Authors' Comments

We would like to thank the editor, reviewers, and community members for their commentary on our manuscript, "Chemical abrasion: The mechanics of zircon dissolution" that will ultimately help to strengthen this contribution. We respond to each of their comments below. If given the opportunity to submit a revised version of this manuscript, some of the major changes we would make in response to feedback include:

1) Focus on the heart of the manuscript more strongly – *textural evidence* for the mechanics of zircon dissolution. Many comments reference the lack of geochemical and geochronological data. We would like to emphasize that a complimentary manuscript that focuses on the geochemical and geochronological evolution of chemically abraded samples is currently in preparation. We would shorten and refocus Sections 4.2 (Implications for ID-TIMS U-Pb Geochronology) and Section 5 (Conclusion) to emphasize that the effectiveness of any chemical abrasion protocol for ID-TIMS U-Pb geochronology will ultimately be sample-dependent and reflect a sample's radiation damage and inclusion content and distribution. We would refrain from prescribing any specific chemical abrasion protocol, since no geochronological and geochemical data are presented in the current work.
2) We would also remove Section 4.3 (Implications for radiation damage annealing models) since it is tangential to the discussion and in need of additional supporting data.
3) Streamline the writing to eliminate wordy text and shorten the manuscript length. We would add two small tables that more succinctly summarize Raman data and basic sample descriptions.

We address each reviewer's specific comments below. Reviewer comments are in black text, and our responses are in blue text.

Community Comment 2 – Magdalena Huyskens

There are quite a few qualitative statements that can and should be backed up with statistical analyses. For example, claiming changes in the slopes between $v3(SiO4)$ and Eg peak after annealing and leaching (lines 254-256) and reporting the average changes and range for the peak width in a raman spectrum for the individual samples and temperature steps.

In the revised manuscript we can included slopes calculated using a simple least-squares linear regression for all unannealed, annealed, and chemically abraded samples in Fig. 5 and Fig. 6 to support our earlier statements. We can also include a new table that summarized the minimum and maximum $\upsilon_3(SiO_4)$ FWHM values for each sample. A similar table could be generated for E_g FWHM values, however, we feel it would be a bit redundant. All measured $\upsilon_3(SiO_4)$ and E_g peak position and FWHM values are included in the Table S1.

For the estimates of volume loss, the method needs to be described in more detail. Right now, I am not sure if it is including interior dissolution features or not.

Volume estimates for these two samples were made using the Dragonfly software's "Upper OTSU" segmentation function. This function differentiates zircon from inclusions, dissolution features, and background (tape/air) based on grayscale intensity. Total volume is calculated by adding the number of selected high-intensity zircon voxels together. The volume of one voxel is ~4.25 μm^3. The volume loss estimates do include interior dissolution features. However, we note that some of the finer-scale dissolution features and inclusions are missed due the dataset's spatial resolution and beam hardening effects. We can add these details to the methods section in revisions.

One of the findings is that some compositional zones are preferentially dissolved. Do you have any compositional data for these? It would been great to know what the difference in composition is and if the solubility is solely based on radiation damage, or some composition otherwise is more soluble.

We agree with the reviewer that the geochemistry of these zones is an important piece of the puzzle. Unfortunately, we do not have compositional data for these specific samples. This study was designed to evaluate the microstructural changes that occur in zircon during chemical abrasion, so geochemical changes are outside the scope of the current investigation. This contribution is intended to lay the groundwork for a second step-leaching study of 3 of the 4 zircon samples that evaluates the geochemistry and geochronology of the dissolved zones.

The one recommendation that is put forward for the CA technique is to increase the temperature: "In most samples regardless of initial damage content, we find that chemical abrasion at 210 °C is more effective at mining out soluble zones from crystal interiors. Based on our mechanistic blueprint, we predict that hotter leaching temperatures are thus more likely to better mitigate Pb-loss in geochronological datasets." I do not find this supported in the data. Yes, the solubility increases with increasing temperature. Increasing it a little bit more or increasing the time will

completely dissolve the entire zircon grain. Since there is no U-Pb data associated with this study, the mitigation of Pb loss is speculative. In addition, there are many zircons that will completely dissolve with such a treatment, in which case no U-Pb date could be collected.

The reviewer is correct that without geochronological data this interpretation is speculative. We will remove this recommendation in revisions. We will note, however, that this interpretation is supported by our step-leaching investigation.

Minor comments:

Misspelling of reference "Bowring and Schmidtz, 2003" (multiple times in the introduction)

We will correct the misspelling.

Figure 2: Is there any way to track which conditions were used for which grains? It would be helpful to get an idea overall how the different samples are behaving under the different conditions. In addition, it would be nice to have images of the zircons before annealing. There are often colour changes associated with this step.

We can modify Figure 2 to better illustrate which samples are shown (AS3, SAM-47, KR18-04, and BOM2A) in Fig. 2b. Labeling the leaching condition for each individual crystal, however, isn't practical given the restricted space, nor can dissolution features be seen at the image's low magnification. Figures 9 – 17 do a much better job providing an overview of how the different samples behave given different leaching conditions. Annealing did induce color changes, but unfortunately, we do not have images of grains prior to annealing.

Figure 5: All panels should have the sample name in them, at roughly the same position. It is confusing that c) is within a). Use the same font type. If one panel has the alpha dose, the other one should have this too….. L 254-260: "We note that relationship between the $v3(SiO4)$ and Eg peak widths is steeper after annealing in each of the four samples, since the two Raman peaks have different temperature sensitivities (Hartel et al., 2021). This observation suggests that laboratory annealing is not simply the inverse of radiation damage accumulation. As such, we caution against using the Váczi and Nasdala (2017) calibration to derive alpha dose estimates from v3(SiO4) peak widths for annealed or chemically abraded samples and omit alpha dose axes from Figures 5b and 6b." This is inconsistent. The alpha dose is noted for the annealed samples, but not the partially leached ones.

We can add sample names to the bottom panels of the Figure 5 and Figure 6. The alpha dose axes in the figures are intended for the unannealed samples *only*. We will modify the axis label to better stress this point. We do not feel it is appropriate to use the alpha dose scale for either the annealed or chemically abraded samples as emphasized in the text, so we will not add the axis to Fig. 5b or Fig. 6b. We will need to leave panel c) within a) because there isn't another good space to place it without vastly expanding the size of the figure.

Figure 7: The choice of color for the 180 °C for 12 h for AS3 & SAM-47 is odd, since it fits the color scheme of samples KR18-04 & BOM2A.

The color scheme in this figure is based on leaching condition as opposed to sample which we feel is more appropriate for easier cross-sample comparison of different leaching conditions. All 12 h leaching experiments are assigned a shade of teal: 180 C, 12 h experiments are dark teal, and 210 C 12 h experiments are light teal. We will change the legend in the figure to better reflect this.

Lines 274-281: "Notably, SAM-47 and BOM2A residues each have at least one data point with a narrower $v3$(SiO4) and Eg peak width than their solely annealed counterparts suggesting that some residues have a higher degree of crystallinity. Further, we find that the residue datapoints for these two samples largely plot below (at lower $v3$ for a given Eg) the annealed datapoints indicating a change in the relationship between the $v3$(SiO4) and Eg peaks. Taken together, these observations could suggest that additional structural recovery occurs in some zircon samples during HF leaching even after dry annealing at significantly higher temperatures."

Is there any reason that this observation can't just be explained by the removal of more damaged zones that were not annealed during the high temperature annealing step? Structural recovery during HF leaching seems impossible to me and would need some further explanation…. … Line 777- 780: "There is also an apparent change in the relationship between the widths of the v3(SiO4) and Eg peak after partial dissolution in HF acid in some samples, and a small number of Raman analyses for chemically abraded residues are more crystalline than their annealed counter parts" Same as for Lines 274-281. Does this not just mean that the parts that were not annealed due to larger radiation damage are still present before leaching?

Dissolution does remove more damaged zones, but dissolution of these zones cannot account for the change in the relationship between the two Raman bands; dissolution would remove material with broader peaks but would not result in a change of slope. We plan to remove Section 4.3 "Implications for Radiation Damage Annealing Models"

which discusses hydrothermal annealing of radiation damage in revisions. There are a few studies that report structural recovering during hydrothermal treatment (Rizvanova et al. 2000; Geisler et al. 2001b, 2002, 2003) that we cite, and the color change evident in grains after chemical abrasion suggests that chemical abrasion anneals color centers. However, we recognize that this discussion is needs additional data to support it and detracts from the main purpose of this paper.

Line 405: "… many most …" remove one of those words

The suggested correction will be made.

The section 4.2.2 Inclusions and zircon trace element analyses is not discussing the impact of dissolving compositional zones within zircons that are observed in this study.

We thank the reviewer for this suggestion, and we will add text regarding this point.

The section "4.4 Imaging radiation damage zoning: Implications for (U-Th)/He thermochronology" seems disconnected from the main point of the paper and is a little distracting.

This section is admittedly disconnected, but we feel it important to include. This paper is the first contribution to demonstrate that μCT can be used to image radiation damage zoning in zircon non-destructively and in 3D. There are big implications for this beyond U-Pb.