussion section.

### LA-ICP-MS (Washington State University)

Twenty-four LA-ICP-MS U-Pb analyses were conducted on polished zircon interiors at Washington State University using a Thermo-Finnigan Element 2 single collector mass spectrometer coupled with a New Wave Nd:YAG UV 213-nm laser (Table S3). Methods follow those outlined in Chang *et al.* (2006) and only a brief summary is presented here. Spots were selected using reflected and transmitted light and were 30  $\mu\text{m}$  in diameter. Elemental and mass-fractionation were corrected by bracketing analyses of GHR1 with analyses of Plešovice zircon (Table 1: Sláma *et al.* 2008). Elemental mass fractions were also calibrated relative to this reference material. No correction for contamination with  $\text{Pb}_c$  was undertaken and grains that reflect high  $\text{Pb}_c$  content were not included in the calculation of dates. Data reduction was done using an 'in house' spreadsheet. External reproducibility was monitored by analysing the 91500 zircon (Table 1: Wiedenbeck *et al.* 1995) and Fish Canyon tuff zircon (Schmitz and Bowring 2001, Wotzlaw *et al.* 2013). Weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  dates and  $2\sigma$  uncertainties for these reference materials are  $1065 \pm 21$  ( $n = 3$ , MSWD = 0.22) for 91500 and  $27.41 \pm 0.64$  Ma ( $n = 4$ , MSWD = 0.22) for the Fish Canyon tuff. The  $^{206}\text{Pb}/^{207}\text{Pb}$  date for 91500 agrees within uncertainty with the published reference value, while the  $^{206}\text{Pb}/^{238}\text{U}$  date for the Fish Canyon Tuff is *ca.* 4% younger than the range of  $^{206}\text{Pb}/^{238}\text{U}$  CA-ID-TIMS zircon dates for this unit (e.g., Wotzlaw *et al.* 2013). One of the twenty-four analyses of GHR1 was discarded because the grain contained high  $\text{Pb}_c$  ( $^{206}\text{Pb}/^{204}\text{Pb} < 1500$ ). Two additional analyses were also excluded as outliers. These grains gave slightly discordant  $^{206}\text{Pb}/^{238}\text{U}$  dates of  $36.5 \pm 1.7$  Ma ( $2\sigma$ ) and  $40.6 \pm 3.1$  Ma ( $2\sigma$ ). We attribute these dates to Pb-loss and discuss their significance in the Discussion section. The remaining twenty-one analyses are shown in Figures 5 and 6 and give a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  date of  $47.99 \pm 0.44$  (0.65) ( $2\sigma$ , MSWD = 0.19), where the first uncertainty is analytical and the second incorporates the long-term reproducibility of zircon reference materials within the laboratory.

### LA-ICP-MS (University of Arizona)

GHR1 zircons were mounted at the University of Arizona and characterised by CL imaging using a Hitachi 3400N SEM and a Gatan Chroma CL system prior to U-Pb analysis by LA-ICP-MS. A total of 114 laser spots of 20  $\mu\text{m}$  diameter and < 10  $\mu\text{m}$  depth were ablated from  $\sim$  100 polished interiors of GHR1 zircon using an Analyte G2 Photon Machines 193-nm excimer laser and analysed for U-Pb geochronology on a Thermo Element2 ICP-MS at the University of Arizona Laserchron Laboratory (Table S4). The methods for these analyses are outlined in Ibañez-Mejía *et al.* (2015) and Pullen *et al.* (*in review*). GHR1 analyses were bracketed by U-Pb isotopic measurements of fragments from the SL2 (Table 1: Gehrels *et al.* 2008), R33 (Table 1: Black *et al.* 2004) and FC-1 (Table 1: Paces and Miller 1991) zircon reference materials, which were used to correct for elemental- and mass-dependent instrumental fractionation as a function of beam intensity. Mass fractions of U and Th were calibrated relative to zircon reference material SL2 (Gehrels *et al.* 2008). Data reduction was done using an 'in-house' spreadsheet.  $\text{Pb}_c$  is assumed to be initial (i.e., from co-crystallised inclusions) and is corrected using the measured  $^{204}\text{Pb}$  and the isotopic composition of crustal Pb at *ca.* 48 Ma (Stacey and Kramers 1975). Six of the 114 analyses were excluded from our age calculations due to high  $\text{Pb}_c$  ( $^{206}\text{Pb}/^{204}\text{Pb} < 1500$ ). These analyses also exhibit discordance following  $\text{Pb}_c$  correction that may indicate that the  $\text{Pb}_c$  budget was controlled by surface contamination with modern crustal  $\text{Pb}_c$  rather than  $\text{Pb}_c$  incorporated in inclusions during zircon crystallisation (Figure 5). A single analysis that gave a date of  $36.7 \pm 1.3$  Ma was also excluded as an outlier and is attributed to Pb-loss. The remaining 107  $^{206}\text{Pb}/^{238}\text{U}$  dates are shown in Figure 6 and give a weighted mean date of  $48.38 \pm 0.19$  (0.71) Ma ( $2\sigma$ , MSWD = 0.80), where the first uncertainty only represents analytical uncertainty and the second includes the reproducibility of zircon reference materials measured during the same measurement session.

### SIMS (Chinese Academy of Sciences)

Thirty-seven zircons from GHR1 were analysed for U-Pb geochronology on a Cameca IMS-1280HR SIMS at the Institute for Geology and Geophysics at the Chinese National Academy of Sciences. The methods for these analyses follow those in Li *et al.* (2009). Zircons were first mounted in epoxy and spots for U-Pb analysis were selected using reflected and transmitted light microscopy. Secondary ions were generated from a using an  $\text{O}_2^-$  beam with a diameter of  $\sim$  30  $\mu\text{m}$  and a depth of 2  $\mu\text{m}$ . U-Pb ratios were calibrated by bracketing GHR1 analyses with analyses of the Plešovice zircon reference material (Table 1: Sláma *et al.* 2008), while U and Th mass fractions were calibrated against zircon reference material 91500 (Table 1: Wiedenbeck *et*



*al.* 1995). Long-term reproducibility of these reference materials is 3% ( $2\sigma$ ) and this uncertainty is propagated to the unknowns following the methods outlined in Li *et al.* (2010). All  $Pb_c$  is attributed to surface contamination and Pb isotopic measurements were corrected for  $Pb_c$  using measured  $^{204}Pb$  and the present day crustal Pb isotopic composition from Stacey and Kramers (1975). Data reduction was done using the Cameca Customisable Ion Probe software package using the methods presented in Li *et al.* (2009). The data is reported in Table S5 and shown in Figures 5 and 6. Ten measurements of Qinghu zircon (Li *et al.* 2013) were conducted to assess external reproducibility and have a weighted mean  $^{206}Pb/^{238}U$  date of  $159.1 \pm 1.5$  Ma ( $2\sigma$ , MSWD = 0.47), which is within the uncertainty of the recommended value (Table 1). Twelve of the analyses contained high  $Pb_c$  ( $^{206}Pb/^{204}Pb < 1500$ ) and are excluded from our age calculations. The twenty-five remaining analyses are shown in Figure 6 and give a weighted mean  $^{206}Pb/^{238}U$  date of  $48.18 \pm 0.31$  Ma ( $2\sigma$ , MSWD = 0.75), where the reported uncertainty incorporates both analytical uncertainty and uncertainty related to the long-term reproducibility of zircon reference materials.

#### **SIMS (USGS/Stanford University)**

Twenty-two U-Pb measurements were performed on GHR1 zircon using a sensitive high-resolution ion microprobe with reverse geometry (SHRIMP-RG) at the Stanford University. All grains were polished and imaged with reflected light on a petrographic microscope, cleaned by rinsing the mount in dilute hydrochloric acid and distilled water, dried in a vacuum oven and coated with a conductive layer of gold. Zircon U-Pb measurements were performed using an  $O_2^-$  primary beam with an intensity ranging from 5.4 to 5.8 nA with analytical spot diameter of  $\sim 30$   $\mu m$  and a pit depth of  $\sim 2$   $\mu m$ . Analyses were performed with a mass resolving power of  $\sim 7000$  (10% peak height) to maximise secondary ion transmission and eliminate isobaric interferences. Measured U/Pb ratios were standardised relative to the Temora-2 zircon (Table 1: Black *et al.* 2004, Mattinson *et al.* 2010), which was analysed repeatedly throughout the duration of the measurement session. Data reduction follows Ireland and Williams (2003) using the Microsoft Excel add-in programs Squid2.51 (Ludwig 2009). Individual spot analyses are reported as  $^{206}Pb/^{238}U$  and  $^{207}Pb/^{206}Pb$  dates and were corrected for  $Pb_c$  using the measured  $^{204}Pb$  and the crustal  $Pb_c$  composition for 48-50 Ma from Stacey and Kramers (1975). All  $^{206}Pb/^{238}U$  ages are reported with  $2\sigma$  uncertainties, including the uncertainty summed in quadrature from the analytical reproducibility of the Temora-2 reference material during the measurement session. The mass fractions of U and Th were calculated relative to 91500 zircon (Wiedenbeck *et al.* 1995) and MAD-559 zircon (Coble *et al.* 2018). The results of the GHR1

analyses are presented in Table S6 and shown in Figures 5 and 6. Two analyses were excluded from the weighted mean due to high  $Pb_c$  ( $^{206}Pb/^{204}Pb < 1500$ ) and two were excluded because they were outliers. One outlier gave a date of  $43.1 \pm 1$  Ma and the other gave a date of  $50.2 \pm 1$  Ma. A weighted mean of the remaining eighteen analyses gives a  $^{206}Pb/^{238}U$  date of  $48.17 \pm 0.35$  Ma ( $2\sigma$ , MSWD = 1.71), where the uncertainty includes both analytical uncertainty and the reproducibility of the Temora-2 reference material during the same measurement session.

A second set of analyses was performed on unpolished surfaces of GHR1 zircon at the USGS/Stanford SHRIMP-RG using the methods described in Matthews *et al.* (2015). The grains were mounted in indium and imaged using a reflected light microscope. Since surface topography can affect mass fractionation in SHRIMP analyses (e.g., Ickert *et al.* 2008, Kita *et al.* 2009), only grains with smooth reflective surfaces were analysed. A total of nineteen surfaces were analysed and yielded  $^{206}Pb/^{238}U$  dates ranging from 43.1 to 49.4 Ma (Figure 7). A weighted mean  $^{206}Pb/^{238}U$  date for these analyses is  $46.69 \pm 0.41$  Ma ( $2\sigma$ , MSWD = 4.04), where the uncertainty includes both analytical uncertainty and the reproducibility of reference materials during the same measurement session. This date is younger than the  $^{206}Pb/^{238}U$  date for zircon interiors analysed by the USGS SHRIMP and the high MSWD indicates that these analyses do not form a coherent population. We discuss the significance of this result in the Discussion section.

### **SIMS (University São Paulo)**

Twenty zircons were analysed using the SHRIMP-IIe at the Institute for Geoscience at the University of Sao Paulo. Zircon grains were mounted with crystals of the Temora-2 and FC1 zircon reference materials and polished prior to analysis. Cathodoluminescence (CL) images were obtained using a FEI Quanta 250 scanning electron microscope (SEM) and an Oxford Instruments XMAX CL detector in order to identify inclusions and growth domains. After imaging, the mount was coated in  $\sim 3$  nm of gold and loaded in the SHRIMP-IIe for U-Pb analyses. Analyses were conducted using a  $\sim 4\text{--}5$  nA  $O_2^-$  beam with a diameter of  $30 \mu m$  and a raster time of 2.5 min. The zircon reference material Z6266 (Table 1: Stern and Amelin 2003) was used to calculate U, Th and Pb mass fractions in unknown samples and the Temora-2 zircon reference material (Table 1: Black *et al.* 2004) was used to normalise the  $^{206}Pb/^{238}U$  ratio. Data reduction follows the methods of Williams (1998) and used the SQUID 2.5 software (Ludwig 2009). All common Pb is assumed to be the result of surface contamination and isotopic ratios were corrected for this contamination using the measured  $^{204}Pb$  and the modern crustal Pb isotopic composition of Stacey and Kramers (1975). FC1

zircons were used to evaluate external reproducibility and eight analyses of these grains gave a weighted mean  $^{207}\text{Pb}/^{206}\text{Pb}$  date of  $1098.8 \pm 6.8$  ( $2\sigma$ , MSWD = 1.10), within uncertainty of the reported value (Table 1). The twenty analyses of GHR1 are reported in Table S7 and shown on Figures 5 and 6. Four analyses were discarded due to high  $\text{Pb}_c$  ( $^{206}\text{Pb}/^{204}\text{Pb} < 1500$ ). The remaining sixteen analyses are shown in Figure 6 and give a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  date of  $48.70 \pm 0.50$  ( $2\sigma$ , MSWD = 1.19), where the uncertainty is analytical only.

## Hf isotopic determinations

### Solution MC-ICP-MS (MIT)

Trace element solutions from ten zircons (za through zj; Table S1) dated at MIT were collected from chemically-abraded zircons following the methods outlined in Schoene *et al.* (2010). These solutions were split into two aliquots, one for measurement of Hf isotopic composition by MC-ICP-MS and another for trace element mass fractions via quadrupole-ICP-MS. Hf was separated from the first set of solutions following methods modified from Goodge and Vervoort (2006) and described in detail in the supplementary material for Eddy *et al.* (2017). Hf isotopic compositions were measured on a Nu Plasma II-ES MC-ICP-MS at MIT and were bracketed by runs of the JMC-475 standard solution at  $25 \text{ ng ml}^{-1}$  concentration to correct for instrumental bias and to assess external reproducibility. Data reduction was done using an 'in-house' spreadsheet. Repeat runs of the JMC-475 standard solution during analyses of GHR1 gave a  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160 \pm 14$  ( $2s$ ,  $n = 13$ ). This value is in good agreement with the published  $^{176}\text{Hf}/^{177}\text{Hf}$   $0.282161 \pm 14$  from Vervoort and Blichert-Toft (1999). It also provides a good estimate of the external reproducibility of  $^{176}\text{Hf}/^{177}\text{Hf}$  measurements produced using solution MC-ICP-MS at MIT. The mean and standard deviation of  $^{176}\text{Hf}/^{177}\text{Hf}$  for all ten analyses of GHR1 is  $0.283050 \pm 0.000017$  ( $2s$ ) and corresponds to an  $\varepsilon\text{Hf}_{(0)}$  of  $+9.4 \pm 0.6$  ( $2s$ ; Figure 8 and Table S8). This is similar to the reproducibility of the JMC-475 standard solution, indicating that the  $^{176}\text{Hf}/^{177}\text{Hf}$  of GHR1 is homogenous within measurement precision.

The Lu/Hf ratio of each analysed zircon was measured from a sub-aliquot of the dissolved zircon solution on an Agilent 7900 quadrupole-ICP-MS at MIT using the methods described in the appendix to Eddy *et al.* (2017). The  $^{176}\text{Lu}/^{177}\text{Hf}$  for each grain was calculated from the measured Lu/Hf using the Lu isotopic composition presented in Vervoort *et al.* (2004) and used to calculate an initial  $^{176}\text{Hf}/^{177}\text{Hf}$  for each grain using the  $^{176}\text{Lu}$  decay constant ( $\lambda = 1.867 \times 10^{-11} \text{ y}^{-1}$ ) presented in Söderlund *et al.* (2004). A mean  $\varepsilon\text{Hf}_{(i)}$  for all ten analysed zircons of GHR1 is  $+10.4 \pm 0.6$  ( $2s$ ), calculated using the values for CHUR presented in Bouvier *et al.* (2008).

### LA-ICP-MS (Washington State University)

Ten Hf isotopic analyses of GHR1 zircon were conducted at Washington State University by LA-ICP-MS. These analyses used a New Wave Nd:YAG UV 213-nm laser coupled with a Thermo-Finnigan Neptune Multi-Collector ICP-MS and used the methods outlined in Gaschnig *et al.* (2011). The spot size was approximately 40  $\mu\text{m}$  in diameter with a depth of  $\sim 40 \mu\text{m}$ , and spots were placed independently of analysed U-Pb ablation pits. Mass dependent fractionation of Hf was corrected by internal normalisation relative to a  $^{179}\text{Hf}/^{177}\text{Hf} = 0.73250$  (Patchett and Tatsumoto 1980), using an exponential law. A correction for the isobaric interference between  $^{176}\text{Yb}$  and  $^{176}\text{Hf}$  was done semi-empirically by monitoring zircon reference materials 91500, FC1 and Mud Tank to calibrate mass bias for Yb and using a  $^{176}\text{Yb}/^{173}\text{Yb}$  adjusted to minimise the offset in the measured  $^{176}\text{Hf}/^{177}\text{Hf}$  in the reference materials as a function of the calculated  $^{176}\text{Yb}/^{177}\text{Hf}$  (e.g., Gaschnig *et al.* 2011, Ibañez-Mejia *et al.* 2015). No correction was done for isobaric interference between  $^{176}\text{Lu}$  and  $^{176}\text{Hf}$ . All data reduction was done using an 'in-house' spreadsheet. Plešovice zircon was used to assess external reproducibility and six analyses gave a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.282472 \pm 52$  (2s), which is in good agreement with the reference value from Sláma *et al.* (2008). Ten analyses of GHR1 zircon gave a  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.283040 \pm 44$  (2s), corresponding to an  $\epsilon_{\text{Hf}(0)}$  of  $+9.0 \pm 1.6$  (2s; Figure 8 and Table S9). The initial  $^{176}\text{Hf}/^{177}\text{Hf}$  was calculated using the measured  $^{176}\text{Lu}/^{177}\text{Hf}$ , the decay constant for  $^{176}\text{Lu}$  ( $\lambda = 1.867 \times 10^{-11} \text{y}^{-1}$ ) presented in Söderlund *et al.* (2004), and the CA-ID-TIMS crystallisation age for GHR1. A mean  $\epsilon_{\text{Hf}(0)}$  for all ten analysed zircons of GHR1 is  $+10.0 \pm 1.5$  (2s), calculated using the values for CHUR presented in Bouvier *et al.* (2008).

### LA-ICP-MS (U. Arizona)

The Hf isotopic composition of GHR1 zircon was measured at the University of Arizona Laserchron centre using a Nu Plasma High Resolution-ICP-MS coupled to a Photon Machines Analyte G2 laser ablation system following methods outlined by Cecil *et al.* (2011) and Ibañez-Mejia *et al.* (2014). Ablation pits were placed over pre-existing U-Pb pits and were  $\sim 40 \mu\text{m}$  in diameter with pits  $< 15 \mu\text{m}$  in depth. Mass numbers 171 through 180 were monitored simultaneously on an array of ten Faraday cups. Mass dependent fractionation of Hf was corrected using the constant  $^{179}\text{Hf}/^{177}\text{Hf} = 0.73250$  (Patchett and Tatsumoto 1980) and Yb fractionation was corrected using the constant  $^{173}\text{Yb}/^{171}\text{Yb} = 1.132338$  (Vervoort *et al.* 2004) for analyses where the total Yb beam is  $> 5 \text{mV}$ . For weaker Yb beams the Hf fractionation factor is applied. The measured  $^{176}\text{Hf}/^{177}\text{Hf}$  was corrected for ( $^{176}\text{Lu}+^{176}\text{Yb}$ ) isobaric interferences by monitoring  $^{175}\text{Lu}$  and using the natural  $^{176}\text{Lu}/^{175}\text{Lu} = 0.02653$  (Patchett 1983) and the

$^{176}\text{Yb}/^{171}\text{Yb} = 0.901691$  (Vervoort *et al.* 2004). Machine parameters were tuned at the beginning and end of the session using a  $10 \text{ ng ml}^{-1}$  solution of JMC-475 with the published  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282161 \pm 14$  (Vervoort and Blichert Toft 1999). Additional JMC-475 solutions doped with varying concentrations of Yb and Lu were measured to confirm the efficacy of the corrections used for isobaric interferences. An in house spreadsheet was used for all data reduction. The  $^{176}\text{Hf}/^{177}\text{Hf}$  of Mud Tank (Table 1: Woodhead and Hergt 2005), Temora-2 (Table 1: Woodhead and Hergt 2005), FC-1 (Table 1: Woodhead and Hergt 2005), 91500 (Table 1: Wiedenbeck *et al.* 1995, Woodhead and Hergt 2005), Plešovice (Table 1: Sláma *et al.* 2008), R33 (Table 1: Fisher *et al.* 2014), and SL2 (Table 1: Woodhead and Hergt 2004) zircon reference materials were analysed during the same session as GHR1 and gave mean  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282518 \pm 0.000056$  (2s),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282621 \pm 92$  (2s),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28219 \pm 12$  (2s),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28228 \pm 10$  (2s),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282465 \pm 75$  (2s),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28276 \pm 0.00012$  (2s),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.283045 \pm 87$  (2s), respectively (Table S10). All of the measured  $^{176}\text{Hf}/^{177}\text{Hf}$  are in good agreement with the published values for these zircon reference materials (Table 1). The mean  $^{176}\text{Hf}/^{177}\text{Hf}$  value for twenty analyses of GHR1 was  $0.283045 \pm 0.000087$  (2s), and corresponds to an  $\epsilon\text{Hf}_{(0)}$  of  $+9.2 \pm 3.1$  (2s: Figure 8 and Table S10). The full dataset contains excess dispersion (MSWD = 3.86), which we attribute to the difficulty of correcting for isobaric interferences in samples with high  $(^{176}\text{Yb}+^{176}\text{Lu})/^{176}\text{Hf}$  (Figure 7). Excluding the seven analyses with  $(^{176}\text{Yb}+^{176}\text{Lu})/^{176}\text{Hf} > 40\%$ , corresponding to  $(^{176}\text{Yb}+^{176}\text{Lu})/^{176}\text{Hf}$  values that greatly exceed those seen in the solution MC-ICP-MS analyses (Figure 9), gives a mean  $^{176}\text{Hf}/^{177}\text{Hf} = 0.283043 \pm 0.000048$  (2s) and reduces the observed dispersion (MSWD = 1.51). The corresponding  $\epsilon\text{Hf}_{(0)}$  for this smaller dataset is  $+9.1 \pm 1.7$  (2s). The initial  $^{176}\text{Hf}/^{177}\text{Hf}$  was calculated for the smaller dataset using the measured  $^{176}\text{Lu}/^{177}\text{Hf}$ , the decay constant for  $^{176}\text{Lu}$  ( $\lambda = 1.867 \times 10^{-11} \text{ y}^{-1}$ ) presented in Söderlund *et al.* (2004), and the CA-ID-TIMS crystallisation age for GHR1. A mean  $\epsilon\text{Hf}_{(t)}$  for these thirteen analyses of GHR1 is  $+10.1 \pm 1.7$  (2s), calculated using the values for CHUR presented in Bouvier *et al.* (2008).

## Discussion

### GHR1 Suitability as a natural reference material for microbeam U-Pb analysis of zircon

The excellent agreement between the CA-ID-TIMS U-Pb geochronology from both MIT and Princeton University highlights the utility of the EARTHTIME initiative in minimising inter-laboratory bias by establishing common isotopic tracers (Condon *et al.* 2015, McLean *et al.* 2015) and data reduction methods for ID-TIMS geochronology (Schmitz and Schoene 2007,

McLean *et al.* 2011). In this case, two independent laboratories produced the same date to within the reported analytical uncertainties of 0.02–0.04%. The twenty-three CA-ID-TIMS  $^{206}\text{Pb}/^{238}\text{U}$  dates for GHR1 zircon also show that there is little to no inter-crystal age dispersion that is resolvable at the reported  $2\sigma$  uncertainty (Figure 3). This observation is consistent with the interpretation that the rapakivi intrusive phase of the Golden Horn batholith rapidly intruded and crystallised without prolonged ( $\gg 100$  ky) melt residence (Eddy *et al.* 2016). The two older analyses produced at Princeton University suggest that rare older grains exist within the GHR1 granite. These grains were likely recycled from older parts of the magmatic system, but are rare. In this study they represent 8% of the total number of grains analysed by CA-ID-TIMS. In both cases, the grains were significantly older (1–4%) than the recommended reference value and can be easily identified during CA-ID-TIMS analysis. Nevertheless, the excellent agreement between independent laboratories and the apparent lack of age dispersion in CA-ID-TIMS  $^{206}\text{Pb}/^{238}\text{U}$  dates further suggests that GHR1 zircon will be useful as a reference material for U-Pb zircon CA-ID-TIMS geochronology.

Microbeam U-Pb analyses from GHR1 zircon show that the  $^{206}\text{Pb}/^{238}\text{U}$  date is reproducible across several laboratories using different analytical methods (Figure 6). However, our study reveals four potential limitations to consider when using GHR1 as a reference material. (1) Like most Cenozoic zircon, GHR1 has low total Pb mass fraction. (2) GHR1 zircon contains abundant inclusions that may contain high  $\text{Pb}_c$ . (3) A spread in ages of whole grain dissolutions without using chemical abrasion (Figure 4) and in zircon surface analyses by SIMS (Figure 7) suggest the presence of either younger overgrowths or Pb-loss. (4) The presence of xenocrysts up to 4% older than the main zircon population, which may bias weighted means of GHR1. We consider all of the limitations listed above to preclude the use of GHR1 as a primary reference material for calibration of U-Pb isotopic measurements during microbeam analyses. Likewise, the variable U mass fraction (150–2000  $\mu\text{g g}^{-1}$  with outliers  $\gg 2000$   $\mu\text{g g}^{-1}$ : Tables S3–S7), variable REE mass fractions (Figure 11 and Table S11), and presence of REE bearing inclusions preclude the use of GHR1 for calibration of elemental mass fractions in zircon during microbeam analyses (Figure 11). However, our data demonstrates the reproducibility of the  $^{206}\text{Pb}/^{238}\text{U}$  ratio in GHR1 zircon interiors across a variety of methods and all participating laboratories produced dates that are in agreement with the CA-ID-TIMS reference date for GHR1 to within  $< 1$ –1.5% (Figure 6 and Table 2). Given the apparent homogeneity of  $^{206}\text{Pb}/^{238}\text{U}$  in GHR1 grain interiors, we suggest that it will provide a useful secondary reference material for assessing the accuracy of fractionation correction and external reproducibility of microbeam U-Pb geochronology of Cenozoic zircon. In this capacity, the inter-crystal variability in U and REE mass fractions will

provide an important check on corrections related to variable matrix composition (e.g., Black *et al.* 2004, Jackson *et al.* 2004) and variable amounts of radiation damage (e.g., Steely *et al.* 2014, Sliwinski *et al.* 2017). Below we offer guidelines for how to best utilise GHR1 zircon in this capacity.

The systematically younger  $^{206}\text{Pb}/^{238}\text{U}$  dates for zircons analysed by ID-TIMS without chemical abrasion (Figure 4) and SIMS surface analyses (Figure 7) suggest some degree of Pb-loss or younger overgrowths in GHR1 zircon. We do not think that these dates incorporate younger zircon growth, because no obvious overgrowths were observed in cathodoluminescence images (Figure 2) and there are no documented magmatic or metamorphic events after 47.729 Ma in the Golden Horn batholith (Eddy *et al.* 2016). Instead, Pb-loss is a more likely explanation for these anomalously young dates. We consider that this Pb-loss is concentrated in the zircon rims because most microbeam analyses of GHR1 zircon interiors reproduced the reference CA-ID-TIMS date (Figure 6), while nearly all of the SHRIMP-RG analyses of zircon surfaces (outermost  $\sim 2\ \mu\text{m}$ ) yielded younger dates (Figure 7). A comparison of U mass fractions measured from grain interiors and surfaces on the SHRIMP-RG at the Stanford University/USGS laboratory also indicates that the surfaces have higher average U content than interiors, and thus, more radiation damage (Table S6). Therefore, we recommend that microbeam analyses of GHR1 zircon avoid zircon edges to reduce the possibility of incorporating zones that could include Pb-loss.

High  $\text{Pb}_c$  in some microbeam zircon analyses of GHR1 interiors resulted in  $^{206}\text{Pb}/^{238}\text{U}$  dates that significantly deviate from the CA-ID-TIMS reference date. We attribute this deviation to the challenges of accurately measuring  $^{206}\text{Pb}/^{204}\text{Pb}$  during microbeam analyses and budgeting the  $\text{Pb}_c$  composition between the composition expected in co-crystallised inclusions and the composition of Pb in modern surficial contamination. These challenges make it difficult to accurately correct isotopic ratios for  $\text{Pb}_c$  contamination and can result in spurious dates. Figure 10 shows the deviation from the CA-ID-TIMS reference date of all  $^{206}\text{Pb}/^{238}\text{U}$  dates produced during microbeam analyses of GHR1 grain interiors relative to measured  $^{206}\text{Pb}/^{204}\text{Pb}$ . Increased deviation from the reference value occurs at  $^{206}\text{Pb}/^{204}\text{Pb} < 1500$ . Consequently, we recommend that microbeam analyses of GHR1 zircon be discarded if  $^{206}\text{Pb}/^{204}\text{Pb} < 1500$ . Using CL or BSE images to avoid inclusions during microbeam analyses may also help increase the number of spots that meet this condition, as the presence of  $\text{Pb}_c$  bearing inclusions is inferred from the

elevated  $Pb_c$  observed in the ID-TIMS analyses that did not undergo chemical abrasion (Table S2).

The occurrence of older ante- or xenocrystic zircon in GHR1 is highlighted by the two CA-ID-TIMS analyses that were  $\sim 1\%$  and  $\sim 4\%$  older than the main zircon population (Table S2). The incorporation of older zircon is common in magmatic systems and these grains likely reflect cannibalisation of zircon from older wall rock. Similar incorporation of ante- or xenocrystic zircon has been identified in ID-TIMS analyses of other natural zircon reference materials (R33: Black *et al.* 2004, Penglai: Li *et al.* 2010) and will likely be a persistent problem in zircon reference materials separated from igneous rocks rather than sub-sampled from large, homogeneous zircon megacrysts. These older grains will be easily identified in CA-ID-TIMS analyses, as they are distinctly older than the main age population. However, the identification of ante- or xenocrysts that are  $< 4\%$  older than the reference age during microbeam analyses is more difficult. Due to the presence of these grains, we recommend that several different individual zircons are analysed during a session and that any grain that consistently produces an older age is excluded. The internal structure of the two older zircon analysed by CA-ID-TIMS was not documented with CL or BSE images prior to dissolution. Future CA-ID-TIMS analyses coupled with CL or BSE images may identify features that can be used during microbeam analyses to avoid these grains. Nevertheless, the good agreement between large-n microbeam U-Pb geochronological datasets and the CA-ID-TIMS reference date suggests that the limited presence of ante- or xenocrystic grains does not have a major effect on these analyses at the current level of age precision that is achievable by LA-ICP-MS and SIMS.

Despite the potential limitations of GHR1 zircon, the homogeneity of the  $^{206}Pb/^{238}U$  ratio in zircon interiors (Figure 6) suggests that it can be a useful secondary reference material. In this respect, the  $48.106 \pm 0.023$  Ma age of GHR1 is important because Cenozoic zircon reference materials for microbeam U-Pb geochronological analyses (Table 1) are currently limited to a single  $38.896 \pm 0.012$  Ma gem-quality zircon crystal (Kennedy *et al.* 2014) and *ca.* 4.4 Ma zircon megacrysts from an alkaline basalt (Li *et al.* 2010) and zircon separated from the Fish Canyon Tuff (Schmitz and Bowring 2001, Wotzlaw *et al.* 2013) that show significant age heterogeneity in ID-TIMS analyses. Thus, the well-characterised age of GHR1 zircon and its practically unlimited supply will help fill this role as the use of microbeam methods for dating Cenozoic igneous and detrital zircons becomes increasingly common.



## Suitability as a natural reference material for microbeam Hf isotope determinations in zircon

The variability seen in solution MC-ICP-MS measurements of  $^{176}\text{Hf}/^{177}\text{Hf}$  from GHR1 zircon is similar to the variability reported for in repeat measurements of the JMC-475 Hf isotopic standard solution, suggesting that there is no resolvable inter-crystal variability in  $^{176}\text{Hf}/^{177}\text{Hf}$ . Consequently, we recommend using our mean  $^{176}\text{Hf}/^{177}\text{Hf} = 0.283050 \pm 17$  (2s) from solution MC-ICP-MS analyses as a reference Hf isotopic value for GHR1 zircon. The mean  $^{176}\text{Hf}/^{177}\text{Hf}$  values measured by both LA-ICP-MS laboratories are in good agreement with this value, demonstrating that it is reproducible by microbeam methods (Figure 8 and Table 3).

Ytterbium and Lu mass fractions from some of the University of Arizona LA-ICP-MS measurements also far exceed those seen in the solution measurements (Figure 9). We attribute this difference to ablation of zircon with elevated REE-content or by contamination of the analysis by REE-bearing inclusions during the laser ablation process. The possibility for high U domains along grain rims may suggest late zircon growth from an evolved liquid that would likely have correspondingly high REE content. Dissolution of these zones during the chemical abrasion process may explain the more restricted range of Yb and Lu seen in the trace element measurements from MIT. Alternatively, ablation of REE-bearing inclusions may be responsible for the elevated REE content observed in some of the microbeam  $^{176}\text{Hf}/^{177}\text{Hf}$  measurements (Figure 11). The removal of these inclusions during chemical abrasion would also explain the lower mass fractions of REE seen in the MIT analyses. Given the ubiquity of inclusions in the GHR1 zircons, the possibility of high-REE growth zones, and the difficulty in correcting for isobaric interferences from REE (e.g.,  $^{176}\text{Yb}$  and  $^{176}\text{Lu}$ ) during the measurement of  $^{176}\text{Hf}/^{177}\text{Hf}$ , we suggest that all grains used as reference material for  $^{176}\text{Hf}/^{177}\text{Hf}$  measurements be imaged prior to analysis so that both inclusions and grain exteriors can be avoided during targeting. Additional screening of analyses with high measured Yb and Lu (i.e.,  $^{176}(\text{Yb}+\text{Lu})/^{176}\text{Hf} > 40\%$ ) may also be effective for removing analyses that yield anomalous  $^{176}\text{Hf}/^{177}\text{Hf}$  values due to excess REE incorporated from inclusions. Regardless, the  $^{176}\text{Hf}/^{177}\text{Hf} = 0.283050 \pm 17$  (2s,  $\varepsilon_{\text{Hf}(0)} = +9.3$ ) of GHR1 zircon is the most radiogenic Hf isotopic composition in any available zircon reference material (Table 1), and should be useful in assessing the external reproducibility of analyses of zircon with high  $\varepsilon_{\text{Hf}(0)}$ .

## Conclusions

Zircon from sample GHR1 are characterised by homogeneous U-Pb and Hf isotopic systematics as evidenced by the highly reproducible  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  by CA-ID-TIMS and solution MC-ICP-MS, respectively. These values are also reproducible by microbeam techniques (LA-ICP-MS and SIMS). The age and geochemical reproducibility, potentially inexhaustible supply,  $48.106 \pm 0.023$  Ma age, and radiogenic  $\epsilon\text{Hf}_{(0)}$  all suggest that GHR1 will provide a useful reference material for assessing external reproducibility of U-Pb analyses of Cenozoic zircon and radiogenic  $^{176}\text{Hf}/^{177}\text{Hf}$  during microbeam analyses. However, care must be taken to avoid analysing REE- and  $\text{Pb}_c$ -bearing inclusions and zircon edges where Pb-loss may have occurred. Zircon separates from this sample are available to interested laboratories through the corresponding authors.

## Acknowledgements

We would like to thank D. McGee and B. Hardt for assistance in making Hf isotopic measurements at MIT. M.I.M benefited from a W.O. Crosby post-doctoral fellowship from the MIT. Thoughtful comments by an anonymous reviewer, J. Vazquez and editorial comments by P. Sylvester improved this manuscript.

## References

**Bauer A.M., Fisher C.M., Vervoort J.D. and Bowring S.A. (2014)**

Coupled zircon Lu-Hf and U-Pb isotopic analyses of the oldest terrestrial crust, the > 4.03 Ga Acasta Gneiss Complex. **Earth and Planetary Science Letters**, **458**, 37–48.

**Black L.P., Kamo S.L., Allen C.M., Davis D.W., Aleinikoff J.N., Valley J.W., Mundil R., Campbell I.H., Korsch R.J., Williams I.S. and Foudoulis C. (2004)**

Improved  $^{206}\text{Pb}/^{238}\text{U}$  microprobe geochronology by the monitoring of a trace-element-related matrix effect: SHRIMP, ID-TIMS, ELA-ICP-MS and oxygen isotope documentation for a series of zircon standards. **Chemical Geology**, **205**, 115–140.

**Bouvier A., Vervoort J.D. and Patchett J.D. (2008)**

The Lu-Hf and Sm-Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. **Earth and Planetary Science Letters**, **273**, 48–57.

**Bowring J.F., McLean N.M. and Bowring S.A. (2011)**

Engineering cyber infrastructure for U-Pb geochronology: Tripolig and U-Pb\_Redux. **Geochemistry, Geophysics, Geosystems**, **12**, Q0AA19

**Cecil M.R., Gehrels G., Ducea M.N. and Patchett P.J. (2011)**

U-Pb-Hf characterization of the central Coast Mountains batholith: Implications for petrogenesis and crustal architecture. **Lithosphere**, **3**, 247–260.

**Chang Z., Vervoort J.D., McClelland W.C. and Knaack C. (2006)**

U-Pb dating of zircon by LA-ICP-MS. **Geochemistry, Geophysics, Geosystems**, **7**, Q05009.

Coble M.A., Vazquez J.A., Barth A.P., Wooden J., Burns D., Kylander-Clark A., Jackson S. and Vennari C.E. (2018)

Trace element characterisation of MAD-559 zircon reference material for ion microprobe analysis. *Geostandards and Geoanalytical Research*, *in press*.

Condon D.J., Schoene B., McLean N.M., Bowring S.A. and Parrish R.R. (2015)

Metrology and traceability of U-Pb isotopic dilution geochronology (EARTHTIME tracer calibration part I). *Geochimica et Cosmochimica*, **164**, 464–480.

Dhuime B., Hawkesworth C.J., Cawood P.A. and Storey C.D. (2012)

A change in the geodynamics of continental growth 3 billion years ago. *Science*, **335**, 1334–1336.

Eddy M.P., Bowring S.A., Miller R.B. and Tepper J.H. (2016)

Rapid assembly and crystallization of a fossil large-volume silicic magma chamber. *Geology*, **44**, 331–334.

Eddy M.P., Jagoutz O. and Ibañez-Mejia M. (2017)

Timing of initial seafloor spreading in the Newfoundland-Iberia rift. *Geology*, **45**, 527–530.

Fisher C.M., Vervoort J.D. and Hanchar J.M. (2014)

Guidelines for reporting zircon Hf isotopic data by LA-MC-ICP-MS and potential pitfalls. *Chemical Geology*, **363**, 125–133.

Gaschnig R.M., Vervoort J.D., Lewis R.S. and Tikoff B. (2011)

Isotopic evolution of the Idaho batholith and Challis intrusive province, northern US Cordillera. *Journal of Petrology*, **52**, 2397–2429.

This article is protected by copyright. All rights reserved.

**Gehrels G.E. (2014)**

Detrital zircon U-Pb geochronology applied to tectonics. **Annual Review of Earth and Planetary Sciences**, **42**, 127–149.

**Gehrels G.E., Valencia V. and Ruiz J. (2008)**

Enhanced precision, accuracy, efficiency, and spatial resolution of U-Pb ages by laser ablation-multicollector-inductively coupled plasma-mass spectrometry. **Geochemistry, Geophysics, Geosystems**, **9**, Q03017.

**Goodge J.W. and Vervoort J.D. (2006)**

Origin of Mesoproterozoic A-type granites in Laurentia: Hf isotope evidence. **Earth and Planetary Science Letters**, **243**, 711–731.

**Guillong M., von Quadt A., Sakata S., Peytcheva I. and Bachmann O. (2014)**

LA-ICP-MS Pb-U dating of young zircons from the Kos-Nisyros volcanic centre, SE Aegean arc. **Journal of Analytical Atomic Spectrometry**, **29**, 963–970.

**Hiess J., Condon D.J., McLean N.M. and Noble S.R. (2012)**

$^{238}\text{U}/^{235}\text{U}$  systematics in terrestrial uranium-bearing minerals. **Science**, **335**, 1610–1614.

**Horstwood M.S.A., Košler J., Gehrels G., Jackson S.E., McLean N.M., Paton C., Pearson N.J., Sircombe K., Sylvester P., Vermeesch P., Bowring J.F., Condon D.J. and Schoene B. (2016)**

Community-derived standards for LA-ICP-MS U-(Th-)Pb geochronology – Uncertainty propagation, age interpretation and data reporting. **Geostandards and Geoanalytical Research**, **40**, 311–332.

**Ibañez-Mejia M., Gehrels G.E., Ruiz J., Vervoort J.D., Eddy M.P. and Li C. (2014)**

Small-volume baddeleyite (ZrO<sub>2</sub>) U-Pb geochronology and Lu-Hf isotope geochemistry by LA-ICP-MS: Techniques and applications. **Chemical Geology**, **384**, 149–167.

**Ibañez-Mejia M., Pullen A., Arenstein J., Gehrels G.E., Valley J., Ducea M.N., More A.R., Pecha M. and Ruiz J. (2015)**

Unravelling crustal growth and reworking processes in complex zircons from orogenic lower-crust: The Proterozoic Putumayo Orogen of Amazonia. **Precambrian Research**, **267**, 285–310.

**Ickert R.B., Hiess J., Williams I.S., Holden P., Ireland T.R., Lanc P., Schram N., Foster J.J. and Clement S.W. (2008)**

Determining high precision, *in situ*, oxygen isotope ratios with a SHRIMP II: Analyses of MPI-DING silicate-glass reference materials and zircon from contrasting granites. **Chemical Geology**, **257**, 114–128.

**Ireland T.R. and Williams I.S. (2003)**

Considerations in zircon geochronology by SIMS. In: **Hanchar J.M. and Hoskin P.W.O. (eds)**, **Zircon: Reviews in Mineralogy and Geochemistry**, **53**, 215–241.

**Jackson S.E., Pearson N.J., Griffin W.L. and Belousova E.A. (2004)**

The application of laser ablation-inductively coupled plasma-mass spectrometry to *in situ* U-Pb zircon geochronology. **Chemical Geology**, **211**, 47–69.

**Kennedy A.K., Wotzlaw J.F., Schaltegger U., Crowley J.L. and Schmitz M. (2014)**

Eocene zircon reference material for microanalysis of U-Th-Pb isotopes and trace elements. **The Canadian Mineralogist**, **52**, 409–421.

**Kita N.T., Ushikubo T., Fu B. and Valley J.W. (2009)**

High precision SIMS oxygen isotope analysis and the effect of sample topography. **Chemical Geology**, **264**, 43–57.

**Li Q.L., Li X.H., Liu Y., Tang G.Q., Yang J.H. and Zhu W.G. (2010)**

Precise U-Pb and Pb-Pb dating of Phanerozoic baddeleyite by SIMS with oxygen flooding technique. **Journal of Analytical Atomic Spectrometry**, **25**, 1107–1113.

**Li X.H., Liu Y., Li Q.L., Guo C.H. and Chamberlain K.R. (2009)**

Precise determination of Phanerozoic zircon Pb/Pb age by multicollector SIMS without external standardization. **Geochemistry, Geophysics, Geosystems**, **10**, Q04010.

**Li X.H., Tang G.Q., Gong B., Yang Y.H., Hou K.J., Hu Z.C., Li Q.L., Liu Y. and Li W.X. (2013)**

Qinghu zircon: A working reference for microbeam analysis of U-Pb age and Hf and O isotopes. **Chinese Science Bulletin**, **58**, 4647–4654.

**Ludwig K.R. (2001)**

Isoplot/Ex version 2.49. **Berkeley Geochronology Center Special Publication 1**, 55pp.

**Ludwig K.W. (2009)**

SQUID 2: A user's manual. **Berkeley Geochronology Center Special Publication 5**, 110pp.

**Matthews N.E., Vazquez J.A. and Calvert A.T. (2015)**

Age of the Lava Creek supereruption and magma chamber assembly at Yellowstone based on  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb dating of sanidine and zircon crystals. **Geochemistry, Geophysics, Geosystems**, **16**, 2508–2528.

**Mattinson J.M. (2005)**

Zircon U-Pb chemical abrasion (“CA-TIMS”) method: Combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages. **Chemical Geology**, **220**, 47–66.

**Mattinson J.M. (2010)**

Analysis of the relative decay constants of  $^{235}\text{U}$  and  $^{238}\text{U}$  by multi-step CA-TIMS measurements of closed system natural zircon samples. **Chemical Geology**, **275**, 186–198.

**McLean N.M., Bowring J.F. and Bowring S.A. (2011)**

An algorithm for U-Pb isotope dilution data reduction and uncertainty propagation. **Geochemistry, Geophysics, Geosystems**, **12**, Q0AA18.

**McLean N.M., Condon D.J., Schoene B. and Bowring S.A. (2015)**

Evaluating uncertainties in the calibration of isotopic reference materials and multi-element isotopic tracers (EARTHTIME tracer calibration II). **Geochimica et Cosmochimica**, **164**, 481–501.

**Paces J.B. and Miller Jr., J.D. (1993)**

Precise U-Pb ages of Duluth Complex and related mafic intrusions, northeastern Minnesota: Geochronological insights to physical, petrogenetic, paleomagnetic, and tectonomagmatic processes associated with the 1.1 Ga Midcontinent Rift System. **Journal of Geophysical Research**, **98**, 13997–14013.

**Padilla A.J., Miller C.F., Carley T.L., Economos R.C., Schmitt A.K., Coble M.A., Wooden J.L., Fisher C.M., Vervoort J.D. and Hancher J.M. (2016)**

Elucidating the magmatic history of the Austurhorn silicic intrusive complex (Southeast Iceland) using zircon elemental and isotopic geochemistry and geochronology. **Contributions to Mineralogy and Petrology**, **171**, 69.

This article is protected by copyright. All rights reserved.



**Patchett J.P. (1983)**

Importance of the Lu-Hf isotopic system in studies of planetary chronology and chemical evolution. **Geochimica et Cosmochimica Acta**, **47**, 81–91.

**Patchett P.J. and Tasumoto M. (1980)**

A routine high-precision method for Lu-Hf isotope geochemistry and chronology. **Contributions to Mineralogy and Petrology**, **75**, 263–267.

**Roberts N.M.W. and Spencer C.J. (2014)**

The zircon archive of continent formation through time. **In: XXX (eds), Geological Society of London Special Publication**, **389**, 187–225.

**Sato K., Tassinari C.C.G., Basei M.A.A., Onoe A.T. and Siga Jr. O. (2016)**

First REE analyses by SHRIMP at Geosciences Institute of São Paulo University: REE diffusion from apatite inclusion inside Temora zircon. **International SHRIMP Workshop**, **8**, 71.

**Schärer U. (1984)**

The effect of initial  $^{230}\text{Th}$  disequilibrium on young U-Pb ages: The Makalu case, Himalaya. **Earth and Planetary Science Letters**, **67**, 191–204.

**Schmitz M.D. and Bowring S.A. (2001)**

U-Pb zircon and titanite systematics of the Fish Canyon Tuff: An assessment of high-precision U-Pb geochronology and its application to young volcanic rocks. **Geochimica et Cosmochimica Acta**, **65**, 2571–2587.

**Schmitz M.D. and Schoene B. (2007)**

Derivation of isotope ratios, errors, and error correlations for U-Pb geochronology using  $^{205}\text{Pb}$ - $^{235}\text{U}$ -( $^{233}\text{U}$ )-spiked isotope dilution thermal ionization mass spectrometric data. **Geochemistry, Geophysics, Geosystems**, **8**, Q08006.

**Schoene B., Latkoczy C., Schaltegger U. and Günther D. (2010)**

A new method integrating high-precision U-Pb geochronology with zircon trace element analysis (U-Pb TIMS-TEA). **Geochimica et Cosmochimica Acta**, **74**, 7144–7159.

**Sláma J., Košler J., Condon D.J., Crowley J.L., Gerdes A., Hanchar J.M., Horstwood M.S.A., Morris G.A., Nasdala L., Norberg N., Schaltegger U., Schoene B., Tubrett M.N. and Whitehouse M.J. (2008)**

Plešovice zircon – A new natural reference material for U-Pb and Hf isotopic microanalysis. **Chemical Geology**, **249**, 1–35.

**Sliwinski J.T., Guillon M., Liebske C., Dunkl I., von Quadt A. and Bachmann O. (2017)**

Improved accuracy of LA-ICP-MS U-Pb ages of Cenozoic zircons by alpha dose correction. **Chemical Geology**, **472**, 8–21.

**Söderlund U., Patchett P.J., Vervoort J.D. and Isachsen C.E. (2004)**

The  $^{176}\text{Lu}$  decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions. **Earth and Planetary Science Letters**, **219**, 311–324.

**Stacey J.S. and Kramers J.D. (1975)**

Approximation of terrestrial lead isotope evolution by a two-stage model. **Earth and Planetary Science Letters**, **26**, 207–221.

**Steely A.N., Hourigan J.K. and Juel E. (2014)**

Discrete multi-pulse laser ablation depth profiling with a single-collector ICP-MS: Sub-micron U-Pb geochronology of zircon and the effect of radiation damage on depth-dependent fractionation. **Chemical Geology**, **372**, 92–108.

**Stelten M.E., Cooper K.M., Vazquez J.A., Calvert A.T. and Glessner J.J.G. (2015)**

Mechanisms and timescales of generating eruptible rhyolitic magmas at Yellowstone caldera from zircon and sanidine geochronology and geochemistry. **Journal of Petrology**, **56**, 1607–1642.

**Stern R.A. and Amelin Y. (2003)**

Assessment of errors in SIMS zircon U-Pb geochronology using a natural zircon standard and NIST SRM 610 glass. **Chemical Geology**, **197**, 111–142.

**Stull R.J. (1969)**

The geochemistry of the southeastern portion of the Golden Horn batholith, Northern Cascades, Washington. **PhD thesis, University of Washington (Seattle)** 127pp.

**Stull R.J. (1978)**

Mantled feldspars from the Golden Horn batholith, Washington. **Lithos**, **11**, 243–249.

**Vervoort J.D. and Blichert-Toft J. (1999)**

Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. **Geochimica et Cosmochimica Acta**, **63**, 533–556.

**Vervoort J.D., Patchett P.J., Söderlund U. and Baker M. (2004)**

Isotopic composition of Yb and the determination of Lu concentrations and Lu/Hf ratios by isotope dilution using MC-ICPMS. **Geochemistry, Geophysics, Geosystems**, **5**, Q11002.

This article is protected by copyright. All rights reserved.

**Viete D.R., Kylander-Clark A.R.C. and Hacker B.R. (2015)**

Single-shot laser ablation split stream (SS-LASS) petrochronology deciphers multiple, short-duration metamorphic events. **Chemical Geology**, **415**, 70–86.

**Vorhies S.H, Ague J.J. and Schmitt A.K. (2013)**

Zircon growth and recrystallization during progressive metamorphism, Barrovian zones, Scotland. **American Mineralogist**, **98**, 219–230.

**Wiedenbeck M., Allé P., Corfu F., Griffin W.L., Meier M., Oberli F., von Quadt A., Roddick J.C. and Spiegel W. (1995)**

Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analysis. **Geostandards Newsletter**, **19**, 1–23.

**Woodhead J.D. and Hergt J.M. (2005)**

A preliminary appraisal of seven natural zircon reference materials for *in situ* Hf isotope determination. **Geostandards and Geoanalytical Research**, **29**, 183–195.

**Wotzlaw J.F., Schaltegger U., Frick D.A., Dungan M.A., Gerdes A. and Günther D. (2013)**

Tracking the evolution of large-volume silicic magma reservoirs from assembly to supereruption. **Geology**, **41**, 867–870.

**Zimmerer M.J., Lafferty J. and Coble M.A. (2016)**

The eruptive and magmatic history of the youngest pulse of volcanism at the Valles caldera: Implications for successfully dating late Quaternary eruptions. **Journal of Volcanology and Geothermal Research**, **310**, 50–57.

## Supporting information

The following supporting information is available in the online version of this article:

Tables S1–7. U-Pb isotopic data for GHR1 from participating laboratories.

Tables S8–10. Hf isotopic data of GHR1 single zircons from participating laboratories.

Table S11. SHRIMP REE determinations (University of Sao Paulo).

Appendix S1. MATLAB code for U-Pb calculations

This material is available from: <http://onlinelibrary.wiley.com/doi/10.1111/ggr.00000/abstract>

(This link will take you to the article abstract).

### Figure captions

**Figure 1.** Location maps for the GHR1 sample showing (a) the location of the Golden Horn batholith relative to other granitoids (black) in the North American Cordillera from Miller *et al.* (2000) and (b) the location of the GHR1 outcrop within the Golden Horn batholith. This figure is slightly modified from Eddy *et al.* (2016).

**Figure 2.** Cathodoluminescence (CL) images of zircon separated from the GHR1 outcrop. Note the oscillatory zoning characteristic of igneous zircon (a, b, c, d), possible small-scale resorption features (c, d), and the presence of inclusions (a, b, c).

**Figure 3.** Chemical abrasion-isotope dilution-thermal ionisation mass spectrometry (CA-ID-TIMS) results from MIT and Princeton University. Results are shown as Wetherill concordia plots and as a rank order plot of Th-corrected  $^{206}\text{Pb}/^{238}\text{U}$  dates for the combined dataset. Note that two analyses of much older zircon (Table S2) are not shown.

**Figure 4.** Wetherill concordia plot comparing the results of ID-TIMS analyses of GHR1 zircon that did not undergo chemical abrasion with the CA-ID-TIMS results. All analyses that did not undergo chemical abrasion prior to dissolution are younger than the CA-ID-TIMS analyses, indicating either the presence of younger zircon overgrowths or Pb-loss. Note the older CA-ID-TIMS analyses that likely represent ante- or xenocrysts.

**Figure 5.** Concordia plots for all microbeam U-Pb analyses by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and secondary ion mass spectrometry (SIMS). The data from Washington State University is not corrected for  $Pb_c$  and is shown on a Tera-Wasserburg concordia plot. The rest of the data is corrected for  $Pb_c$  using the methods described for each individual laboratory and is shown on Wetherill concordia plots. All dates are reported with  $2\sigma$  uncertainty and mean square weighted deviation (MSWD). \*The uncertainty for the dates from the University of Arizona and Washington State University are reported in the format  $\pm A/B$ , where A represents the analytical uncertainty and B includes the external uncertainty related to the reproducibility of zircon reference materials. Please refer to the text for the uncertainty reporting procedures from each of the other laboratories.

**Figure 6.** Rank order plot comparing the  $^{206}Pb/^{238}U$  dates from microbeam U-Pb measurements relative to the preferred crystallisation date for GHR1 determined by chemical abrasion-isotope dilution-thermal ionisation mass spectrometry (CA-ID-TIMS). Individual bars represent single analyses and are shown with  $2\sigma$  uncertainty. Weighted mean dates are also reported with  $2\sigma$  uncertainty. Dashed lines were excluded from the weighted mean calculation and correspond to grains with high  $Pb_c$  or grains that were outliers. Only data between 56 Ma and 40 Ma is shown. The mean and  $2\sigma$  uncertainty for each laboratory are shown as thin black lines and grey boxes, respectively. \*The uncertainty for the dates from the University of Arizona and Washington State University are reported in the format  $\pm A/B$ , where A represents the analytical uncertainty and B includes the external uncertainty related to the reproducibility of zircon reference materials. Only the full uncertainty (B) is shown on the figure. Please refer to the text for the uncertainty reporting procedures from each of the other laboratories.

**Figure 7.** A Wetherill concordia plot (a) and a rank order plot of  $^{206}\text{Pb}/^{238}\text{U}$  dates (b) from analyses of unpolished surfaces (outermost 2  $\mu\text{m}$ ) of GHR1 zircon measured by SIMS. The dates show significant scatter and many are younger than the CA-ID-TIMS reference date (b). These younger dates suggest either the presence of younger zircon overgrowths or Pb-loss in zircon rims.

**Figure 8.** Rank order plot comparing the  $^{176}\text{Hf}/^{177}\text{Hf}$  results from solution multi-collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) with those from laser ablation (LA)-ICP-MS. The dashed analyses from the University of Arizona contained  $(^{176}\text{Lu}+^{176}\text{Yb})/^{176}\text{Hf} > 40\%$  and are not included in the calculation of the mean. All uncertainty is reported at  $2\sigma$  and the means are reported as  $2s$ .

**Figure 9.** Plot of  $^{176}\text{Hf}/^{177}\text{Hf}$  for GHR1 measured by LA-ICP-MS compared with the per cent of mass 176 represented by isobaric interferences ( $^{176}\text{Yb}$  and  $^{176}\text{Lu}$ ). The plot shows a greater divergence in measured  $^{176}\text{Hf}/^{177}\text{Hf}$  values from the mean of solution ICP-MS measurements when there are high levels of interference, suggesting that the increased scatter in the LA-ICP-MS data may be related to the difficulty of making interference corrections. The range of  $(^{176}\text{Yb} + ^{176}\text{Lu})/^{176}\text{Hf} \%$  measured in the trace element aliquots of the solution analyses is also shown. The greater range of  $(^{176}\text{Yb} + ^{176}\text{Lu})/^{176}\text{Hf} \%$  in LA-ICP-MS analyses may reflect analyses that incorporated REE-rich inclusions such as apatite. These inclusions were removed from the solution analyses during the chemical abrasion step. All uncertainty bars are reported at  $2\sigma$ .

**Figure 10.** The % deviation from the CA-ID-TIMS reference date of microbeam analyses compared with the analysed  $^{206}\text{Pb}/^{204}\text{Pb}$ . The full dataset is shown in (a), while (b) highlights the analyses with the lowest  $^{206}\text{Pb}/^{204}\text{Pb}$ . We notice a marked increase in deviation from the reference date at low  $^{206}\text{Pb}/^{204}\text{Pb}$  and recommend that analyses with  $^{206}\text{Pb}/^{204}\text{Pb} < 1500$  be treated as unreliable.

**Figure 11.** (a) CL image showing the location of spots analysed for REE mass fractions at São Paulo University. (b) Chondrite normalised (using the values reported in McDonough and Sun 1995) rare earth element (REE) spider plots of spots analysed on GHR1 zircons. Elevated REE content (1.2, 3.2 and 3.3), relative to the content seen in 'clean' zircon (1.1, 1.3, 3.1) is correlated with the presence of inclusions in the analysed volume. However, given that the matrix of inclusion-bearing analyses (1.2, 3.2, 3.3) differs from the reference material (91500 zircon: Wiedenbeck *et al.* 2004) used to calculate the sensitivity factor between NIST 610 glass and zircon, we emphasise that these measurements should only be considered qualitative. Energy-dispersive X-ray spectroscopy (EDS) measurements of these inclusions identified them as apatite. REE analyses follow the methods of Sato *et al.* (2016) and are reported in Table S11.



Table 1.  
Zircon reference materials for microbeam U-Pb and Hf isotopic analyses

| Name      | ID-TIMS age (Ma) <sup>a</sup> | 2 $\sigma$ | Reference <sup>b,c</sup>                     | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2 $\sigma$ | Reference <sup>d,e</sup>                  | Host lithology     | Quantity  |
|-----------|-------------------------------|------------|--|--------------------------------------|------------|---|--------------------|-----------|
| Penglai   | 4.4                           | 0.1        | Li <i>et al.</i> (2010) <sup>b</sup>         |                                      |            |   |                    |           |
| FCT       | 28.196 - 28.638               | -          | Wotzlaw <i>et al.</i> (2013) <sup>b</sup>    | 0.282906                             | 0.000001   | Li <i>et al.</i> (2010) <sup>d</sup>      | Alkaline Basalt    | Unlimited |
| AUS_z2    | 38.896                        | 0.012      | Kennedy <i>et al.</i> (2014) <sup>b</sup>    | -                                    | -          | -   | Dacite             | Unlimited |
| GHR1      | 48.106                        | 0.023      | <i>This Study</i> <sup>c</sup>               | -                                    | -          | -   | Single Crystal     | Limited   |
| Qinghu    | 159.5                         | 0.2        | Li <i>et al.</i> (2009) <sup>b</sup>         | 0.283050                             | 0.000017   | <i>This Study</i> <sup>e</sup>            | Rapakivi Granite   | Unlimited |
| Plešovice | 337.13                        | 0.37       | Sláma <i>et al.</i> (2008) <sup>b</sup>      | 0.283002                             | 0.000004   | Li <i>et al.</i> (2013) <sup>e</sup>      | Quartz Monzonite   | Unlimited |
| Temora-1  | 416.75                        | 0.24       | Black <i>et al.</i> (2003) <sup>c</sup>      | 0.282482                             | 0.000013   | Sláma <i>et al.</i> (2008) <sup>d,e</sup> | Potassic Granulite | Unlimited |
| Temora-2  | 418.37                        | 0.14       | Mattinson (2010) <sup>b</sup>                | 0.282685                             | 0.000011   | Wu <i>et al.</i> (2006) <sup>e</sup>      | Gabbroic Diorite   | Unlimited |
| R33       | 420.53                        | 0.16       | Mattinson (2010) <sup>b</sup>                | 0.282686                             | 0.000008   | Woodhead and Hergt (2005) <sup>e</sup>    | Gabbro             | Unlimited |
| Z6266     | 559.0                         | 0.2        | Stern and Amelin (2003) <sup>c</sup>         | 0.282764                             | 0.000014   | Fisher <i>et al.</i> (2014) <sup>d</sup>  | Monzodiorite       | Unlimited |
| SL        | 563.5                         | 3.2        | Gehrels <i>et al.</i> (2008) <sup>c</sup>    | -                                    | -          | -   | Single Crystal     | Limited   |
| Peixe     | 564                           | 4          | Chang <i>et al.</i> (2006) <sup>c</sup>      | 0.281630                             | 0.000010   | Woodhead and Hergt (2005) <sup>e</sup>    | Single Crystal     | Limited   |
| GJ-1      | 608.5                         | 1.5        | Jackson <i>et al.</i> (2004) <sup>c</sup>    | -                                    | -          | -   | Alkaline Complex   | Unlimited |
| Mud Tank  | 732                           | 5          | Black and Gulson (1978) <sup>c</sup>         | 0.282000                             | 0.000005   | Morel <i>et al.</i> (2008) <sup>e</sup>   | Single Crystal     | Limited   |
| 91500     | 1065.4                        | 0.3        | Wiedenbeck <i>et al.</i> (1995) <sup>c</sup> | 0.282507                             | 0.000006   | Woodhead and Hergt (2005) <sup>e</sup>    | Carbonatite        | Unlimited |
| FC-1      | 1098.47                       | 0.16       | Mattinson (2010) <sup>b</sup>                | 0.282306                             | 0.000008   | Woodhead and Hergt (2005) <sup>e</sup>    | Single Crystal     | Limited   |
| OG1       | 3467.05                       | 0.63       | Stern <i>et al.</i> (2009) <sup>b</sup>      | 0.282184                             | 0.000016   | Woodhead and Hergt (2005) <sup>e</sup>    | Gabbro             | Unlimited |
|           |                               |            |  | -                                    | -          | -   | Diorite            | Unlimited |

<sup>a</sup> These dates correspond to those used for standardization during microbeam analyses as part of this study.

<sup>b</sup> Chemical abrasion (CA)-ID-TIMS

<sup>c</sup> Traditional ID-TIMS

<sup>d</sup> Laser ablation MC-ICP-MS

<sup>e</sup> Solution MC-ICP-MS

<sup>f</sup> CA-ID-TIMS analyses by Wotzlaw *et al.* (2013) show significant age dispersion in FCT relative to the original U-Pb ID-TIMS date of Schmitz and Bowring (2001).

Table 2.

Summary of U-Pb geochronology results

| Laboratory                  | Method <sup>1</sup> | No. of analyses  | Weighted Mean <sup>206</sup> Pb/ <sup>238</sup> U Date (Ma, 2 $\sigma$ ) <sup>2</sup> | MSWD <sup>3</sup> |
|-----------------------------|---------------------|------------------|---|-------------------|
| MIT                         | CA-ID-TIMS          | $n = 15$ of 15   | $48.105 \pm 0.024^4$  | 1.52              |
| Princeton University        | CA-ID-TIMS          | $n = 10$ of 12   | $48.108 \pm 0.025^4$  | 1.70              |
| Washington State University | LA-ICP-MS           | $n = 21$ of 24   | $47.99 \pm 0.44^5$  | 0.19              |
| University of Arizona       | LA-ICP-MS           | $n = 107$ of 114 | $48.38 \pm 0.71^6$  | 0.80              |
| Chinese Academy of Sciences | SIMS                | $n = 25$ of 37   | $48.18 \pm 0.31^6$  | 0.75              |
| USGS/Stanford               | SIMS                | $n = 18$ of 22   | $48.17 \pm 0.35^5$  | 1.71              |
| University of Sao Paulo     | SIMS                | $n = 16$ of 20   | $48.70 \pm 0.50^5$  | 1.50              |

<sup>1</sup> CA-ID-TIMS: Chemical abrasion-isotope dilution-thermal ionization mass spectrometry, LA-ICP-MS: Laser ablation-inductively coupled plasma-mass spectrometry, SIMS: Secondary ion mass spectrometry

<sup>2</sup> All weighted means were calculated using either ET\_Redux (Bowring *et al.* 2011) or the MATLAB function included in online supporting information.

<sup>3</sup> Mean Square Weighted Deviation (Wendt and Carl 1992) calculated using MATLAB function included in the online supporting information.

<sup>4</sup> CA-ID-TIMS dates include contributions to uncertainty from analytical sources and the calibration of the isotopic tracer.

<sup>5</sup> LA-ICP-MS and SIMS dates from Washington State University, USGS/Stanford, and the University of São Paulo include analytical uncertainty only.

<sup>6</sup> LA-ICP-MS and SIMS dates from the University of Arizona and Chinese Academy of Sciences includes both analytical uncertainty and systematic external errors related to reproducibility of zircon reference materials.

Table 3.

Summary of Hf isotopic results

| Laboratory                  | Method <sup>1</sup> | No. of analyses | $^{176}\text{Hf}/^{177}\text{Hf}$ | 2s       | MSWD <sup>2</sup> | $\epsilon\text{Hf}(0)$ |
|-----------------------------|---------------------|-----------------|-----------------------------------|----------|-------------------|------------------------|
| MIT                         | Solution MC-ICP-MS  | $n = 10$ of 10  | 0.283050                          | 0.000017 | 1.11              | 9.4                    |
| Washington State University | LA-ICP-MS           | $n = 10$ of 10  | 0.283040                          | 0.000044 | 1.90              | 9.0                    |
| University of Arizona       | LA-ICP-MS           | $n = 13$ of 20  | 0.283043                          | 0.000048 | 1.51              | 9.1                    |

<sup>1</sup> Solution MC-ICP-MS: Solution multi-collector-inductively coupled plasma-mass spectrometry, LA-MC-ICP-MS: Laser ablation-multi-collector-inductively coupled plasma-mass spectrometry

<sup>2</sup> Mean square weighted deviation (Wendt and Carl 1992). Calculated using the MATLAB script in the online supporting information.























