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.

Editorial comment – Daniel Condon

The paper mixes a set of quantitative data that is linked to observations and qualitative data derived from it. As a result, the description of the data is rather wordy and at times difficult to follow – wonder if some form of tabulation wouldn't help? Also, lots of the discussion/generalisation seems reasonable, its worth making it clear that this if for four samples and a wider range of samples need to be characterised, and perhaps a wider range of parameters (i.e., the annealing in addition to the leaching that his manuscript focusses on).

We would re-organize and refocus sections as described elsewhere to improve manuscript readability. We would add a new table that summarizes key sample information including age and degree of radiation damage and text that emphasizes that dissolution mechanics are strongly sample-dependent. In the conclusion we would add lines recommending that future studies should evaluate a wider range of zircon samples. We address the comment regarding the annealing conditions below.

Fractures – the use of this term implies that planar features are a result of stress that is applied to the material. There is a good argument to be made for this process and it seems likely to be a common occurrence in some samples. My comment is that calling all planar features fractures implies a certain causative process (differential stress). Are all planar features fractures? Maybe they are.

Yes, all planar features are interpreted as fractures, and we attribute their formation to differential stress caused by volume expansion/reduction related to radiation damage accumulation/annealing or inclusions. Differential stresses may be caused either by geological processes or during thermal annealing in the laboratory. We would state this more clearly in revised text. Non-planar features are not interpreted as fractures, and we refer to them in the text simply as acid paths.

Rim to core dissolution. A lot of different mechanisms and processes are discussed and the authors do a good job of introducing these and tracking them through the discussions. Whilst the images/analyses support that rim to core dissolution is not typical the authors do state (line 680) that there is a progressive rim to core dissolution

The reviewer is correct that rim-to-core dissolution is not typical. We only expect rim-to-core dissolution (with the caveat along the crystallographic c-axis) in highly crystalline grains only in the event that there are no acid paths to the grain interior (i.e. no fractures, surface reaching inclusions, or overlapping defects that reach the grain surface). We can clarify this in revision.

Much of the focus in the discussion, and in the community, is around the leaching temperature as being the thing that is most significant. Perhaps it is but what above the duration of the annealing, or the rate of cooling? This paper focusses on samples that have bene annealed for 48 hours but it should be acknowledged in the manuscript that practitioners quote a range of annealing durations, typically 48 or 60 hours. I assume this is the time between turning the furnace on and off, and often cooling can take several hours although the rate of cooling can be increased by opening the furnace…. and "How does the duration/temperature of the annealing impact the crystal structure and precondition it for reaction to leaching?" … Line 251 – how does this look for 60 hours? Is there any published data for this?

We selected our annealing temperature (900 °C) based on the recommendations of Huysken et al. (2016) who showed that increasing the annealing temperature can lower the solubility of domains affected by residual Pb-loss. Annealing studies of radiation damage in zircon demonstrate that annealing is strongly dependent on temperature and weakly dependent on heating duration (Zhang et al., 2000; Ginster et al., 2019). The difference between 48 and 60 h or oven cooling times is expected to have negligent effect on the crystallinity of zircon based on these previous studies (Ginster et al., 2019, their Figure 1). We can add these points to the manuscript.

The zircon crystals studied have not been analysed for high-precision U-Pb – but data does exist for the samples (AS3 – Schoene et al., GCA, 2005, coherent U-Pb; SAM-47 – no U-Pb data published? KR18-04 – MacLennan et al., Sci Adv, 2020 – overdispersion, Pb loss? BOM2A, Basu et al., 2020, single population). Have these analyses been conducted at experimental conditions analogous to those deployed in this study? I appreciate that the precision/resolution may not be at the level to preclude Pb-loss but presenting the data might help frame the discussion around the implications for zircon U-Pb systematics and age interpretations

There is currently no published U-Pb data for SAM-47, and not all published U-Pb analyses were conducted at analogous experimental conditions. As such it would be difficult to extrapolate our textural findings to how well any specific leaching condition eliminates Pb-loss for these samples. As such, we would shorten the U-Pb discussion section in revisions and refrain from prescribing recommended leaching conditions. We would instead refocus this paper on describing dissolution textures. The goal of this manuscript is to lay the mechanistic groundwork for a second contribution that will include geochronological and geochemical data for three of the four samples and focus on how different chemical abrasion conditions affect zircon U-Pb and trace element systematics. This second piece will link the textural results presented here to both the literature data cited and the new U-Pb data. Efforts to include textural, geochronological, and geochemical data in a single contribution proved unwieldy.

The paper seems focussed around leaching mechanisms/processes applied to whole crystals – however the process will often be applied to fragments and/or grains that has been polished for CL, on both cases exposing the interior of the grains. Would be useful to mention for the non-practitioners that not all zircons will come as complete crystals.

The reviewer is correct. We can this point to the discussion.

It is a long paper and much of the qualitative observational data based upon examination of many observations from the four samples, which a subset of representative images presented. One issue is around readability – could some of the generalised observational data/interpretations be tabulated to make it more accessible? Personally, I found it challenging, going back and forth to try and compare what is said for the different samples and leaching temperatures. I felt the use of tables may be helpful for compiling this qualitative information and making it more readily accessible.

If asked to submit a revised manuscript, we would shorten the manuscript considerably, reorganize, and refocus the results and discussion sections as described elsewhere to improve manuscript readability. In particular, the Discussion sections 4.1.1 and 4.1.2 would be reorganized to better summarize key findings from the results section and their implications for the dissolution of higher and lower damage grains. We will strongly consider adding more tables as suggested (we can definitely add a small table that summarizes basic sample information), but we are not convinced that a reasonably-sized table that summarizes results can be designed or would significantly improve readability.

Conclusion section – is it possible to draw out the observations and how they record a progression of processes?

This is an excellent suggestion. We can retool the conclusion to better reflect a progression of processes.

Bowring and Schmitz, not Bowring and Schmidtz - We can corrected this typo.

also mention the rare occurrences of reverse discordance seen in some samples? - We can add this point to the introduction.

thermal annealing instead of laboratory annealing – We can change all occurrences of laboratory annealing to thermal annealing

remove more soluble – We can corrected this.

bias, yes, but more realistically this should be considered an additional source of uncertainty in the assigned age – We can add this point to the introduction.

also prompted the community to question/explore a range of interpretative frameworks for such datasets – We can add this point to the introduction.

Line 96 – could the sample information be tabulated?

We can add a table with basic sample information including U-Pb age and alpha dose estimates.

Line 146 – what portion (percentage of grains) didn't survive the leaching and was their anything distinctive about those grains? Did any grains break apart?

AS3 and SAM-47 residues are *extremely* fragile. Many of the AS3 and SAM-47 grains broke in the process of transferring the crystals from the Teflon microcap to the tape or disintegrated entirely. Touching the residue with a tweezer tip was sometimes all that it took for a grain to disintegrate. Examples of several broken crystals are shown in the SE and μCT collages. The only distinctive characteristic of broken grains was either large, pre-existing fractures visible in μCT images or more generally samples with high initial radiation damage (i.e. all AS3 and SAM-47 grains). A large percentage of grains were also dropped or lost during pipetting. Lab notes do not distinguish between disintegrated and misplaced, so calculating a percentage of broken is not possible. These are important points to make that we can add to the results section.

Figure 2 A is reflected light, what is the light source for B? I assume AS3 is top left etc., for Panel B but there is space to add label, or state this in the figure caption. The images are low resolution – will higher resolution version be submitted as a supplement? Also, the top right panel indicated the images contain residues that have been leached for varying times (4 and 12 hours) – how does the reader distinguish these different grains?

Both A and B are reflected light images. We can modify the figure 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. We do not have photomicrographs at higher resolution – The SEM images in Figures 9 – 17 do much better at showing high resolution images of dissolution textures.

Line 262 – were replicate raman determinations made on any of the crystals to assess variation within a crystal?

Yes, replicate analyses were made on some zircon crystals. Most grains exhibit intracrystalline variations to some extent as discussed in the results section. Graphically, intracrystalline variations are best illustrated in Figure 5a by the core and rim measurements made for SAM-47. The sample names in Table S1 in the Supplementary Material indicates which samples have replicate analyses. We can add text to the result section more clearly indicating that replicate analyses were made.

Figure 8 – what is the 2D nature of the 3D rendering in figure 8?

The 2D image is a single slice of the image stack used to render the 3D grain in B. We can change the figure caption to clarify.

376 – remove interestingly.

We can make the suggested change.

678 – ID-TIMs analyses represent an integrated analyses of the residue post-leaching – this could be core-rim, or more core, or more rim – seems that is will be sample and duration dependent?

Yes. This is a key point. We will added this point to the text.

687 – "hot leaching" (210C)? Or should this be hotter leaching? Or longer leaching?... 702 – yes, but in lower radiation damaged samples it may also impact an age-bias towards the core/older material…723 – and could this be a mechanism that results in the rare cases of reverse discordance we see in CA ID-ITMS data for some old zircons? Could we be seeing this in samples but not at a resolvable level, where the zonation is favourable?

That is indeed possible on both points. However, including these points in the text may be too speculative since we do not present complimentary geochronological data in this study. Based on the suggestions of some of the other reviewers we would remove these lines from the text.

741 – yes but sometimes the inclusion rich zircon may be the ones we want to date…

This is true. We can add this point to text.

781 – is hydrothermal annealing a thing? Can you provide a reference? Looking at the literature I couldn't find anything in materials science – do you mean hydrothermal treatment? This sounds odd – how robust are the few data this discussion is based up?

There are a few studies that report structural recovering during hydrothermal treatment (Rizvanova et al. 2000; Geisler et al. 2001b, 2002, 2003), and this remains our preferred interpretation to explain some characteristics of our Raman data (i.e. changes in the relationship between the two Raman bands post-leaching). However, we recognize that this discussion needs additional data to support it and detracts from the main purpose of this paper. We would remove this section in revisions.

784 - Widmann. We can correct the typo.

865 – Okay – then what impact does the annealing temperature/duration/cool down rate have on the formation of micro fractures? All the discussion is around varying the leaching parameters but should we also be considering the annealing step?

To the best of our knowledge previous radiation damage annealing studies have not focused on how different temperature conditions affect zircon micro fracturing. We can add text to the conclusion section suggesting that future studies should evaluate how different annealing conditions affect micro fracturing in zircon and the rate of zircon dissolution.

839 – four samples covering a range of ages and radiation damage accumulation.

We can make the suggested correction.

888 - … removal of excess closed system material AND potential age bias in lower radiation damaged materials?

We would remove these lines from a revised manuscript.