



1 Increased accuracy and precision in igneous and detrital zircon 2 geochronology using CA-LA-ICPMS

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

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30 1. Introduction

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32 Detrital zircon U-Pb geochronology is a common and widely-used tool with a broad range of applications
33 across multiple subdisciplines of geology. As the efficiency, accuracy, and precision of U-Pb geochronology
34 measurements continue to improve (e.g., Carrapa, 2010; Gehrels, 2012; Gehrels, 2014; Pullen et al., 2014; Sundell et
35 al., 2021), the production of large detrital zircon datasets by laser ablation-inductively coupled plasma-mass
36 spectrometry (LA-ICP-MS) has become more common. In basin analysis and tectonics, these datasets are often used
37 to determine sediment provenance, characterize source terranes, and reconstruct ancient sediment routing pathways
38 (Fedo et al., 2003; Anderson 2005; Smith et al., 2023). The resulting data is typically interpreted using kernel density
39 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



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

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

69 70 **2. U-Pb Zircon Geochronology Approach and Methods**

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



78 zircon analyzed to encompass 28.5 – 3467 Ma. This increased age range of the tested reference materials provides a
 79 more complete understanding of LA-ICP-MS U-Pb systematics on chemically abraded zircon and whether a single
 80 primary standard can be used for a wide range of zircon dates and U content. Second, we assess the ability of chemical
 81 abrasion to mitigate Pb-loss in an igneous sample that has experienced substantial radiation damage by comparing
 82 chemically abraded and non-chemically abraded $^{206}\text{Pb}/^{238}\text{U}$ LA-ICP-MS zircon analyses to a newly produced CA-ID-
 83 TIMS reference date for the same sample. Finally, we assess how CA affects detrital zircon (DZ) age spectra by
 84 comparing chemically abraded and untreated aliquots of two detrital samples. One sample is Cenozoic in age and
 85 contains both Phanerozoic (100-300 Ma) and Precambrian (1000-1200 Ma) zircon age populations, whereas the
 86 second sample is Proterozoic and contains zircon age populations between 2000-3500 Ma.
 87

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

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91 2.1 Methods for Thermal Annealing and Chemical Abrasion

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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 HNO₃ 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 H₂O. Chemically abraded aliquots were then sent to the University of Arizona



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

104

105 **2.2 LA-ICP-MS Zircon U-Pb Geochronology**

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

123

124 **2.3 CA-ID-TIMS Zircon U-Pb Geochronology**

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



137 NBS981 Pb reference material. We assume that all ^{204}Pb is from laboratory contamination and correct for it using a
138 laboratory Pb isotopic composition of $^{206}\text{Pb}/^{204}\text{Pb} = 18.82 \pm 0.74$ (2σ), $^{207}\text{Pb}/^{204}\text{Pb} = 15.52 \pm 0.63$ (2σ), $^{208}\text{Pb}/^{204}\text{Pb} =$
139 37.93 ± 1.60 (2σ) derived from repeat total procedural blank measurements run during 2022. Uranium was run as an
140 oxide (UO_2) and isotopic measurements were made statically using Faraday detectors and corrected for fractionation
141 using the known ratio of $^{233}\text{U}/^{235}\text{U}$ in the EARTHTIME ^{205}Pb - ^{233}U - ^{235}U isotopic tracer (Condon et al., 2015; McLean
142 et al., 2015) and assuming a zircon $^{238}\text{U}/^{235}\text{U}$ value of 137.818 ± 0.045 (Hiess et al., 2012). Data reduction was done
143 using the ET_Redux software package (Bowring et al., 2011) and the decay constants of Jaffey et al. (1971). All
144 isotopic data measured via CA-ID-TIMS are presented in Table S15.

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147 3. Results

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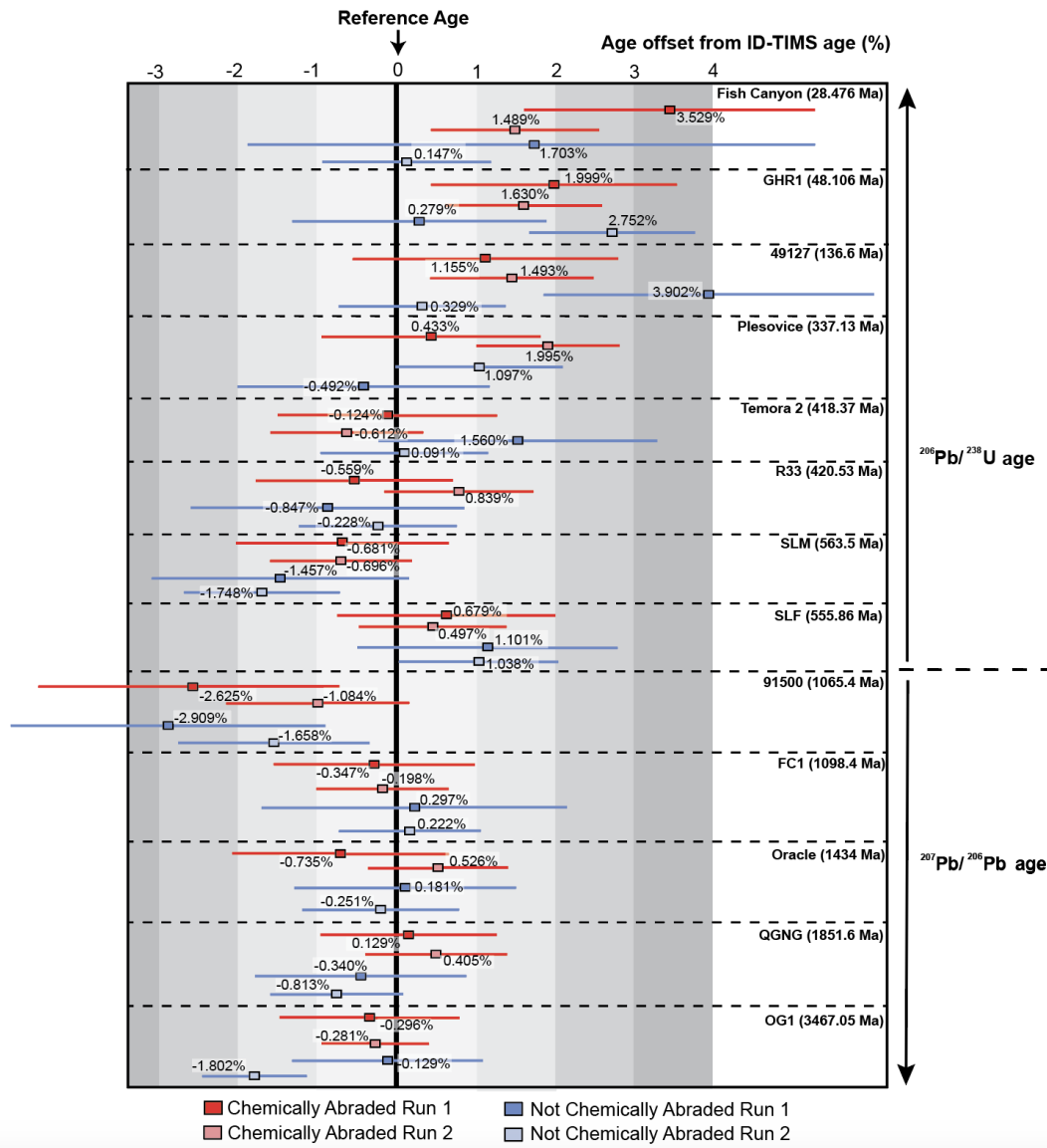
149 3.1 CA-LA-ICP-MS U-Pb Geochronology of Zircon Reference Materials

150 Treated and untreated aliquots of thirteen different zircon U-Pb reference materials (Table 1) were analyzed in this
151 study to further assess whether chemical abrasion systematically biases U-Pb dates. The reference materials were
152 analyzed during two round-robin runs. The first run targeted 15 zircon grains from treated and untreated aliquot of
153 reference materials. During the second run, 30 zircon grains were targeted. Because FC-1 was used as a primary
154 reference material for calibration of the LA-ICP-MS, approximately 30 FC-1 zircons were analyzed during run 1 and
155 87 were analyzed during run 2 per treated and untreated aliquots. The total number of zircons analyzed was 657 in
156 each of the chemically abraded and untreated aliquots of reference materials. Of the 657 grains in the chemically
157 abraded aliquot, 635 analyses (96.6%) were retained following filtering for discordance, whereas 608 analyses
158 (92.5%) were retained in the untreated aliquot. These results further confirm that CA helps mitigate Pb-loss and
159 improve precision in LA-ICP-MS analyses (e.g., Crowley et al., 2014; von Quadt et al., 2014). The most extreme
160 change in concordance and data retention occurred between treated and untreated FC-1 zircon (1098.4 Ma). Of the
161 117 grains analyzed per treated and untreated aliquot, 97.4% of analyses were retained in the chemically abraded
162 aliquot versus 82.1% in the untreated aliquot. Discordance criteria used for filtering the above data were reverse
163 discordance larger than 5% and/or $^{206}\text{Pb}/^{238}\text{U}$ errors larger than 10%.

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



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



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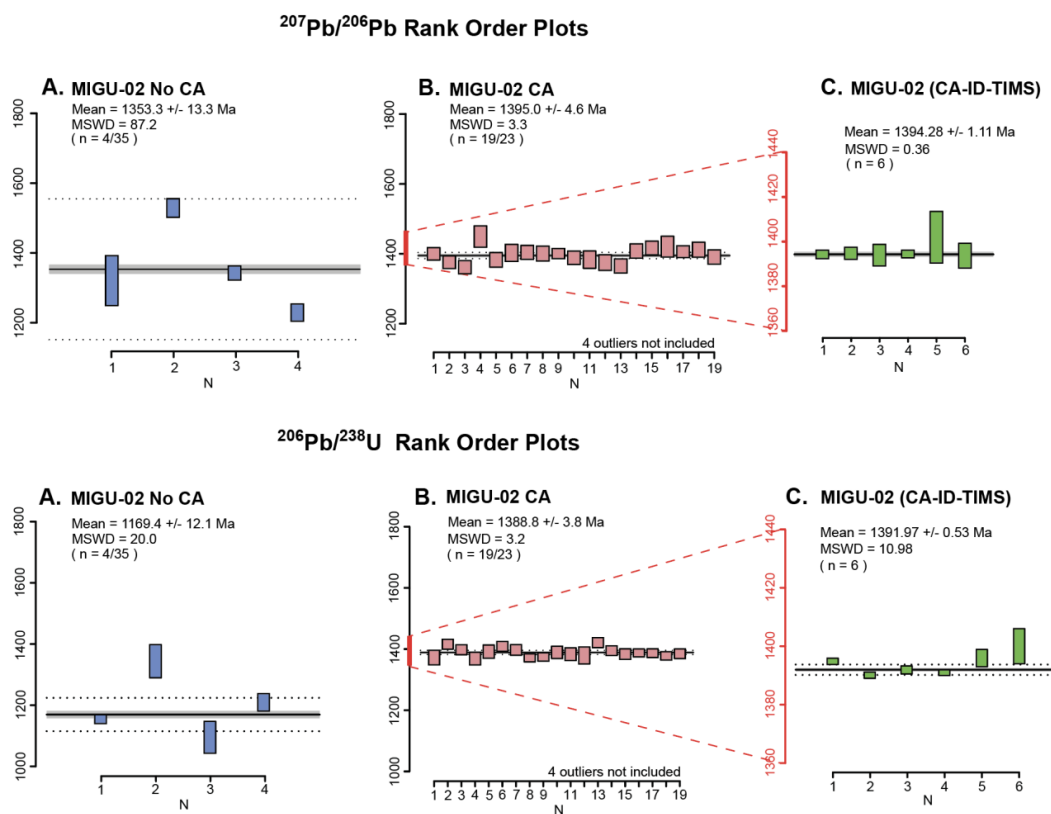
185 The scatter in the CA-LA-ICP-MS dates for both treated and untreated aliquots is similar for all age ranges.
186 The greatest scatter in calculated weighted mean ages (~4 to 0.2% age offset from reference date) is in both the treated
187 and untreated Mesozoic to Cenozoic reference materials. This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

200

201 3.2 Untreated and CA- U-Pb Zircon LA-ICP-MS Analyses of Metamict Zircon

202 A Precambrian granite sample from the Parguaza Complex in the North Guyana Shield (MIGU-02; N 5° 21'
203 3.70"; W 67° 41' 33.41") that has experienced substantial radiation damage was analyzed to assess the effects of
204 chemical abrasion on grains with significant Pb-loss. Untreated (n = 35) and treated aliquots (n = 23) of MIGU-02
205 were analyzed at the ALC and compared to a reference age determined by CA-ID-TIMS at Purdue University
206 (n=6)(Fig. 2; Tables S14 and S15). During the bulk chemical abrasion process, 80-85% of MIGU-02 grains fully
207 dissolved, leaving only a small fraction of the original aliquot to be used for analyses.

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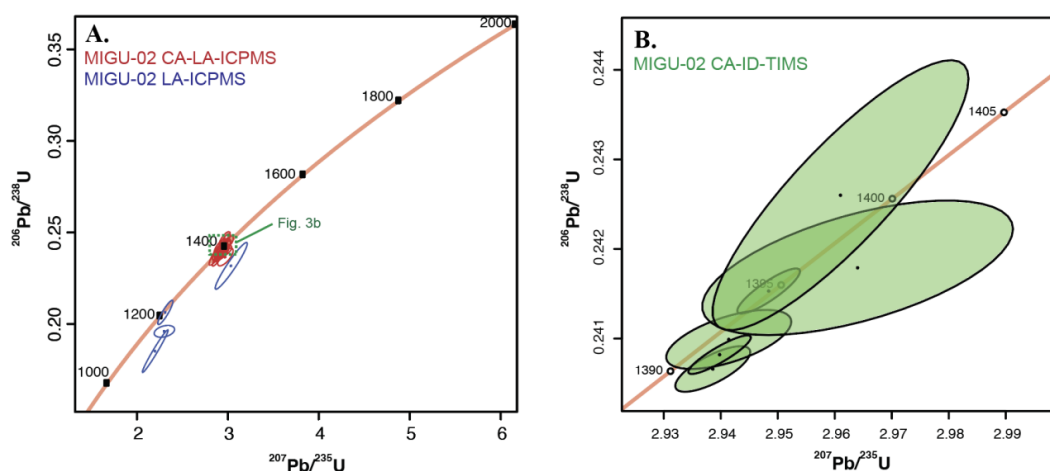
210 **Figure 2.** Rank order plots of calculated $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages for treated and untreated MIGU-02 aliquots
211 and of the reference age for MIGU-02 obtained using CA-ID-TIMS. **A.** Untreated samples of MIGU-02 show large
212 degree of scatter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

215

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



226 significantly older $^{207}\text{Pb}/^{206}\text{Pb}$ dates (1571-1900 Ma) than the CA-ID-TIMS reference date (Table S14) and are likely
227 xenocrystic. The weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date from the untreated MIGU-02 aliquot is 1353.3 ± 13.3 Ma ($n = 4/35$;
228 $\text{MSWD} = 87.5$) and the treated aliquot is 1395.0 ± 4.6 Ma ($n = 19/23$; $\text{MSWD} = 3.3$). The mean $^{206}\text{Pb}/^{238}\text{U}$ date of
229 the untreated aliquot is 1169.4 ± 12.1 Ma ($\text{MSWD} = 20.0$) and the mean $^{206}\text{Pb}/^{238}\text{U}$ date of the treated aliquot is
230 1388.8 ± 3.8 Ma ($\text{MSWD} = 3.2$). Thus, the dates from treated zircon show a significant increase in concordance,
231 precision, and accuracy relative to the reference date as determined by CA-ID-TIMS (Fig. 2).
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233
234 **Figure 3. A.** Untreated and treated aliquots of MIGU-02 shown on a concordia plot. Non-CA MIGU-02 dates are
235 reversely discordant whereas CA dates fall on concordia and overlap the reference age. **B.** All CA-ID-TIMS analyses
236 of MIGU-02 shown on a concordia plot. One date shows reverse discordance whereas all other dates fall on concordia
237 or have slight normal discordance.

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

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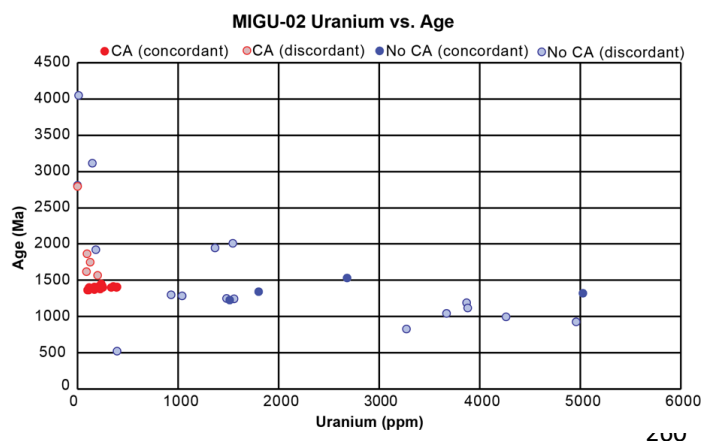


Figure 4. Uranium concentrations (ppm) plotted against $^{207}\text{Pb}/^{206}\text{Pb}$ age (Ma) for both treated and untreated aliquots of MIGU-02. Both concordant and discordant analyses are shown. Uranium concentration is directly proportional with radiation damage in zircon with the same low-temperature cooling history. The restricted range of low U

261 concentrations in the CA-treated grains suggests that CA was effective at dissolving high U zircon that was more
262 likely to have Pb-loss.

263 3.3 Untreated and CA- U-Pb Zircon LA-ICP-MS Analyses of Detrital Zircon

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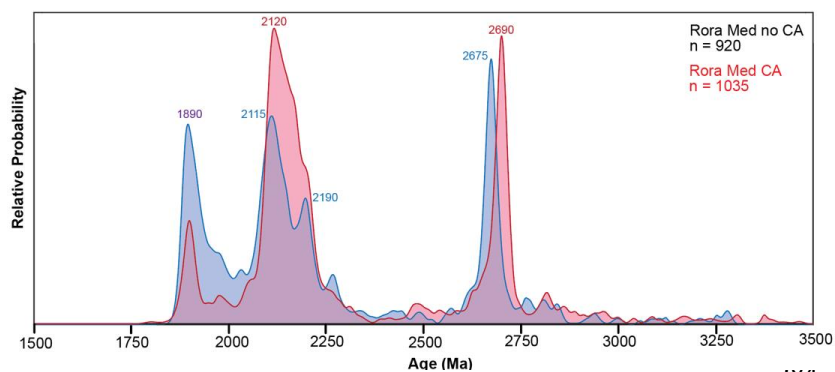


Figure 5. Comparison of U-Pb detrital zircon age spectra of not chemically abraded (blue) and chemically abraded (red) aliquots of Rora Med. Areas where age spectra overlap are shaded in purple. We aimed for

285 n=1000 for each aliquot because Pullen et al (2014) shows the distribution of analyzed zircon ages is thought to
286 approach the ‘true’ age distribution of the sample.



287 In the Precambrian sample (Rora Med), there are subtle changes in the DZ age spectra between the treated
 288 and untreated aliquots. Overall, the CA treated aliquot shows improved concordance (Fig. 7) and age spectra show
 289 narrowing of peak age populations, changes in the number of peaks present, and a slight but noticeable shift in peak
 290 age populations to older ages (Fig. 5). Of note, the 1890 Ma peak narrows in the treated aliquot compared to the broad
 291 peak that covers a range of ages between 1890 and 2000 Ma in the untreated aliquot. There is also a change in the
 292 shape and number of peaks between the treated and untreated aliquots for the 2100-2300 Ma range. In the untreated
 293 aliquot, there are three distinct peak age populations (~2115, 2190, & 2260 Ma), whereas in the treated aliquot, there
 294 is only one broad peak age population that spans between ~2120-2190 Ma. There is also a distinct shift in the untreated
 295 aliquot 2675 Ma peak age population to fifteen million years older in the treated aliquot (Fig. 5).
 296

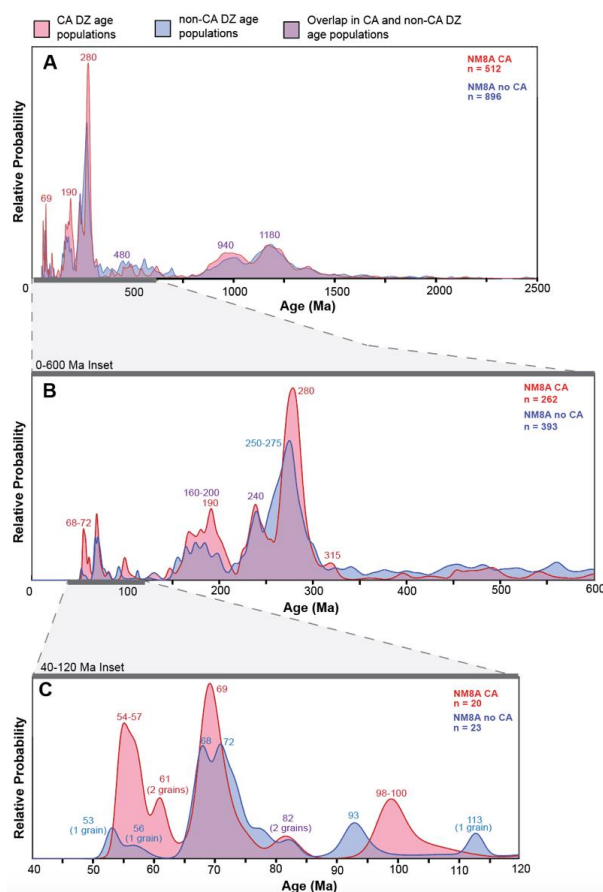


Figure 6. Comparison of U-Pb detrital age spectra of not chemically abraded (blue) and chemically abraded (red) aliquots of NM8A. Areas where age spectra overlap are shaded in purple. We aimed for n=1000 for each aliquot as the distribution of analyzed zircons ages is thought to approach the ‘true’ age 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

320 and 200 Ma in the untreated aliquot sharpens to a more distinct peak at 190 Ma, with two subordinate peaks between
 321 150 and 175 Ma in the treated aliquot. We also see a zone of two broadly defined peaks at 68 and 72 Ma in the
 322 untreated aliquot sharpen to a singular peak at 69 Ma in the treated aliquot. There is also an older shift from the 93
 323 Ma peak in the untreated aliquot to ~98 Ma in the treated aliquot. Other shifts and changes in peak age populations



324 that are <120 Ma (Fig. 6c) cannot be confidently constrained due to the low number of analyses that define those
325 populations (1-2 grains). Concordance is indistinguishable between treated and untreated aliquots of NM8A (Fig. 7).
326
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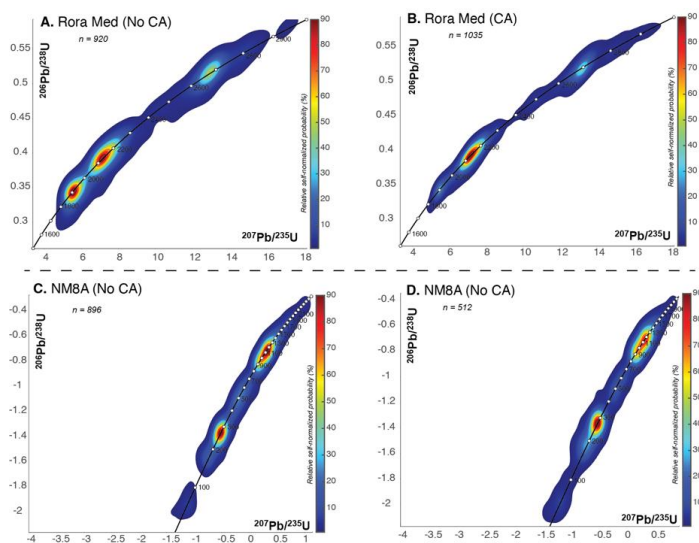


Figure 7. Density contour concordia diagrams for not chemically abraded and chemically abraded aliquots of detrital zircon samples NM8A and Rora Med (A-D). There is substantial improvement in concordance of the Proterozoic Rora Med sample from the not chemically abraded to the chemically abraded aliquot (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

342 logarithmic scale.

343

344

345 4. Discussion

346 Our study shows that chemical abrasion prior to LA-ICP-MS analysis does not negatively affect resulting U-
347 Pb dates provided chemically abraded reference materials are used as the primary standard (e.g., Crowley et al., 2014;
348 von Quadt et al., 2014). We also show that chemical abrasion is extremely effective in mitigating the effects of Pb-
349 loss in LA-ICP-MS U-Pb dating of zircon that has experienced substantial radiation damage. Significant improvement
350 was observed in both $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates of MIGU-02 zircon relative to ID-TIMS results, and also the
351 efficiency of the analyses was dramatically improved by focusing LA-ICP-MS analyses on only those
352 grains/fragments that survived the chemical abrasion process and had not sustained significant radiation damage.
353 These results reinforce the observations of previous studies that used this approach (Crowley et al., 2014; von Quadt
354 et al., 2014) and suggested that the CA-LA-ICP-MS method can be valuable for studies that need increased precision
355 and accuracy in LA-ICP-MS U-Pb zircon analyses.

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



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

363 We posit that mitigation of Pb-loss is behind the observed sharpening of Neoproterozoic through Cenozoic
364 age populations in our samples because zircon dates in this age range are best determined using $^{206}\text{Pb}/^{238}\text{U}$, and the
365 accuracy of this date can be compromised by Pb-loss that is difficult to identify since Pb-loss trajectories for zircon
366 of this age range will closely follow concordia. These effects can be seen most clearly in sample NM8A where age
367 peaks narrowed and became more defined (e.g., 250-300 Ma peak age populations) following chemical abrasion and
368 some peak age populations shifted to slightly older dates (Fig. 6). Assuming that the zircons that form these
369 populations cooled below the temperature at which radiation damage is effectively annealed at a similar time, then U
370 content can be used as a proxy for radiation damage (Nasdala et al., 2005; Widmann et al., 2019; McKanna et al.,
371 2023). This is clearly observed for the treated and untreated aliquots of igneous sample MIGU-02, where the treated
372 aliquot has substantially lower U concentrations and increased accuracy and concordance of measured $^{206}\text{Pb}/^{238}\text{U}$ dates
373 (Figs. 2, 3, and 4). However, the thermal history is not known *a priori* for detrital zircon datasets, meaning this same
374 assessment applied to NM8A and Rora Med is more uncertain.

375 To examine whether the reduced Pb-loss we observed in the chemically abraded aliquot reflects the selective
376 dissolution of zircon with radiation damage, we compared zircon U concentrations from a particular age range (250-
377 320 Ma) as a first-order approximation. We assume that the populations in this range likely have the same low-T
378 cooling history, although with the caveat that this assumption remains unknown and cannot be tested with our data.
379 We also note that these populations showed the most significant sharpening following chemical abrasion (Fig. 6B).
380 Figure 8 shows that the average U concentration of treated grains in this age range is similar and indistinguishable to
381 the untreated aliquot, indicating that we cannot determine if chemical abrasion selectively removed analyses that had
382 Pb-loss. Note, however, that due to the unknown thermal history of the detrital zircon in this sample and sample NM8
383 itself, it is much more difficult to directly compare U concentrations between detrital zircon aliquots than it is between
384 igneous zircon from the same unit (e.g., MIGU-02) since we cannot assume that all zircons of the same age have
385 experienced the same thermal history.

386

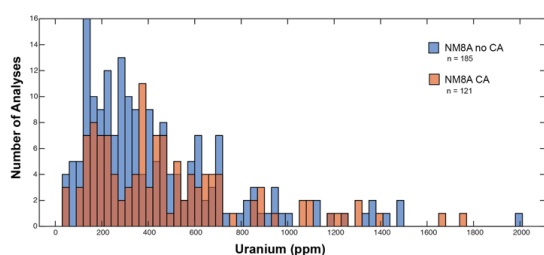


Figure 8. Histogram showing U concentration (ppm) for zircons in the peak age population between 250-320 Ma in detrital zircon sample NM8A. On the detrital zircon spectra, this age population narrows from one broad peak in the untreated aliquot to a well-defined, narrow peak in the treated aliquot (Fig.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

394 treated and untreated aliquots are overall similar and indistinguishable.

395

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



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

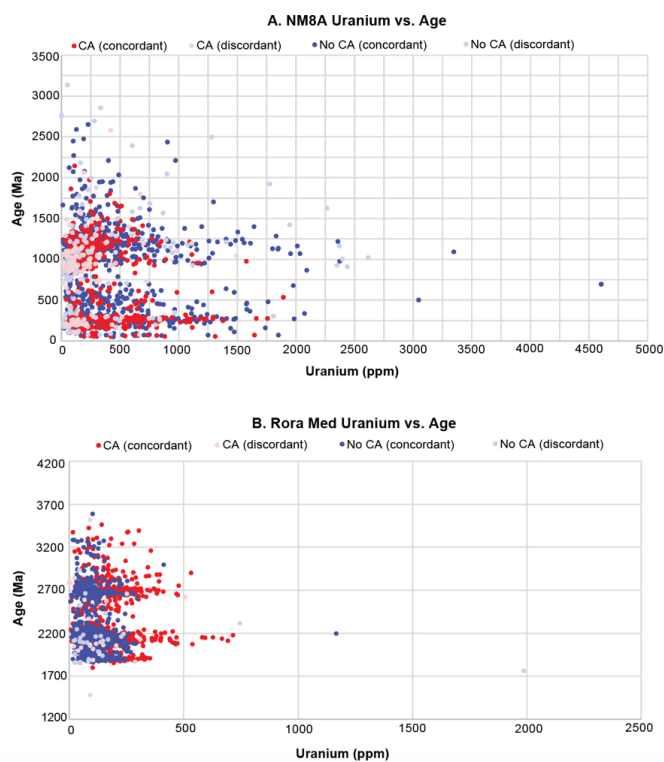


Figure 9. Scatter plot of uranium concentrations (ppm) plotted against the age (Ma) for both treated and untreated aliquots of **A.** NM8A and **B.** Rora Med. Both concordant and discordant analyses are shown. CA appears to reduce the scatter in U concentrations for Precambrian ages compared to the 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.

42 /

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-Mejía 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 (Fedó et al., 2003; Hay and Dempster, 2009a). In particular, Hay and Dempster (2009a) argue that inclusion-



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

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

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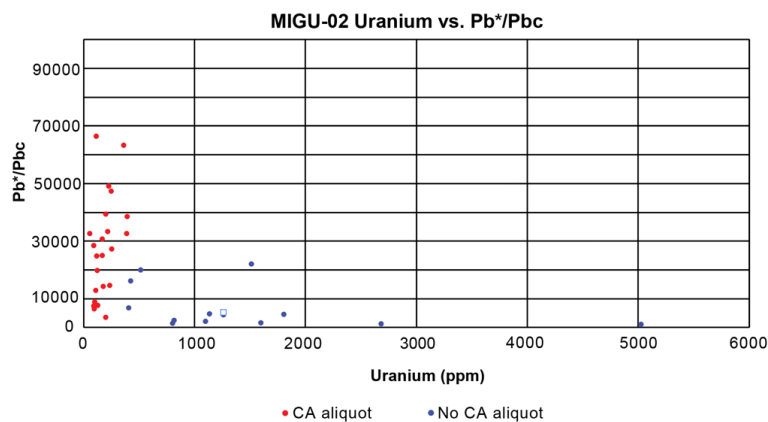


Figure 10. Pb^*/Pb_c ratios are plotted against uranium for MIGU-02. The Pb^*/Pb_c ratios in the treated aliquot of MIGU-02 are significantly higher than the untreated aliquot for similar concentrations of U. Higher Pb^*/Pb_c ratios in the treated aliquot of MIGU-02 can be attributed to reduction of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

471 removal of inclusions.



472 5. Conclusions and Recommended Applications

473 Chemical abrasion is a widely used tool in the zircon U-Pb ID-TIMS community (*see reviews in* Schoene,
474 2014; Schaltegger et al., 2015), where it has been repeatedly shown to mitigate the negative effects on age accuracy
475 introduced by Pb-loss (Mundil et al., 2004; Mattinson, 2005; Widmann et al., 2019). Recent efforts to extend chemical
476 abrasion to LA-ICP-MS analyses have also shown that this pre-treatment can be beneficial (Crowley et al., 2014; Von
477 Quadt et al., 2014; McKanna et al., 2023; Sharman and Malkowski, 2023). The extension of this pre-treatment to
478 large-n detrital zircon analyses is a natural outgrowth of these efforts. Our results indicate no negative effects from
479 chemical abrasion prior to LA-ICP-MS analyses and that the technique results in improved concordance, precision,
480 and, at least for the highly radiation damaged igneous sample we studied here, accuracy of measured U-Pb dates. For
481 DZ samples, these benefits appear to translate to more defined and slightly older $^{206}\text{Pb}/^{238}\text{U}$ age peaks for Phanerozoic
482 zircon, and more concordant analyses, and in some cases slightly older $^{207}\text{Pb}/^{206}\text{Pb}$ dates, for Precambrian zircon. One
483 potential drawback of this pre-treatment is the possibility that age populations characterized by high-U zircon may be
484 selectively dissolved during chemical abrasion. We did not observe this effect in either of our tested samples.
485 However, we remain wary of its possibility in other samples with highly damaged Precambrian zircon populations,
486 and so future practitioners are advised caution. The differences between age distributions in our analyzed detrital
487 zircon spectra are slight and indicate that the Pb-loss present in typical untreated analyses would not significantly alter
488 the interpretation of sediment source terranes at a broad scale. However, chemical abrasion did sharpen several
489 Phanerozoic peak ages and increased concordance in Precambrian zircon populations, indicating that the pre-treatment
490 may be useful in certain scenarios in which researchers may require increased resolution of detrital zircon age spectra
491 to distinguish fine-scale variations in provenance, sediment source terranes, or source characteristics.

492

493 Supplement

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

495

496 Author contribution

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

499

500 Competing Interests

501 The authors declare no competing interests.

502

503 Acknowledgments

504 We thank the Arizona LaserChron Center (ALC) for sharing samples and reference materials and for helping
505 analyze these samples. Specifically, we thank G. Gehrels, M. Pecha, D. Alberts, and Wai Allen. We also thank R.
506 Ickert for help designing a system for bulk CA at Purdue. All LA-ICPMS measurements were made at the Arizona
507 LaserChron Center under NSF-EAR 2050246 for support of the Arizona LaserChron Center and all CA steps and
508 CA-ID-TIMS measurements were completed at Purdue University's Radiogenic Isotope Geology Lab (RIGL) under
509 NSF-EAR-2151277 to M. Eddy.



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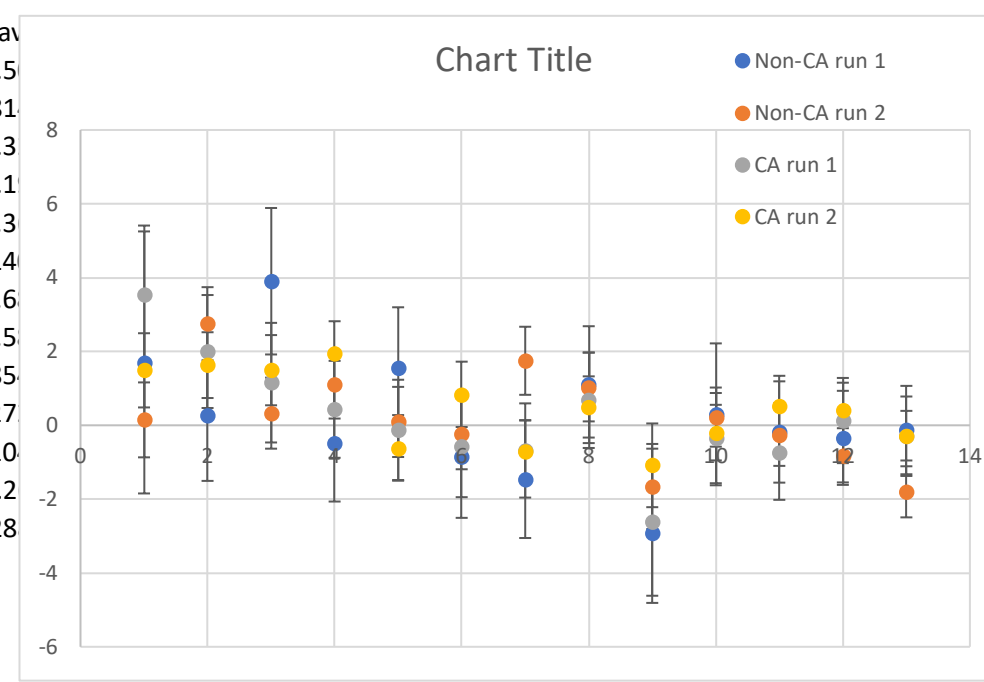
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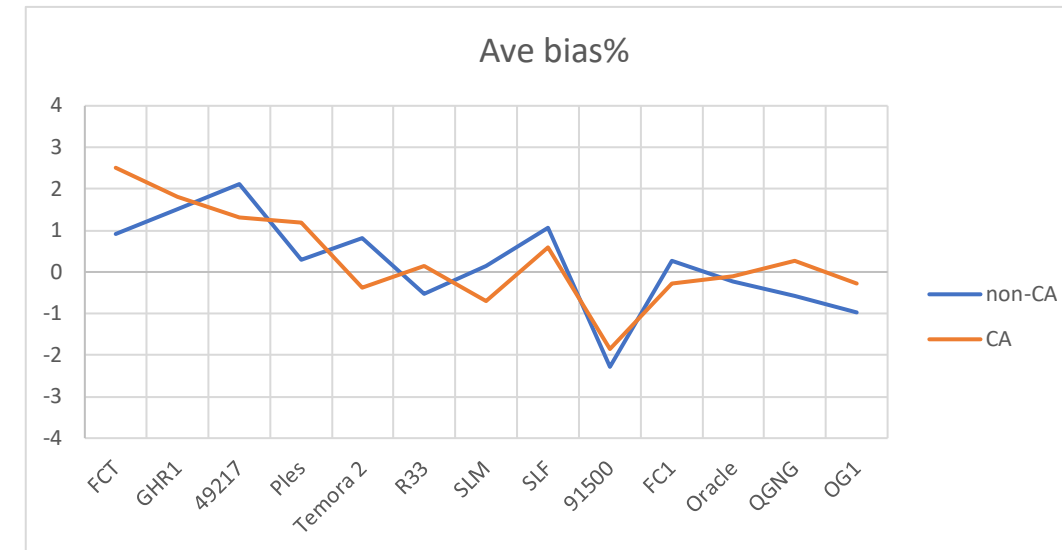
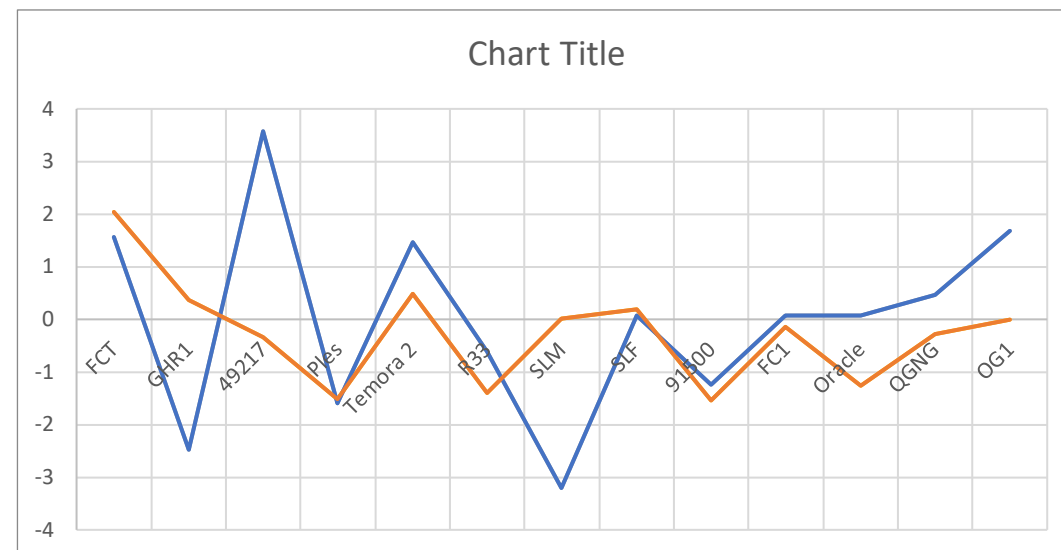
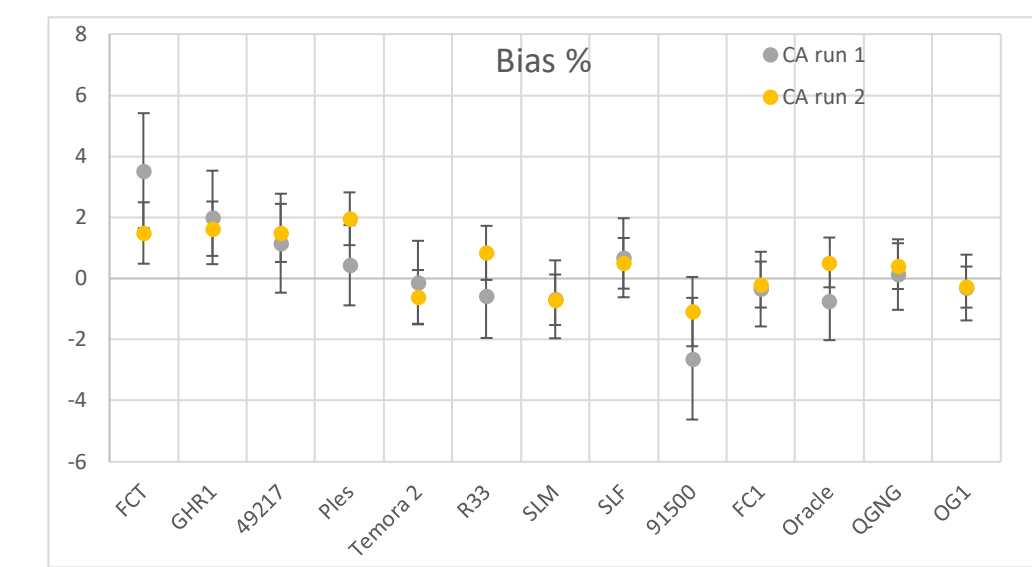
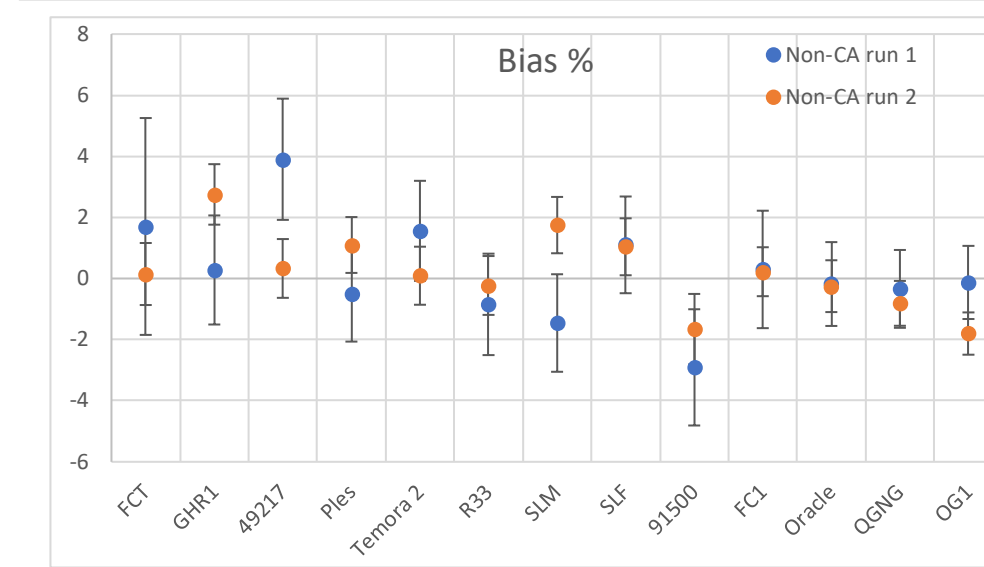
	Non-CA Run 1		Non-CA Run 2		bias% ave
	bias%	unc%	bias%	unc%	
FCT	1.703	3.549	0.147	1.015	0.925
GHR1	0.279	1.785	2.752	0.99	1.5155
49217	3.903	1.984	0.329	0.962	2.116
Ples	-0.492	1.573	1.097	0.914	0.3025
Temora 2	1.56	1.637	0.091	0.95	0.8255
R33	-0.847	1.66	-0.228	0.963	-0.5375
SLM	-1.457	1.596	1.748	0.922	0.1455
SLF	1.101	1.583	1.038	0.932	1.0695
91500	-2.909	1.902	-1.658	1.153	-2.2835
FC1	0.297	1.922	0.222	0.801	0.2595
Oracle	-0.181	1.372	-0.251	0.848	-0.216
QGNG	-0.34	1.274	-0.813	0.734	-0.5765
OG1	-0.129	1.197	-1.802	0.692	-0.9655

	CA Run 1		CA Run 2		bias% av
	bias%	unc%	bias%	unc%	
FCT	3.529	1.882	1.489	1.005	2.5
GHR1	1.999	1.53	1.63	0.891	1.81
49217	1.155	1.62	1.493	0.951	1.3
Ples	0.433	1.313	1.955	0.864	1.1
Temora 2	-0.124	1.358	-0.612	0.889	-0.3
R33	-0.558	1.389	0.839	0.885	0.14
SLM	-0.682	1.276	-0.696	0.827	-0.6
SLF	0.679	1.293	0.497	0.829	0.5
91500	-2.625	1.992	-1.084	1.134	-1.85
FC1	-0.347	1.222	-0.198	0.753	-0.27
Oracle	-0.735	1.284	0.526	0.815	-0.10
QGNG	0.129	1.154	0.405	0.749	0.2
OG1	-0.296	1.076	-0.281	0.672	-0.28



	non-CA bias diff run1-run2
FCT	1.556
GHR1	-2.473
49217	3.574
Ples	-1.589
Temora 2	1.469
R33	-0.619
SLM	-3.205
SLF	0.063
91500	-1.251
FC1	0.075
Oracle	0.07
QGNG	0.473
OG1	1.673

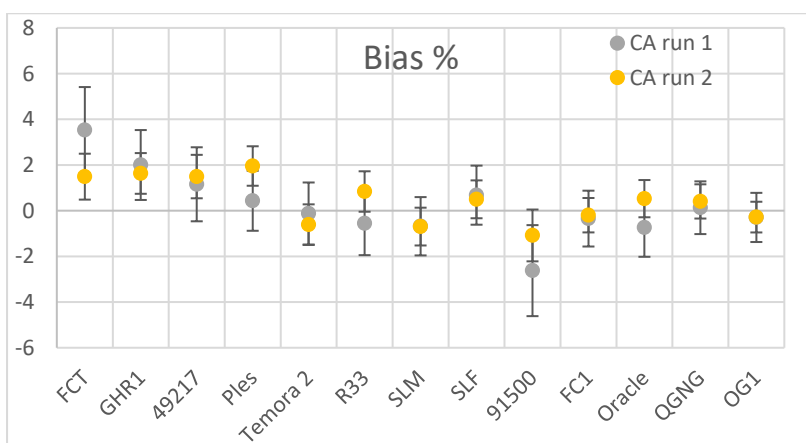
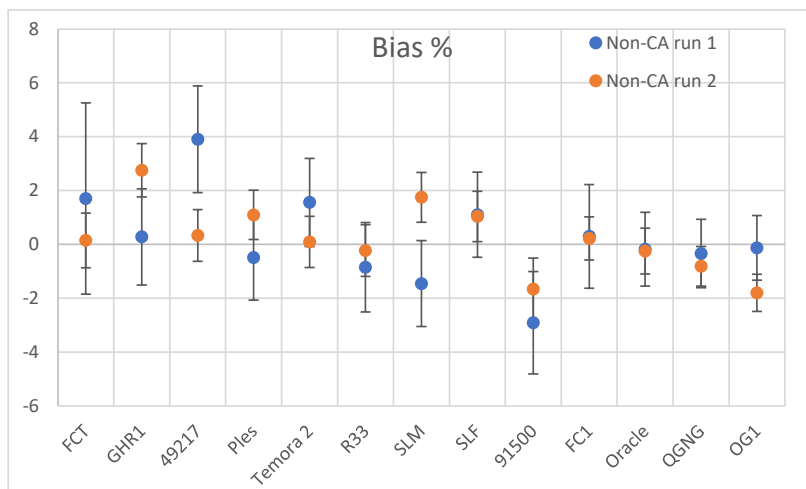
	CA bias diff run1-run2
FCT	2.04
GHR1	0.369
49217	-0.338
Ples	-1.522
Temora 2	0.488
R33	-1.397
SLM	0.014
SLF	0.182
91500	-1.541
FC1	-0.149
Oracle	-1.261
QGNG	-0.276
OG1	-0.015



Review of Donaghy et al – Increased accuracy and precision in igneous and detrital zircon geochronology using CA-LA-ICPMS.

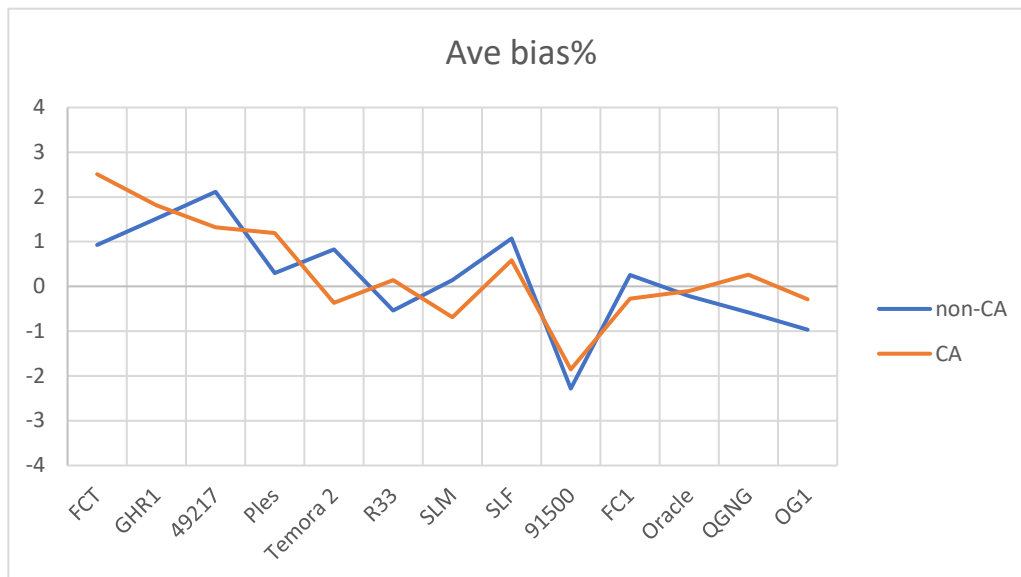
The authors look to demonstrate improved accuracy and precision of U-Pb data acquired utilising a chemical abrasion sample preparation method, compared to laser ablation analysis without using this. I have provided comments in the attached pdf, but some key points are:

- 1) Please state the uncertainty level in all figures (including supplementary).
- 2) Uncertainties should be quoted to 2 significant figures with ages/ratios/values quoted to the same number of decimal places as the uncertainty.
- 3) MSWD's should be quoted to 2 significant figures
- 4) Please provide a metadata table for the LA-ICP-MS work (and ideally ID-TIMS also).
- 5) What reference values were used for FC-1 as the primary reference material?
- 6) Imaging and targeting to avoid zonation/inclusions/xenocrysts, especially in the younger zircons, may have avoided some of the issues discussed. For balance, the usefulness of imaging for this purpose could be mentioned.
- 7) Resolution of concordance is mentioned a lot with CA stated as improving concordance and resolution of concordance. However, it is equally stated that the same accuracy is achieved between CA'd and non-CA'd datasets. Illustration of this discussion would be much easier if the bias of the reference materials was tabulated in the manuscript since this is the fundamental premise of the paper. Taking the biases quoted in the supplementary plots, it can be seen in the figures below that the bias and pattern of both treated and untreated runs are equivalent.



Note the negative bias for 91500 might be accounted for by using CA'd reference values from (Schoene et al 2006 or Horstwood et al 2016) rather than the non-CA values (Wiedenbeck et al 1995).

These plots highlight the reduced scatter in the CA data whilst not changing the overall bias. Plotting the data another way, as the average bias between runs 1 & 2 for CA'd and non-CA'd aliquots, highlights the similarity in bias between the two data sets. In this example then, CA doesn't appear to improve concordancy (since the bias isn't changing at the +/-1% level), but is improving scatter.



In this respect, CA can probably be said to be improving the resolution of concordancy, however, stated in the way of the manuscript, this assertion is unquantified. The language around 'improved resolution and precision' is very loose and should be tightened with better quantification using the data acquired. This would be aided by being able to link the analyses to the nature of the material targeted but I appreciate this wasn't the approach taken. However, when looking at 'resolution' of detrital zircon spectra, knowing that some of the many analyses were not straddling age zones would be important, so that the shape and resolution of the age peak can be quantified and compared with another, by reducing the 'baseline' of potentially mixed measurements. In the absence of being able to do this, perhaps a different form of words or better explanation of some of the constraints on peak shape and dispersion might be useful, followed by described quantification of these. The outcome would be more supportive of the authors arguments for improvements resulting from CA-LA-ICPMS.