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Increased accuracy and precision in igneous and detrital zircon geochronology using CA-LA-ICPMS

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Abstract. Detrital zircon geochronology by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a widely-used tool for determining maximum depositional ages, sediment provenance, and reconstructing sediment routing pathways. Although the accuracy and precision of U-Pb geochronology measurements has improved over the past two decades, Pb-loss continues to impact the ability to resolve zircon age populations by biasing affected zircon toward younger apparent ages. Chemical abrasion (CA) has been shown to reduce or eliminate the effects of Pb-loss in zircon U-Pb geochronology, but has yet to be widely applied to large-n detrital zircon analyses. Here, we assess the efficacy of the chemical abrasion treatment on zircon prior to analysis by LA-ICP-MS and discuss the advantages and limitations of this technique in relation to detrital zircon geochronology. We show that i) CA does not systematically bias LA-ICP-MS U-Pb dates for thirteen reference materials that span a wide variety of crystallization dates and U concentrations; ii) CA-LA-ICP-MS U-Pb zircon geochronology can reduce, or eliminate, Pb-loss in samples that have experienced significant radiation damage; and iii) bulk CA prior to detrital zircon U-Pb geochronology by LA-ICP-MS improves the resolution of Neoproterozoic to present zircon age populations and the percentage of concordant analyses in Mesoproterozoic and older age populations. The selective dissolution of zircon that has experienced high degrees of radiation damage suggests that some detrital zircon age populations could be destroyed or have their abundance significantly modified during this process. However, we did not identify this potential effect in either of the detrital zircon samples that were analyzed as part of this study. We conclude that pre-treatment of detrital zircon by bulk CA may be useful for applications that require increased resolution of detrital zircon populations.

1. Introduction

Detrital zircon U-Pb geochronology is a common and widely-used tool with a broad range of applications across multiple subdisciplines of geology. As the efficiency, accuracy, and precision of U-Pb geochronology measurements continue to improve (e.g., Carrapa, 2010; Gehrels, 2012; Gehrels, 2014; Pullen et al., 2014; Sundell et al., 2021), the production of large detrital zircon datasets by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become more common. In basin analysis and tectonics, these datasets are often used to determine sediment provenance, characterize source terranes, and reconstruct ancient sediment routing pathways (Fedo et al., 2003; Anderson 2005; Smith et al., 2023). The resulting data is typically interpreted using kernel density estimates (KDEs) or probability density plots (PDPs) and assessed by comparing the means, heights, widths, and modes of peaks in detrital zircon age spectra using similarity/dissimilarity metrics. One factor that may limit the

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resolution of these peaks is Pb-loss which can smear zircon age populations toward younger apparent U-Pb dates. This issue may not bias data in which Pb-loss is a recent phenomenon provided that the $^{207}Pb/^{206}Pb$ date is used for zircon crystallization. However, protracted or complicated histories of Pb-loss can make it difficult to interpret $^{207}Pb/^{206}Pb$ dates (Nemchin and Cawood, 2005) and many labs only use this system to constrain a zircon crystallization date if it is concordant. The precision of the $^{207}Pb/^{206}Pb$ chronometer also typically limits its use to Mesoproterozoic and older zircon. The most precise date for Neoproterozoic or younger zircon is generally obtained with the $^{206}Pb/^{238}U$ chronometer, but these dates are more susceptible to open-system behavior. Zircon age populations that are affected by Pb-loss in this age range can be difficult to identify since Pb-loss trajectories closely follow Concordia and may result in analyses that are concordant within analytical uncertainty but have spuriously young $^{206}Pb/^{238}U$ dates. The effect of Pb-loss on detrital zircon analyses is consequently two-fold. It reduces the number of concordant Mesoproterozoic and older zircons, making populations in this age range more difficult to identify, and it will cryptically smear Neoproterozoic and Phanerozoic zircon age populations along concordia toward spuriously young dates, making it difficult to resolve differences between distinct but similarly aged populations.

The chemical abrasion method, in which thermally annealed zircon is partially dissolved in hydrofluoric acid (HF) prior to analysis has been shown to successfully mitigate Pb-loss (e.g., Mundil et al., 2004; Mattinson, 2005; Widmann et al., 2019; Sharman and Malkowski, 2023) and is widely used in isotope dilution-thermal ionization-mass spectrometry (ID-TIMS) U-Pb zircon geochronology (*see reviews in* Schoene, 2014; Schaltegger et al., 2015). The technique likely benefits analyses in two ways. First, it selectively dissolves zones of the zircon crystal that have experienced extensive radiation damage and possible Pb-loss (Widmann et al., 2019). Second, the partial dissolution process dissolves inclusions that may harbor non-radiogenic Pb, leading to a higher proportion of zircon-hosted radiogenic Pb (Pb*) in the measured analysis. Over the last decade, several groups have analyzed chemically abraded zircon by LA-ICP-MS and shown that this approach can successfully mitigate Pb-loss, resulting in the increased concordance, precision, and, presumably, accuracy of U-Pb dates (Crowley et al., 2014; Von Quadt et al., 2014). These results suggest that chemical abrasion prior to large-n detrital zircon analyses may also be useful when the resolution of closely spaced Neoproterozoic and Phanerozoic peak age populations is desired or when high degrees of discordance obscure the interpretation of Mesoproterozoic and older age populations. Here, we assess the benefits and drawbacks of this pre-treatment with a particular focus on whether the resolution of younger zircon age populations is increased, whether it improves concordance for Precambrian detrital zircon populations, and/or whether the selective removal of metamict zircon will bias age populations.

2. U-Pb Zircon Geochronology Approach and Methods

We have divided our study into three distinct parts. First, we compare chemically abraded and untreated zircon from 13 zircon reference materials (Table 1) to test whether chemical abrasion systematically biases U-Pb dates analyzed by LA-ICP-MS. Crowley et al. (2014) demonstrated that chemically abraded zircon ablate more slowly and experience greater down-hole fractionation than untreated zircon. These differences are likely related to differences in the ability of the laser to couple with zircon that has been etched by the chemical abrasion process. While no negative effects of chemical abrasion were seen in Crowley et al. (2014) or von Quadt et al. (2014), provided that chemically abraded reference materials were used as primary standards, we have expanded the age range of reference

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zircon analyzed to encompass 28.5 – 3467 Ma. This increased age range of the tested reference materials provides a more complete understanding of LA-ICP-MS U-Pb systematics on chemically abraded zircon and whether a single primary standard can be used for a wide range of zircon dates and U content. Second, we assess the ability of chemical abrasion to mitigate Pb-loss in an igneous sample that has experienced substantial radiation damage by comparing chemically abraded and non-chemically abraded $^{206}Pb/^{238}U$ LA-ICP-MS zircon analyses to a newly produced CA-ID-TIMS reference date for the same sample. Finally, we assess how CA affects detrital zircon (DZ) age spectra by comparing chemically abraded and untreated aliquots of two detrital samples. One sample is Cenozoic in age and contains both Phanerozoic (100-300 Ma) and Precambrian (1000-1200 Ma) zircon age populations, whereas the second sample is Proterozoic and contains zircon age populations between 2000-3500 Ma.

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

Name	ID-TIMS age (Ma)	2s	References	Host lithology	Quantity
Fish Canyon tuff	28.476	0.029	Schmitz and Bowring (2001)[a]	Dacite	Unlimited
GHR1	48.106	0.023	Eddy et al. (2019)[b]	Rapakivi Granite	Unlimited
49127	136.6		Gehrels et al. (2008)[b]		Uncertain
Plesovice	337.13	0.37	Slama et al. (2008)[a]	Potassic Granulite	Unlimited
Temora 2	418.37	0.14	Mattinson (2010)[a]	Gabbro	Unlimited
R33	420.53	0.16	Mattinson (2010)[a]	Monzodiorite	Unlimited
SLM	563.5	3.2	Gehrels et al. (2008)[b]	Single Crystal	Limited
SLF	555.86	0.68	Wang et al. (2022)[b]	Single Crystal	Limited
91500	1065.4	0.3	Wiedenbeck et al. (2008)[b]	Single Crystal	Limited
FC1	1098.47	0.16	Mattinson (2010)[a]	Gabbro	Unlimited
Oracle	1434	8	Gehrels et al. (2008)[b]	Granite	Uncertain
QGNG	1851.6	0.6	Black et al. (2004)[b]	Quartz gabbro gneiss	Uncertain
OG1	3467.05	0.63	Stern et al. (2009)[a]	Diorite	Unlimited

[a] Chemical abrasion CA-ID-TIMS
[b] Traditional ID-TIMS

2.1 Methods for Thermal Annealing and Chemical Abrasion

All chemically abraded zircon aliquots were treated at Purdue University following methods modified from Mattinson (2005) and similar to those described in Eddy et al. (2019). Zircon separates were first thermally annealed in quartz crucibles for 60 hours at 900°C in a muffle furnace and then loaded in 3 mL savillex hex beakers with ~1 mL of 28M HF and 0.1 mL of 8M HNO_3 for bulk chemical abrasion. Four hex beakers were then stacked in the PTFE liner for a 125 mL Parr acid dissolution vessel. To ensure vapor exchange during partial dissolution a small hole was drilled through each beaker cap. The fully assembled Parr acid dissolution vessel was then held at 210°C for 12 hours. Once the chemical abrasion process was completed, the leachate was removed from each beaker using a pipette and the zircons were rinsed three times with H_2O. Chemically abraded aliquots were then sent to the University of Arizona

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LaserChron Center (ALC) for mounting and LA-ICP-MS analyses. Methods for chemical abrasion of zircon prior to the ID-TIMS analyses reported in this paper are similar to those described above, except individual zircon were chemically abraded in 200 µL Ludwig style microcapsules and repeatedly rinsed in distilled 7M HCl and ultrapure H_2O prior to spiking and complete dissolution.

2.2 LA-ICP-MS Zircon U-Pb Geochronology

Zircon aliquots were mounted in 2.5-cm-diameter epoxy plugs, polished, and imaged by cathodoluminescence using a Hitachi 3400N SEM and a Gatan Chroma CL system prior to analysis by LA-ICP-MS. Chemically abraded zircon were only mounted with chemically abraded zircon reference materials, while untreated zircon aliquots were mounted with untreated reference materials. U-Pb isotopic analyses were obtained via LA-ICP-MS using a Thermo Element2 single-collector ICP-MS coupled with a Teledyne Photon Machines Analyte G2 excimer laser at the ALC. The diameter of the laser spot was set to 30 microns. Elemental- and mass-dependent instrumental fractionation were corrected by bracketing unknown analyses with analyses of primary reference material FC1 following the methods described in Pullen et al. (2018). Only chemically abraded primary standards were used for calibration of chemically abraded samples and only untreated primary standards were used for untreated samples following the recommendations of Crowley et al. (2014). Bracketing occurred every 10-11 analyses for the round-robin comparison of zircon reference materials, every 2-3 analyses for igneous zircon analyses, and every 5 analyses for detrital zircon samples. Data reduction was completed using an in-house Matlab script, AgeCalcML v.1.42 (Sundell et al., 2021). This program allows the user to filter data by maximum $^{206}Pb/^{238}U$ and/or $^{207}Pb/^{206}Pb$ uncertainty (typically set to 10%), reverse discordance (typically 5%), and normal discordance (typically 20%). For the purposes of this study, we de-activated all uncertainty and discordance filters in AgeCalcML and all isotopic data measured via LA-ICP-MS that is from clearly ablated zircon are reported in Tables S1-S13. However, age interpretations of igneous and detrital zircon data use filtered data (Tables S14-S19).

2.3 CA-ID-TIMS Zircon U-Pb Geochronology

Sample MIGU-02, a granitoid from the Guyana Shield, was analyzed by ID-TIMS at Purdue University to provide a reference date to compare the chemically abraded and untreated LA-ICP-MS analyses. Following the chemical abrasion methods described above, individual zircons were spiked with the EARTHTIME ^{205}Pb-^{233}U-^{235}U isotopic tracer (Condon et al., 2015; McLean et al., 2015) and loaded into a Parr acid digestion vessel with 28M HF. The vessel was then held at 210°C for 60 hours for zircon dissolution. After dissolution, the samples were dried down and then converted to chloride form, by adding 75 µl 7M HCl, reassembling the Parr acid digestion vessel, and holding it at 180°C for 12 hours. After conversion to chloride form, the solution was converted to 3M HCl in preparation for anion exchange chromatography. Pb and U were purified from these solutions using AG-1x8 anion exchange resin following procedures modified from Krogh (1973). The resulting aliquots were dried down to a chloride salt before being dissolved in silica gel, dried onto rhenium filaments, and loaded into an IsotopX Phoenix TIMS for analysis. Pb isotopic measurements were made by peak hopping on a Daly detector and corrected for mass dependent isotopic fractionation using an $\alpha = 0.147 \pm 0.028$ (%amu) and deadtime = 29.9 ns, derived from repeat measurements of the

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NBS981 Pb reference material. We assume that all ^{204}Pb is from laboratory contamination and correct for it using a laboratory Pb isotopic composition of $^{206}Pb/^{204}Pb = 18.82 \pm 0.74$ (2σ), $^{207}Pb/^{204}Pb = 15.52 \pm 0.63$ (2σ), $^{208}Pb/^{204}Pb = 37.93 \pm 1.60$ (2σ) derived from repeat total procedural blank measurements run during 2022. Uranium was run as an oxide (UO_2) and isotopic measurements were made statically using Faraday detectors and corrected for fractionation using the known ratio of $^{233}U/^{235}U$ in the EARTHTIME ^{205}Pb-^{233}U-^{235}U isotopic tracer (Condon et al., 2015; McLean et al., 2015) and assuming a zircon $^{238}U/^{235}U$ value of 137.818 ± 0.045 (Hiess et al., 2012). Data reduction was done using the ET_Redux software package (Bowring et al., 2011) and the decay constants of Jaffey et al. (1971). All isotopic data measured via CA-ID-TIMS are presented in Table S15.

3. Results

3.1 CA-LA-ICP-MS U-Pb Geochronology of Zircon Reference Materials

Treated and untreated aliquots of thirteen different zircon U-Pb reference materials (Table 1) were analyzed in this study to further assess whether chemical abrasion systematically biases U-Pb dates. The reference materials were analyzed during two round-robin runs. The first run targeted 15 zircon grains from treated and untreated aliquot of reference materials. During the second run, 30 zircon grains were targeted. Because FC-1 was used as a primary reference material for calibration of the LA-ICP-MS, approximately 30 FC-1 zircons were analyzed during run 1 and 87 were analyzed during run 2 per treated and untreated aliquots. The total number of zircons analyzed was 657 in each of the chemically abraded and untreated aliquots of reference materials. Of the 657 grains in the chemically abraded aliquot, 635 analyses (96.6%) were retained following filtering for discordance, whereas 608 analyses (92.5%) were retained in the untreated aliquot. These results further confirm that CA helps mitigate Pb-loss and improve precision in LA-ICP-MS analyses (e.g., Crowley et al., 2014; von Quadt et al., 2014). The most extreme change in concordance and data retention occurred between treated and untreated FC-1 zircon (1098.4 Ma). Of the 117 grains analyzed per treated and untreated aliquot, 97.4% of analyses were retained in the chemically abraded aliquot versus 82.1% in the untreated aliquot. Discordance criteria used for filtering the above data were reverse discordance larger than 5% and/or $^{206}Pb/^{238}U$ errors larger than 10%.

The dates of CA and non-CA reference materials are all within 0.1 – 4% of the reference ages determined by ID-TIMS (Fig. 1). Therefore, despite an increased concordance of treated grains relative to untreated grains, weighted means of acceptable analyses are indistinguishable and indicate that it is unlikely that chemical abrasion biases U-Pb dates within LA-ICPMS uncertainty. Concordant analyses in both treated and un-treated aliquots have similar U concentrations suggesting that zones with high U concentrations (Tables S1-S13) were not selectively removed by chemical abrasion despite the correlation between high U concentrations, radiation damage, and Pb-loss (e.g., Widmann et al., 2019). However, reference materials are chosen for their homogeneous nature regarding isotopic compositions, so it is not surprising that U concentrations are indistinguishable between the two aliquots. The reproducibility of U-Pb dates for all of the reference materials is strong evidence that a single primary reference material (FC-1 in this case) can be used to correct for instrumental fractionation across a wide range of zircon ages, U content, and trace element compositions for chemically abraded zircon.

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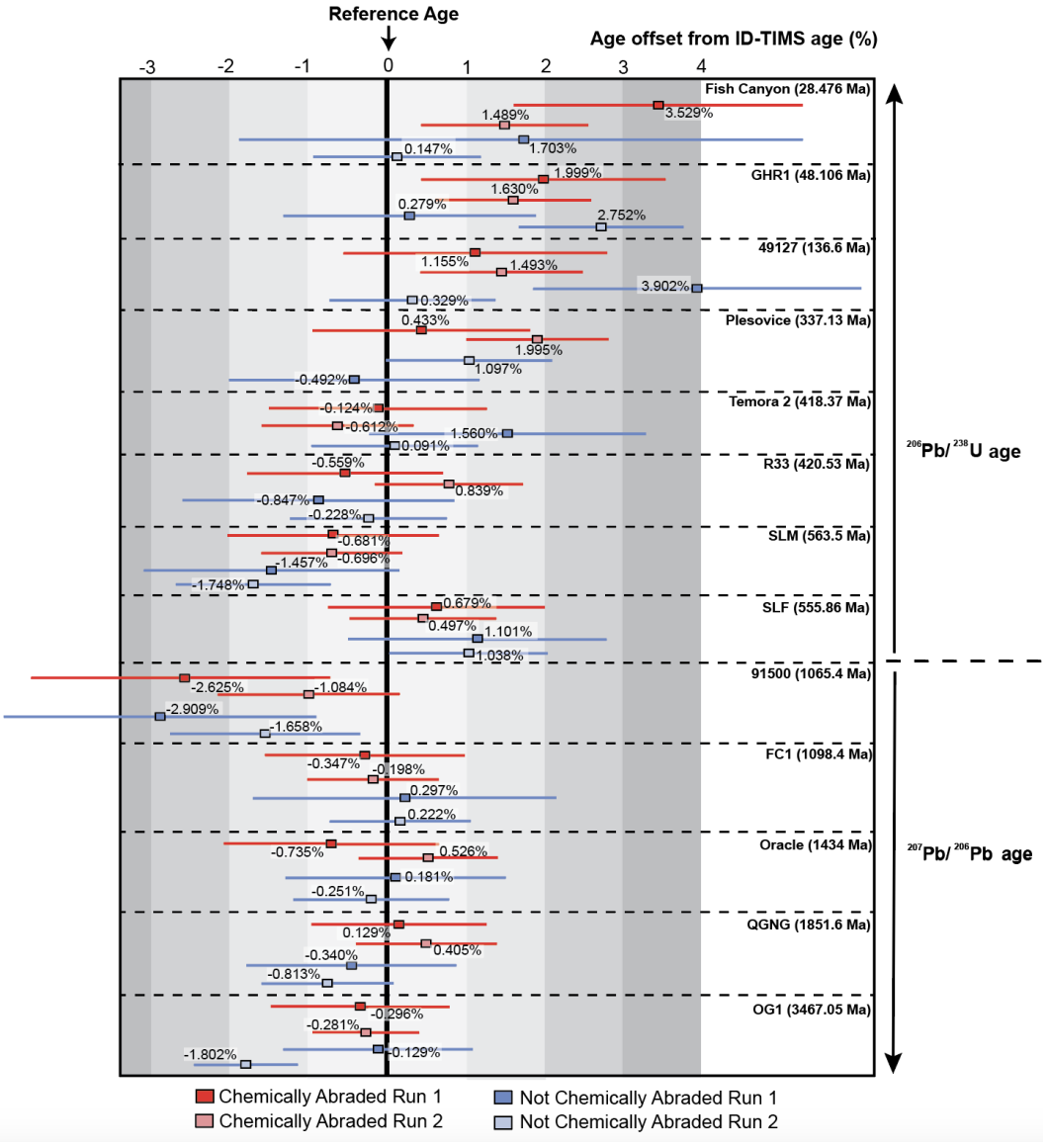

Figure 1. Comparison of $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ (CA)-LA-ICP-MS ages with CA-ID-TIMS ages for thirteen reference materials that range in age from 28 to 3467 Ma. Each square is the weighted mean of a set of (CA)-LA-ICP-MS measurements shown as the percent offset from the known reference age (ID-TIMS). The uncertainty is reported as 2-sigma standard error of the weighted mean. Chemical abrasion of treated aliquots was conducted at Purdue University and laser ablation analyses were conducted at Arizona LaserChron Center on the Thermo Element2 single-collector ICP-MS. Methods for LA-ICP-MS at LaserChron using the Element2 are described by Pullen et al. (2018).

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The scatter in the CA-LA-ICP-MS dates for both treated and untreated aliquots is similar for all age ranges. The greatest scatter in calculated weighted mean ages (~4 to 0.2% age offset from reference date) is in both the treated and untreated Mesozoic to Cenozoic reference materials. This scatter in age offset is improved by chemical abrasion for Paleozoic reference materials (2.0 to -0.8% age offset) and excellent for Proterozoic and Archean aliquots (0.6% to -0.7%). However, when comparing treated and untreated aliquots, the behavior of some reference materials warrants further discussion below. The CA-LA-ICP-MS weighted mean $^{206}Pb/^{238}U$ dates for two Cenozoic reference materials were older than the CA-ID-TIMS reference date. Chemical abrasion of GHR1 zircon led to increased concordance, but an older $^{206}Pb/^{238}U$ weighted mean date (Fig. A2). We attribute this difference to the presence of slightly older xenocrysts within the sample (e.g., Eddy et al., 2019). We see a similar result for Fish Canyon tuff zircon where the CA aliquot showed increased concordance, but the calculated mean age was offset more from the reference age than the no-CA aliquot (Fig. S1). This sample contains significant antecrysts that might bias its results (e.g., Wotzlaw et al., 2013). Indeed, increased precision and accuracy in analyses of young suites of igneous zircon routinely find overdispersion that can be related to protracted zircon growth or the presence of xenocrysts/antecrysts. Thus, the slight variability in weighted mean dates for GHR1 and Fish Canyon samples in CA-LA-ICP-MS analyses is not entirely unexpected and therefore unlikely to reflect of a systematic bias of the CA-LA-ICPMS method.

3.2 Untreated and CA- U-Pb Zircon LA-ICP-MS Analyses of Metamict Zircon

A Precambrian granite sample from the Parguaza Complex in the North Guyana Shield (MIGU-02; N 5° 21' 3.70"; W 67° 41' 33.41") that has experienced substantial radiation damage was analyzed to assess the effects of chemical abrasion on grains with significant Pb-loss. Untreated (n = 35) and treated aliquots (n = 23) of MIGU-02 were analyzed at the ALC and compared to a reference age determined by CA-ID-TIMS at Purdue University (n=6)(Fig. 2; Tables S14 and S15). During the bulk chemical abrasion process, 80-85% of MIGU-02 grains fully dissolved, leaving only a small fraction of the original aliquot to be used for analyses.

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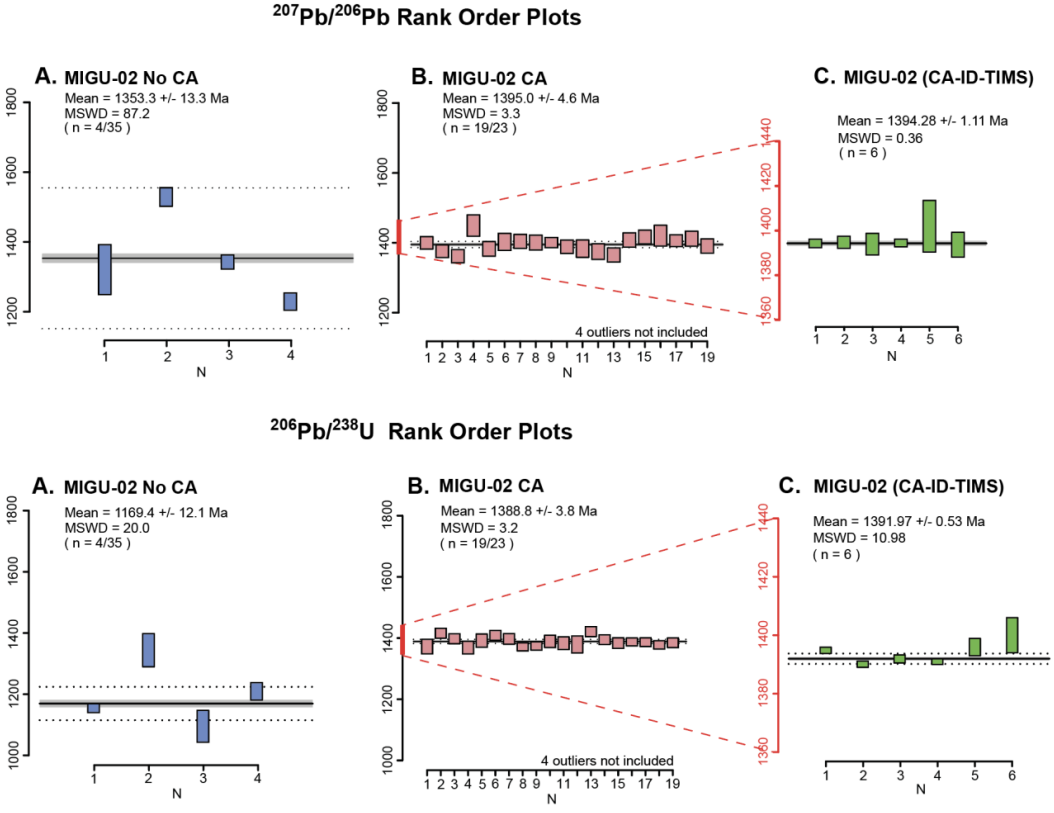

Figure 2. Rank order plots of calculated $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ages for treated and untreated MIGU-02 aliquots and of the reference age for MIGU-02 obtained using CA-ID-TIMS. **A.** Untreated samples of MIGU-02 show large degree of scatter in dates and substantial deviation from the reference age. **B.** Treated zircons show a significant increase in precision and accuracy of ages relative to the reference age. **C.** Reference age for MIGU-02 determined using the weighted mean of six grains. See text for discordance criteria.

The $^{207}Pb/^{206}Pb$ CA-ID-TIMS reference age for MIGU-02 is 1394.28 +/- 1.11 Ma (n=6, MSWD = 0.36), while the $^{206}Pb/^{238}U$ dates are more scattered (Fig. 2). The scatter indicates that U/Pb elemental fractionation occurred during chemical abrasion in one analysis (slight reverse discordance) and residual Pb-loss remained in others (normal discordance)(Fig. 3). Nevertheless, a weighted mean date of the $^{206}Pb/^{238}U$ CA-ID-TIMS dates is 1391.97 +/- 0.55 Ma (n = 6, MSWD = 10.98) and indicates that residual Pb-loss only affects the dates at the <0.5% level. Untreated LA-ICP-MS analyses of MIGU-02 show significant discordance (Fig. 3) and only 4 analyses (n=4/20; 80% discordant) were retained after filtering by AgeCalcML v.1.42. Chemical abrasion substantially increased the number of concordant analyses (n = 23/23). Fifteen analyses were removed from the untreated aliquot dataset and seven analyses were removed from the treated aliquot dataset because they hit epoxy, and are not included in the totals. Although all grains were concordant in the treated aliquot, four grains were not included in the weighted mean because they had a

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significantly older $^{207}Pb/^{206}Pb$ dates (1571-1900 Ma) than the CA-ID-TIMS reference date (Table S14) and are likely xenocrystic. The weighted mean $^{207}Pb/^{206}Pb$ date from the untreated MIGU-02 aliquot is 1353.3 +/- 13.3 Ma (n = 4/35; MSWD = 87.5) and the treated aliquot is 1395.0 +/- 4.6 Ma (n = 19/23; MSWD = 3.3). The mean $^{206}Pb/^{238}U$ date of the untreated aliquot is 1169.4 +/- 12.1 Ma (MSWD = 20.0) and the mean $^{206}Pb/^{238}U$ date of the treated aliquot is 1388.8 +/- 3.8 Ma (MSWD = 3.2). Thus, the dates from treated zircon show a significant increase in concordance, precision, and accuracy relative to the reference date as determined by CA-ID-TIMS (Fig. 2).

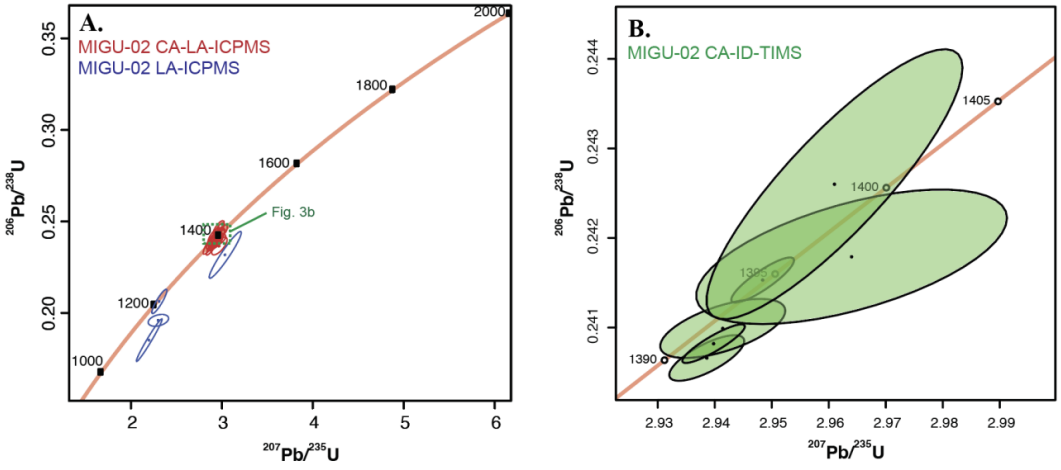

Figure 3. A. Untreated and treated aliquots of MIGU-02 shown on a concordia plot. Non-CA MIGU-02 dates are reversely discordant whereas CA dates fall on concordia and overlap the reference age. **B.** All CA-ID-TIMS analyses of MIGU-02 shown on a concordia plot. One date shows reverse discordance whereas all other dates fall on concordia or have slight normal discordance.

When both untreated and treated MIGU-02 dates are plotted against uranium concentration, all the CA-treated analyses have low uranium concentrations (<500 ppm), while untreated grains show significant variation in uranium concentration (Fig. 4). Most of the high uranium concentration analyses from untreated zircon are >±20% reversely discordant. Since uranium concentration is correlated to radiation damage in old zircon, this result reinforces the observation that CA is an effective tool for removing damaged zones of the zircon (Nasdala et al., 2005; Widmann et al., 2019).

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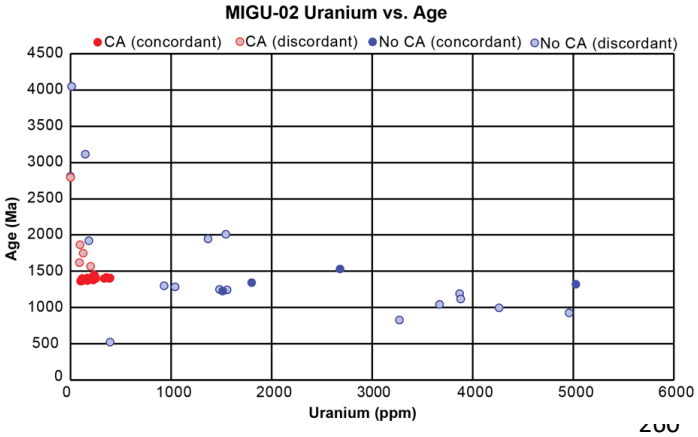

Figure 4. Uranium concentrations (ppm) plotted against $^{207}Pb/^{206}Pb$ age (Ma) for both treated and untreated aliquots of MIGU-02. Both concordant and discordant analyses are shown. Uranium concentration is directly proportional with radiation damage in zircon with the same low-temperature cooling history. The restricted range of low U concentrations in the CA-treated grains suggests that CA was effective at dissolving high U zircon that was more likely to have Pb-loss.

3.3 Untreated and CA- U-Pb Zircon LA-ICP-MS Analyses of Detrital Zircon

One Phanerozoic (NM8A) and one Precambrian sample (Rora Med) were analyzed in this study to determine how detrital zircon age distributions in samples with a wide range of age populations compare between chemically abraded and untreated aliquots. We followed the 'Large-n' approach of Pullen et al. (2014) for this study, to obtain a more robust distribution of ages, their modes, peak widths, and abundances of all analyzed samples – treated and untreated. For NM8A, we analyzed 512 individual zircon in the treated aliquot and 896 zircon in the untreated aliquot. In Rora Med, we analyzed 1035 zircon in the treated aliquot and 920 zircon in the untreated aliquot. Our results show that chemical abrasion (CA) changed the number and distribution of apparent peak age populations in both DZ samples compared to the non-CA age spectra (Figs. 5 and 6). Most notably, the Phanerozoic age peaks in sample NM8A narrowed, became more defined, and, in some cases, shifted to slightly older dates.

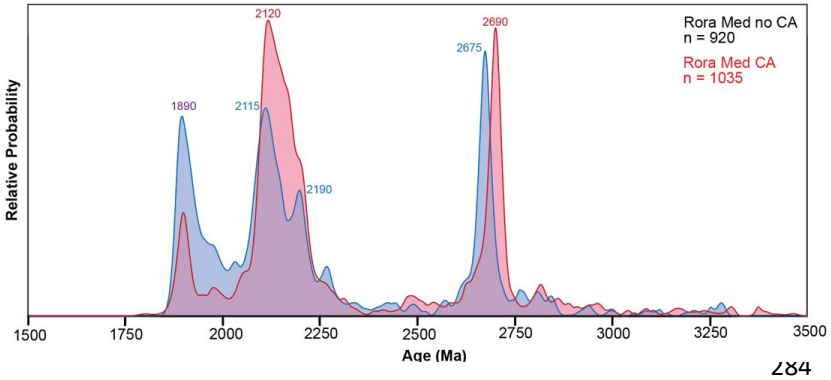

Figure 5. Comparison of U-Pb detrital zircon age spectra of not chemically abraded (blue) and chemically abraded (red) aliquots of Rora Med. Areas where age spectra overlap are shaded in purple. We aimed for n=1000 for each aliquot because Pullen et al (2014) shows the distribution of analyzed zircon ages is thought to approach the 'true' age distribution of the sample.

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In the Precambrian sample (Rora Med), there are subtle changes in the DZ age spectra between the treated and untreated aliquots. Overall, the CA treated aliquot shows improved concordance (Fig. 7) and age spectra show narrowing of peak age populations, changes in the number of peaks present, and a slight but noticeable shift in peak age populations to older ages (Fig. 5). Of note, the 1890 Ma peak narrows in the treated aliquot compared to the broad peak that covers a range of ages between 1890 and 2000 Ma in the untreated aliquot. There is also a change in the shape and number of peaks between the treated and untreated aliquots for the 2100-2300 Ma range. In the untreated aliquot, there are three distinct peak age populations (~2115, 2190, & 2260 Ma), whereas in the treated aliquot, there is only one broad peak age population that spans between ~2120-2190 Ma. There is also a distinct shift in the untreated aliquot 2675 Ma peak age population to fifteen million years older in the treated aliquot (Fig. 5).

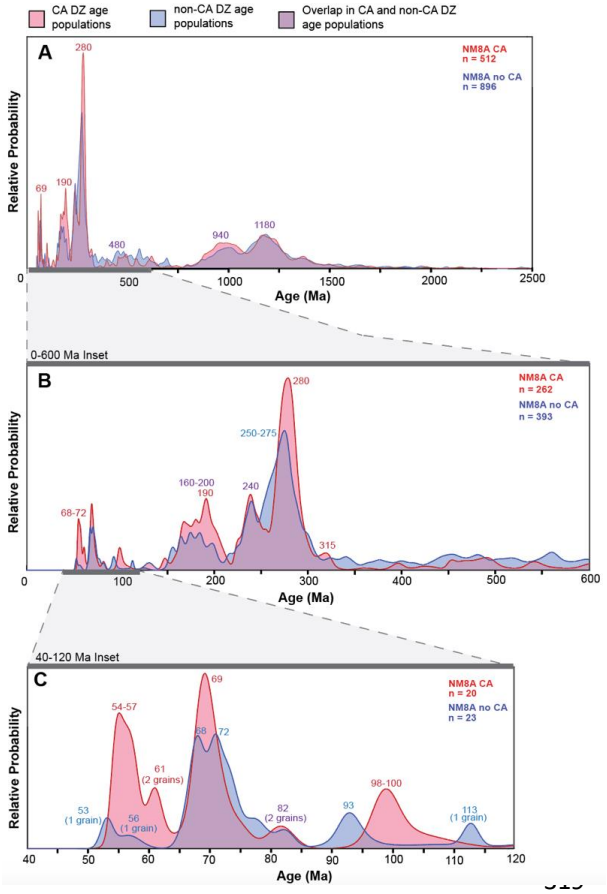

Figure 6. Comparison of U-Pb detrital age spectra of not chemically abraded (blue) and chemically abraded (red) aliquots of NM8A. Areas where age spectra overlap are shaded in purple. We aimed for n=1000 for each aliquot as the distribution of analyzed zircons ages is thought to approach the 'true' age distribution of the sample (Pullen et al. 2015). Insets A-C show variations of the scale on the x-axis.

There are also subtle changes in the number of peaks and peak shapes between the treated and untreated aliquots of NM8A. The most significant changes observed are increased resolution and definition of Phanerozoic peak age populations between 0 and 300 Ma for the treated aliquot (Fig. 6). For example, between 200-300 Ma, two broad peaks in the untreated aliquot sharpen and narrow to two well-defined peak age populations in the treated aliquot (Fig. 6b). Additionally, a broad population between 150 and 200 Ma in the untreated aliquot sharpens to a more distinct peak at 190 Ma, with two subordinate peaks between 150 and 175 Ma in the treated aliquot. We also see a zone of two broadly defined peaks at 68 and 72 Ma in the untreated aliquot sharpen to a singular peak at 69 Ma in the treated aliquot. There is also an older shift from the 93 Ma peak in the untreated aliquot to ~98 Ma in the treated aliquot. Other shifts and changes in peak age populations

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that are <120 Ma (Fig. 6c) cannot be confidently constrained due to the low number of analyses that define those populations (1-2 grains). Concordance is indistinguishable between treated and untreated aliquots of NM8A (Fig. 7).

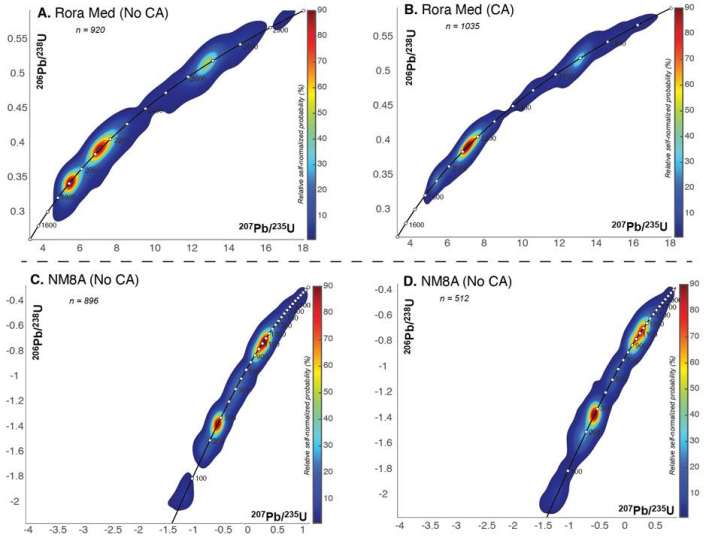

Figure 7. Density contour concordia diagrams for not chemically abraded and chemically abraded aliquots of detrital zircon samples NM8A and Rora Med (A-D). There is substantial improvement in concordance of the Proterozoic Rora Med sample from the not chemically abraded to the chemically abraded aliquot (A-B). However, both aliquots of the Phanerozoic NM8A sample are indistinguishable (C-D). Please note that the concordia diagrams for NM8A (C-D) are plotted on a logarithmic scale.

4. Discussion

Our study shows that chemical abrasion prior to LA-ICP-MS analysis does not negatively affect resulting U-Pb dates provided chemically abraded reference materials are used as the primary standard (e.g., Crowley et al., 2014; von Quadt et al., 2014). We also show that chemical abrasion is extremely effective in mitigating the effects of Pb-loss in LA-ICP-MS U-Pb dating of zircon that has experienced substantial radiation damage. Significant improvement was observed in both $^{206}Pb/^{238}U$ and $^{207}Pb/^{238}U$ dates of MIGU-02 zircon relative to ID-TIMS results, and also the efficiency of the analyses was dramatically improved by focusing LA-ICP-MS analyses on only those grains/fragments that survived the chemical abrasion process and had not sustained significant radiation damage. These results reinforce the observations of previous studies that used this approach (Crowley et al., 2014; von Quadt et al., 2014) and suggested that the CA-LA-ICP-MS method can be valuable for studies that need increased precision and accuracy in LA-ICP-MS U-Pb zircon analyses.

Given the apparent benefits of chemical abrasion to LA-ICP-MS analyses, it is natural to extend the technique to detrital zircon and test the advantages and disadvantages afforded by this method. Crowley et al. (2014) first used this approach on an Archean graywacke and showed that it did not significantly bias their results. However, this technique has not been widely used over the last decade. Our results indicate that a chemical abrasion pre-treatment may help resolve finer scale features in detrital zircon spectra from the Cenozoic to the Archean. We attribute this

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increased resolution mainly to the mitigation of Pb-loss leading to increased accuracy of the resulting LA-ICP-MS dates.

We posit that mitigation of Pb-loss is behind the observed sharpening of Neoproterozoic through Cenozoic age populations in our samples because zircon dates in this age range are best determined using $^{206}Pb/^{238}U$, and the accuracy of this date can be compromised by Pb-loss that is difficult to identify since Pb-loss trajectories for zircon of this age range will closely follow concordia. These effects can be seen most clearly in sample NM8A where age peaks narrowed and became more defined (e.g., 250-300 Ma peak age populations) following chemical abrasion and some peak age populations shifted to slightly older dates (Fig. 6). Assuming that the zircons that form these populations cooled below the temperature at which radiation damage is effectively annealed at a similar time, then U content can be used as a proxy for radiation damage (Nasdala et al., 2005; Widmann et al., 2019; McKanna et al., 2023). This is clearly observed for the treated and untreated aliquots of igneous sample MIGU-02, where the treated aliquot has substantially lower U concentrations and increased accuracy and concordance of measured $^{206}Pb/^{238}U$ dates (Figs. 2, 3, and 4). However, the thermal history is not known *a priori* for detrital zircon datasets, meaning this same assessment applied to NM8A and Rora Med is more uncertain.

To examine whether the reduced Pb-loss we observed in the chemically abraded aliquot reflects the selective dissolution of zircon with radiation damage, we compared zircon U concentrations from a particular age range (250-320 Ma) as a first-order approximation. We assume that the populations in this range likely have the same low-T cooling history, although with the caveat that this assumption remains unknown and cannot be tested with our data. We also note that these populations showed the most significant sharpening following chemical abrasion (Fig. 6B). Figure 8 shows that the average U concentration of treated grains in this age range is similar and indistinguishable to the untreated aliquot, indicating that we cannot determine if chemical abrasion selectively removed analyses that had Pb-loss. Note, however, that due to the unknown thermal history of the detrital zircon in this sample and sample NM8 itself, it is much more difficult to directly compare U concentrations between detrital zircon aliquots than it is between igneous zircon from the same unit (e.g., MIGU-02) since we cannot assume that all zircons of the same age have experience the same thermal history.

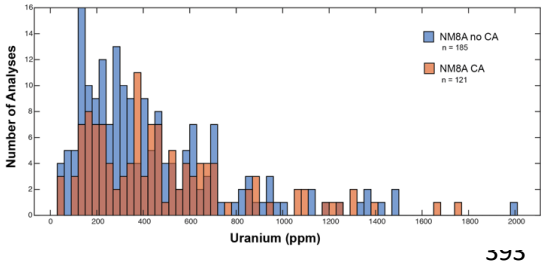

Figure 8. Histogram showing U concentration (ppm) for zircons in the peak age population between 250-320 Ma in detrital zircon sample NM8A. On the detrital zircon spectra, this age population narrows from one broad peak in the untreated aliquot to a well-defined, narrow peak in the treated aliquot (Fig. 6b). Measured U concentrations from this peak age population of treated and untreated aliquots are overall similar and indistinguishable.

Reduced Pb-loss in Mesoproterozoic and older zircon also benefits detrital zircon studies because ancient Pb-loss can bias $^{207}Pb/^{206}Pb$ dates of moderately discordant or even (analytically) concordant zircon toward

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398 erroneously young values (Nemchin and Cawood, 2005). This effect has led many laboratories to filter for discordance
399 within their datasets. Thus, improving concordance will increase the proportion of dates that can be retained in a
400 detrital zircon study and improve confidence in the identification of peak age populations. One potential issue with
401 this approach is the possibility that entire zircon populations will be removed during chemical abrasion if they have
402 high degrees of radiation damage. Surprisingly, we did not see this effect in either NM8A nor Rora Med. This result
403 is surprising and may be sample specific, since Rora Med zircon from all age populations have low U concentrations
404 (<500 ppm; Fig. 9b). Although our RoraMed sample did not preferentially lose any age populations during CA, this
405 feature may be unique to Precambrian samples with overall low zircon U concentrations and/or recent exhumation to
406 low temperature conditions where radiation damage can accumulate and Pb-loss occurs.
407

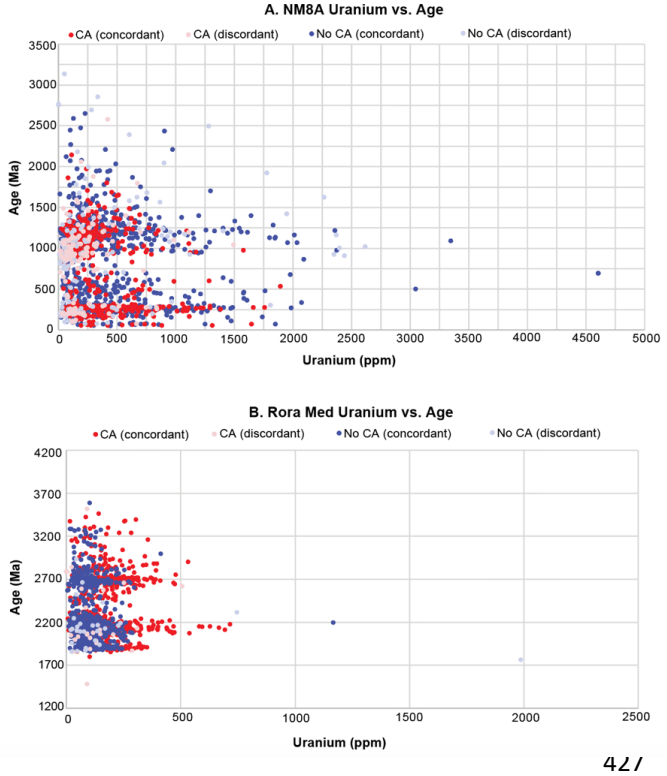

Figure 9. Scatter plot of uranium concentrations (ppm) plotted against the age (Ma) for both treated and untreated aliquots of **A.** NM8A and **B.** Rora Med. Both concordant and discordant analyses are shown. CA appears to reduce the scatter in U concentrations for Precambrian ages compared to the untreated aliquot in NM8A. Overall, all analyzed zircons in treated and untreated aliquots of Rora Med have low U concentrations (<500 ppm), and therefore minor differences in U concentrations are seen between treated and untreated aliquots.

427
428
429 The nature of sediment transport may also work to remove metamict zircon prior to deposition in certain
430 environments. Hydraulic sorting, mechanical abrasion, and weathering, can naturally bias detrital zircon populations
431 present in a different lithologies (Malusa et al., 2013; Ibañez-Mejia et al., 2018). For example, Ewing et al. (2003)
432 noted that metamictization leads to structural damage of the zircon crystal structure and that this can be correlated to
433 a decrease in density and hardness. These changes lead metamict zircon to be more prone to destruction during river
434 transport (Fedo et al., 2003; Hay and Dempster, 2009a). In particular, Hay and Dempster (2009a) argue that inclusion-

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rich and metamict zircon are broken during sediment transport, and that these fragments do not survive being incorporated into clastic sandstone deposits. Instead, these smaller fragments can be swept out to more distal depositional environments. Small zircon are also typically lost during sample preparation (Hietpas et al., 2011; Slama and Kosler, 2012), meaning that both natural and laboratory processes may preferentially lead to a high proportion of undamaged zircon in sandstone samples. Thus, while we did not observe the removal of specific age populations following chemical abrasion in the two detrital zircon samples that were analyzed in this study and there are reasons to suspect that natural and laboratory processes will favor the analysis of undamaged zircon anyway, we recognize that other samples may behave differently. Future users of this technique should carefully consider this possibility in their datasets.

Another potential benefit of chemical abrasion is the preferential dissolution of inclusions within zircon during the partial dissolution step (McKanna et al., 2023). Inclusions harbor Pb_c that can be incorporated into the analyzed volume during laser ablation, reducing the Pb^*/Pb_c and limiting measurement precision and accuracy. When comparing the Pb^*/Pb_c ratios of treated and untreated aliquots of MIGU-02, we see a clear distinction that treated zircons have a much higher Pb^*/Pb_c ratio for similar ranges in U concentration (Fig. 10). We note that the overall U concentrations for the treated aliquot of MIGU-02 are low compared to the untreated aliquot, as we have already shown that CA for metamict zircon effectively removes high-U zones where Pb-loss is most likely to have occurred (see above discussion; Fig. 4). Regardless, the increased Pb^*/Pb_c ratio for the treated aliquot of MIGU-02 shows that this method is also efficient in removing inclusions with high Pb_c content and/or highly damaged domains where Pb_c might have been introduced by fluids. These two effects are correlated with increased concordance, precision, and accuracy observed in $^{206}Pb/^{238}U$ zircon dates of the treated aliquot of MIGU-02, supporting the benefits of utilizing CA prior to LA-ICP-MS measurements in metamict igneous zircon suites. It is likely that this same effect occurs in detrital zircons suites that are treated by chemical abrasion. Although, it is difficult to isolate since detrital zircons are sourced from various terranes and we cannot confidently compare the Pb*/Pbc of zircon with the same age, U concentration, and thermal history.

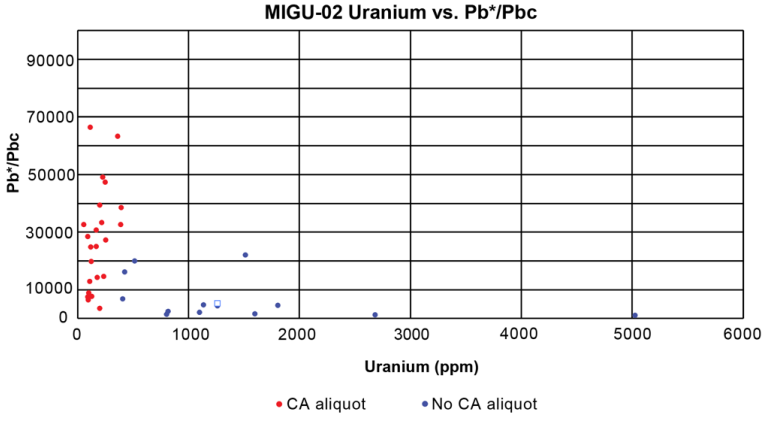

Figure 10. Pb*/Pbc ratios are plotted against uranium for MIGU-02. The Pb*/Pbc ratios in the treated aliquot of MIGU-02 are significantly higher than the untreated aliquot for similar concentrations of U. Higher Pb*/Pbc ratios in the treated aliquot of MIGU-02 can be attributed to reduction of Pbc by removal of inclusions.

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5. Conclusions and Recommended Applications

Chemical abrasion is a widely used tool in the zircon U-Pb ID-TIMS community (*see reviews in* Schoene, 2014; Schaltegger et al., 2015), where it has been repeatedly shown to mitigate the negative effects on age accuracy introduced by Pb-loss (Mundil et al., 2004; Mattinson, 2005; Widmann et al., 2019). Recent efforts to extend chemical abrasion to LA-ICP-MS analyses have also shown that this pre-treatment can be beneficial (Crowley et al., 2014; Von Quadt et al., 2014; McKanna et al., 2023; Sharman and Malkowski, 2023). The extension of this pre-treatment to large-n detrital zircon analyses is a natural outgrowth of these efforts. Our results indicate no negative effects from chemical abrasion prior to LA-ICP-MS analyses and that the technique results in improved concordance, precision, and, at least for the highly radiation damaged igneous sample we studied here, accuracy of measured U-Pb dates. For DZ samples, these benefits appear to translate to more defined and slightly older $^{206}Pb/^{238}U$ age peaks for Phanerozoic zircon, and more concordant analyses, and in some cases slightly older $^{207}Pb/^{206}Pb$ dates, for Precambrian zircon. One potential drawback of this pre-treatment is the possibility that age populations characterized by high-U zircon may be selectively dissolved during chemical abrasion. We did not observe this effect in either of our tested samples. However, we remain wary of its possibility in other samples with highly damaged Precambrian zircon populations, and so future practitioners are advised caution. The differences between age distributions in our analyzed detrital zircon spectra are slight and indicate that the Pb-loss present in typical untreated analyses would not significantly alter the interpretation of sediment source terranes at a broad scale. However, chemical abrasion did sharpen several Phanerozoic peak ages and increased concordance in Precambrian zircon populations, indicating that the pre-treatment may be useful in certain scenarios in which researchers may require increased resolution of detrital zircon age spectra to distinguish fine-scale variations in provenance, sediment source terranes, or source characteristics.

Supplement

All datasets utilized in this study are available in the Supplementary Materia online at:

Author contribution

EED and MPE designed experiments and EED conducted the experiments. All authors participated in the interpretation and discussion of results. EED prepared the figures and manuscript.

Competing Interests

The authors declare no competing interests.

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