Avoid short sections: for example, combine sections 2.1.2, 2.1.3 and 2.1.5 (2.1.4 is missing?) into a single section under the title "Reference values".

2. The Introduction needs significant rewriting, focusing on the main scope of the manuscript, which needs to be more clearly defined. The historical review can be omitted (lines 43-54), the sections on CA-TIMS could be shortened (60-69), unwarranted comments should be removed (55-59), statements should always be supported by references (e.g. 72-74). In this context, the recent publication by Donaghy et al 2024 in Geochronology https://gchron.copernicus.org/preprints/gchron-2023-20/ should be considered, together with the others suggested by the reviewers.

good *Or know how the so-stay — lead advancements.* *and Axel & hills*

3. I recommend that U-Pb becomes the focus of the MS and that oxygen is also considered, whereas trace elements and Hf should be of secondary importance. In the results, present the U-Pb first, then the oxygen, and finally the trace elements and Hf; keep this order throughout the text, also for methods and discussion. In section 4.2, start by discussing the main results (improvement of U-Pb age scatter by CA, such as on line 547) from the data (do not start with a conclusion statement), discussing all samples and building the argument with a more linear logic. The comparison with previous studies should come after the summary of your own data. *→ Hayslews + order fishes* The part on comparison with CA-ID-TIMS is less clear and insightful (lines 515-525 report a lot of ages without much explanation, a table of these may be needed). The section on the different calibration slope for 91500 is a tangent that could be removed from the discussion (lines 552-555). *→shrink, figure to appendix or out *Check res.h* The discussion of common Pb composition and abundance is sometimes unclear, with things being presented but not explained or leading to any conclusion (e.g. 576, 579-583). *· Grados volcanic; scatter.* *↳ organize more* *Rewrite+ restrive*

4. The SHRIMP d18O discussion is inconclusive for TEM2 and the mix-up in sample preparation is unfortunate. New data for TEM2 are needed to clarify its performance after CA or this sample should be excluded from this comparison. References to processes such as "core-rim diffusive re-equilibration" (line 660) require proper discussion of the evidence or should be avoided.

5. Trace elements and Lu-Hf are less relevant (less frequently performed or not performed by SIMS) and should be reduced to a dedicated short section with the results, with data mostly presented as a supplement, or omitted altogether.
The discussion of the REE is not particularly insightful and I do not think the fit to the O'Neill et al. polynomial is useful for the main message of the paper. I recommend removing this part, including the reconstruction and significance of the La content (686-701), which is a different topic altogether. ✓

Shorter +c too

6. Overall, the description and interpretation of the results should be kept as factual as possible, with quantification whenever possible, leaving out unwarranted comments and opinions. Discussion should focus on the main message, and tangential arguments should be deleted (no addition of data for dissolution channels, no addition of data for OG1 if its SIMS age has already been commented on by previous work). Repetitions should be identified and removed. Data that do not contribute to the main scope of the paper should be omitted. Similarly, the conclusion should be factual and a summary of the main points of the discussion, and should not introduce new lines of reasoning or secondary thoughts (725, 728) or comparisons with previous studies (729-731).

discussion more to

I reiterate that the extensive study you have carried out has value and is in principle suitable for publication in Geochronology, but not in the current form. In view of the extensive revision that will be required, the revised MS will have to be resubmitted to the reviewers, in addition to further checks by the editor.
Kind regards
Daniela Rubatto
Associate Editor

I guess this gives me something to do in March.
-Chuck

-----Original Message-----
From: editorial@copernicus.org <editorial@copernicus.org>
Sent: Thursday, February 29, 2024 2:04 AM
To: Charles Magee <Charles.Magee@ga.gov.au>

Response to reviewers

We would like to thank both reviewers for their time and effort in reviewing our paper.

Response to review #1:

We agree with reviewer #1 that they have found our paper challenging and- missed the main point, although we disagree with their assessment of our writing style as the reason.

To clarify, the main point of our paper is that chemically abraded reference ages should not be used for non-chemically abraded reference zircons for SIMS U-Pb analysis. We reproduce chemically abraded CAIDTIMS reference ages for chemically abraded SIMS targets, and untreated CAIDTIMS reference ages for untreated SIMS targets. This is the most important and urgent part of this paper, as many SIMS analysts currently use CA ages for natural material. While the differences for most reference zircons are too small to distinguish in an individual session, this will produce systematic errors over time.

Our secondary point, and the reason the study was conducted, is to see if the chemical abrasion process interferes with measurements of other chemical and isotopic systems, either by mobilizing elements, or by altering the matrix in a way that interferes with the analysis.

Our tertiary point is that if SIMS U-Pb analysts wish to achieve sub-percent accuracy and precision, chemical abrasion will be necessary, but not sufficient, for all but the least radiation-damaged zircons, as natural zircon is not reliably closed system at sub-percent levels. For high precision projects where tighter uncertainty in reference ages is required, we have published in table 1 reference ages recalculated using the tracer calibration which we present in this paper.

Many of the questions raised by reviewer #1 relate to our analyses of the zircons from the S-type Mount Painter Volcanics. Fortunately, many of these issues have already been answered in the literature.

While we were preparing this manuscript for submission we failed to notice the publication of Vogt et al. (2023), which describes the chemical abrasion and subsequent SIMS analysis of S-type zircons from Central Europe.

Like the study of Kryza et al., Vogt et al. (2023) chemically abrade only their unknown sample, and do not look at the effect of CA on well-characterised zircons. However, they provide SIMS U-Pb, d18O, and trace element results for both untreated and chemically abraded samples which answer many of Reviewer #1's speculations on this topic.

We will obviously need to rewrite our introduction to incorporate this study, but we are confident that the very different aims of our study and Vogt et al.'s (2023) should make explaining their complementarity fairly straightforward.

As for their specific points:

We are well aware of the McKanna et al. (2023) study, as I (CM, the corresponding author) provided a community comment during the review process. It is complementary to our work, as their imaging of ever-smaller channels of dissolution down to the resolution of their instrument is consistent with our observation that the removal of low level Pb loss is pervasive at the scale of our SHRIMP spot.

Almost all SIMS U-Pb data are scattered beyond the statistical expectations of the grouped spots. This is why it was noteworthy that the chemically abraded reference zircon analytical session (170123) did not require any spot-to-spot error component. A spot-to-spot error for all the samples

to migration of U and radiogenic Pb. The third is better understanding the sources and formation conditions of the zircons and their host rocks through analysis of zircon trace elemental, radiogenic and stable isotopic compositions.

45 In the last 30 years, significant progress has been achieved in all three areas. In zircon dating by isotope dilution thermal ionisation mass spectrometry (ID-TIMS), precision and accuracy were improved by development of highly efficient ion emitters (Gerstenberger and Haase 1997) and by introduction of U and Pb double spikes made of high-purity synthetic isotopes (Chen and Wasserburg 1981, Todt et al. 1996), and combining these spikes for precise and accurate U-Pb and Pb-isotopic dating (Amelin and Davis 2006, Condon et al. 2015). Among the developments that help analysing closed U-Pb systems, chemical abrasion (Mattinson 2005; Mundil et al. 2004) is arguably the most important. Combining these developments, together with preparation of large quantities of carefully calibrated isotopic tracers in the Earthtime initiative (Condon et al. 50 2015; McLean et al. 2015), raised analytical precision and accuracy of U-Pb dating to a new level. At the same time, the measurement of multiple isotopic systems in individual zircon grains, in particular SIMS stable oxygen isotopes (Schuhmacher et al. 2004; Ickert et al. 2008) and the Lu-Hf system by both solution and laser ablation MC-ICPMS techniques (Amelin et al. 1999, Harrison et al. 2005, Hiess et al. 2009) has built geologic context around the U-Pb age, in terms of constraining the source material and petrogenesis of the melt from which the zircon crystallized.

55 Many, perhaps even most, of these developments are based on empirical findings enabled by researchers' intuition and refined through extensive experimenting, rather than being deduced from theory. As a result, these new techniques are often used without clear understanding of exactly how they work, and to what degree the various analytical techniques may interfere with one another. For example, we are not aware of any studies which determine whether chemical abrasion improves or complicates the analyses of stable oxygen isotope ratios by SIMS or Lu-Hf isotopic measurements by laser ICP-MS.

60 Chemical abrasion is applicable to analytical protocols other than TIMS U-Pb geochronology which involve analysis of dissolved zircon. Schoene et al. (2010) developed an approach to recover many elements (including Lu and Hf) from zircon dissolved for U-Pb geochemistry. This allows for their later use in elemental, Lu-Hf isotopic analysis as well as other isotopic systems such as $^{238}U/^{235}U$ (Hiess et al. 2012, Tissot et al. 2019) and Zr isotopes (Ibanez-Mejia and Tissot 2019) that emerge with ongoing analytical advances. However, dissolution of zircon in hydrofluoric acid makes recovering the zircon oxygen 65 and silicon isotopic compositions impossible. Also, phosphorus and titanium, the elements that are required for calculation of phosphorus saturation and for zircon crystallisation thermometry, were reported to be lost during zircon dissolution or chemical separation of Pb and U (Schoene et al. 2010). McKanna et al. (2023b) show that incompatible LREE are preferentially leached from zircon during the partial dissolution phase of chemical abrasion, but they only have trace element data on REE, Y, Nb, Hf, Ta, and Hf.

70 Several laser ICPMS studies (e.g. Crowley et al. 2014) have shown that chemical abrasion introduces matrix effects which cause apparent U-Pb age offsets of up to several percent. In contrast, SIMS studies have shown no appreciable effect for young zircons with low radiation damage (Watts et al. 2016), but results from zircons with more extensive radiation damage are consistent with the chemical abrasion process ameliorating Pb loss (Kryza et al. 2012, 2014). With the suggestion by Magee et al. (2023) that minor, cryptic Pb loss may be common in SIMS U-Pb dates from early Paleozoic and older zircons, SIMS 75 U-Pb dating of chemically abraded material could conceivably improve the precision and/or accuracy.

In-situ microbeam analysis of untreated zircon, both as unknowns and standards, involves an unresolved issue surrounding the standardization of U-Pb analysis. The CA-ID-TIMS revolution has bequeathed the in-situ geochronology community with a variety of newer, more precise reference ages for many of the zircons used as primary or secondary reference materials, many of which were initially characterised by ID-TIMS before the advent of chemical abrasion. For example, the laboratory 80 intercomparison study of Webb et al. (2023) shows that participating SIMS and LA-ICPMS labs use at least three different reference ages for a single reference zircon (91500). These ages are from both chemically abraded and untreated material.

One area where TIMS precision has improved over the last few decades is tracer uncertainty. Ideally we would use reference ages for all four reference zircons in both the chemically abraded and untreated state, determined using a single tracer. However, such a study has not yet been published. Instead, we chose reference ages calculated using the minimum number of
125 different tracers for which we could find information.

There are three isotopic tracers used in our choice of reference values. They are (with samples used on):

- The Royal Ontario Museum (ROM) tracer (T2U, QNU, OGU, OGC); Black et al. (2003); Black et al. (2004); Stern et al. (2009);
- Earthtime 535 tracer (91U, QNC, T2C); Schoene et al. (2006), Schaltegger et al. (2021); and
130 - Earthtime 2535 tracer (91C, T2C); Horstwood et al. (2016), Schaltegger et al. (2021).

The two Earthtime tracers have identical $^{205}Pb/^{235}U$ ratios, which is the key ratio in determination of $^{206}Pb/^{238}U$ ages, and are considered to be the same for the purposes of this study, as Schaltegger et al. (2021) show no systematic difference in the age of TEMORA 2.

Using the published uncertainties for these tracers complicates intercomparison of untreated and chemically abraded material
135 because the published uncertainty on the ROM tracer given in Black et al. (2003) is an order of magnitude higher than the Earthtime (McLean et al. 2015) tracer uncertainties. This causes the tracer uncertainty for the Black et al. (2003, 2004) and Stern et al. (2009) results to dominate the total uncertainty budget. Reducing this order of magnitude difference in tracer uncertainty makes intercomparison of CA and untreated results more straightforward.

The Earthtime project, in addition to creating the Earthtime tracer, also involved widely distributing several gravimetric
140 solutions, which can be used to more precisely and accurately determine the isotopic ratios of tracer solutions. We are publishing ROM tracer results determined using all three of the gravimetric solutions described by Condon et al. (2015). These data were acquired after the Black et al. (2003, 2004) data, but before the Stern et al. (2009) data, making them relevant for the ROM lab at the time these reference values were determined. This allows us to reduce the reference value uncertainty for the (mostly untreated) samples analysed at the ROM to a level more commensurate with the Earthtime tracer, and well below
145 SHRIMP analytical uncertainty.

For consistency, we recalculate all reference values using a single methodology. We take the weighted mean of the individual aliquots where available, and calculate the analytical uncertainty by multiplying the standard deviation of these results by Student's t. Where the probability of fit is less than 0.05, we also multiply by the square root of the MSWD. We also include four new aliquots for OGC, intended for the Stern et al. (2009) paper but not included in the final manuscript. For consistency,
150 we apply the same calculation to the $^{206}Pb/^{238}U$ ratios from all of the reference analyses, generating the reference values and uncertainties given in Table 1. This difference in methodology accounts for the difference in these Table 1 values and their uncertainties compared to the headline numbers in the source papers.

Reference values derived from analyses using the same isotopic tracer do not need to propagate the tracer uncertainty when being compared to each other; similarly, the isotopic tracer uncertainty portion of the reference value uncertainty does not need
155 to be propagated within SHRIMP sessions comparing two zircon reference values derived from the same tracer.

SHRIMP uncertainty propagation is described in Magee et al. (2023); In short, SHRIMP results in a single session can be compared to each other using just the sample analytical uncertainties (internal errors of Stern & Amelin 2003). However, when SHRIMP dates are compared to a TIMS reference value, the uncertainty of the SHRIMP reference zircon measurement for that session needs to be considered, as does the uncertainty on the SHRIMP reference zircon value. However, if a SHRIMP
160 age is being compared to a TIMS reference age which used the same tracer as the reference zircon for the SHRIMP session, the tracer component of the reference zircon value should not be propagated. So, for example, a SHRIMP session using untreated TEMORA 2 (Black et al. 2004) as the reference zircon would not include the tracer portion of the reference zircon uncertainty when comparing the SHRIMP age for untreated QGNG to the reference TIMS age published in Black et al. (2003), as Black et al. (2003) and Black et al. (2004) both used the same tracer.

245 ions were detected using an ETP electron multiplier. The retardation lens was not used. Electron multiplier dead time (25 ns) had previously been determined using Ti isotopic ratios in rutile. Analytical spots were programmed daily and run in approximately 23 hour batches.

For the standard zircons (mount GA6363, session 170123), after an initial concentration standard (zircon M127; Nasdala et al. 2016) was run, 42 spots were run on each of the eight zircon samples in a round robin fashion. A 100 μm Kohler aperture was

250 used, to produce an elliptical flat-bottomed sputter crater approximately 22 μm x 16 μm across and roughly 0.8μm deep. The primary beam monitor (PBM) measured a net sample current of 1.9 nA, which corresponds to a true primary beam current of 1.2 nA when analysing zircon. The acquisition table consisted of six scans through a 10 mass station run table: $^{90}Zr_2{}^{16}O$ (2 s), ^{204}Pb (20 s), Background ($^{204}Pb+0.05$ amu), (20 s), ^{206}Pb (15 s), ^{207}Pb (40 s), ^{208}Pb (5 s), ^{238}U (5 s), $^{232}Th{}^{16}O$ (2 s), $^{238}U{}^{16}O$ (2 s), $^{238}U{}^{16}O_2$ (2 s).

255 For the S-type zircons (mount GA6364, session 170124), 36 rims from both the CA and untreated aliquots of Mount Painter Volcanics zircon were run. This was followed by approximately 70 core analyses on each sample, in the manner of a sedimentary detrital zircon study. Untreated TEMORA 2 (Black et al. 2004) zircon was used as the primary reference zircon, with untreated 91500 and untreated OG1 zircon run as the secondary reference zircon and $^{207}Pb/^{206}Pb$ reference zircon, respectively. The run table and other analytical conditions were unchanged from the previous session. A quick follow-up

260 session (210046) was run using the same settings on those chemically abraded Mount Painter Volcanics rims which initially had anomalously young or old ages.

SHRIMP U-Pb data were processed using Squid 2.5 (Ludwig 2009). This software deadtime-corrects, background subtracts, and normalizes the data to the secondary beam monitor (SBM) to remove the effects of changes in the secondary beam intensity, before using Dodson (1978) interpolation to calculate isotopic ratios. The ^{204}Pb isotope was used for common Pb

265 correction of both the reference zircon and the unknowns, as ^{204}Pb overcounts were within uncertainty of zero for all sessions. While routine geochronology at Geoscience Australia is done using a ln(Pb/U) vs ln(UO/U) calibration with slope 2 (Claoue-Long et al. 1995), a detailed examination of these data showed that only three of the eight calibration slopes were within uncertainty of that value (Figure 2). Furthermore, the slope for zircon 91500 was shallower than the slopes of the other reference zircons. Chemical abrasion did not seem to have any substantial effect on calibration slope (Figure 2).

270 In this experiment, we choose to apply a calibration slope of 1.8. This is the best fit for the three non-megacryst samples, and it is the value which the Geological Survey of Canada (GSC) uses for their SHRIMP data reduction (Rayner, pers. comm.). Whether a systematic error component is required for 91500 data for having a shallow slope will be addressed in the discussion section.

Stern and Amelin (2003) determined that using the GSC SHRIMP, the spot-to-spot variability in calibrated Pb/U ratios in 610

275 glass was on the order of 1%. As the glass is homogenous for these elements at this level, this "spot-to-spot error" was accounted for in most subsequent SHRIMP data reduction procedures, with minimum values somewhere between 1% or 0.5% often used in data reduction. As the purpose of this study is to see if chemical abrasion, automated analysis and piezoelectric positioning can improve this number, for this study we start with a default spot-to-spot error of zero, and assign spot-to-spot uncertainty expansion only if the probability of fit for the calibration line in the primary reference material is less than 0.05.

280 ### 2.4.3 SHRIMP δ¹⁸O

The analytical procedures for SHRIMP SI oxygen isotope analysis closely follows those employed by Avila et al. (2020). A ca. 5 nA Cs⁺ primary ion beam is focused to a 25x20 μm spot. Charging is neutralised through focusing of a 2.2 kV electron beam on to the sputter area. Oxygen isotopes were measured in multiple collection mode with ^{16}O and ^{18}O measured across 10^{11} Ω resistors. Data were reduced with the ANU data reduction program POXI.

3 Results

3.1 ROM calibration and reference zircon age recalculation.

Seven aliquots of the gravimetric reference solutions described by Condon et al. (2015) were run at the Royal Ontario Museum. These were three replicates each of the JMM and RP solutions, and one of the MIT solution. The results are given in supplementary table S1. The weighted mean $^{235}U/^{205}Pb$ ratio of the ROM tracer solution was 106.569 ± 0.1 (2σ), with a MSWD of 0.177 and a very high probability of fit of 0.983. This is well within the previous estimate of 106.54 ± 0.28 (2σ) given in Black et al. (2003). Following the advice of Condon et al. (2015), the central value, and therefore the reference $^{206}Pb/^{238}U$ ratio of the reference zircons, was not changed.

McLean et al (2015) show that the contribution of the tracer uncertainty is smaller than the total analytical uncertainty due to error correlations in the calculations of the tracer solution composition. As we used the same gravimetric solutions as McLean et al. (2015) and the ROM tracer has a similar $^{235}U/^{205}Pb$ ratio of ~100, we scale the tracer uncertainty contribution by 0.53, in a conservative approximation of the scaling of McLean et al. (2015). This gives us a tracer uncertainty contribution of approximately 0.05% to the systematic uncertainty.

Using this new uncertainty value, we recalculated the reference values for all reference zircons, which are given in Table 1.

3.2 SHRIMP U-Th-Pb results of reference zircons

SHRIMP session 170123 generally ran without incident; only a single analysis (T2C.39.1) had to be discarded due to instrumental instability producing a nonsensical downhole fractionation pattern. ^{204}Pb overcounts were within error of zero, and the $^{207}Pb/^{206}Pb$ ratio (Tables S3, S4) for both untreated and chemically abraded OG1 were within error of their respective reference values, indicating no detectable mass-based isotopic fractionation. Individual spot data reduced using the T2U as the primary reference material and Black et al. (2004) as reference value is presented in Supplementary Table S3. Individual spot data reduced using T2C as the primary reference zircon and the reference value of Schaltegger et al. (2021) are presented in Supplementary Table S4. Measured weighted mean ages of all samples, relative to either T2U or T2C, are shown in Table 2. Weighted means of the spot averages using T2C as the primary reference material, and their comparison to the TIMS reference values are shown in Figure 3, panels 1-7. Calibration slope probabilities of fit were better than 0.05 for all chemically abraded samples, and for the T2U and 91U zircons, indicating that no excess spot-to-spot error was required in the reduction of this data set for those reference zircons known to reliably exhibit closed system U-Pb behaviour.

In all cases, chemical abrasion reduced the 95% confidence envelope of the mean, reduced the MSWD, and increased the probability of fit for the weighted mean for unknowns, regardless of which zircon was chosen as the primary reference. On average, the chemically abraded grains have slightly larger intraspot uncertainty, but this is consistent with worse counting statistics from lower average uranium contents, which we attribute to survivor bias in the chemical abrasion process. The lower MSWD for the chemically abraded samples is not simply a result of larger single spot uncertainty; the central values are also less dispersed. For the chemically abraded samples, the analytical 95% confidence interval on the means was on the order of ± two permille. All chemically abraded ages were within uncertainty of their reference TIMS ages, when either T2U or T2C is used as the primary reference material.

The ages for 91U and 91C were within uncertainty of each other, as were T2U and T2C. OGU and QNU, however were younger, and had a dispersed population and a high MSWD, compared to their chemically abraded counterparts. The population mean, however, had an age consistent with the TIMS ages of untreated, not chemically abraded zircon (Stern et al. 2009 and Black et al. 2003), and not with the chemically abraded ages for those samples (Table 2, Figure 3, Figure 4).

Of course, any of these zircons can be used as the reference zircon instead of TEMORA 2. The only pairing of reference zircon and unknown which does not result in the samples being within error of their reference values is the pair of 91U and OGC (or vice versa), which report an offset on the unknown relative to the reference value of approximately 0.45% (younger if 91U is

smaller grainsize than untreated 91500 and suffered more burn-through analyses as a result, appears to have been more affected by common Pb. This may be a surface or epoxy contaminant entrained into the gas flow to the torch when the laser burned through the back or sides of the grain. Spot by spot laser U-Pb data are presented in supplementary table S10.

490 ### 3.6.2. LASS trace element results

Trace elements were analysed in the same quad ICP mass cycles as the U-Pb isotopes. Due to the dwell time required for Pb isotopes, the LREE aside from cerium were often below detection limits. Many samples had lanthanum and praseodymium below detection limit (BLD), and in 91500 most of the LREE were BLD. As a result, orthogonal polynomial coefficients (O'Neill 2016) were not calculated. Spot by spot results are listed in supplementary table S11.

495 ### 3.6.3. LASS Lu-Hf results

The laser ablation split stream sent half the ablated material from the U-Pb and trace element analyses described above to a multicollector ICPMS for Yb-Lu-Hf isotopic analysis. The number of samples is therefore the same as mentioned above. The multicollector-based Yb/Hf ratio for each spot is consistent with the trace element data. Table 8 and Figure 10 show the weighted mean initial Hf isotopic compositions, as ratios and as εHf(t). As these geochronology reference zircons have variable

500 Lu-Hf ratios, the mean measured Hf isotopic values are of course more scattered due to variable amounts of ingrowth, particularly for the older zircons (QGNG and OG1). The spot-to-spot data, including the measured $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ are in supplementary Table S12.

4 Discussion

4.1 ROM tracer recalibration and reference values

505 The recalibration of the ROM tracer reduces the systematic uncertainty by a factor of five relative to the values published in Black et al. (2003, 2004). This in turn reduces the uncertainty in the reference ages by 140-290%, depending on the reference zircon (noting that only Black et al. (2004) explicitly report an uncertainty including the tracer; Black et al. (2003) and Stern et al. (2009) leave that calculation as an exercise for the reader). As a result, the tracer uncertainty is now much smaller than any of the other uncertainty components from these U-Pb SHRIMP results, allowing us to compare the results without the

510 complication of an order-of-magnitude tracer uncertainty difference. We recommend the reference values in Table 1 be used for all listed non-chemically abraded reference zircons used to standardize in-situ analyses for this reason.

4.2 SHRIMP U-Pb analyses of reference zircons

SHRIMP U-Pb analyses of both chemically abraded and untreated zircon show that both CA and untreated material can be used interchangeably and dated against each other, so long as the corresponding reference value is used. Analyses of CA

515 material are more precise, without any systematic discrepancies appearing at the 0.25-0.4% level. This suggests that for well-behaved reference zircons, using a piezo stage, automated analyses, and chemical abrasion, $^{206}Pb/^{238}U$ precision substantially better than the 1-3% value quoted by Schaltegger et al. (2015) can be achieved without sacrificing accuracy.

We can test the dependence of the apparent high accuracy and precision of the CA-SHRIMP results on our choice of reference

520 values by comparing them to a different set of internally consistent CA-ID-TIMS data. Huyskens et al. (2016) present CA-ID-TIMS results for TEMORA 2, OG1, and M16401 (the source rock for the 91500 zircon). By reducing our OGC and 91C results to the Huyskens et al. (2016) T2C value, we can look at accuracy & precision within the session and without intertracer uncertainties.

Reducing the data to the T2C values of Davydov et al. (2010), Ickert et al. (2015), or Von Quadt et al. (2016) instead of the Schaltegger (2021) or Huyskens (2016) values does not significantly alter the results.

Chemical abrasion appears to ameliorate Pb loss at the scale of the 22μm x 16μm x 0.8μm sputter craters. SHRIMP ages of chemically abraded OG1 and QGNG zircon are within uncertainty of the CA-ID TIMS ages, but not the untreated TIMS ages. In contrast, the SHRIMP ages of untreated OG1 and QGNG (whether standardized to T2U or T2C) are within uncertainty of the least discordant population of the TIMS results of untreated zircon, even after discordant grains are excluded to form a coherent population (Figure 4). This supports the claim made both by Black et al. (2003) for QGNG and by Stern et al. (2009) and Magee et al. (2023) for OG1, that the pooled untreated TIMS ^{206}Pb/^{238}U age represents the ^{206}Pb/^{238}U age of SHRIMP spots on untreated material better than the ^{207}Pb/^{206}Pb TIMS age (with or without chemical abrasion), or the chemically abraded ^{206}Pb/^{238}U TIMS age.

Bodorkos et al. (2009) suggested that sufficiently careful SHRIMP spot placement might avoid areas of Pb loss, while Magee et al. (2016) showed (Supplementary figures DR12 and DR 13) that in Paleoarchean detrital zircons, 1 μm deep SHRIMP spots show less Pb loss than 10-20 μm deep laser-ICPMS craters. However, the data presented here imply that there is a level of subtle discordance that cannot be avoided in SHRIMP analyses by spot selection using transmitted, reflected, and cathodoluminescence imaging. In other words, the dissolution of discordant zircon visible in the form of dissolved zones and channels is not the only change to the zircon; the remaining visually intact material also undergoes a subtle change in U-Pb ratio as a result of chemical abrasion. McKanna et al. (2023a) show that chemical abrasion removes material from the mm scale all the way down to the submicron resolution of their SEM images, which is consistent with our SHRIMP U-Pb data. The removal of pervasively distributed radiation damage confined to dislocation loops on the scale of 10 nm described by Peterman et al. (2021) might account for this seemingly homogenous change on the submicron scale. At the much lower annealing temperatures of chemical abrasion (900C vs 1450C), the closed system U-Pb behaviour suggests that U and Pb are not diffusively separated. TEM and atom probe studies on chemically abraded zircon might yield insights on nanoscale processes not spatially resolvable at the scale of a SHRIMP spot.

Use of chemical abrasion on the younger reference zircons 91500 and TEMORA 2 modestly reduces their scatter. For older, slightly discordant reference zircons OG1 and QGNG, the reduction in analytical uncertainty from the CA treatment is more substantial. Based on these results, we predict that the routine use of chemically abraded reference zircons could reduce the reference zircon component of total uncertainty associated with SHRIMP U-Pb calibrations, even when analysing untreated unknowns, as chemically abraded and untreated zircons appear to cross calibrate.

The 91500 age is unlikely to be significantly affected by the shallower ln(UO/U) vs ln (Pb/U) slope for 91500 zircon (figure 2) compared to the other reference zircons, as the ln(UO/U) values are only 0.4% lower for the 91500 grains than for the TEMORA 2 CA reference zircons. For a difference in slope of 0.5, this would yield ages 0.2% older for both 91500 samples, which is less than the analytical uncertainty for both the untreated and CA 91500 datasets.

It is worth noting that the source rocks for the TEMORA 2, QGNG, and OG1 reference zircons, the Middledale Gabbroic Diorite (TEMORA-2), Quartz Gabbronorite Gneiss from the Donington Suite (QGNG), and the Owens Gully Diorite (OG1), respectively, are all intermediate-to-mafic rocks. If any fractionation effects related to rock type exist, they are unlikely to be perceived in this study. Zircon 91500 is derived from a porphyroblastic syenite gneiss (Wiedenbeck 1995). The shallower calibration slope may relate to this, and its lower actinide, Hf, and REE contents which result from a different petrogenesis.

Deleted

91500 slope - continue + appendix

4.3 SHRIMP U- Pb of Mount Painter zircons

4.3.1 Igneous Rims

The analyses of the zircons from the Mount Painter Volcanics have several interesting features. Firstly, the chemically abraded rims are much lower in common Pb than the untreated ones. The untreated rims have common ^{206}Pb contents reaching as high as 16% (Figure 11). The seven grains which have common ^{206}Pb above 0.5% have been excluded from the weighted mean age, but the common Pb correction works well enough for them to yield a coherent age of 430.3 ± 1.2 / 1.6 Ma, if included. This well-behaved common Pb correction suggests that the common Pb is close to the model age in composition, and is not Proterozoic industrial or environmental contaminant lead. If the Pb is contained in micro or nano inclusions, its presence in the rims might be explained by the rims on these volcanic zircons having crystallized rapidly and subsumed inclusions during a volcanic eruption. The lack of common Pb in the chemically abraded zircons is consistent with the chemical abrasion process dissolving Pb-bearing mineral or melt inclusions less resistant to HF than zircon.

Such a hypothesis would predict that the rims on S-type granitic (not dacitic) zircons which crystalized more slowly would not contain as much common Pb. For comparison, eight ~430 Ma S-type granitic zircon overgrowths from Bodorkos et al. (2015) were re-examined to look for high common Pb. In three of these samples, no spots in the igneous overgrowth group had any statistically significant common Pb. Three more had a single common Pb-containing outlier with a raw ^{207}Pb/^{206}Pb ratio of less than 0.075. The last two samples had, respectively, two and seven spots with detectable common Pb, but in no case was the total ^{207}Pb/^{206}Pb ratio higher than 0.075 (which is about 1.5% ^{206}Pb$_c$ in the Devonian). So compared to these granitic S-type zircons of Bodorkos et al. (2015), our dacitic zircon rims have unusually high common Pb contents.

Unlike the reference zircons TEMORA 2, 91500, QGNG, and OG1, the MPC rims were not less scattered than the untreated rims. The chemically abraded rims were more scattered. Whether or not the high common Pb rims were excluded, the MPU rims yielded a single population with a probability of fit (Pof) of either 0.11 or 0.3. In contrast, the chemically abraded zircons had a PoF below 0.001, even after excluding a spot which may have hit part of a core. This is not a case of the common Pb correction expanding the individual spot errors on the untreated grains to accommodate a similar level of dispersion.

Interestingly, the 18 chemically abraded cores which were the same age (within uncertainty) as the rims did not have excess scatter. The 18 MPC cores all defined a single coherent population with a PoF of 0.13, and an age (431.3 ± 2.1 Ma) within uncertainty of the MPC rim age (431.8 ± 1.7 Ma). It is only the chemically abraded rims which show excess geochronological scatter.

The much larger population of syn-eruptive cores in the CA-treated grains as opposed to the untreated grains is interpreted as survivor bias, as the core-rim interface presents an area of weakness for the HF to attack during partial dissolution. Zircon dissolution along this boundary was noted in some surviving grains (Figure 1).

The igneous ages from the MPC rims are about 1.5 to 2 million years older than those from the MPU rims. This 1/3 to ½ percent difference is consistent with the offset seen in TEMORA 2, QGNG, and OG1. While we have no self-annealing closure ages for QGNG and Mount Painter, Magee et al. (2017) give U-Th-He dates for OG1 and TEMORA that yield irradiation levels of up to 6.5x10^{17} α/g For TEMORA 2 and up to 2x10^{18} α/g for OG1 zircons. These are both over the 6x10^{17} α/g damage limit proposed by McKanna et al. (2023b) where Pb loss may occur. The eruption age is unlikely to be the final cooling age for the Mt Painter Volcanics, as this unit was buried and deformed during the Lachlan Orogen. However, a closure time similar to TEMORA 2 (from the same orogen) would yield higher damage levels due to the higher uranium content of the Mt Painter zircon rims (tables 3 and 6b) relative to TEMORA 2.

The increase in scatter in the chemically abraded Mount Painter rims is more difficult to explain, and it occurs in both the younger and older directions. Although Pb diffusion can happen in zircon at 950°C, it is unlikely to proceed over tens of microns in the space of 15 hours. Even if the partial dissolution process enhances diffusion, the HF partial dissolution step comes after, not before, the high temperature annealing.

Given the number of high common Pb rims in the untreated rims (7 of 36), it is conceivable that the dissolution of included phases in the rims was incomplete, leaving orphaned U (in the case of the young grain), or orphaned Pb (in the case of the old two).

610 Alternatively, the dissolution of inclusions and metamict zones in the rims may have compromised the sputtering surface. In theory, a nanospongiform surface texture from partial dissolution could cause ion emittance issues that might invalidate the $^{206}Pb/^{238}U$ vs $^{254}(UO)/^{238}U$ calibration equation. It is not clear why this would be apparent only in the Mount Painter zircons and not the reference material grains, but it could be that the increased dissolution proportion of these grains has increased the probability of any particular spot having anomalous Pb^+ - U^+ - UO^+ ion emission behaviour.

615 To constrain these various possibilities, the individual zircon grains whose rims did not group in the igneous age group were re-analysed (session 210046) to see if there was a reproducible difference in the $^{206}Pb/^{238}U$ ratio, or if the scatter was unreproducible. Both cores and rims were analysed to determine if the cores were higher or lower in total ^{206}Pb than the rims. The results, shown in Figure 12, show that the outlier grains from the original session 170124 are not consistently anomalous in $^{206}Pb/^{238}U$ ratio or age. This implies an analytical effect relating to the sputtering and emission surface, not a compositional

620 one due to Pb migration across zircon subdomains or orphaned U or Pb from incomplete dissolution.

It is worth noting that the SHRIMP instrument performed unusually well during reference zircon session 170123. The T2U grains formed a coherent population (probability of fit > 0.05) without the addition of any spot-to-spot error (Ludwig 2009). Currently in the Geoscience Australia SHRIMP laboratory, this only happens in approximately 20-30% of SHRIMP geochronology sessions; The majority of sessions have a calculated spot-to-spot error between 0.5% and 1%, such as session

625 170124, in which the Mt Painter zircons were run (spot-to-spot error 0.66%). Continuing analytical development is necessary in order to understand the sources of this uncertainty. This may involve more rigorous control of ion source stability, instrument tuning, mount preparation, or stage movement and spot placement. However, chemical abrasion seems to ameliorate that component of spot-to-spot scatter caused by failure of untreated zircon to be completely closed to Pb mobilisation. What instrumental issues remain the next largest source of uncertainty, how to ameliorate them, and where the ultimate limit of

630 SIMS ^{206}Pb-^{238}U geochronology lies remains to be seen.

4.3.2 Mount Painter Volcanics cores

Compared MPU, MPC has more igneous age cores, and a smaller population of Ediacaran-Cambrian aged cores recognised as part of the Pacific Gondwana Suite (Fergusson et al. 2001). This is consistent with the Pacific Gondwana grains being more susceptible to loss during the chemical abrasion procedure than other zircons in the sample. Similarly, the increase in the

635 proportion of igneous age grains in the chemically abraded sample is consistent with single generation zircons being more resistant to destruction by the chemical abrasion process than those with overgrowths, where the contacts can be damaged by the partial dissolution step of chemical abrasion (figure 1) . — Eddy group & ref ✓

Geologically, the dominance of Pacific Gondwana Ediacaran-Cambrian zircons with a somewhat subordinate population of 1000-1200 Ma grains is typical of early Palaeozoic sediments in Queensland (Fergusson et al. 2002, 2007; Purdy et al. 2016),

640 Victoria (Keay et al. 1999), South Australia (Ireland et al. 1998) and the NSW Lachlan fold belt to the South and East of Mount Painter (Fergusson et al. 2001). So their presence in the Mount Painter Volcanics is consistent with this unit being an S-type dacite sourced from the melting of early Paleozoic sediments (Chappell and White 1974). The relative dearth of ~450-480 Ma zircons in the Mount Painter Volcanics zircon cores may indicate derivation from Cambrian or early Ordovician sediments. Alternatively, it may reflect sedimentary transport effects which deprived the source sediments of zircon younger than ~480

645 Ma.

4.4 SHRIMP δ¹⁸O discussion

For the 91500, OG1, and QGNG zircons, the change in $\delta^{18}O$ mean values between the chemically abraded and unabraded populations was negligible. However, the chemically abraded TEMORA grains were approximately 0.7‰ lighter than the untreated grains. This is probably a sample handling error. Schmitt et al. (2019) show that the TEMORA 2 zircon distributed by Geoscience Australia has variable $\delta^{18}O$ values, which differ depending on which batch of zircon is used. While the original plan was to split a single vial of TEMORA 2 zircon, a sample preparation miscommunication resulted in an entire vial being chemically abraded. Even though both the original and the replacement vials were labelled as being the older material (heavier in $\delta^{18}O$) described in Schmitt et al. (2019), we suspect an old vial was refilled with more recent material with lighter $\delta^{18}O$. Otherwise, it is hard to explain why the TEMORA 2 zircon would change oxygen isotopic composition while the more metamict OG1 and QGNG samples remained unchanged. We repeat the warning from Schmitt et al. (2019) that TEMORA 2 oxygen isotope values from the Geoscience Australia mineral separation facility are heterogeneous.

The Mount Painter Volcanics zircon rims showed substantially more scatter in $\delta^{18}O$ composition than the reference zircons. This is consistent with previous observations that S-type granites have variable rim $\delta^{18}O$ (Ickert 2010). None-the-less, the mean $\delta^{18}O$ value is consistent between the untreated and chemically abraded rims, and is well within uncertainty.

The Mount Painter Volcanics zircon cores have a wide range of $\delta^{18}O$ values, as might be expected of sedimentary zircons. For the dozen or so grains of each sample where core and rim analyses were performed on the same zircon, there is no evidence that the $\delta^{18}O$ composition of the core influences the $\delta^{18}O$ composition of the rim. Given the relatively low Ti-in-zircon rutile equilibration temperatures of 690°C (from both untreated and chemically abraded rims), this is not surprising. Similarly there appears to have been no core-rim diffusive re-equilibration on the tens-of-micron spot diameter scale during the annealing phase of chemical abrasion.

It is worth noting that not all the Mount Painter Volcanics zircon cores are detrital. Those cores which are the same age (within uncertainty) as the rims are probably related to some sort of pre-eruptive igneous process. While the geochronology results show that the Th/U ratios of these cores are often higher than the rims, no other trace elemental analyses were done on the cores. However, ten of these young cores were analysed for $\delta^{18}O$. These results were similar to the rims (between 7 and 10 ‰, with an average of 8.6 ±1 ‰), and were not within uncertainty of mantle $\delta^{18}O$ values.

4.5 Trace element discussion

While the OH/O ratio in zircons was measured in both the first (mass 16-17-18) and second (mass 17-18-19) SHRIMP SI sessions, the OH background was high, presumably due to the epoxy mounting material. This background decreased over time, so the OH/^{18}O data from the (17-18-19) session, which was run on the same mounts without any sample exchange, had lower backgrounds. The same trends were present in both sessions, but the lower signal / background ratio in the first (16-17-18) session increased the scatter.

Although we do not have a way of standardizing OH, the OH/O measurements in the untreated OG1 were both more variable and higher than in the chemically abraded OG1. In all other samples, there was no significant difference in OH between the chemically abraded and untreated samples. This is consistent with OG1 being the most open system zircon we looked at, and thus having the most metamictisation-related hydration, which the partial dissolution step of chemical abrasion removes. Overall, the low OH/O in 91500 and S-type Mount Painter Volcanics cores relative to the I-type OG1, QGNG, and TEMORA 2 zircons is consistent with the observation of Mo et al. (2023) that S-type zircons are dryer than I-type zircons.

Fluorine contents in both the chemically abraded and untreated samples is unchanged. The lack of fluorine uptake in OGC is consistent with hydrous material being preferentially dissolved, and not with the exchange of fluorine with OH bound in structurally sound zircon. Fluorine measured as $^{19}F^-$ by SHRIMP SI relative to $^{18}O^-$ and $^{19}F^+$ relative to $^{30}Si^+$ by SHRIMP 2 gave generally similar values, with the median values for all samples in the low teens of ppm, compared to a standard value of 15 ppm for 91500 (Coble et al. 2018).

For the other trace elements, little change was noticed. U and Th contents in the chemically abraded OG1 were slightly lower. We attribute this to survivor bias, where higher U and Th grains would accrue more radiation damage, and be less likely to survive the chemical abrasion treatment. The Ti contents and indicated temperatures are unchanged. Burnham (2020) describes how to use the shape coefficients of O'Neill (2016)'s orthogonal polynomials to quantitatively describe REE concentrations. Median calculated shape coefficients are listed in Table 6, and spot by spot values are listed in supplementary tables 6 and 7. In the case of the laser trace element data, the requirement to also collect Pb isotopes has compromised the detection limits for the LREE, and the lack of odd HREE in the run table means that the orthogonal polynomial calculations overfit the data due to the relatively few degrees of freedom caused by unanalysed odd HREE and BDL LREE. Thus laser lambda values are not reported for the laser REE data. With the SHRIMP data, the lambda values for the curve defined by the median concentrations were fairly similar to the median lambda values as calculated for each spot for λ_0 and λ_1, vaguely similar for λ_2, and generally not well matched for λ_3.

Summarize / Relet

The laser REE data show that for 4 of the 30 untreated QGNG and OG1 zircons, the chondrite-normalized lanthanum concentration was above 1. Additionally, in one of the OGC zircon, the chondrite-normalized lanthanum concentration was above 10. As lanthanum is highly incompatible in the zircon structure, these analyses probably indicate either inclusions or radiation damage associated alteration and element mobility. To the extent that they were above the detection limit, praseodymium and neodymium were also elevated in these samples. In contrast, none of the chemically abraded samples had high lanthanum concentrations, indicating that these LREE-enriched zones present in the untreated samples were removed by the chemical abrasion process.

None of the SHRIMP REE patterns had chondrite-normalized La concentrations above 1. We attribute this to the smaller analytical volume and shallower pit depth of SHRIMP relative to laser allowing the analyst to miss inclusions or metamict areas. The chemically abraded TEMORA 2 and OG1 zircons showed lower median LREE than the untreated samples, consistent with the idea that a significant LREE budget in zircon comes from metamict zones or nanoinclusions of other minerals where the LREE are more compatible. However, QGNG shows the opposite trend, which we cannot explain.

4.6 Lu-Hf discussion

The Hf isotopic results are similar for both chemically abraded and untreated reference zircons. Of the eight analysed reference zircons, only the initial Hf composition of the 91U was not within uncertainty of the reference values. There was no pattern in the direction of Hf isotopic change between the chemically abraded and untreated samples, but the chemically abraded results generally had a larger uncertainty. QGNG (both) and OGU were the only reference zircons where the probability of fit for all spot measurements was greater than 5%.

5 Overall conclusions

The most important conclusion from this study is that untreated and chemically abraded reference values and samples are not interchangeable in SHRIMP U-Pb analyses, if they differ significantly. SHRIMPing chemically abraded zircons returns the chemically abraded TIMS age; SHRIMPing untreated zircons returns the TIMS age derived from zircons which did not undergo chemical abrasion. All chemically abraded reference zircon results in this study are more precise, but for the younger reference zircons (TEMORA 2 and 91500), this is a modest effect. Using CA-ID-TIMS reference ages for untreated older reference zircons such as OG1 or QGNG will almost certainly produce a systematic bias on the order of half a percent: the difference between the reference ages for the untreated and chemically abraded grains observed using both SHRIMP and TIMS geochronology.

This study shows that zircons such as OG1 and QGNG, which have suffered minor Pb loss, will not reproduce the CA-ID-TIMS age when analysed by SHRIMP, unless the SHRIMP targets are also chemically abraded. This suggests that there is

pervasive low-level Pb loss in the untreated samples, which is corrected in the chemically abraded material. This would mean that there is a subtle change in the surviving material, and it isn't just the visible channels and cavities (Figure 1) where zircon

730 has been dissolved that are affected by the chemical abrasion process.

As the SHRIMP ages of both untreated OG1 and untreated QGNG were about half a percent lower than the chemical abraded ages (either SHRIMP or TIMS), it would not be surprising if many older and/or actinide-rich zircons also showed minor Pb loss. This is consistent with the conclusions of Magee et al. (2023), where a comparison of untreated SHRIMP ages to CA-ID-TIMS ages showed that Cambrian zircons tended to have younger SHRIMP ages, with a magnitude similar to the OG1 and

735 QGNG offset demonstrated here.

This experiment demonstrates that when the SHRIMP instrument is running well, on chemically abraded reference zircons, accuracy and precision in the 2.5 to 4 ‰ range is possible. This represents a substantial improvement in the performance of in-situ geochronology. Whether this level of accuracy and precision will be achievable for unknown zircons with more complex geologic history or higher accumulated radiation damage than well-established reference zircons remains to be seen, as the

740 Mount Painter Volcanics results suggest that there could be complicating factors. While we cannot guarantee that chemical abrasion will improve SIMS U-Pb geochronology, we think these results are promising enough to warrant further experimentation.

Chemical abrasion has little additional effect on zircon mineral chemistry beyond the U-Pb system, and does not seem to have

745 compromised the ability to measure any of the elements or isotopes presented in this paper with microbeam mass spectrometry. OG1 showed a loss of OH, which is consistent with chemical abrasion dissolving altered, hydrated zircon. As this was not accompanied by an increase in F, we dismiss crystal structure F-OH substitution during HF treatment as a cause. Aside from OH, there was a tendency for highly incompatible elements such as the LREE, Ca, and common Pb to be reduced in the chemically abraded samples compared to the untreated samples, but this was not universal. Hafnium and oxygen isotopes were

750 undisturbed.

Author contributions

CM, SB, TI, and YA designed the project, CM and SB wrote the graduate project proposal for the project, SK did the gravimetric solution and OG1 ID-TIMS, CK and YA did the chemical abrasion for microanalysis, CK did SHRIMP analyses for U-Pb and $\delta^{18}O$, KW and NE did the LASS analyses, CM did the SHRIMP TE analyses, CK, CM, and NE reduced the data,

755 CM, CK, YA, SK, and NE wrote the text, CK and CM did the figures, and CK, CM, SK, and NE did the tables.

Competing interests

At least one of the co-authors is a member of the editorial board of Geochronology.

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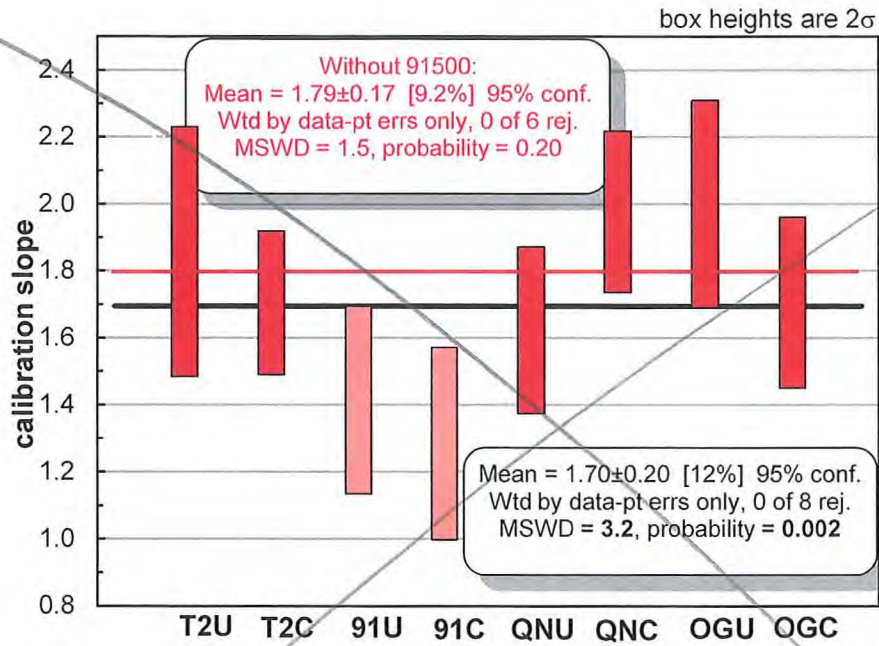
Figure 2: The calibration slopes for all 8 samples on mount GA6363, when each is defined as the reference zircon. Number of analyses is 41 for T2C, 42 for all other samples.

990

All new T-W diagrams
for all data

✳ Consistent format ✳

- delete TEMORA δ¹⁸O pnel
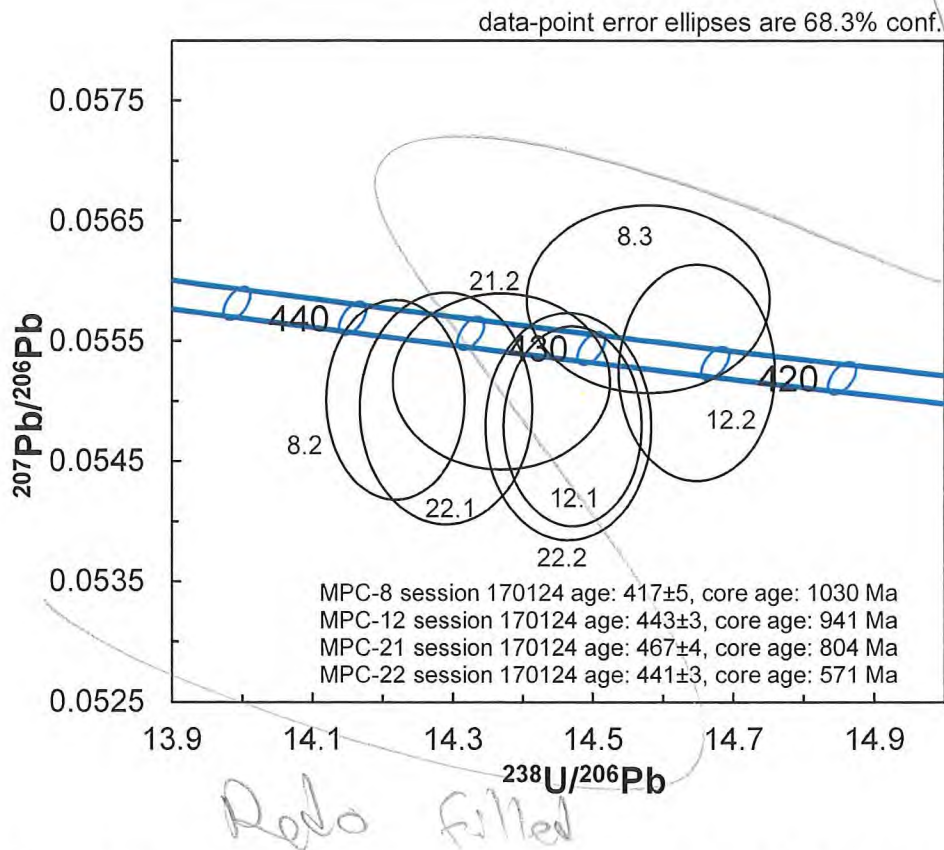
Figure 12: Repeat analyses of Mount Painter Volcanics zircon rims with anomalous rim ages in the first analytical session (170124).

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Tables:

Table 1: Reference values recalculated from literature using consistent uncertainty treatment and reduced tracer uncertainty from gravimetric solution analyses:

Zircon	$^{206}Pb/^{238}U$ ratio	No tracer 95% *	Tracer 95%	Tracer+ random 95%	n	MS WD	Age Ma	±No tracer 95% Ma	±With tracer 95% Ma	Tracer	Reference
T2U	0.066789	0.098%	0.051%	0.110%	9	0.56	416.78	0.39	0.44	ROM	Black et al. (2004)
T2C	0.066896	0.012%	0.030%	0.032%	59	3.89	417.36	0.05	0.13	Both ET	Schaltegger et al. (2021)
91U	0.17937	0.025%	0.030%	0.039%	7	0.58	1063.55	0.25	0.38	ET535	Schoene et al. (2006)
91C	0.17937	0.049%	0.030%	0.058%	7	1.10	1063.51	0.49	0.57	ET2535	Horstwood et al. (2016)
QNU	0.33097	0.229%	0.051%	0.235%	8	2.94	1843.08	3.68	3.77	ROM	Black et al. (2003)
QNC	0.33213	0.054%	0.030%	0.062%	7	2.21	1848.70	0.86	0.99	ET535	Schoene et al. (2006)
OGU	0.70503	0.125%	0.051%	0.135%	6	1.46	3439.68	3.33	3.59	ROM	Stern et al. (2009)
OGC	0.71074	0.106%	0.051%	0.118%	7	0.22	3461.25	2.85	3.15	ROM	Stern et al. (2009)

* 95% confidence interval is Std Er x Student's t x square root of MSWD, if probability of fit < 0.05.

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Table 6. SHRIMP median sample trace elemental concentrations measured as positive ions on SHRIMP 2 and median derived values. A: Session 220029, on the reference zircon mount GA6363. B: Session 220028, on Mount Painter Volcanics mount GA6364. "Setup 91500" is co-analysed 91500 zircon on setup mount GA5040. T (Ti): Titanium-in-zircon thermometer of Ferry and Watson (2007), assuming titanium activity=1. P sat: Phosphorus saturation of Burham and Berry (2017). Orthogonal polynomials (λ) of O'Neill (2016).

A	G8	M127	T2U	T2C	91U	91C	QNU	QNC	OGU	OGC
F ppm	46	15	15	14	16	17	14	15	16	16
Al ppm	1.5	3.9	1.9	4.1	11.8	9.7	0.1	0.1	1.9	2.2
P ppm	81	190	128	193	11	10	259	220	166	127
Ca ppm	2.3	2.6	2.5	2.5	2.5	3.5	2.5	1.6	2.5	3.2
Ti ppm	9.5	5.8	9.6	7.7	4.4	4.6	15.6	14.4	8.1	6.3
Fe ppm	4.2	2.1	1.1	4.0	3.7	3.1	5.1	4.5	38.1	55.5
Y ppm	456	780	1186	1037	121	132	809	1033	1142	635
				-						
La ppm	0.005	0.005	0.016	0.003	0.005	0.007	0.006	0.023	0.032	0.007
Ce ppm	15.4	16.0	3.7	3.7	2.2	2.2	18.3	18.2	12.3	10.2
Pr ppm	0.091	0.092	0.208	0.044	0.009	0.011	0.087	0.232	0.273	0.068
Nd ppm	1.2	1.9	3.6	1.0	0.1	0.2	1.5	4.3	4.8	1.3
Sm ppm	2.3	3.9	6.0	3.0	0.3	0.4	3.6	7.0	7.6	2.6
Eu ppm	0.07	0.26	1.13	0.85	0.18	0.23	0.41	1.19	1.98	0.97
Gd ppm	9.7	16.2	25.3	16.8	1.7	1.8	16.4	29.2	27.0	11.1
Tb ppm	3.3	5.6	8.5	6.4	0.7	0.7	5.8	9.2	8.4	3.7
Dy ppm	39	67	106	85	10	11	71	103	98	47
Ho ppm	13	25	40	34	4	4	28	36	37	20
Er ppm	57	120	189	165	21	23	124	154	169	102
Tm ppm	12	28	41	37	5	6	26	31	38	25
Yb ppm	104	291	418	387	62	70	257	292	386	288
Lu ppm	16	52	71	69	11	13	43	49	69	55
Hf ppm	11351	11472	7960	8668	5388	5233	10196	9977	8261	8759
Th ppm	254	397	78	118	23	23	128	207	134	86
U ppm	1349	851	156	283	70	71	166	230	138	150
T (Ti), °C	741	697	743	722	673	679	790	782	727	705
P sat	0.34	0.40	0.17	0.30	0.14	0.11	0.61	0.33	0.23	0.38
λ_0	3.2	3.8	4.3	3.7	1.8	2.0	3.7	4.3	4.4	3.6
λ_1	-53	-58	-55	-65	-58	-56	-58	-51	-51	-58
λ_2	-216	-202	-176	-202	-32	-2	-206	-197	-150	-130
λ_3	-1161	-1669	-1384	-692	590	720	-996	-1078	-1379	-1375

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