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Examination of SHRIMP U-Pb zircon geochronology accuracy from samples dated by both SHRIMP and CA-TIMS

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Abstract. Estimations of the reproducibility of U-Pb ages from SHRIMP instruments are based on data from studies nearly two decades old. Since that time, refinement of analytical procedures and manufacturing and installation improvements may have reduced the fundamental uncertainties of SHRIMP U-Pb analysis. This paper investigates 35 SHRIMP-TIMS double-dated "real-world" geologic samples from a variety of igneous rock types to better understand both geological and analytical sources of disagreement between the two dating methods.

Geoscience Australia's (GA) use of high-precision chemical abrasion thermal ionization mass spectrometry (CA-TIMS) for chronostratigraphy in Australian sedimentary basins has produced a substantial selection of precisely dated zircons, which we can use to cross-correlate the SHRIMP and CA-TIMS ages throughout the Phanerozoic. Thirty-two of the 35 ages were reported with external SHRIMP uncertainties less than 1% (95% confidence), below previous estimates of the reproducibility limits of the SHRIMP. Six of eight cases where the CA-TIMS age was outside the SHRIMP uncertainty envelope were in samples where the reported SHRIMP age had a sub-0.66% uncertainty, suggesting that SHRIMP analyses of untreated zircon which report smaller uncertainties are probably overoptimistic.

The mean age-offset between SHRIMP and TIMS is 0.097%, but the distribution is bimodal. Geological explanations for SHRIMP-CA-TIMS age discrepancies are uncovered by considering intrusive and extrusive age results separately. All but one sample where the SHRIMP age is more than 0.25% older are volcanic. This offset could be explained by the better single-grain age-resolution of TIMS, allowing identification and exclusion of antecrysts from the eruptive population, while SHRIMP does not have a sufficient single-grain precision to deconvolve these populations – leading to an apparent older SHRIMP age. In contrast, SHRIMP ages from plutonic rocks- particularly plutonic rocks from the early Paleozoic- are typically younger than the CA-TIMS ages from the same samples, most likely reflecting Pb loss from non-chemically-abraded SHRIMP zircons, while chemical abrasion of zircons prior to TIMS analysis destroyed or corrected these areas of Pb loss.

1 Introduction

1.1 Background and previous work

In recent decades, uranium-lead (U-Pb) geochronology has progressed from being one of many multi-grain geochronological techniques to being the most widespread and trusted method of determining deep time.

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As uranium has two long-lived isotopes, ^{235}U, and ^{238}U, there are three potential isotope ratios which can be used for radiometric dating. The $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ daughter/parent ratios directly measure the decay of the respective isotopes of uranium, and the near-constant ratio of uranium isotopes allows the $^{207}Pb/^{206}Pb$ ratio also to be used for age determination. This paper deals exclusively with the $^{206}Pb/^{238}U$ system, which is the primary uranium-lead method for the Phanerozoic.

One of the most important developments over the last 15 years has been the use of chemical abrasion on single zircons prior to isotope dilution thermal ionization mass spectrometry (CA-TIMS). CA-TIMS has yielded previously unattainable precision and accuracy in the determination of geologic time from the radioactive decay of ^{238}U to ^{206}Pb (Mundil et al. 2004, Mattinson 2005).

Since this CA-TIMS revolution, there have been relatively few recent studies of the accuracy and precision limits in Secondary Ion Mass Spectrometry (SIMS) geochronology. There are two large radius SIMS instruments which do the bulk of SIMS U-Th-Pb geochronology: The 1270/1280/1300 series (from CAMECA) and the SHRIMP I/II/RG/V series (from the Australian National University (ANU) and Australian Scientific Instruments (ASI)). In recent years, the only new work relating to the accuracy and precision of U-Pb geochronology is Jeon and Whitehouse (2014) for the 1280 instrument. There have been no recent corresponding studies for the SHRIMP. Assuming that CA-TIMS is the best method currently available to ascertain the crystallization age of igneous zircon, then comparing SHRIMP ages to CA-TIMS ages of the same zircons should give us some measure of accuracy. As CA-TIMS ages are generally about an order of magnitude more precise than SHRIMP ages, the precision of the SHRIMP analysis is the main determinant of whether the dates from the two methods agree. Thus, understanding the potential sources of uncertainty in SIMS geochronology is critically important to this study, and the history and methodology of calculating SIMS U-Pb uncertainties are reviewed below.

The chief source of uncertainty in SIMS geochronology is the method of correcting for elemental ionization differences between U and Pb in the sputtering process. The raw ionization efficiency differs by approximately a factor of three (Magee et al. 2014). This differing ionization efficiency and mass spectrometric transmission of U and Pb must be accurately determined and corrected for in each individual spot analysis in order to translate the ratio of detected Pb and U ionic species into the true ratio of U and Pb in the sample. This correction ratio is referred to in the geochronology SIMS community as the "calibration".

The calibration is generally an equation that uses the covariance between Pb ionization efficiency and high field strength element (HFSE) or actinide oxide ion production to calculate the ionization variability. Jeon and Whitehouse (2014) showed that for the 1280 model of large SIMS instrument, the calibration with the least variance correlates the Pb^+/UO^+ ratio to the UO_2^+/UO^+ ratio. However, that study does not address the issue of accuracy. Calibrations are instrument specific, and no equivalent study to Jeon and Whitehouse (2014) has been done this century for SHRIMP; Claoué-Long et al. (1995) is still the most recent calibration study for this instrument, so the $\ln(Pb^+/UO^+)$ vs $\ln(UO^+/U^+)$ calibration was used both for published SHRIMP data by the authors listed in Table 1, and for the new data we present.

Schmitt and Vazquez (2017), and Schaltegger et al. (2015), put the 2σ reproducibility of SIMS in the 1-2% to 1-3% range, respectively. In both cases, this number seems to be derived from a daisy chain of references ultimately referring to Claoué-Long et al. (1995) and/or Stern and Amelin (2003). Stern and Amelin (2003) state in the abstract that "for both glass and zircon standards, there remained on average about ± 1% (1σ) unaccounted variation per $^{206}Pb^+/^{238}U[O_x]^+$ analysis." Stern & Amelin (2003) also takes a more detailed look at the nature of the uncertainty from SHRIMP data, and how their treatment of uncertainties are applied to SHRIMP (and other SIMS) measurements today.

In summary, Stern and Amelin (2003) divide the uncertainties of SHRIMP U-Pb geochronology into three categories of "error". The first, or within spot, errors are simply the uncertainty associated with each analytical spot, and is generally associated with counting statistics, instrumental instability, and/ or sample heterogeneity on the scale of the spot (if the latter two are present). The second class of errors are the within session, or "internal errors" (Stern and Amelin 2003). The spot-to-spot error falls into this category, as it represents the additional uncertainty required to make the calibration equation statistically meaningful for the (nominally) uniform primary reference material. Finally,

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there are external errors, or errors related to comparing the results of a session to wider geochronology results. These include the standard error on the calibration constant, the uncertainty in the reference age of the zircon, and also the decay constant errors, if the U-Pb SIMS age is compared to ages from systems other than U-Pb. As this paper only discusses ^{206}Pb-^{238}U isotopic system, we will not consider decay constant errors further.

The spot-to-spot error is added to within-spot errors for zircons grouped into a given population, before those spots are grouped by population to determine the sample age and associated uncertainty (Ludwig 2001). However, because the standard error of the weighted mean is reduced by an increasing number of analyses, and the calibration constant standard error (not standard deviation) is used in the external errors, measuring a large number of spots may reduce the total reported uncertainty to below the level of the spot-to-spot error. For example, an analytical session with a 1% spot-to-spot error can have samples with grouped spot ages reported to better than 1% precision, provided that a high enough number of samples have been analysed, and that the spots in each sample are close enough in age. This feature has been overlooked by authors of recent review papers, and whether there is a fundamental limit to accuracy that precludes the use of high n sessions to improve precision is not an area which has been extensively investigated.

Jeon and Whitehouse (2015) reported that all studied SIMS calibrations on their 1280 SIMS instrument yielded ages of their secondary Temora-2 (Black et al. 2004) zircon that were accurate to within 1% of the reference value. In contrast, Metcalfe et al. (2015) describe the SHRIMP geochronology of Eastern Australia's Permo-Triassic basins as "unreliable", especially older data analysed by university SHRIMP instruments using the SL13 reference zircon. In contrast, Laurie et al. (2016) show that zircons from the same geologic province (and in some cases, the same samples as Metcalfe et al. (2015)) analysed by the Geoscience Australia SHRIMP using the Temora-2 reference zircon (Black et al. 2004) instead of SL13, are generally within 1% (at the 95% confidence level) of the CA-TIMS ages. Understanding how such discrepancies can arise requires a brief overview of the physical mechanisms of each analytical technique.

In order for geochronology to preserve a crystallographic formation age, both the daughter and parent isotopes must remain locked in the crystal lattice. Thus Pb loss from zircon due to crystallographic damage is a major confounding factor in high-precision zircon dating. Chemical abrasion preferentially removes damaged zircon which may have suffered Pb loss; Mundil et al. (2004) show that the CA-TIMS procedure increases the apparent age of some zircons by approximately 4%, due to the removal of the areas which have suffered Pb loss. Several attempts at analyzing zircons before and after chemical abrasion using SIMS show similar changes in age from chemical abrasion, which range from 4% to undetectable (Kryza et al. 2012, Kryza et al. 2014, Watts et al. 2016).

How often rectification of Pb loss by chemical abrasion exceeds the precision of the SIMS analysis is then a key issue as to whether SIMS dating of untreated zircon yields the CA-TIMS age. This depends on two things; the prevalence of zircons with Pb loss which cannot be corrected or avoided by spot placement, and the magnitude of that Pb loss relative to the precision of the SIMS analytical method.

The CA-TIMS method works by dissolving all of the zircon where crystallographic lattice damage is sufficient to allow Pb loss prior to analysis (Mundil et al. 2004, Mattinson et al. 2005, Huyskens et al. 2016, Widmann et al. 2019). When these areas of damage are not removed, such as in untreated, natural zircon, the inclusion of these damaged areas in the analytical volume can yield an erroneous (usually younger) age, if the lattice damage has allowed Pb loss. When analysing natural zircon, SIMS operators aim to use optical, compositional, and/or cathodoluminescence imagery of zircon to avoid these damaged areas, and instead target undamaged zircon by using the ion beam to extract a small (<1000 μm3) volume of the best-looking near-surface (~1 μm) material for analysis. So if a zircon has lost Pb from damaged areas sufficient to change the age beyond the precision of the SIMS analytical technique, and if the SIMS analyst cannot identify and avoid these areas, then we would expect the SIMS age to be younger than the CA-TIMS age.

In addition to this isotopic disturbance issue, comparing U-Pb ages from TIMS and SIMS requires that zircon from the same zircon crystallization event is dated by both methods. The small volume of individual SIMS analyses, combined with the 1-2% useful yield of Pb

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ions (Magee et al. 2014) in SHRIMP, means that multiple spot analyses need to be performed to build up the counting statistics necessary for a precise date. The SIMS sputter crater erodes the conductive gold coat on the SHRIMP mount, and zircon is not a conductor, so old SIMS sputter craters can build up electric charge. This charge can change the ion extraction trajectories from nearby craters in a way that fractionates U and Pb ions. As a result, SHRIMP spots generally need to be spaced out to a degree (e.g. 10 to 20 µm of gold between rastered areas) such that the several dozen spots which are to be pooled to calculate a date need to be placed on different zircon grains. If these grains crystallized in different geologic events (such as a volcanic eruption entraining older zircons from previous magmatic pulses), and the analyst is unable to determine this visually, then the calculated date will be a mixture of two geologic ages. This is particularly problematic in intermediate to silicic volcanic rocks, where zircons from early volcanic events in the lifecycles of the volcanic edifice can be mixed in with zircons from later explosive eruptions. In the Phanerozoic, CA-TIMS has the precision to differentiate between sub-million year events of this type, while SIMS does not. As the Metcalfe et al. (2015) and Laurie et al. (2016) papers studied Permian silicic volcanic rocks, the presence of antecrysts in some of their samples may explain their differing interpretations of SHRIMP-TIMS comparison. Thus there is at least one analytical (the uncertainty surrounding the mechanism and reliability of the calibration equation) and two geological (lead loss and multiple indistinguishable crystallization events) problems which could result in TIMS-SHRIMP discrepancies.

As a result of the Metcalf et al. (2015) and Laurie et al. (2016) studies, as well as other projects distributed throughout the Palaeozoic and Mesozoic, Geoscience Australia has access to a large amount of accurate, high precision CA-TIMS geochronology data for the Phanerozoic. In addition, our SHRIMP laboratory, now in its thirteenth year of operation, has a database of zircon samples dated by SHRIMP. Cross-referencing samples dated by both techniques allows us to assess the accuracy of the SHRIMP U-Pb ages generated in our laboratory, relative to the CA-TIMS method. This study consists of 35 samples- considerably more than the seven double dated samples from Metcalf et al. (2015) or the nine (four of which were repeats from Metcalfe et al. (2015)) from Laurie et al. (2016). Thirty-two of the 35 ages were reported with external SHRIMP errors less than 1%, so this study will provide an assessment as to whether reporting sub-percent level uncertainty can drive SHRIMP-TIMS age differences outside their respective uncertainties. As the samples in our database were collected for geologic reasons, and not as potential reference zircons, this study allows us to assess the precision and accuracy of SHRIMP U-Pb geochronology "in the wild" from rock types and geologic units which are pertinent to current geologic questions.

1.2 Sample descriptions

Geoscience Australia databases were searched for samples measured by both SHRIMP and TIMS. TIMS ages acquired before the adoption of chemical abrasion were not used. Neither were data on reference zircons. SHRIMP data was limited to that taken on the SHRIMP IIe at Geoscience Australia between 2008 and 2015. All SHRIMP data used the Temora-2 zircon as the primary U-Pb reference material, and the Black et al. (2004) U/Pb age of 416.8 Ma as the reference age for that zircon. All 35 samples found were Phanerozoic, and just over half (18) were Permian, illustrating the importance of Permian coal deposits in Australian stratigraphic research.

All GA sample numbers presented here refer to zircon-rich heavy mineral separates which were concentrated by the Geoscience Australia mineral separation laboratory. In some cases grains selected for TIMS analysis were plucked directly from the SHRIMP mount. In others they were selected from the same zircon-rich heavy mineral separation fraction from which the SHRIMP mount zircons were picked.

The zircons dated by both SHRIMP and CA-TIMS in this study are summarized in Table 1, and come from the following previous work:

There are a total of 19 Permian-to-early Triassic samples, roughly half of which are from volcanic units in Eastern Australia coal deposits. Nine samples had Permian to lower Triassic CA-TIMS and SHRIMP dates published in Laurie et al. (2016). A further three samples had

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Permian CA-TIMS dates published in Metcalf et al. (2015), but were not included in Laurie et al. (2016). Both of these studies use high precision CA-ID-TIMS to constrain a variety of biostratigraphic problems, including absolute ages for stage boundaries in Australia, Correlation between basins, and temporal correlation between the East Coast coal basins and marine sequences in Western Australia. Samples GA1978294, GA1978295, and GA1978296 are tuffs in the Lightjack Formation from commercial drill core in the Canning Basin. Samples GA2000865, GA2000869, and GA2122750 are tuffs in the Kaloola member of the Bandanna Formation from two commercial drill holes in the Bowen Basin. Sample GA2122736 is a tuff from the Tinowon Formation in one of the same Bowen Basin holes. There are five samples from four separate commercial drill holes and a road cut in the Sydney Basin. The four drill holes, all from the Hunter region, are: Sample GA2005145, the Nalleen Tuff Member, sample GA2031207, a tuff from the Rowen Formation, GA2031203 from the Awaba Tuff Member of the Newcastle Coal Measures, and GA2031204 from the Nobbys Tuff Member of the Newcastle Coal Measures. Sample GA2005209 is from Garie Formation, sampled from a road cut near Wollongong. We publish the SHRIMP data for all the above samples which were not in Laurie et al. (2016).

Three Permian SHRIMP ages from Cross and Blevin (2010) and Brownlow and Cross (2010) were originally published using data reduced with the SQUID 1 data processing software (Ludwig 2001). These have been reprocessed in Squid 2 (Ludwig 2009). The reprocessed SHRIMP data are presented here. Sample GA1683223 is the Dundee Rhyodacite, a volcanic unit at the top of the Wandsworth Volcanic Group, which was dated by SHRIMP and TIMS to resolve issues with an old Rb/Sr date placing it in the Triassic. The Brownlow and Cross (2010) ID-TIMS age predates the adoption of chemical abrasion at UBC, and is not considered further. Samples GA1954029, Parlour Mountain Leucomonzogranite and GA1954030, the Gwydir River Monzogranite (originally called an adamellite in Cross and Blevin (2010)) both intrude the Wandsworth Volcanics, and thus provide a youngest constraint for that group (Cross and Blevin 2010). CA-ID-TIMS data for all these samples appear in Chapman et al. (2022).

The Wandsworth Volcanic Group was later directly dated, and four dates are presented here. Three geographically widely dispersed samples of the Wandsworth Volcanic Group (GA2120074, GA2120076, and GA2120077) have SHRIMP dates by Chisholm et al. (2014). An additional sample of the Emmaville Volcanics, also part of the Wandsworth Volcanic Group, had a SHRIMP date published by Cross and Blevin (2013). The CA-ID-TIMS data for all Wandsworth Volcanic Group samples are in Chapman et al. (2022).

There are six Devonian samples in this study. Five are felsic volcanic rocks from the Hill End Trough region of eastern Australia, selected for SHRIMP and CA-TIMS analysis based on their good biostratigraphic control and relevance to the Geologic Time Scale (Bodorkos et al., 2012, 2017; see also Gradstein et al., 2020). In the Cowra Trough, the Bulls Camp Volcanics (sample GA1594761) are of earliest Lochkovian age, as the unit is conformably underlain by a terminal Silurian graptolite assemblage, and overlain by rocks containing middle-Lochkovian conodonts (Pogson and Watkins 1998). In the Hill End Trough, a middle Lochkovian age is indicated for the lower Turondale Formation (sample GA1528019; Jagodzinski and Black 1999), because the upper part of the unit incorporates 'detrital' conodonts of late Lochkovian age in allochthonous limestone blocks (Packham et al. 2001). Overlying the Turondale Formation is the Merrions Formation, with three samples from its type-section (samples GA1528025, GA1528027, and GA1530245; Jagodzinski and Black 1999) each assigned an early Pragian age, based on the presence of Pragian index fossils in overlying sedimentary strata (Packham et al. 2001). Although Bodorkos et al. (2012, 2017) summarised these CA-TIMS and SHRIMP dates in abstract form, the underlying analytical data are presented here for the first time. Unusually for SHRIMP data, Bodorkos et al. (2012) presented these dates with an uncertainty envelope which included the uncertainty on the Temora-2 reference ID-TIMS age (see uncertainty treatment section below for details).

The sixth Devonian sample is the subvolcanic porphyritic Yithan Rhyolite (GA2097849), which is associated with tin mineralisation in the Central Lachlan Orogen. Bodorkos et al. (2013) published the SHRIMP results; the CA-TIMS data are presented here.

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Lewis et al (2015; 2016) undertook geochronological analysis eight compositionally diverse igneous rocks associated with the Cambrian Mount Stavely Volcanic Complex to better understand the chronology of felsic-intermediate magmatism in the Grampians-Stavely Zone. GA2254431 and GA2254432 are samples of the Buckeran Diorite; a medium-coarse grained, equigranular, hornblende-bearing diorite that intrudes the Glenthompson Sandstone. Samples GA2254430 and GA2254436 are from the the Bushy Creek Granodiorite; a variably medium to coarse grained, generally equigranular, slightly quartz-phyric to biotite-bearing granodiorite that intrudes the Glenthompson Sandstone. Samples GA2167510, GA2169175, and GA2172148 are all various subvolcanic porphyritic dacites (both molybdenite-bearing and barren) that cross cut the deformed co-magmatic Mount Stavely Volcanic Complex and older Glenthompson Sandstone. Finally GA1486519, the Narrapumelap Road Dacite Member, is a dark pink-grey dacitic to rhyolitic lava within the Towanway Tuff—part of the Mount Stavely Volcanic Complex. . Lewis et al. (2015, 2016) published SHRIMP ages and CA-TIMS summaries, while the details of the CA-TIMS analyses are presented here.

In addition to these samples, new data using both SHRIMP and CA-TIMS are presented from two unrelated samples.

Sample GA2121671 is a calcilutite from exploration hole, Alaric 1 (2890-2940 mRT), in the Northwest Shelf, Western Australia. This interval was originally logged as Triassic age. Upon further micropaleontological analysis, the sampled interval intersects Triassic to Cretaceous strata, where the top of the core section is interpreted as Cretaceous-aged Forestier Claystone, while the bottom is interpreted as Triassic-aged Mungaroo Formation (Helby et al. 2004). The interval yielded Cretaceous zircon with no signs of sedimentary transport.

Sample GA1977984 is the nominally Ordovician Saddington Tonalite, in Queensland. The Saddington Tonalite is a term used to group felsic intrusions of the Gray Creek Complex and Judea Formation which range from diorite to tonalite (Henderson et al. 2011). This sample was dated to supersede an unpublished laser date with multiple age populations.

2 Methods

2.1 Analytical methodology

2.1.1 SHRIMP analytical methodology

The 35 samples whose data are presented here were analysed in a total of 16 different SHRIMP analytical sessions, run by seven different operators, between 2008 and 2015. Additional details for published work are given in the references listed in Table 1. Session-specific information is given in Table 2. In general, the SHRIMP configuration was typically a 1.6-2.5 nA O_2^- beam on the Primary Beam Monitor (PBM), which measures net sample current (generally 1.6 times the true primary beam in zircon, when positive secondary ions are extracted). The mass filtered primary beam is projected through a 100 µm aperture to form a ~14x20 µm evenly illuminated spot on the zircon. Although pit depths were not directly measured, the pit depth measurements from Magee et al. (2014) from this instrument running under the same analytical conditions yield a sputter rate for a 100 µm Köhler aperture of 0.34 nm s^{-1} nA^{-1} of O_2^- primary beam, meaning that the sputtering craters were generally 700-1000 nm deep, with occasional depths as little as 500 nm or as much as 1350 nm.

The secondary mass spectrometer was set up with a 110 µm source slit and a 100 µm collector slit, yielding an average mass resolution of about 5000 at the 1% level for Pb isotope peaks. HfO_2^+ was resolved from Pb^+ to within the limits of detection. The energy window was approximately -40 to +55 electron volts, relative to the 10 keV secondary acceleration energy.

In most analytical sessions, the magnet cycled through 10 mass stations 6 times. The masses corresponded to the following species: $^{90}Zr_2{}^{16}O$; ^{204}Pb; Background (^{204}Pb+0.05 amu); ^{206}Pb; ^{207}Pb; ^{208}Pb; ^{238}U; $^{248}Th^{16}O$; $^{254}U^{16}O$; $^{270}U^{16}O_2$. Count times were generally 20 seconds for ^{204}Pb and background, 15 seconds for ^{206}Pb, 40 seconds for ^{207}Pb, and 2-5 seconds on all other peaks. Additional mass stations and altered

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count times were used in session 110088 (Magee et al. 2017). A calibration slope of two was used for all sessions except 90001 (slope 1.52) and 100127 (slope = 1.77). Common Pb was corrected for using either the ^{207}Pb (assuming concordance) or the ^{204}Pb isotope, with ^{204}Pb generally preferred for older zircons, and ^{207}Pb for younger ones.

2.1.2 TIMS methodology

For the TIMS dates from Boise State University, U-Pb dates were obtained by the chemical abrasion isotope dilution thermal ionization mass spectrometry (CA-TIMS) method, modified after Mattinson (2005), from analyses composed of single zircon grains. Zircon picked from mounts or separates provided by Geoscience Australia was placed in a muffle furnace at 900°C for 60 hours in quartz beakers.

Zircon was put into 3 ml Teflon PFA beakers and loaded into 300 µl Teflon PFA microcapsules. Fifteen microcapsules were placed in a large-capacity Parr vessel and the zircon partially dissolved in 120 µl of 29 M HF for 12 hours at 180°C or 190°C. Zircon was returned to 3 ml Teflon PFA beakers, the HF was removed, and zircon was immersed in 3.5 M HNO_3, ultrasonically cleaned for an hour, and fluxed on a hotplate at 80°C for an hour. The HNO_3 was removed and zircon was rinsed twice in ultrapure H_2O before being reloaded into the 300 µl Teflon PFA microcapsules (rinsed and fluxed in 6 M HCl during sonication and washing of the zircon) and spiked with the Boise State University mixed ^{233}U-^{235}U-^{205}Pb tracer solution (BSU-1B) or EARTHTIME mixed ^{233}U-^{235}U-^{205}Pb tracer solution (ET535). Zircon was dissolved in Parr vessels in 120 µl of 29 M HF with a trace of 3.5 M HNO_3 at 220°C for 48 hours, dried to fluorides, and re-dissolved in 6 M HCl at 180°C overnight. U and Pb were separated from the zircon matrix using an HCl-based anion-exchange chromatographic procedure (Krogh, 1973), eluted together and dried with 2 µl of 0.05 N H_3PO_4.

Pb and U were loaded on a single outgassed Re filament in 5 µl of a silica-gel/phosphoric acid mixture (Gerstenberger and Haase, 1997), and U and Pb isotopic measurements made on a GV Isoprobe-T multicollector thermal ionization mass spectrometer equipped with an ion-counting Daly detector. Pb isotopes were measured by peak-jumping all isotopes on the Daly detector for 100 to 160 cycles and corrected for 0.16 ± 0.03%/a.m.u. or 0.18 ± 0.03%/a.m.u. (1σ) mass fractionation. Transitory isobaric interferences due to high-molecular weight organics, particularly on ^{204}Pb and ^{207}Pb, disappeared within approximately 60 cycles, while ionization efficiency averaged 10^4 cps/pg of each Pb isotope. Linearity (to ≥1.4 x 10^6 cps) and the associated deadtime correction of the Daly detector were monitored by repeated analyses of NBS982. Uranium was analyzed as UO_2^+ ions in static Faraday mode on 10^{12} ohm resistors for 300 cycles, and corrected for isobaric interference of $^{233}U^{18}O^{16}O$ on $^{235}U^{16}O^{16}O$ with an $^{18}O/^{16}O$ of 0.00206. Ionization efficiency averaged 20 mV/ng of each U isotope. U mass fractionation was corrected using the known $^{233}U/^{235}U$ ratio of the tracer solution.

U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007), calibration of BSU-1B tracer solution of $^{235}U/^{205}Pb$ of 77.93 and $^{233}U/^{235}U$ of 1.007066, calibration of ET535 tracer solution (Condon et al., 2015) of $^{235}U/^{205}Pb$ = 100.233, $^{233}U/^{235}U$ = 0.99506, and $^{205}Pb/^{204}Pb$ = 11268, U decay constants recommended by Jaffey et al. (1971), and $^{238}U/^{235}U$ of 137.818 (Hiess et al., 2012). $^{206}Pb/^{238}U$ ratios and dates were corrected for initial ^{230}Th disequilibrium using $D_{Th/U}$ = 0.20 ± 0.05 (1σ) and the algorithms of Crowley et al. (2007), resulting in an increase in the $^{206}Pb/^{238}U$ dates of ~0.09 Ma. All common Pb in analyses was attributed to laboratory blank and subtracted based on the measured laboratory Pb isotopic composition and associated uncertainty. U blanks are estimated at 0.013 pg.

Weighted mean $^{206}Pb/^{238}U$ dates are calculated from equivalent dates (probability of fit >0.05) using Isoplot 3.0 (Ludwig, 2003). Errors on weighted mean dates are given as ± x / y / z, where x is the internal error based on analytical uncertainties only, including counting statistics, subtraction of tracer solution, and blank and initial common Pb subtraction, y includes the tracer calibration uncertainty propagated in quadrature, and z includes the ^{238}U decay constant uncertainty propagated in quadrature. Internal errors should be considered when comparing our dates with $^{206}Pb/^{238}U$ dates from other laboratories that used the same tracer solution or a tracer solution that was cross-

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calibrated using EARTHTIME gravimetric standards. Errors including the uncertainty in the tracer calibration should be considered when comparing our dates with those derived from other geochronological methods using the U-Pb decay scheme (e.g., laser ablation ICPMS). Errors including uncertainties in the tracer calibration and ^{238}U decay constant (Jaffey et al., 1971) should be considered when comparing our dates with those derived from other decay schemes (e.g., $^{40}Ar/^{39}Ar$, ^{187}Re-^{187}Os). The 2σ uncertainties were converted to 95% confidence intervals after data delivery to Geoscience Australia in the same manner as the UBC TIMS data, whose analytical method is described next.

For the TIMS analyses performed at the University of British Columbia, the methodology was modified from what is described in Scoates & Friedman (2008). Individual zircon crystals were placed in a muffle furnace at 900°C for 60 hours in quartz beakers to anneal minor radiation damage and prepare the crystals for subsequent chemical abrasion (Mattinson, 2005). Zircon crystals were subjected to a modified version of the chemical abrasion method of Mattinson (2005), whereby single crystal fragments were individually abraded in a single step with concentrated HF. Zircon was put into 3 ml Teflon PFA beakers, rinsed in 3.5 M HNO_3 three times before being and loaded into 300 µl Teflon PFA microcapsules. Microcapsules were then placed in a large-capacity Parr vessel and the zircon partially dissolved in 100 µl of 29 M HF for 12 hours at 180°C. Zircon was returned to 3 ml Teflon PFA beakers, HF was removed, and zircon was immersed in 6 M HCl, ultrasonically cleaned for 30 minutes, and fluxed on a hotplate at 80°C for an hour. Zircon was dissolved in Parr vessels in 120 µl of 29 M HF with a trace of 3.5 M HNO_3 at 220°C for 48 hours, dried to fluorides, and re-dissolved in 6 M HCl at 180°C overnight. Solutions were subsequently dried down with 2 µl of 0.05 N H_3PO_4 and are ready for mass spectrometry.

Pb and U were loaded on a single outgassed zone-refined Re filament in 2 µl of a silica-gel/phosphoric acid mixture (Gerstenberger and Haase, 1997), and U and Pb isotopic measurements made on a VG Sector 54S thermal ionization mass spectrometer with Sector 54 electronics equipped with an analog Daly detector. Pb isotopes were measured by peak-jumping all isotopes on the Daly detector for 100 cycles and corrected for 0.18 ± 0.05%/a.m.u. (1σ) mass fractionation from repeated measurements of NBS-982. Transitory isobaric interferences due to high-molecular weight organics, particularly on ^{204}Pb and ^{207}Pb, disappeared within approximately 60 cycles and monitored on masses ^{201}Pb and ^{203}Pb. Uranium was analyzed as UO_2^+ ions by peak-jumping all isotopes on the Daly detector for 100 cycles and corrected for isobaric interference of $^{233}U^{18}O^{16}O$ on $^{235}U^{16}O^{16}O$ with an $^{18}O/^{16}O$ of 0.00206. U mass fractionation was corrected using the known $^{233}U/^{235}U$ ratio of the tracer solution.

U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007), calibration of ET535 tracer solution (Condon et al., 2015) of $^{235}U/^{205}Pb$ = 100.233, $^{233}U/^{235}U$ = 0.99506, and $^{205}Pb/^{204}Pb$ = 11268, U decay constants recommended by Jaffey et al. (1971), and $^{238}U/^{235}U$ of 137.818 (Hiess et al., 2012). $^{206}Pb/^{238}U$ ratios and dates were corrected for initial ^{230}Th disequilibrium using a Th/U in the magma of 3. All common Pb in analyses was attributed to laboratory blank and subtracted based on the measured laboratory Pb isotopic composition and associated uncertainty. U blanks are estimated at 0.020 pg. Weighted mean $^{206}Pb/^{238}U$ dates are calculated from equivalent dates (probability of fit >0.05) using Isoplot 3.0 (Ludwig, 2003).

To make uncertainty treatments of all TIMS results consistent with those from Laurie et al. (2016), the uncertainty of the weighted mean was multiplied by the square root of the MSWD, if it was greater than 1, and Student's t, which resulted in an increased uncertainty envelope. This is especially pronounced for those samples where there were only three grains in the mean.

2.2 SHRIMP uncertainty treatment

For the TIMS analyses, the reported uncertainty includes the analytical uncertainty as well as the spike uncertainty (as the data reported here originate from two labs). For the SHRIMP analyses, the reported uncertainty includes the analytical uncertainty of the unknowns, the session mean (the standard error of the individual spot calibration constant measurements made on the reference zircon Temora-2), and the

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uncertainty on the reference age assigned to the Temora-2 (Black et al. 2004) reference zircon. This is calculated by adding twice the 1σ spike uncertainty (2 x 0.13% = 0.26%) in quadrature to the analytical uncertainty (0.08%) reported by Black et al. (2004), yielding a reference zircon value of 416.78 ± 1.13 Ma (an uncertainty of 0.27%). As the uncertainty of reference values of reference materials is rarely incorporated into published uncertainty, the 95% confidence envelopes presented in this paper may differ to those in the original sources. As all measurements take place within the U-Pb system, no uncertainties associated with the ^{238}U or ^{235}U decay constants are propagated. In all cases, the SHRIMP uncertainty is substantially larger than that from CA-TIMS. The additional 0.707% error incorporated into the Laurie et al. (2016) uncertainties in not included here, as that error covered differences between SHRIMP instruments at different institutions, and the use of different reference zircons. Because all SHRIMP data in this paper were produced at Geoscience Australia using Temora-2 as the primary reference material, this error enhancement serves no purpose, and may obscure subtle systematic effects which we hope to observe. Thus the uncertainties shown in this study are smaller than those reported in Laurie et al. (2016) for the same SHRIMP data.

There are four CA-TIMS analyses whose ages were published by both Metcalf et al. (2015) and Laurie et al. (2016). Although both papers report numbers from the same analytical sessions, the reported numbers differ because of differences in the reporting of uncertainties (2 σ vs 95% confidence determined using Student's t and sqrt MSWD where greater than 1). We use the Laurie et al. (2016) numbers as the uncertainty calculated using Student's t is more robust. For those samples where the TIMS data has not yet been published, the results are listed in the results section, below. The full datasets for both the new TIMS data and the new SHRIMP data are in the electronic data tables (see results section for details).

3 Results

3.1 CA-TIMS ages

CA-TIMS analyses of 5-12 individual single zircon crystals from the zircon concentrates from each sample yielded groups of 3-12 concordant grains. These were interpreted as the igneous age of the zircons samples. Only four of the 35 samples had younger outliers, consistent with the hypothesis that chemical abrasion removes zircon which has suffered lattice damage sufficient to cause Pb loss. In contrast, 19 of the samples had inherited grains. Two of the eleven intrusive rocks had inherited grains, as did 17 of the 24 volcanic rocks. This is consistent with the observation in modern volcanoes that zircon ages in any given eruption span the range of the volcanic edifice (Claiborne et al. 2010), and that CA-TIMS dating is sufficiently precise that Palaeozoic zircons hundreds of thousands of years older than the igneous population may be resolvable. Full data from Boise State University are presented in electronic Table S1, while UBC data are presented in electronic Table S2. The new TIMS ages (n = 16) are summarized in the text below to make them more easily searchable in the literature.

3.1.1 Mesozoic Northwest Shelf

CA-TIMS results from 7 of 9 zircons from a ditch cuttings sample from the North West Shelf Alaric 1 drillhole (GA2121671) yield an age of 139.15 ± 0.09 Ma (Table S-1). The c. 139 Ma zircon age is inconsistent with the Triassic (252-201 Ma) age originally assigned to the core based on microfossils low in the section. If the zircons are from an unrecognised ash-fall layer, then the c. 139 Ma age is the age of deposition. If they are detrital, it is a maximum deposition age. The minimum age, as defined by dinocysts (Helby et al. 2004) in overlying cuttings samples (2655–2720 mRT and 2870–2900 mRT)—upper to lower Batioladinium reticulatum Zone (c. 141.4–140.2 Ma) and upper Cassiculosphaeridia delicata Zone (143.6–142.6 Ma), respectively—is Berriasian.

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Although this stratigraphy appears at first glance to be inverted, the age- stratigraphy correlations of Helby et al. (2004) predate the invention of CA-TIMS. So it is possible that their calibration of fossil stratigraphy to radiometric time calibration is based on obsolete isotopic geochronological measurements. More recently, Lena et al (2019) bracket the Jurassic/Cretaceous boundary at between 140.7 and 140.9 Ma using CA-TIMS, almost 5 million years younger than Helby et al. (2004), and putting our 139.15 Ma age comfortably in the early Berriasian.

330 **3.1.2 Devonian (Bodorkos et al. (2012)**

Bodorkos et al. (2012) presented the comparison of five SHRIMP and TIMS ages in abstract form. The complete CA-TIMS data from that report are given here.

Five zircons from the Bulls Camp Volcanics (GA1594761) yield a group of three concordant ages and two analyses interpreted to have been affected by Pb loss. (Table S-2-B) The three concordant grains yield an age of 417.75 ± 0.88 Ma.

335 Six zircons from the Turondale Formation (GA1528019) yield an age of 415.56 ± 0.51 Ma (Table S-2-C).

Five zircons from the Merrions Formation (GA1528025) yield two older concordant ages which are interpreted as inherited and three younger grains with a combined age of 412.73 ± 0.96 Ma (Table S-2-D).

Six zircons from the Merrions Formation (GA1528027) yield two older ages, and a group of four concordant analyses with a combined age of 411.71 ± 0.89 Ma. (Table S-2-E).

340 Five zircons from the Merrions Formation (GA1530245) yield a group of four concordant ages and one younger, less precise zircons which is interpreted as having lost Pb (Table S-2-F). The four older grains yield a combined age of 413.76 ± 0.76 Ma.

3.1.3 Other Devonian

Seven of eight zircons from GA2097849 (Yithan Rhyolite) yielded an age of 414.27 ± 0.26 Ma (Table S-1).

3.1.4 Ordovician

345 Six chemically abraded zircons from the Saddington Tonalite (GA1977984) yield a weighted mean $^{206}Pb/^{238}U$ age of 487.07 ± 0.70 Ma (Table S-2-A). Henderson et al. (2011) describe the Saddington Tonalite as a suite of diorite to tonalite intrusions of the Bendigonian graptolite-bearing Judea Formation, and the older Gray Creek formation. The Bendigonian corresponds to the middle Floian in the ICS 2020 timescale (Gradstein et al. 2020). The age of 487.07 ± 0.70 Ma is within uncertainty of the Cambrian-Ordovician boundary, so further work on the geochronology, stratigraphy, and contact relationships of this region may be required, as this particular sample is young enough to
350 intrude the Gray Creek formation, but not the Judea Formation.

3.1.5 Cambrian Stavely

Sample GA2254430, the Bushy Creek Granodiorite, yielded a CA-TIMS age of 501.55 ± 0.31 Ma from six of seven zircons (Table S-1).
Sample GA2254436, the Bushy Creek Granodiorite, yielded a CA-TIMS age of 501.65 ± 0.29 Ma from six of six zircons (Table S-1).
Sample GA2254431, the Buckeran Diorite, yielded a CA-TIMS age of 504.83 ± 0.30 Ma from eight of eight zircons (Table S-1).
355 Sample GA2254432, also the Buckeran Diorite, yielded a CA-TIMS age of 505.00 ± 0.36 Ma from seven of seven zircons (Table S-1).

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Sample GA1486519, the Narrapumelap Road Dacite Member, yielded a CA-TIMS age of 507.21 ±0.39 Ma from seven of eight zircons (Table S-1).

Sample GA2167510, the 'Victor Porphyry', yielded a CA-TIMS age of 504.17 ± 0.31 Ma from five of six zircons (Table S-1).

Sample GA2169175, also the 'Victor Porphyry', yielded a CA-TIMS age of 503.80 ± 0.29 Ma from six of six zircons (Table S-1).

Sample GA2172143, a molybdenite porphyry, yielded a CA-TIMS age of 504.53 ± 0.31 Ma from eight of eight analyses (Table S-1).

3.2 SHRIMP ages

The 35 SHRIMP ages compiled in this paper were obtained in a total of 16 SHRIMP sessions. Data from twelve of those sessions have been previously published. Of those, two (80101 and 80104) were originally published using SQUID1 data reduction software (Ludwig 2001). These have been reprocessed using SQUID 2 (Ludwig 2009). The details of the samples and sessions are in Table 1 and Table 2. The spot by spot results for new data are in Table S3, and the final ages with comparisons are in Table 3. SHRIMP ages are not listed in the text as we feel the TIMS ages are more appropriate as ages of record for these samples. Additional information is available in the Geoscience Australia Geochronology Delivery Service: http://www.ga.gov.au/geochron-sapub-web/geochronology/shrimp/search.htm

4 Discussion

4.1 Summary of SHRIMP-TIMS comparison

Figure 1 and Table 3 show 35 samples for which U-Pb dates have been determined using both SHRIMP and CA-TIMS. The difference (SHRIMP age – TIMS age) per sample is given in terms of Ma, percent of the total CA-TIMS age, and number of SHRIMP 95% confidence intervals. The SHRIMP confidence interval is used because the mean SHRIMP 95% confidence interval is almost eight times larger than the mean CA-TIMS 95% confidence interval, and therefore dominates the uncertainty. In eight of the 35 samples, the TIMS age lay beyond the SHRIMP 95% confidence interval. In five of these the SHRIMP age was younger, and in three the SHRIMP age was older than the TIMS age. The average 95% confidence interval for all 35 SHRIMP results was 0.72%, while the average for the 8 samples where the TIMS age lay outside that interval was 0.66%. This suggests that the SHRIMP confidence intervals are optimistic, as the expected number of the 35 samples to lie outside the 95% confidence interval is 35 x 0.05 = 1.75.

Of the three samples where the reported SHRIMP uncertainty envelope was greater than 1%, one sample had a TIMS age outside the SHRIMP uncertainty envelope (33%). Of the six samples with a SHRIMP uncertainty between 1% and 0.75%, none had TIMS ages outside the uncertainty envelope (0%). Of the 24 samples where the SHRIMP uncertainty envelope was between 0.75% and 0.5%, six TIMS ages were outside the SHRIMP uncertainty envelope (25%). Of the two samples where the reported uncertainty envelope was less than 0.5%, one had a TIMS age outside the SHRIMP uncertainty envelope (50%). In summary, six of the eight cases where the TIMS age lay outside the uncertainty envelope of the SHRIMP data had reported SHRIMP uncertainties of less than 0.66%. This suggests that reported SHRIMP uncertainties below two thirds of a percent are increasingly likely to be inaccurate as the 95% confidence envelope contracts. Possible reasons for this, and potential approaches to overcome this barrier are discussed below.

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4.2 Possible explanations and approaches

4.2.1 Primary beam species

GA2122736 and GA2122750 were analysed on the SHRIMP using an $^{18}O_2^-$ primary beam instead of a $^{16}O_2^-$ beam (Magee et al. 2014, Magee et al. 2017). This does not seem to have resulted in any statistically meaningful change in the SHRIMP result accuracy relative to CA-TIMS, compared to the other 33 samples, which were analysed using $^{16}O_2^-$, as both are within the offset range of the samples measured using $^{16}O_2^-$. Thus we discount this as a factor in the observed offsets.

4.2.2 Outlier discussion

In only two samples did the SHRIMP and TIMS ages differ by more than 1%. One of these, sample GA2031207, is a Guadalupian tuff from the Rowan Formation, with a TIMS age of 271.60 ± 0.13 Ma, where the SHRIMP date is younger, at 268.7 ± 1.9 Ma. An earlier analysis of a similar sample on an older SHRIMP using the SL13 reference zircon gave a similar age-offset (Roberts et al. 1996; Laurie et al. 2016). Wu et al. (2017) find that Kuhfeng Formation (Yangtze Basin, China) samples with 272.95-271.04 Ma CA-TIMS age ranges also come out 1.4% and 1.6% younger when dated by SIMS (a CAMECA 1280, not an ASI SHRIMP). Wu et al. (2017) interpret this as Pb loss which is remediated by chemical abrasion, but which was not avoided by placing ion probe spots on what appear to be undamaged zones of the zircons when viewed in cathodoluminescence or photomicroscopy. The Rowan Formation was deposited between the P2 and P3 Permian glaciations (Metcalfe et al. 2015). In addition to being synchronous, the Rowan Formation and the Kuhfeng Formation are both marine sediments overlain by coal-bearing terrestrial sediments. Perhaps there are diagenetic effects in this sort of environment which would result in Pb loss from zircon for 3-5 million years after deposition. This would suggest a geological, not analytical problem, which is confounded by comparing chemically abraded ages to SIMS analyses of natural zircon.

Sample GA1978296, from the Canning Basin, is 6 Ma, (2.2%) older by SHRIMP than by CA-TIMS. We have no explanation for this, and that result seems to be an inexplicable outlier (Figure 1). Our only suggestion is that we analysed relatively few (n=7) zircons by SHRIMP, so may not have had the statistics to understand the U-Pb systematics of this sample.

4.2.3 Age difference probability density

Figure 2 shows that the distribution of the SHRIMP-TIMS age, expressed in percent, is not Gaussian. Rather, it is bimodal, with approximately two-thirds of the SHRIMP ages up to 0.75% older, and approximately one-third between 0.25 and 1% younger. Including the uncertainties of these differences yields a skewed probability density function. Grouping all 35 samples into a single population requires an excess external (sample to sample) 2σ error of 0.77%. Added to the lowest SHRIMP uncertainty of 0.47% yields a minimum 2σ confidence interval of ± 1.24%. This is within the range of 1-2% uncertainty stated by Schmitt and Vazquez (2017). However, the curve clearly contains at least two populations (not including the outliers mentioned above), so the mean accuracy is not a particularly meaningful statistic.

Figure 2 shows that the grains where the SHRIMP age is older are predominantly Permian, where the grains with older TIMS ages include most of the Cambrian grains. Figure 3 plots the age of the grains vs the percent difference (SHRIMP minus TIMS), and shows a reasonable linear regression. Although not perfect, removal of the two >1% outliers described above p-hacks the probability of fit to 0.29. Additionally, the zero intercept is quite close to the age of the Temora 2 reference zircon age. This could be interpreted as suggesting that there is a time-dependent linear mismatch between SHRIMP and TIMS. However, such an interpretation would be erroneous, for the following reasons.

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4.2.4 Refutation of linear TIMS-SHRIMP age offset

Most SHRIMP geochronology reported in the scientific literature is used for samples from the Precambrian, not Phanerozoic. Extrapolation of this linear trend into the Precambrian (Figure 3) shows that by the Mesoproterozoic the age mismatch is several percent. This difference is well within the precision of SHRIMP to detect when comparing $^{207}Pb/^{206}Pb$ vs $^{206}Pb/^{238}U$ ages, but despite thousands of SHRIMP papers being published on this part of the time scale, such a systematic deviation from concordance has not been observed.

Furthermore, there is additional data from most of the sessions used in this study. In addition to the Temora-2 calibration standard and the unknown zircons, 14 of the 16 SHRIMP analytical sessions also contained multiple analyses of the Paleoarchean OG1 zircon (Stern et al. 2009). The trend-line from Figure 3 predicts that this zircon will have a $^{206}Pb/^{238}U$ age that is 7% younger than the CA-TIMS age (Figure 3). As Figure 4 shows, the offset is more than an order of magnitude smaller. The mean SHRIMP $^{206}Pb/^{238}U$ age from the 14 sessions where OG1 was analysed is lower than the CA-TIMS age, but only by about 0.6%. So no linear age-based calibration offset was present in those analytical sessions.

Although the weighted mean OG1 SHRIMP age from the 14 sessions of 3440.8 ± 8.4 Ma is about 0.6% lower than the CA-ID TIMS age, it is statistically identical to the NON-chemically abraded ID-TIMS age for OG1 of 3440.7 ± 3.2 Ma (Stern et al. 2009). The obvious sub-millimeter damage done to zircons which have undergone chemical abrasion (Huyskens et al. 2016) might be interpreted as suggesting that chemical abrasion is a large scale process wherein damaged crystallographic domains are dissolved away and the zircon which survives chemical abrasion is untouched. The size and morphology of the dissolved areas implies that a microbeam technique should be able to avoid the damaged areas and return the chemically abraded age. However, our OG1 data suggest that microbeam targeting of the best-looking areas of untreated zircons return the NON-chemically abraded age for untreated zircons instead of the chemically abraded age. This implies that even the portions of the zircon which have survived the partial dissolution step of the chemical abrasion process are still somehow corrected for Pb loss on the scale of a 20x15x1 µm SHRIMP spot.

4.2.5 Geological explanation

If chemically abraded material has a fundamentally different U/Pb ratio than natural material, then our study may not be telling us anything at all about errors in calibration or systematic biases in the SHRIMP methodology. Rather, it could simply be documenting geologic or crystallographic effects which are remediated by chemical abrasion or avoidable as a result of the excellent single-grain analytical precision of TIMS being able to differentiate zircons from different events only separated in time by a few permil of their age. This explanation is consistent with the Rowan Formation (GA2031207) results observed above, with the caveat that for some reason the Rowan Formation experienced roughly twice as much Pb loss as the Devonian-Cambrian samples.

For example, zircons from plutonic rocks may have suffered sub-percent Pb loss which chemical abrasion can remedy, but which cannot be avoided by SIMS analytical spot selection. Applying this hypothesis to our data requires us to reclassify it. In Figure 5, we have reclassified the 35 samples of this study, not by age, but by rock type. The “Volcanic” relates to volcanic rocks and ashfall. “Plutonic” is granites, granodiorites, tonalities, porphyries, and other coarse-grained rocks.

All but one of these samples where the SHRIMP age is more than 0.25% older are volcanic, and the TIMS dates may be younger because the better age-resolution of TIMS on each grain allows sub-million year eruptive edifice-scale antecrysts to be resolved and removed from the best estimate of the eruptive age. This cannot be done for SHRIMP due to the poor counting statistics on individual spots, and the result is ages biased slightly (usually not resolvably) older.

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The simplest explanation for the zircons with a SHRIMP age younger than the CA-TIMS age is that the zircons have suffered Pb loss. This population is chiefly made up of plutonic zircons, which are more likely to have accumulated enough radiation damage to have undergone minor Pb loss.

If SIMS ages return natural ages for natural zircons and chemically abraded ages for chemically abraded zircons, and if most of the disagreement between SHRIMP and TIMS is due to the SHRIMPed zircons not being chemically abraded, then the overall accuracy and precision of the SHRIMP methodology may be sufficient to resolve the ~0.6% difference in natural and chemically abraded OG1 $^{206}Pb/^{238}U$ ages. A follow-up manuscript describing SHRIMP analyses of this and other less discordant reference zircons both with and without chemical abrasion is currently in preparation.

5 Conclusions

The comparison of 35 zircon populations dated by both CA-TIMS and SHRIMP methods shows that the results generally agree to within 1% on most samples. Reporting a SHRIMP age of natural zircon with a precision better than ~0.7% increases the chance of that age being different to the CA-ID-TIMS age. The non-Gaussian distribution of the differences makes the relevance of assigning a Gaussian uncertainty envelope for the accuracy of our SHRIMP results dubious. However, the structure of this mismatch suggests that geologic factors may be part of the disagreement in ages. It is somewhat ironic that what began as a database comparison project has required going back to the actual rocks to find the best explanation.

If confirmed, this geologic explanation has two main implications. Firstly, SIMS geochronology is not the best method in geologic settings where grains may have real differences in crystallization age that are smaller than the precision of a single spot, but larger than the precision of the final age of the pooled spot values. Permian volcanic rocks which mix eruption-aged zircons grains with zircon crystallized earlier in the history of the volcanic edifice are one such example. However, the precision of individual spot analyses will depend on the U and Pb content of the zircon, and the size of the analysed volume, with the recognition that as sputter pits deepen to increase volume, effects such as charging of pit walls and ripple formation in the bottom of the crater will eventually disturb the calibration.

Secondly, if much of the analytical error in SHRIMP measurements can be attributed to geologic factors such as Pb loss or antecrysts, then it is possible that the actual uncertainty in the calibration is less than traditionally stated. The Stern and Amelin (2003) estimate of ~1% was based in part on glass, which should not suffer from these effects. However, that study is almost 20 years old, so refinement of analytical procedures and improvements in SHRIMP manufacturing and installation may have reduced the fundamental uncertainty associated with the calibration equation. We suggest improvements to the SIMS geochronological technique are most likely to occur through detailed characterization of the calibration using instances where confounding geologic factors have been minimized.

6. Author Contributions

CM, SB, and CL produced the new SHRIMP data. J.C. and RF produced the new TIMS data and made tables S1 and S2. SB created the GA geochronology databases used in this study and designed the study with CM. CM recalculated everything as needed, initially interpreted the results and put together all figures and tables except provided new TIMS data. CM, SB, CL, JC and CW wrote the text.

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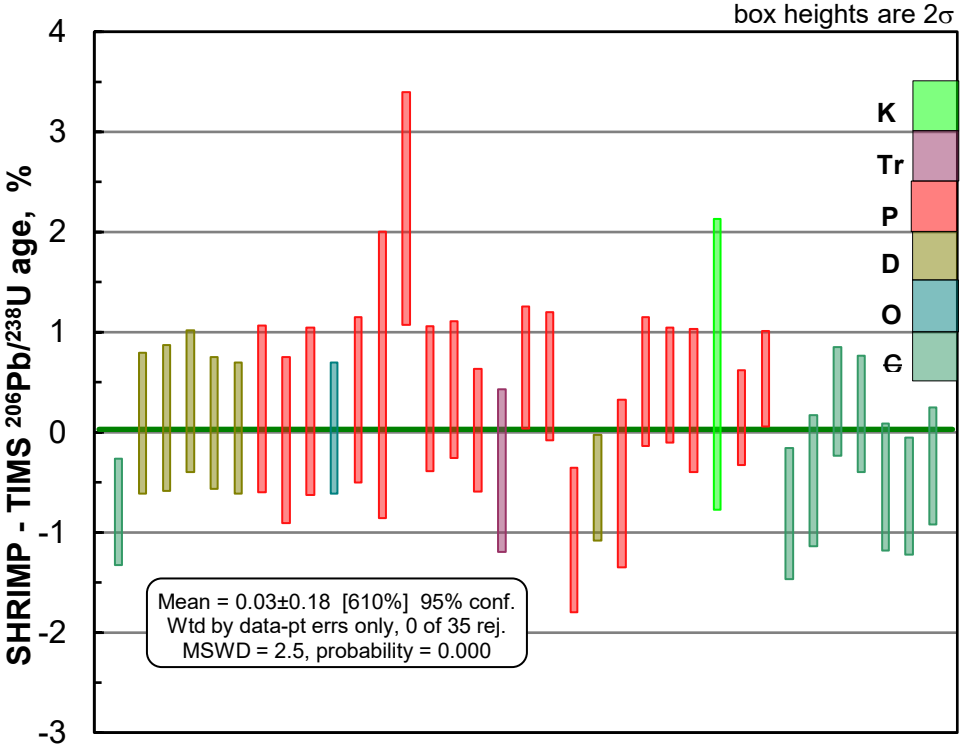

Figure 1: The average difference of all 35 doubly dated samples, in percent (100 x (SHRIMP age- TIMS age)/TIMS age). Samples are listed in GA sample number order. Error bars are coloured by geologic period.

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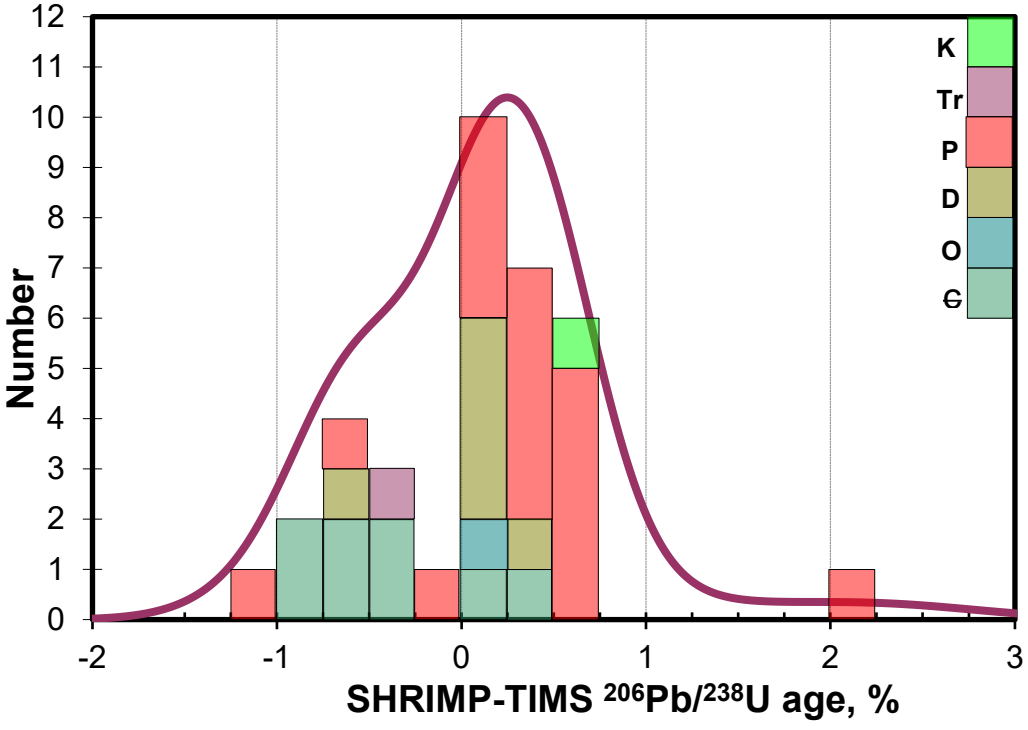

Figure 2: Histogram and probability density plot for all 35 date comparisons. Histogram is coloured by geologic period.

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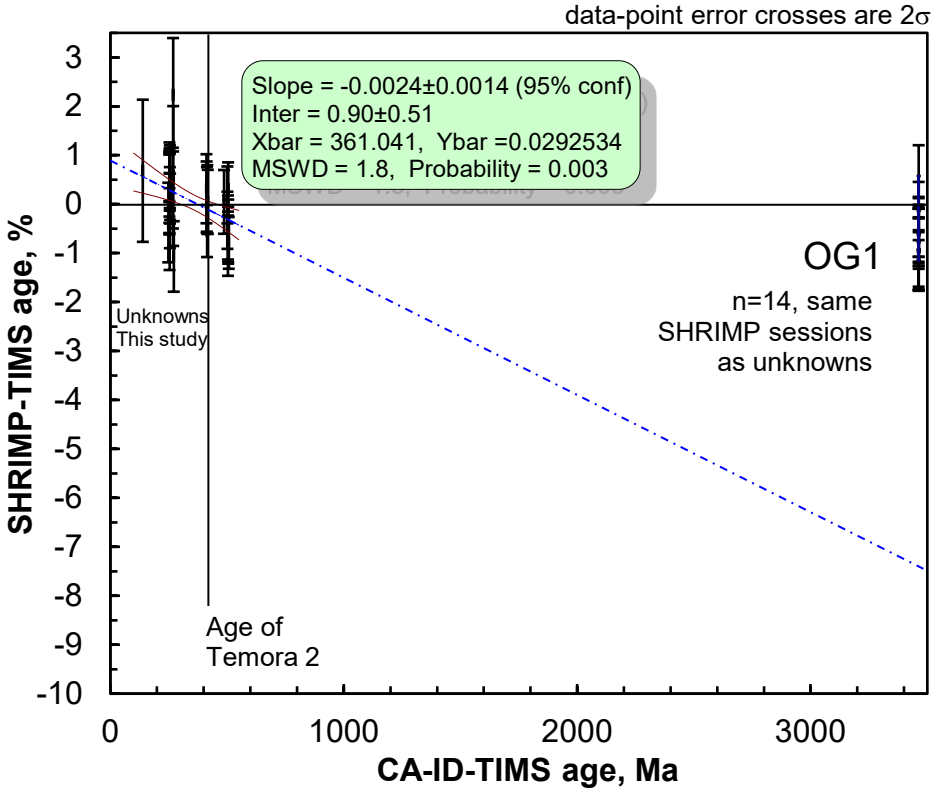

Figure 3: The average age difference (in percent) of all 35 doubly dated samples, vs the CA-TIMS age of the samples. Cherry picking away the two >1% outliers will p-hack this fit to 0.29, but will not address the fundamental arguments against its validity discussed in the text, as shown by the $^{206}Pb/^{238}U$ age of the secondary reference zircon OG1, whose primary use is for monitoring of $^{207}Pb/^{206}Pb$ isotopic fractionation.

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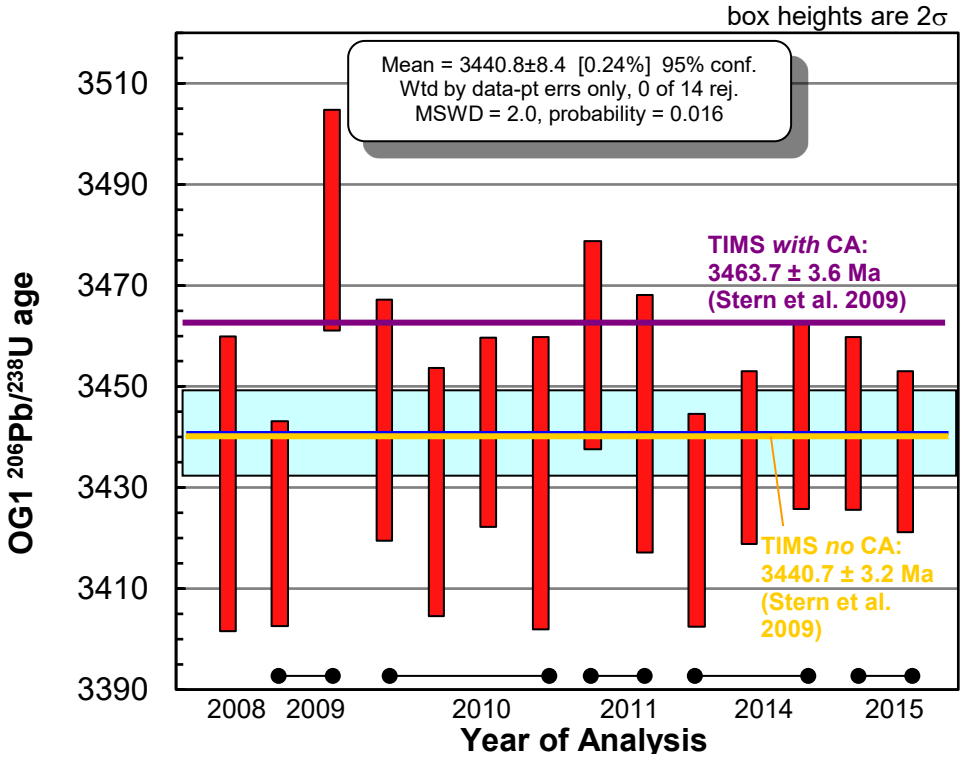

Figure 4: Weighted mean $^{206}Pb/^{238}U$ age of OG1 analyses from 14 sessions whose data is included in this paper. The weighted mean is similar to the non-chemical abrasion age, and about 0.4% lower than the chemical abrasion age.

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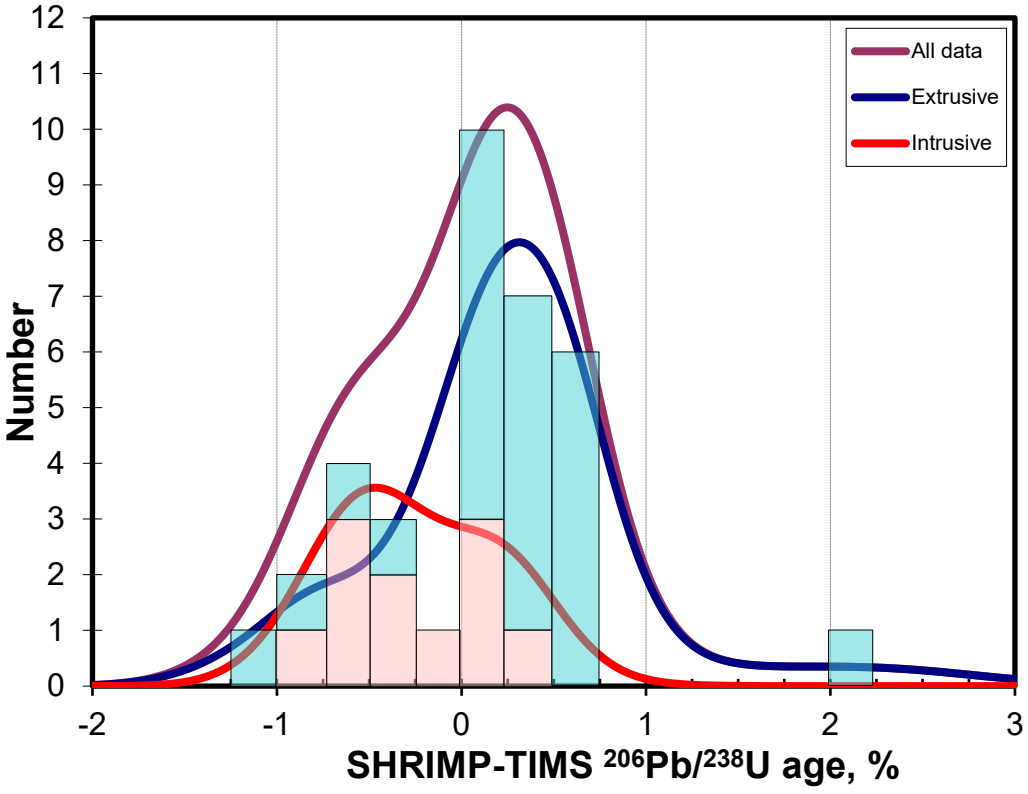

Figure 5: The same probability curve-histogram combination as Figure 2, but with the histograms recoloured by geologic rock type. Volcanic rocks are blue, plutonic rocks are pink.

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Table 1: Summary information for the 35 samples in the Geoscience Australia database dated using both CA-TIMS and SHRIMP:

GA number	*Formation*	*Logged Rock Type*	*SHRIMP reference*	*TIMS reference*	*Mount*	*Session*	*SHRIMP Year*
1486519	Narrapumelap Road Dacite Member	Dacite	Lewis et al. 2016	Lewis et al. 2017 †	GA6294	150010	2015
1528019	Turondale Formation	Massive volcanic siliciclastic siltstone	Bodorkos et al. 2012†	Bodorkos et al. 2012†	GA6075	90001	2009
1528025	Upper Merrions Formation	Massive volcanic siliciclastic siltstone	Bodorkos et al. 2012†	Bodorkos et al. 2012†	GA6075	90001	2009
1528027	Lower Merrions Formation	Massive volcanic siliciclastic siltstone	Bodorkos et al. 2012†	Bodorkos et al. 2012†	GA6075	90001	2009
1530245	Middle Merrions Formation	Porphryritic Volcanic Rock	Bodorkos et al. 2012†	Bodorkos et al. 2012†	GA6075	90001	2009
1594761	Bulls Camp Volcanics	Welded Ignimbrite	Bodorkos et al. 2012†	Bodorkos et al. 2012†	GA6075	90001	2009
1683223	Dundee Rhyodacite	Rhyolite	Brownlow&Cross 2010*	Chapman et al. 2022	GA6058	80101	2008
1954029	Parlour Mountain Leucomonzogranite	Granite	Cross & Blevin 2010*	Chapman et al. 2022	GA6057	80104	2008
1954030	Gwydir River Monzogranite	Granite	Cross & Blevin 2010*	Chapman et al. 2022	GA6057	80104	2008
1977984	Saddington Tonalite	Tonalite	This Study	This Study	GA6086	90038	2009
1978294	Lightjack Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6122	100044	2010
1978295	Lightjack Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6122	100044	2010
1978296	Lightjack Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6122	100044	2010
2000865	Kaloola Member, Bandanna Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6112	100012	2010
2000869	Kaloola Member, Bandanna Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6112	100012	2010
2005145	Nalleen Tuff Member	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6113	100103	2010
2005209	Garie Formation	Felsic Tuff	This Study	Metcalfe et al. 2015	GA6113	100103	2010
2031203	Awaba Tuff	Tuff	This Study	Metcalfe et al. 2015	GA6113	100103	2010
2031204	Nobbys Tuff	Felsic Tuff	This Study	Metcalfe et al. 2015	GA6113	100103	2010
2031207	Rowan Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6113	100103	2010
2097849	Yithan Rhyolite	Porphyritic Rhyolite	Bodorkos et al. 2013	This Study	GA6140	100127	2010

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GA number	*Formation*	*Logged Rock Type*	*SHRIMP reference*	*TIMS reference*	*Mount*	*Session*	*SHRIMP Year*
2105111	Emmaville Volcanics	Volcaniclastic	Cross & Blevin 2013	Chapman et al. 2022	GA6139	100128	2010
2120074	Wandsworth Volcanic Group	Ignimbrite	Chisholm et al. 2014	Chapman et al. 2022	GA6152	110005	2011
2120076	Wandsworth Volcanic Group	Ignimbrite	Chisholm et al. 2014	Chapman et al. 2022	GA6152	110005	2011
2120077	Wandsworth Volcanic Group	Crystal tuff	Chisholm et al. 2014	Chapman et al. 2022	GA6152	110005	2011
2121671	unknown	Calcilutite	This Study	This Study	GA6155	110011	2011
2122736	Tinowon Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6169	110088	2011
2122750	Kaloola Member, Bandanna Formation	Tuff	Laurie et al. 2016	Laurie et al. 2016	GA6169	110088	2011
2167510	"Victor Porphyry"	Porphyry	Lewis et al. 2015	Lewis et al. 2017 †	GA6268	140028	2014
2169175	"Victor Porphyry"	Porphyry	Lewis et al. 2015	Lewis et al. 2017 †	GA6272	140035	2014
2172143	Unnamed porphyry hosting molybdenite	Porphyry	Lewis et al. 2016	Lewis et al. 2017 †	GA6282	140082	2014
2254430	Bushy Creek Granodiorite	Granodiorite	Lewis et al. 2016	Lewis et al. 2017 †	GA6302	150060	2015
2254431	Buckeran Diorite	Diorite	Lewis et al. 2016	Lewis et al. 2017 †	GA6302	150060	2015
2254432	Buckeran Diorite	Diorite	Lewis et al. 2016	Lewis et al. 2017 †	GA6302	150060	2015
2254436	Bushy Creek Granodiorite	Granodiorite	Lewis et al. 2016	Lewis et al. 2017 †	GA6302	150060	2015

** Reprocessed using SQUID 2.5*

† Full data in this paper

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Table 2: Summary information for the 16 SHRIMP analytical sessions in which these data were collected. N Tem= number of Temora-2 analyses as the primary reference material; n Tem Excl- number of excluded standard spots; 1σ er f mean- uncertainty of calibration; spot to spot er- additional error for each spot to give MSWD=1; Temora common Pb isotope- common Pb isotope used for primary reference material; Unknown common Pb isotope- common isotope of Pb used for unknowns in session; n OG1 number of OG1 analyses used to determine $^{207}Pb/^{206}Pb$ fractionation; OG1 $^{206}Pb/^{238}U$ age- the U-Pb age (not the $^{207}Pb/^{206}Pb$ age) of the $^{207}Pb/^{206}Pb$ standard material; OG1 c95% abs WITH ref er of tem mean- uncertainty on OG1 $^{206}Pb/^{238}U$ age:

session	*n Tem*	*n Tem excl*	*1σ er of mean, %*	*spot - to spot er %*	*^{204}Pb over-counts/ s from ^{207}Pb*	*over-count 95% conf*	*Temora common Pb isotope*	*Unknown common Pb isotope*	*n OG1*	*n OG1 excl*	*OG1 $^{206}Pb/^{238}U$ age*	*OG1 c95% abs WITH ref er of tem mean*
80101	17	0	0.30	0.86	-0.01	0.03	207	207	0			
80104	37	0	0.27	1.42	-0.01	0.02	207	207	16	0	3430.9	29.1
90001	72	0	0.15	1.00	-0.01	0.02	204	204	18	0	3422.9	20.3
90038	21	0	0.18	0.75*	0.01	0.02	204	204	10	0	3483.0	21.8
100012	24	0	0.22	0.75	0.00	0.02	207	207	11	0	3443.4	23.8
100044	20	0	0.19	0.75*	0.01	0.03	207	207	8	0	3429.2	24.6
100103	46	0	0.16	0.77	0.01	0.01	207	207	20	0	3441.0	18.7
100128	31	0	0.26	1.10	0.01	0.02	204	204	14	1	3430.9	28.9
110005	36	1	0.17	1.00*	**0.02**	**0.02**	204	204	26	0	3458.2	20.6
110011	78	5	0.23	1.62	**0.04**	**0.02**	204	207	31	0	3442.7	25.4
110088	79	1	0.11	0.83	0.02	0.02	207	207	0			
140028	31	0	0.17	0.75*	0.02	0.02	204	204	14	0	3423.6	21.0
140035	51	1	0.14	0.75*	0.01	0.01	204	204	11	0	3436.1	17.1
140082	40	0	0.12	0.75*	**0.02**	**0.01**	204	204	16	0	3444.3	18.4
150010	76	0	0.13	0.85	0.00	0.01	204	204	27	1	3442.8	17.1
150060	70	0	0.12	0.75*	**0.02**	**0.01**	204	204	28	0	3437.2	15.9

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Table 3: Summary of SHRIMP – CA-TIMS comparison. TIMS older- antecryst zircons analysed; TIMS grouped for age- n of zircons used in age calculation; TIMS younger- younger ungrouped zircons: SHRIMP older- antecryst zircons analysed; SHRIMP grouped for age- n of zircons used in age calculation; SHRIMP younger- younger ungrouped zircons; Diff (Ma) difference in age in Ma; Diff %- difference in age in % of the TIMS age; Diffc95% difference in age in numbers of SHRIMP 95% confidence intervals.

GA Sample No	*TIMS older*	*TIMS group-ed for age*	*TIMS young-er*	*SHRMP older*	*SHRMP grouped for age*	*SHRMP younger*	***CA-TIMS*** *$^{206}Pb/^{238}U$ age*	*± c95% (random + tracer)*	***SHRIMP*** *$^{206}Pb/^{238}U$ age*	*± c95% (random + session + reference)*	Diff (Ma)	Diff %	*Diff c95%*
1486519	1	7	0	2	34	0	507.21	0.39	503.2	2.7	-4.01	-0.79	-1.5
1528019	0	6	0	0	32	0	415.56	0.51	416	2.9	0.44	0.11	0.2
1528025	2	3	0	0	32	0	412.73	0.96	413.3	3.0	0.57	0.14	0.2
1528027	2	4	0	1	30	1	411.71	0.89	413	2.9	1.29	0.31	0.4
1530245	0	4	1	1	31	0	413.76	0.76	414.2	2.7	0.44	0.11	0.2
1594761	0	3	2	0	33	0	417.75	0.88	417.9	2.7	0.15	0.04	0.1
1683223	0	6	0	0	19	0	253.10	0.15	253.7	2.1	0.60	0.24	0.3
1954029	0	6	0	0	30	0	255.08	0.16	254.9	2.1	-0.18	-0.07	-0.1
1954030	3	3	0	2	28	0	252.76	0.26	253.3	2.1	0.54	0.21	0.3
1977984	0	7	0	2	30	0	487.07	0.70	487.3	3.2	0.23	0.05	0.1
1978294	0	7	0	10	13	3	268.02	0.16	268.9	2.2	0.88	0.33	0.4
1978295	0	8	0	0	6	4	269.25	0.10	270.8	3.9	1.55	0.58	0.4
1978296	1	8	0	3	7	1	268.79	0.14	274.8	3.2	6.01	2.24	1.9
2000865	0	8	0	0	19	1	252.64	0.10	253.5	1.8	0.86	0.34	0.5
2000869	1	12	0	1	33	2	253.11	0.08	254.2	1.7	1.09	0.43	0.6
2005145	1	7	2	1	19	1	253.14	0.09	253.2	1.6	0.06	0.02	0.0
2005209	0	8	0	4	17	4	248.23	0.19	247.3	2.0	-0.93	-0.37	-0.5
2031203	1	7	0	2	20	1	253.25	0.13	254.9	1.6	1.65	0.65	1.1
2031204	1	7	0	1	24	0	255.26	0.14	256.7	1.6	1.44	0.56	0.9
2031207	2	6	0	1	23	4	271.60	0.13	268.7	1.9	-2.9	-1.07	-1.5
2097849	1	7	0	6	29	6	414.27	0.26	412.0	2.2	-2.27	-0.55	-1.0
2105111	1	5	0	0	27	0	253.59	0.17	252.3	2.1	-1.29	-0.51	-0.6
2120074	2	4	0	0	26	0	254.70	0.19	256.0	1.6	1.30	0.51	0.8
2120076	0	6	0	0	25	0	254.58	0.15	255.8	1.5	1.22	0.48	0.8
2120077	1	5	0	0	25	0	255.48	0.17	256.3	1.8	0.82	0.32	0.4
2121671	2	7	0	4	11	1	139.15	0.09	140.1	2.0	0.95	0.68	0.5

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GA Sample No	*TIMS older*	*TIMS group-ed for age*	*TIMS young-er*	*SHRMP older*	*SHRMP grouped for age*	*SHRMP younger*	***CA-TIMS*** *$^{206}Pb/^{238}U$ age*	*± c95% (random + tracer)*	***SHRIMP*** *$^{206}Pb/^{238}U$ age*	*± c95% (random + session + reference)*	Diff (Ma)	Diff %	*Diff c95%*
2122736	6	4	0	0	50	1	256.01	0.11	256.4	1.2	0.39	0.15	0.3
2122750	1	8	0	0	36	0	252.54	0.09	253.9	1.2	1.36	0.54	1.1
2167510	1	5	0	2	24	1	504.17	0.31	500.1	3.3	-4.07	-0.81	-1.2
2169175	0	6	0	2	24	1	503.80	0.29	501.4	3.3	-2.40	-0.48	-0.7
2172143	0	8	0	0	39	1	504.53	0.31	506.1	2.7	1.57	0.31	0.6
2254430	1	6	0	3	31	2	501.55	0.31	502.5	2.9	0.95	0.19	0.3
2254431	0	8	0	2	21	2	504.83	0.30	502.1	3.2	-2.73	-0.54	-0.9
2254432	0	6	1	0	24	1	505.00	0.36	501.8	2.9	-3.20	-0.63	-1.1
2254436	0	6	0	4	28	2	501.65	0.29	500.0	2.9	-1.65	-0.33	-0.6
										Median Absolute Deviation	0.8	0.3	0.7
										Median	0.54	0.15	0.51
										Simple Mean	0.021	0.097	0.146

Table S-1: Grain-by-Grain CA-TIMS data from Boise State University (Electronic).

Table S-2: Grain-by-Grain CA-TIMS data from University of British Columbia (Electronic).

Table S-3: Spot by spot data for new SHRIMP results from Geoscience Australia SHRIMP (Electronic).