



Mitigating the role of Pb loss on Maximum Depositional Age estimation using Chemical Abrasion-Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

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Abstract. It is increasingly recognized that Pb loss in zircon of even Cenozoic age is pervasive and can lead to $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates that are younger than the mineral's crystallization date. Therefore, applications of U-Pb geochronology that rely on identifying a sample's youngest age component, like the determination of a detrital zircon sample's maximum depositional age (MDA), can be compromised if Pb loss is not mitigated. Here, we test whether the use of bulk chemical abrasion (CA) prior to laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) detrital zircon U-Pb geochronology can eliminate Pb loss, specifically to improve low-n MDA estimation methods of Cenozoic zircon. We analyzed CA-treated and untreated aliquots of two Cenozoic sandstones from southern Alaska and found all untreated fractions have zircon with younger apparent $^{206}\text{Pb}/^{238}\text{U}$ dates than treated zircon fractions. To assess whether this discrepancy is a result of Pb loss, the youngest zircon grains in all aliquots were extracted and dated using chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS). All chemically abraded date pairs agree within 2σ uncertainty, whereas untreated LA-ICP-MS analyses give $^{206}\text{Pb}/^{238}\text{U}$ dates that are distinctly younger than their corresponding CA-ID-TIMS dates by 4.1–15.9%. We conclude the CA-LA-ICP-MS method provides an avenue to improve the accuracy of low-n MDA estimations and subsequent geological interpretations.

1. Introduction

Basin analysis studies commonly implement detrital zircon U-Pb geochronology to aid in understanding sediment provenance and routing systems (Fedó et al., 2003; Smith et al., 2023). Depositional age constraints in these studies are critical for understanding the rates at which sedimentary basins record tectonic and paleoenvironmental change. Ideally, basin strata include interbedded volcanics that can be dated using high-precision ^{40}Ar - ^{39}Ar or U-Pb geochronology. However, in their absence, a sandstone sample's youngest detrital zircon crystal (or age group) has been used to define a maximum depositional age (MDA: Brown and Gehrels, 2007; Dickinson and Gehrels, 2009; Gehrels, 2014; Schaltegger et al., 2015; Herriott et al., 2019; Sharman and Malkowski, 2020). This approach has become particularly popular because large-n detrital zircon U-Pb datasets can be quickly generated using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS: Pullen et al., 2014; Coutts et al., 2019; Copeland, 2020).

MDA estimations using LA-ICP-MS assume that the youngest zircon within a sample have remained closed systems. However, low-temperature, open system behavior of the U-Pb system in zircon, known as Pb loss, is



notoriously difficult to identify in Mesozoic and Cenozoic zircon because their Pb loss trajectories parallel Concordia (Bowring and Schmitz, 2003; Andersen et al., 2019). Pb loss can occur *in situ* in magmatic rocks post crystallization and/or after deposition into sedimentary basins, ultimately skewing age interpretations (Nasdala et al., 2005; Reiners, 2005; Keller et al., 2019; Senger et al., 2023). MDA estimation techniques that are based on low-n clusters of young zircon ages (Dickinson and Gehrels, 2009; Herriott et al., 2019; Coutts et al., 2019; Sharman and Malkowski, 2020; Vermeesch, 2021), Pb loss can be especially problematic and significantly skew zircon dates toward younger, inaccurate, age estimations. Additionally, matrix-effects, even if small, can also be linked to systematic age shifts in reported U-Pb ages (Allen and Campbell, 2012; Sliwinski et al., 2017; Herriott et al., 2019; 2025). Matrix-effects are a result of variations in laser ablation behavior between the primary reference materials and unknowns due to differences in their zircon matrices (Allen and Campbell, 2012; Marillo-Sialer et al., 2014, 2016; Howard et al., 2025): including differing degrees of radiation damage (Allen and Campbell, 2012; Sliwinski et al., 2017) and trace element composition (Black et al., 2004). Radiation damage is often correlated to higher uranium [U] concentration in older zircon (Nasdala et al., 2005; Widmann et al., 2019), thus making matrix-effects especially problematic for young zircon because they often have lower U concentrations when compared to older reference materials.

The chemical abrasion (CA) technique was developed to mitigate zircon Pb loss in isotope dilution-thermal ionization-mass spectrometry (ID-TIMS) U-Pb geochronology (Mattinson, 2005; Widmann et al., 2019; Schoene, 2014; McKanna et al., 2023; Sharman and Malkowski, 2024). Recent detrital zircon studies have leveraged the CA technique for MDA estimations by tandem dating the youngest detrital zircons identified during LA-ICP-MS using CA-ID-TIMS (Herriott et al., 2019; 2025; Howard et al., 2025), but this approach remains time consuming and costly. Few studies have implemented a bulk CA technique of detrital zircons prior to LA-ICP-MS (Crowley et al., 2014; von Quadt et al., 2014) and here, we show this technique (e.g., Donaghy et al., 2024) mitigates Pb loss and enables more rapid and accurate MDA estimations using solely CA-LA-ICP-MS data.

2. U-Pb Zircon Geochronology Methods

The samples used in this study were collected ~200 km apart within the Yakutat terrane in southeastern Alaska and are from the lowermost part of the Tokun (MT1-215) and Kulthieth (SK2-535) Formations (early to middle Eocene in age: Plafker, 1987 and references therein). Zircons were separated from both samples and divided into two aliquots. One aliquot remained untreated, whereas the other was treated using the bulk CA technique outlined in Donaghy et al. (2024). The two aliquots were then mounted in epoxy, polished, imaged by cathodoluminescence (CL) using a Hitachi 3400N SEM and a Gatan Chroma CL-system, and analyzed by LA-ICP-MS using a Teledyne Iridia excimer laser coupled with a Thermo Element2 single-collector ICP-MS at the University of Arizona Laserchron Center. The methods for these analyses are presented in Pullen et al. (2018) and Donaghy et al. (2024). Data reduction was completed using the AgeCalcML v1.42 Matlab script (Sundell et al., 2021). Data were filtered by maximum $^{206}\text{Pb}/^{238}\text{U}$ and/or $^{207}\text{Pb}/^{206}\text{Pb}$ uncertainty (10%), reverse discordance (5%), and normal discordance (20%). Density contour concordia plots and [U] scatter plots are included in Appendix A. All LA-ICP-MS data collected in this study are presented in (Tables S1-S4). We used Saylor and Sundell (2016) DZstats program to aid in the quantitative comparison of treated and untreated detrital zircon aliquots (Table S5) and Sundell et al. (2024) DZmda program to aid in the calculation of MDAs.



The youngest zircon identified during LA-ICP-MS analyses were then plucked from their epoxy mounts for tandem-dating (Table 1). Untreated grains were subjected to chemical abrasion prior to ID-TIMS U-Pb analyses, whereas treated grains were immediately dissolved for analysis via ID-TIMS without additional treatment. All CA-ID-TIMS measurements were made at Purdue University (Table S6) following the methods for chemical abrasion, sample digestion, ion chromatography, and TIMS isotopic measurements outlined in Donaghy et al. (2024). Data reduction was done using the ET_Redux software package (Bowring et al., 2011).

3. Results

Detrital zircon age spectra for the Eocene Kulthieth (SK2-535) and Tokun (MT1-215) Formations are largely indistinguishable between treated and untreated aliquots, and between formations, with high values for cross-correlation (>0.90), likeness (>0.84), and similarity (>0.97) coefficients (Fig. 1; Table S5). Due to the lack of abundant Cenozoic detrital zircon ages in Donaghy et al. (2024), this is the first study to contribute a robust comparison of treated and untreated Cenozoic zircon. The majority of zircon ages range between 100–40 Ma in both treated and untreated aliquots of the Kulthieth and Tokun Formations, but despite the similar proportions of zircon in the same age range, there are some distinct changes in the shape and number of peaks. Most notably, the 70–50 Ma peak shape is broader with two defined peaks in the untreated aliquot of both formations versus the narrow, well-defined peak in the treated aliquot (Fig. 2). The other substantial change in age spectra from the untreated to treated aliquots of both samples is the overall decrease in 100–85 Ma ages. In the untreated aliquots, a single broad peak spans the 100–85 Ma age range versus two distinct peaks (75 Ma and 90–85 Ma) in the treated aliquot (Fig. 2).

Table 1. Comparison of (CA)LA-ICP-MS and tandem CA-ID-TIMS zircon dates.

Sample	LA-ICP-MS Ages				CA-ID-TIMS Ages		Percent Difference	
	U (ppm)	238U (cps)	206Pb* 238U (Ma)	± 2s	206Pb* 238U (Ma)	± 2s	% dif.	average
Untreated Tokun Fm. (MT1-215) NO CA; tandem dated grains								
MT1-214 52	642	2663854	44.6	1.4	53.05	0.68	-15.9	
MT1-214 276	473	1959668	49.1	1.4	51.971	0.097	-5.5	-9.1
MT1-214 22	152	630573	49.9	2.4	53.01	0.25	-5.9	
Treated Tokun Fm. (MT1-215 CA); tandem dated grains								
MT1-214CA 65	411	1385712	51.2	3	52.83	0.13	-3.1	
MT1-214CA 42	144	486240	51.9	2.6	52.98	0.13	-2.0	
MT1-214CA 212	106	357482	52.1	3.3	53.50	0.67	-2.6	-2.5
MT1-214CA 225	224	755764	52.3	2.2	53.49	0.90	-2.2	
Untreated Kulthieth Fm. (SK2-535) NO CA; tandem dated grains								
SK2-535 113	617	3583325	42.7	1.6	44.921	0.035	-4.9	
SK2-535 141	357	2070979	42.7	1.6	44.876	0.063	-4.8	-4.6
SK2-535 312	175	1017284	42.7	2	44.51	0.39	-4.1	
Treated Kulthieth Fm. (SK2-535 CA); tandem dated grains								
SK2-535CA 289	785	2487647	42.6	2.9	44.724	0.099	-4.7	
SK2-535CA 120	386	1223966	42.9	3	44.960	0.046	-4.6	
SK2-535CA 179	339	1076133	43.1	3.1	44.711	0.040	-3.6	-3.5
SK2-535CA 220	372	1180655	43.2	1.8	44.69	0.23	-3.3	
SK2-535CA 116	615	1949049	43.6	1.8	44.718	0.039	-2.5	
SK2-535CA 1	412	1307385	43.7	2.3	44.704	0.096	-2.2	



Despite overall minor changes in detrital zircon age spectra, there are significant differences between the dates of the treated and untreated youngest few zircons tandem dated by LA-ICP-MS and ID-TIMS (Table 1). Individual LA-ICP-MS zircon dates are 4.1–15.9% younger than their corresponding CA-ID-TIMS dates. On the other hand, individual CA-LA-ICP-MS dates are only 2.0–4.7% younger than their corresponding CA-ID-TIMS dates and within the reported 2σ uncertainty (Fig. 2). To better quantify how MDAs compare between the different tandem-dated datasets, we applied three frequently used metrics for low-n MDA calculations: weighted mean, maximum likelihood age (MLA), and youngest single grain (YSG) (Coutts et al., 2019; Vermeesch, 2021). Additionally, we also applied common MDA estimation techniques to the full (CA)LA-ICP-MS age spectra, including youngest peak population (YPP), youngest gaussian fit (YGF), and youngest statistical population (YSP) to better characterize the statistical distribution of the youngest age group relative to low-n estimation methods, which could be subject to outliers (Fig. 2; Table 2).

4. Discussion

4.1 Impacts of bulk CA prior to LA-ICP-MS on Cenozoic detrital zircon age groups

The similarity of DZ spectra between treated and untreated aliquots for the Kulthieth (SK2-535) and Tokun Formations (MT1-215) is strong support that bulk chemical abrasion (CA) does not negatively impact or bias DZ spectra (Fig. 2). This similarity is demonstrated by the high values for cross-correlation (>0.90), likeness (>0.84), and similarity (>0.97) coefficients. Negligible effects to the overall age distribution suggest the CA-LAICPMS method could be a valuable tool for studies that need increased accuracy in determining U-Pb age groups, especially for young zircon. Additionally, our results build on Donaghy et al. (2024) and show young zircon (<100 Ma) can be susceptible to Pb loss and can significantly bias MDA estimations toward younger apparent ages.

While the treated and untreated aliquots are overwhelmingly similar, there are some minor changes between spectra that warrant further discussion with respect to the bulk CA technique and mitigation of Pb loss. The 70–50 Ma peak age group in the untreated aliquots of both the Kulthieth and Tokun Formations narrowed to a well-defined 60–50 Ma peak in the corresponding treated aliquots. Additionally, the broad single 100–85 Ma peak in untreated aliquots splits to distinct peaks at 75 Ma and 90–85 Ma in treated aliquots. These shifts in the shape and number of peaks in age spectra are consistent with improved accuracy of apparent DZ ages following mitigation of Pb loss (Donaghy et al., 2024). We also observed the loss of some zircon age groups from untreated to treated aliquots that can be associated with the full dissolution of some zircon due to high uranium [U] content (Crowley et al., 2014; Donaghy et al., 2024). This is most apparent in the Proterozoic grains of the Tokun Formation. Approximately 6.3% of the total zircons in the untreated aliquot of the Tokun Fm. were Proterozoic, which decreased to 3.7% in the treated aliquot. Older grains are more associated with Pb loss due to radiation damage (Nasdala et al., 2005; Widmann et al., 2019), and the shifts and disappearance in some Proterozoic age groups is evidence that some of these grains fully dissolved during the CA process. A similar shift was observed in the Kulthieth Formation, where 2.7% of the total grains in the untreated aliquot are between 350–250 Ma. This age group disappears almost entirely after bulk CA, and only 0.7% of the total grains fall within this range in the treated aliquot (Fig. 2a). Despite these minor variations, DZ spectra between treated and

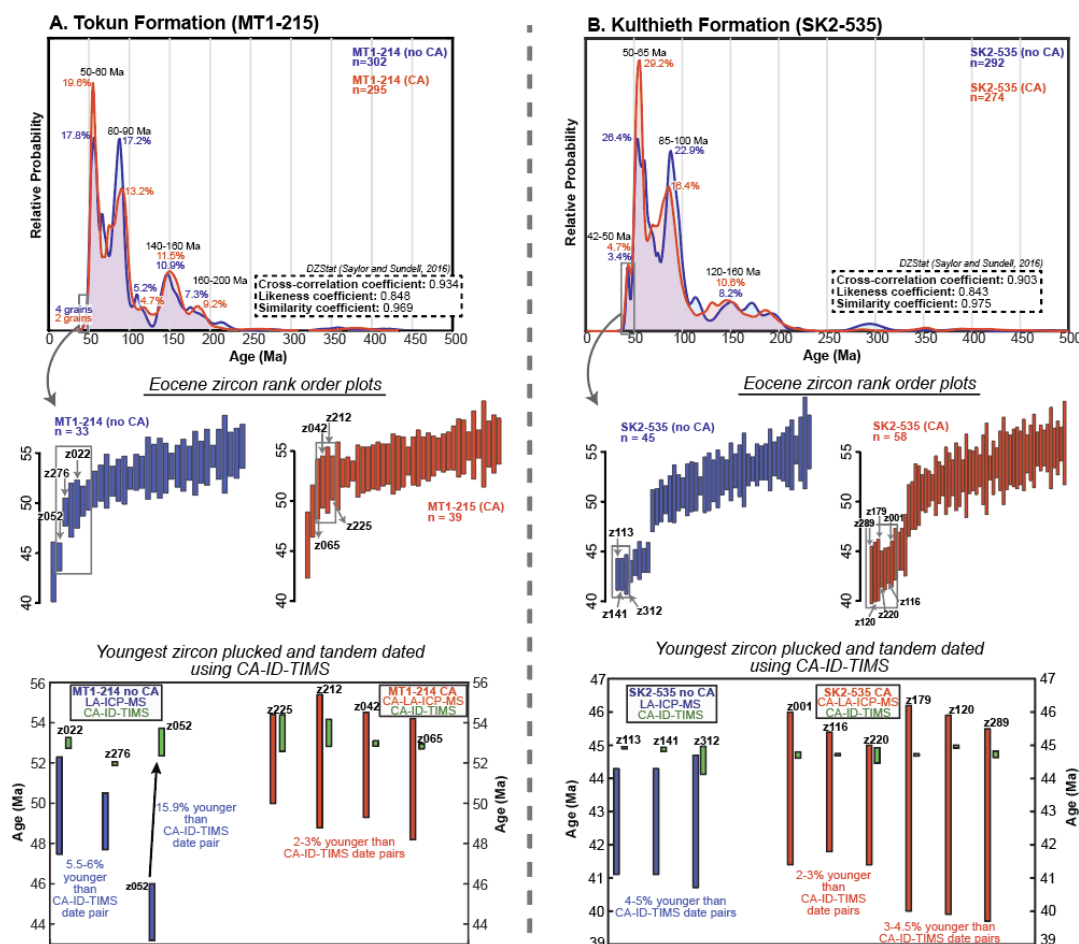


Figure 1. Comparison of U-Pb detrital zircon age spectra of non-chemically abraded (blue) and chemically abraded (red) aliquots of the (A) Tokun (MT1-214) and (B) Kulthieth (SK2-535) Formations. Rank order plots directly beneath detrital zircon age spectra show the spread of U-Pb zircon dates for all individual zircon grains that comprise the Eocene age group. Additional bar plots of calculated $^{206}\text{Pb}/^{238}\text{U}$ ages show the youngest zircon plucked from the Eocene age group in treated and untreated aliquots compared with their respective tandem CA-ID-TIMS age.

untreated aliquots of Tokun and Kulthieth Formations are indistinguishable from the perspective of sediment provenance interpretation.

We also plotted treated and untreated analyses for both samples on density contour concordia diagrams to determine if CA improved the scatter of concordant analyses in addition to improving the resolution of some peak age populations (Fig. A1). The most pronounced improvement in the scatter of concordant analyses is observed in the Kulthieth Formation. While there is also significant improvement in the scatter of concordant analyses in the Tokun Formation, the shift of individual analyses back to concordia is not as severe as observed in the Kulthieth Formation



(Fig. A1). The greatest improvement of scatter for the Tokun Formation is for zircon ages between 100–80 Ma (Fig. A1). This is of particular interest because the 80–100 Ma peak age population was one of the age groups that was most significantly impacted by CA in both Tokun and Kulthieth Formations. Furthermore, although there are not significant changes to the DZ spectra (Fig. 2a) for Cenozoic samples, this is evidence that cryptic Pb loss still negatively impacts and biases young zircon dates (Howard et al., 2025; Sharman and Malkowski, 2024).

155

Table 2. Comparison of MDA estimations between treated and untreated aliquots of Tokun and Kulthieth Formations.

	Tokun Formation (MT1-214)				Kulthieth Formation (SK2-535)			
	No CA	(noCA) TIMS	CA	(CA) TIMS	No CA	(noCA) TIMS	CA	(CA) TIMS
1. weighted mean (tandem)	47.29 ± 0.92 (n=3)	52.12 ± 0.09 (n=3)	51.90 ± 1.34 (n=4)	52.922 ± 0.091 (n=4)	42.70 ± 0.98 (n=3)	44.908 ± 0.031 (n=3)	43.29 ± 0.94 (n=6)	44.773 ± 0.022 (n=6)
2. MLA (tandem dated)	44.7 ± 1.8 (n=3)	51.97 ± 0.11 (n=3)	51.9 ± 1.3 (n=4)	52.90 ± 0.38 (n=4)	n/a	44.908 ± 0.031 (n=3)	43.29 ± 0.94 (n=6)	44.708 ± 0.039 (n=5)
3. MLA (full ICP-MS dataset)	48.8 ± 1.1 (n=303)	n/a	53.4 ± 0.6 (n=295)	n/a	43.2 ± 1.5 (n=292)	n/a	43.7 ± 1.6 (n=274)	n/a
4. YSG (tandem dated)	44.6 ± 1.4 (z052)	51.970 ± 0.097 (z276)	51.2 ± 3.0 (z065)	53.49 ± 0.90 (z225)	42.7 ± 1.6 (z113)	44.51 ± 0.39 (z312)	42.6 ± 2.9 (z289)	44.69 ± 0.23 (z220)
5. YSG (full ICP-MS dataset)	43.1 ± 3.0	n/a	45.6 ± 3.3 (z153)	n/a	42.7 ± 1.6 (z113)	n/a	42.6 ± 2.9 (z289)	n/a
6. YPP (full ICP-MS dataset)	44.5	n/a	55.0	n/a	43.5	n/a	43.8	n/a
7. YGF (full ICP-MS dataset)	44.5 ± 0.9	n/a	55.0 ± 5.2	n/a	43.5 ± 2.1	n/a	43.8 ± 2.9	n/a
8. YSP (full ICP-MS dataset)	44.3 ± 1.2 (n=2)	n/a	53.0 ± 0.4 (n=25)	n/a	43.5 ± 0.5 (n=8)	n/a	43.9 ± 0.7 (n=11)	n/a
Percent Difference from tandem-dated CA-ID-TIMS MDA								
	No CA	CA			No CA	CA		
1. weighted mean (tandem)	-9.3	-1.9			-4.9	-3.3		
2. MLA (tandem dated)	-14.0	-1.9			NA	-3.2		
3. MLA (full ICP-MS dataset)	NA	NA			NA	NA		
4. YSG (tandem dated)	-14.2	-4.3			-4.1	-4.7		
5. YSG (full ICP-MS dataset)	NA	NA			NA	NA		
	No CA aliquot % difference to CA aliquot	No CA to TIMS WM	CA to TIMS WM		No CA aliquot % difference to CA aliquot	No CA to TIMS WM	CA to TIMS WM	
6. YPP (full ICP-MS dataset)	-19.1	-14.6	3.9		-0.7	-3.1	-2.2	
7. YGF (full ICP-MS dataset)	-19.1	-14.6	3.9		-0.7	-3.1	-2.2	
8. YSP (full ICP-MS dataset)	-15.7	-15.0	0.1		-1.0	-3.1	-1.9	

4.2 Systematic negative bias in Cenozoic treated and untreated MDA estimations

Our results indicate Pb loss in Cenozoic zircon compromises accuracy for the youngest analyzed zircon during LA-ICP-MS analyses leading to underestimation of MDAs. This issue is likely magnified in older samples that have accumulated more radiation damage (Donaghy et al., 2024; Howard et al., 2025), however, Pb loss can also occur at low-temperature conditions in sedimentary basins due to processes associated with hydrothermal fluids and from



alpha damage to the zircon crystal lattice at temperatures below the annealing threshold (Bowring and Schmitz, 2003; Keller et al., 2019; Herrmann et al., 2021). A comparison of the youngest zircon ages in our untreated and treated
165 detrital zircon aliquots to their tandem CA-ID-TIMS dates shows a significant improvement in the average negative
bias from 4.1–15.9% to 2.0–4.7%, respectively (Table 1; Figs. 1-2). Additionally, zircon in treated aliquots overall
have less scatter and lower ^{238}U (uranium) beam intensities, decreased scatter in concordance, and higher radiogenic
to common Pb ratios (Figs. A1-A2). This improvement in CA-treated samples is strong support that CA prior to LA-
ICP-MS mitigates Pb loss (Herriott et al., 2019; Donaghy et al., 2024; Howard et al., 2025). Mitigation of Pb loss
170 directly impacts MDA estimation, as all low-n techniques (e.g., weighted mean, YSG) result in age interpretations for
the untreated samples that are inaccurately young, whereas the treated aliquots provide estimates that are within
uncertainty of the CA-ID-TIMS analyses (Fig. 2). Low-n MDA estimation techniques that focus on the youngest
individual grains in the youngest age group in general are particularly vulnerable to outliers in the tail of the age
distribution from either Pb loss or analytical uncertainty. Therefore, we also compared common MDA estimation
175 techniques used for large-n samples (e.g., MLA, YPP, YGF, and YSP). For this analysis, we did not target the youngest
individual grains for tandem CA-ID-TIMS dating in all samples (Fig. 2; Table 2). Overall, we found that remediation
of Pb loss using CA is consistent with previous studies comparing detrital zircon ages and MDAs using tandem dating
by LA-ICP-MS and CA-TIMS (Crowley et al., 2014; von Quadt et al., 2014; Herriott et al., 2019, 2025; Donaghy et
al., 2024; Howard et al., 2025; Sharman and Malkowski, 2024).

180 In the case of this study, untreated zircon using all MDA estimations techniques results in age interpretations
that are inaccurate (Fig. 2), especially for the Tokun Formation. The youngest untreated zircon in the Tokun Formation
range between 49–43.1 Ma ($n=4$; Table S3). However, tandem-dating of an ~44.6 Ma grain yields a CA-ID-TIMS
date of ~53.05 Ma (Table 1), indicating a ~15.9% negative age bias in the LA-ICP-MS date. If an age interpretation
is made from the YSG in the untreated aliquot (~43 Ma), it would underestimate the age by up to 10 million years
185 (Fig. 2). This substantial negative age bias is not isolated to the YSG approach. For tandem-dated aliquots, all untreated
Tokun Formation MDA estimations range between 9.3–14.2% younger than their correlative CA-ID-TIMS MDAs
(Fig. 1; Table 2). Additionally, the YPP, YGF, and YSP also yield MDA estimations that are between 14–15% younger
than the CA-ID-TIMS weighted mean and maximum likelihood age MDA for the untreated Tokun aliquot. In contrast,
most of the <50 Ma grains are not present in the treated aliquot and there is a distinct shift to older zircon dates in the
190 age spectra (Fig. 1), consistent with mitigation of Pb loss. As a result, the absence of <50 Ma grain and larger
proportion of 60–50 Ma zircon ages yield YPP, YGF, and YSP MDA estimations that are 0.1–4% older than the CA-
ID-TIMS weighted mean and maximum likelihood age MDA for the treated Tokun aliquot (Table 2). The youngest
zircon in treated and untreated aliquots of the Kulthieth Formation are closer in age and experience less of a negative
age bias in the untreated aliquot (Fig. 2). Despite the similar MDA estimations between tandem-dated aliquots of the
195 Kulthieth Formation, we still observe a slight improvement in the negative age bias from 4.1–4.9% to 3.2–4.7% (Fig.
2). The YPP, YGF, and YSP estimation methods yielded similar MDAs between treated and untreated aliquots of the
Kulthieth Formation, but overall, all MDAs have a negative age bias (1.5–3.1%) relative to the CA-ID-TIMS weighted
mean and maximum likelihood MDAs. These results support that Pb loss can impact even young zircon and emphasize



the importance of considering these impacts in age estimations of sedimentary strata using solely MDA estimations, especially low-n estimation methods, from untreated zircon.

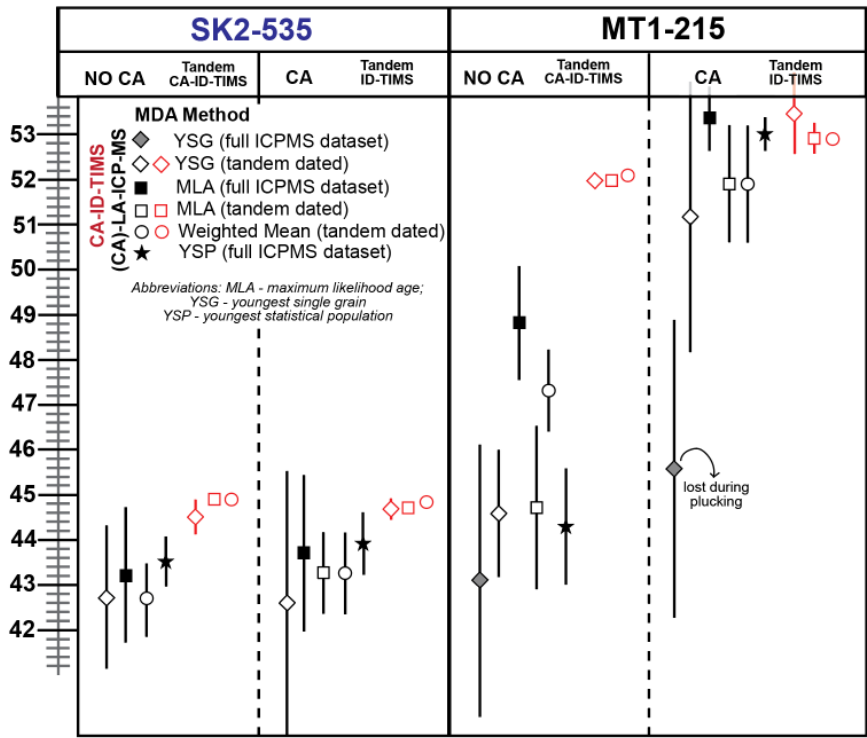


Figure 2. Bar plot comparing LA-ICP-MS and CA-LA-ICP-MS MDA estimations using three different techniques. The length of the bars represents the 2σ uncertainty. The ‘tandem dated’ MDA estimations refer to grains plucked for CA-ID-TIMS and estimations can be directly compared to their CA-ID-TIMS MDA.

Another indicator of Pb loss in zircon are high uranium concentrations [U], as they are typically correlated to increased radiation damage (Nasdala et al., 2005; Widmann et al., 2019; Donaghy et al., 2024). The degree of radiation damage likely depends on a variety of factors including the zircon source, transport, and basin thermal history (Hay and Dempster, 2009; Sharman and Malkowski, 2024). We note that zircon in the Kulthieth Formation have [U] that are 20–55% higher than zircon from the Tokun Formation across all age groups (Table S7). This is possibly attributed to differences in sediment transport and storage processes between formations (Hay and Dempster, 2009), as the alluvial-fluvial to nearshore Kulthieth Formation is inferred to be deposited more proximal to potential sources relative to the marine Tokun Formation (Plafker, 1987). Additionally, in both Kulthieth and Tokun Formations, the treated aliquot has, on average, 35–40% less [U] than the untreated aliquot (Table S7). Lower [U] in the treated aliquots indicates the chemical abrasion treatment preferentially dissolved zones of higher [U] that are associated with Pb loss. Higher analytical uncertainties in some of the treated zircon (Fig. 1) could possibly be linked to lower [U]. Regardless,



these results support that even young zircon can accumulate significant radiation damage resulting in substantial Pb loss that is remediated by the CA.

220 Low- n estimation methods are highly sensitive to individual grain ages and can be heavily affected by Pb loss or, simply, the expected analytical dispersion (Coutts et al., 2019; Vermeesch, 2021; Howard et al., 2025). Increasing the sample size by pooling n zircons that comprise the youngest age group can help mitigate the effects of analytical dispersion (e.g., YPP, YGF, and YSP), but it may also dilute the power of MDA estimation by including grains that are older than the youngest population. For example, this problem is obvious in the comparison of YPP
225 and YGF estimation methods to the CA-ID-TIMS weighted mean and maximum likelihood MDA estimation method of the treated Tokun aliquot. It also does not address Pb loss. Mitigating Pb loss, on the other hand, allows the use of low- n MDA estimations. Nevertheless, our data indicate that an average negative age bias of 2.5–3.5% remains in treated aliquots (Figs. 1-2). This result is consistent with recent studies by Howard et al. (2025) and Herriott et al. (2025) report an average negative bias of ~2-3% for $^{206}\text{Pb}/^{238}\text{U}$ dates from untreated detrital zircon. Such bias could
230 be related to incomplete mitigation of Pb loss with the bulk CA technique or matrix-effects during LA-ICP-MS analysis. One possible source of matrix-effects is the typical use of older zircon (e.g., FC-1) as primary reference materials relative to young (<100 Ma) zircon. These grains may behave differently during CA because reference materials are selected for their relatively low [U] and date reproducibility (i.e., little to no Pb loss). These differences may lead to changes in how the laser couples with the reference material relative to the unknown, and, ultimately, to
235 different mass and/or elemental instrumental fractionation during LA (see discussion in Howard et al., 2025). A majority of the untreated zircon aliquots in Howard et al. (2025) were thermally annealed (TA) prior to LA-ICP-MS, a technique that has been shown to help remediate matrix-effects by healing defects in the zircon crystal lattice to create more homogenous surfaces between unknowns and references materials during ablation (Marillo-Sialer et al., 2016; Herriott et al., 2019). The implementation of this method can help explain the differences between average
240 negative bias in untreated aliquots in those studies (2-3%) versus the average of 6-7% in untreated aliquots in this study. Future studies targeting the impact of bulk CA on matrix-effects will be fundamental for the LA-ICP-MS community, such as comparison of thermally annealed (TA)- vs. CA-LA-ICP-MS datasets to untreated aliquots. Such a persistent negative age bias in young zircon further highlights the importance of having well-characterized, age and compositionally appropriate reference materials for detrital zircon studies.

245

5. Conclusions

Pb loss is likely pervasive in zircon and is hard to identify in Phanerozoic zircon. When present, Pb loss biases $^{206}\text{Pb}/^{238}\text{U}$ analyses of zircon toward dates that are younger than the mineral's crystallization age. Our results have shown that Pb loss impacts even Cenozoic zircon, and that bulk CA prior to LA-ICP-MS helps mitigate this
250 issue. A slight (2–4%), but persistent, negative bias between CA-LA-ICP-MS and CA-ID-TIMS dates may be related to matrix-effects induced by differences between reference materials and unknowns following CA. However, this bias is significantly improved from untreated aliquots, small, and typically within the uncertainty of a single LA-ICP-MS $^{206}\text{Pb}/^{238}\text{U}$ analysis. Thus, CA-LA-ICP-MS U-Pb detrital zircon geochronology is poised to become a new tool for rapid and more accurate MDA estimates via LA-ICP-MS without the need for laborious and time-consuming tandem



255 CA-ID-TIMS geochronology. We encourage future studies, especially those poised to quantify matrix-effects and the
 use of larger n datasets, to continue to assess the effectiveness of the CA-LA-ICP-MS for MDA estimations.

260 Appendix A

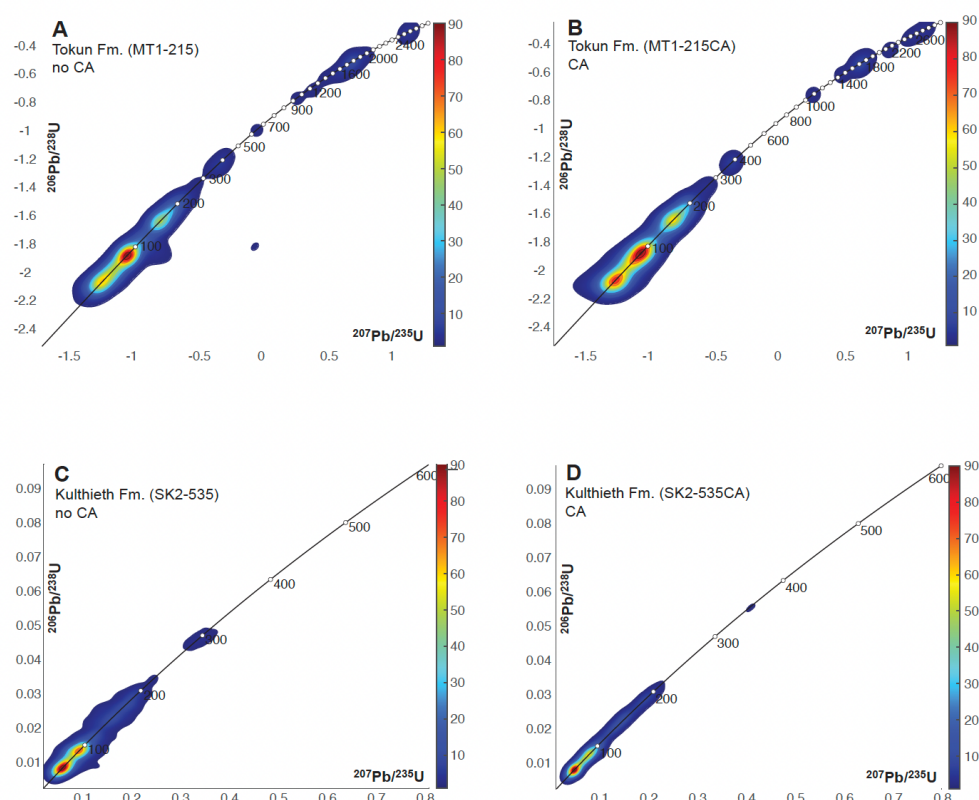


Figure A1. Density contour concordia diagrams for non-chemically abraded and chemically abraded aliquots of detrital zircon samples from the Tokun (MT1-215) and Kulthieth (SK2-535) Formations (A-D). Both aliquots of the Tokun Formation are indistinguishable (A-B). However, there is substantial improvement in the scatter of concordant
 265 analyses in the chemically abraded aliquot of the Kulthieth Formation compared to the untreated aliquot (C-D).

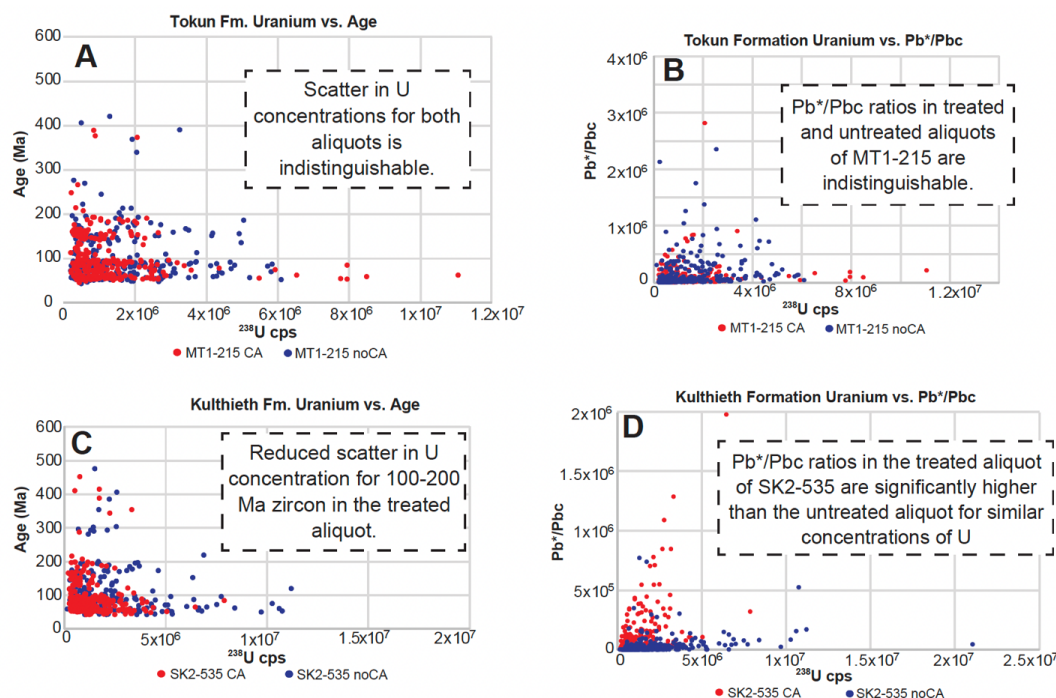


Figure A2. Scatter plots of ^{238}U cps plotted against age (Ma) and Pb^*/Pbc for both treated and untreated aliquots of the (A-B) Tokun (MT1-215) and (C-D) Kulthieth (SK2-535) Formations. See Figure S1 in Supplementary Material for scatter plots of alpha dose against age (Ma). Abbreviations: Pb^* - radiogenic Pb; Pbc - common Pb.

Code availability

DZstats is a free, MATLAB-based program available for download from GitHub (Saylor and Sundell (2016)). DZmda is a free, MATLAB-based program available for download from GitHub (Sundell et al., 2024).

Data availability

All (CA)LA-ICP-MS and CA-ID-TIMS individual measurements are included in the Supplementary Material.

Supplement

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

Author contribution

EED, MPE, and MIM all helped design experiments for treated and untreated zircon aliquots. EED prepared all bulk chemically abraded aliquots and conducted CA-ID-TIMS experiments. EED conducted LA-ICP-MS and CA-LA-ICP-MS 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.

295

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 300 ICPMS measurements were made at the Arizona LaserChron Center under NSF-EAR 2342541 and all CA steps and CA-ID-TIMS measurements were completed at Purdue University's Radiogenic Isotope Geology Lab under NSF-EAR-2151277 to M. Eddy.

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