Response to Reviewer 2's comments on manuscript gchron-2023-6 "Modeling apparent Pb loss in zircon U-Pb geochronology"

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Reviewer #2 provides an overall critical assessment of our manuscript with comments that focused on (1) the novelty of our study, (2) criteria for what types of data should be included in a modeling study, and (3) parts of the text with overstated or imprecise language. Although we generally disagree with Reviewer #2's characterization of points (1) and (2) and provide a rebuttal below, there are many aspects of Reviewer #2's comments that are well taken and that we will incorporate into a future revision. For instance, we now appreciate that there is a need to better describe how our study relates to previously published work on Pb loss modeling in general and to better articulate the specific aims of this study.

Below, we provide a response to Reviewer #2's comments and explain how we will specifically incorporate suggestions in a future revision with ***bold, italic text***. We also provide Reviewer #2's comments below with line numbers, which we reference in our response.

We would like to note that although Reviewer #2 provided extensive comments, this review lacked an assessment of the paper's central thesis – that apparent Pb loss may be characterized by mathematical convolution. Indeed, the review does not use the word "convolution" and does not include comments on the feasibility of the approach – either positive or negative.

1. Novelty of the study

Reviewer #2 questions the novelty of our study. For example, Reviewer #2 suggests that "there are already well-established, more appropriate, and more powerful mechanisms" that involve geochemical characterization (U, Fe, Ca, REE, OHO, etc.), analysis via Raman spectroscopy, and internal mineral texture (lines 7-11). Reviewer #2 goes on to provide examples of 'similar population-based approaches' (lines 96-112), citing Morris et al. (2015), Kirkland et al. (2017), Kirkland et al. (2020), and others. Similarly, Reviewer #2 suggests that our treatment of detrital zircon has already been addressed (lines 137-143).

Although we appreciate the suggestions for additional references that relate to the general topic, we would like to emphasize that none of the studies mentioned by Reviewer #2 relate to the specific topic of this paper: assessing distributions of apparent Pb loss magnitude through mathematical convolution. Some of these papers focus on modeling the timing of Pb loss (Morris et al., 2015; Kirkland et al., 2017) and one correcting for common Pb (Anderson, 2002). We thus contest Reviewer #2's assertion that the central thesis of our manuscript has already been published (lines 7-12). None of the references that Reviewer #2 provides mention convolution or attempt to model distributions of apparent Pb loss magnitude. In our future revision, ***we will revisit the introductory text to make sure that we avoid overstating the novelty of this work through specific and precise language about the contribution provided.***

2. Criteria for a Modeling Study

Reviewer #2 cites a general community preconception, or skepticism, of model-based studies in that they are "unreliable to the point of being unproductive" (lines 27-32). Reviewer #2 goes on to suggest that new model-based approaches should satisfy two specific set of conditions (lines-27-55). These conditions include specific data types (paired LA-ICP-MS and TIMS, known timing of Pb loss, detailed petrologic data, CL + BSE images, Raman spectroscopy, and mineral chemistry data) (lines 34-55).

Although we don't dispute that the dataset described would likely make an excellent study of Pb loss, we contend that there is no single way to study Pb loss. The type of data collected for a given study should depend on the goals and objective of the study, not a preconditioned list of items specified *a priori*. Reviewer #2 does not explain why the framework of mathematical convolution fails without these data.

There are several reasons why the types of data suggested would be challenging to collect for the purpose of our study. It is not our goal to characterize Pb loss in any single zircon crystal, but rather to characterize the *distribution* of Pb loss magnitude that has influenced an entire sample. This requires ideally many U-Pb analyses from numerous zircon crystals, versus detailed characterization of fewer grains. Specifically, the geochemical data requested (e.g., Fe, Ca, OHO) are not routinely collected during *in-situ* U-Pb geochronology. Routine datasets provide only U and Th concentrations and isotopic ratios ($^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$). We don't dispute that collecting additional data types (e.g., REE) could be useful, and we specifically mentioned this in our original submission (lines 460-462).

This study simply presents a mathematical concept (convolution) for quantifying the distribution of Pb loss magnitude. The datasets we analyze are from, in part, previously published studies that we view in high esteem (e.g., von Quadt et al., 2014; Watts et al., 2016), and the point of our paper mirrors their own: that an offset exists between non-CA and CA U-Pb dates. Our contribution is to provide a mathematical framework for better quantifying that offset in terms of a distribution, rather than as a simple percentage shift. It seems that this simple aim might have been lost on Reviewer #2 (e.g., lines 139-143). In our revision, ***we will revisit the introductory text to make sure that the aim of this paper is clearly communicated.***

Although we disagree with Reviewer #2's criteria for what must be in a modeling study, we do appreciate that the geochronology community is broad and diverse, and that our manuscript might be better received if we were more specific about the context and purpose of this study. In our future revision, ***we will revisit the introductory text to better communicate the aims and context of this paper. We will also better articulate the intended audience of this work (i.e., in-situ U-Pb community) and the expected value. We would also consider changing the title of our paper to be more specific.***

3. Other Points

Reviewer #2 highlights several places in the text where our language is vague, overstated or imprecise. Reviewer #2 also highlights opportunities to improve our referencing. We provide a bullet list of these comments and our responses. Overall, these comments will be helpful in improving the revised manuscript.

- Improve the description of causes of radiogenic Pb, specifically by clarifying that fluids are needed to remove Pb (lines 62-65). ***In our revision, we will review the suggested literature and revise the Introductory text appropriately to more completely describe causes of Pb loss.***
- Mention potential causes of non-Gaussian distributions of U-Pb dates, specifically the common Pb correction (see also comment by Reviewer #1) and complexities related to zircon growth (lines 66-84). ***In our revision, we will include improved discussion surrounding our assumption of a starting Gaussian distribution and situations for which this assumption may not be appropriate. We will also clarify that our assumption of Gaussian distribution is one of convenience – mathematical convolution could be done with any distribution type that reflects the underlying non-Pb loss perturbed U-Pb date distribution.***
- Consideration of how the various distributions might relate to geologic processes (lines 113-120). This is a good suggestion, and in our revision ***we will include discussion of potential mechanistic links between geologic processes and distribution types.*** For example, we find it intriguing that the Weibull distribution, which was the best-fitting function for apparent Pb loss distributions, has also been applied to modeling particle size distributions (Zobeck et al., 1999).
- Avoid suggesting that "Pb loss in natural samples has not been well characterized" in the abstract (line 122). In our revision ***we will take care to use more precise language and avoid broad statements***. We agree with the reviewer that much work has been done on open-system behavior in the U-Pb system, and did not intend to imply otherwise.
- Include a more comprehensive list of references (lines 131-133). In our revision, ***we will make more effort to cite relevant studies by a broader diversity of authors, including those mentioned by Reviewer #2***.
- Revise the statement relating to how analyses are pulled off concordia during Pb loss (lines 134-136, referencing line 34 of the original submission). In our revision, ***we will clarify that the analyses may not be pulled completely off of Concordia depending on magnitude of Pb loss and measurement precision, and we will clarify that this takes place during the timing of Pb loss.***
- Mention the fact that open-system behavior is itself useful geologic information that is removed via CA (lines 144-151). This point is well taken. It is not the goal of our work to study the geologic processes associated with Pb loss (e.g., timing). However, this does not mean that this is not useful information for geologic studies. In our revision, ***we will include statements in the discussion that clarify this point***.
- Be more specific about the aim of future data collection (lines 152-161). This is a point well taken. In our revision, ***we will include a better description of the overall goal for which the data collection strategy is oriented***. This goal is to better quantify the distributions of apparent Pb loss magnitude in untreated, *in-situ* LA-ICP-MS analyses.
- Avoid appealing to increasing precision to identifying Pb loss (lines 162-167). We believe that this assertion is valid, as shown by Fig. 8. The complexities mentioned here seem to arise from our assumption of the underlying age distribution being Gaussian. ***We will incorporate additional statements related to this assumption*** (see also lines 66-84 above).

- Consider the implications for thermochronology (lines 168-170). We view this suggestion as being outside of the scope of our study. We are uncertain why the passage of zircon through its closure temperature (He or fission track?) is relevant to the modeling framework that we present.

References

Andersen, T.: Correction of common lead in U-Pb analyses that do not report ^{204}Pb. Chemical Geology 192, 59-79, 2002.

Kirkland, C.L., Abello, F., Danišik, M., Gardiner, N.J., and Spencer, C.: Mapping temporal and spatial patterns of zircon U-Pb disturbance: A Yilgarn Craton case study. Gondwana Research 52, 39-47, 2017.

Kirkland, C.L., Barnham, M., and Danišik, M.: Find a match with triple-dating: Antarctic sub-ice zircon detritus on the modern shore of Western Australia. Earth and Planetary Science Letters 531, 115953, 2020.

Morris, G.A., Kirkland, C.L., and Pease, V.: Orogenic paleofluid flow recorded by discordant detrital zircons in the Caledonian foreland basin of northern Greenland. Lithosphere 7, 138-143, 2015.

von Quadt, A., Gallhofer, D., Guillong, M., Peytcheva, I., Waelle, M., and Sakata, S.: U-Pb dating of CA/non-CA treated zircons obtained by LA-ICP-MS and CA-TIMS techniques: impact for their geological interpretation. J. Anal. At. Spectrom 29, 1618-1629, 2014.

Watts, K.E., Coble, M.A., Vazquez, J.,A., Henry, C.D., Colgan, J.P., and John, D.A.: Chemical abrasion-SIMS (CA-SIMS) U-Pb dating of zircon from the late Eocene Caetano caldera, Nevada. Chemical Geology 439, 139-151, 2016.

Zobeck, T.M., Gill, T.E., and Popham, T.W.: A two-parameter Weibull function to describe airborne dust particle size distributions. Earth Surface Processes and Landforms 24, 943-955, 1999.

The work by Sharman and Malkowski presents a model-based consideration of the effects of radiogenic-Pb loss in zircon. Such effects are well known in the U-Pb community and a discussion on the diagnosis of open system behaviour of widespread importance for U-Pb geochronology. Nonetheless, there are some significant concerns with aspects of the study that preclude me recommending publication in its current form.

Specifically, the work apparently seeks to better characterise radiogenic-Pb loss in situations that it may be cryptic. However, there are already well-established, more appropriate, and more powerful mechanisms to do this. For example, simple comparison of isotopic ratios to geochemistry (uranium, iron, calcium, REE, raman, OHO, etc) and / or internal mineral texture will already provide a much simpler but much more powerful way to demonstrate the presence of

Pb loss. In short, it is unclear how the proposed models provide a tool that will be used to advance geochronology interpretations.

I am sorry to do this, but I think this work needs to be considered in the historical context of U-Pb geochronology because it is relevant to perceptions around model-based U-Pb approaches and (as I get to) has implications for key tests for this work. In the 1960s U-Pb isotopic analyses of zircon clearly demonstrated that in many cases zircon behaves in an open system fashion (e.g. is discordant). Now many researchers at that time also attempted to extract primary ages (and secondary overprinting) by interpreting linear and indeed non-linear arrays on concordia diagrams using models that rapidly increased in complexity (for example; Tilton 1960 JGR, Silver and Deutsch 1963 Journal of Geology, Steiger and Wasserburg 1966 JGR). Other developments also happened at around the time model-based interpretations were in vogue. Namely, isotope dilution analysis of single zircon grains with air abrasion and magnetic separation (e.g. Krogh) and of course insitu dating via ion microprobe dating (e.g. Compston). These analytically based developments set zircon U-Pb geochronology on the pathway of identification, extraction, and dating of grain domains with closed U-Pb systems (or specific targeting of open system domains where geochemical evidence could also be brought to bear on the subject).

Now my point (and I am aware of this from my own experience in reviews) the general community has a strong preconception that model-based approaches are generally unreliable to the point of being unproductive (given the numerous processes that can lead to the same distribution). Hence, works that try to revive a model-based approach to U-Pb geochronology, in an effort, to enhance understanding and make such models helpful to better understand geology, must allay this perception. In order to achieve this outcome of an advance then what can be done: Well, it would seem logical to this reviewer, that any new model-based approach needs to satisfy two conditions:

1/ It must be quantitatively calibrated against high quality closed-system geochronological data AND known times of disturbance. The choice of the samples where both primary and secondary ages are determined by precise, accurate and model-independent methods for such tests is crucial. Unfortunately, the sample choice in this work failed this criterion as the same grains were not analysed after LA-ICPMS by TIMS and in fact, in some cases the choosen studies have used even a different isotopic system to constrain the "true" age. Moreover, the timing of overprinting processes has not been clearly independently determined on the same material to the level needed. Hence, to demonstrate the use of this work and continue this study, such condition really needs to be passed. Such tests would significantly benefit from including detailed geological and petrologic information so the geological context and implications of the proposed models can be understood. This would necessitate detailed characterization of the grains, for example CL and BSE images before and after analyses, the latter showing ablation spots (and potentially also Raman spectroscopy) so any relationship between these grain level observations and isotopic ratios could be made, as they would serve as prima facie evidence of open system conditions.

2) It must be demonstrated that the new approach yields new information that is not available and unobtainable with modern closed system methods or simple relationships already at hand. This is a big challenge because by combination of mineral chemistry with isotopic ratios already can yield much more rigorous insight into geological processes than by this strongly model based example of age distribution fitting. Furthermore, any ages calculated, or more specifically in this case,

distributions proposed with such new methods really needs to be accompanied by uncertainty intervals that include the model-related uncertainty around the distribution. This is a very difficult goal to achieve.

In this current study, there appears to be a signficant way to go to satisfactorily address both these conditions.

Significant issues

Precision in the language. There are numerous cases where the level of precision in the text could lead to miss-interpretation by a reader. Moreover, there are specific inaccuracies. Please refer to the specific points below which document some of these.

The discussion of the causes of radiogenic Pb loss appears incomplete. While a damaged crystal structure is clearly a factor it isn't the sole prerequisite for open system processes. Please see the work of Silver / Pigeon which clearly demonstrates that fluids are also needed to strip Pb. In short, a more accurate description of radiogenic-Pb loss is needed.

Assumption of a gaussian distribution for the undisturbed zircon state of U-Pb ratios. There are several primary processes that could lead to a non-gaussian distribution that should at least be mentioned. While the simplifying assumption of a gaussian distribution is a reasonable starting position for certain growth processes, the work would be improved with a consideration of the natural complications to this situation. For example: Common Pb – it's presence and form of correction. Specifically, a non-uniform common Pb composition (while unlikely to be of significant concern in zircon and of more relevance for minerals with typically higher common Pb loads e.g. apatite and titanite) will invalidate the assumption of a gaussian distribution. Furthermore, there would be expected to be a complex interrelationship between radiogenic-Pb loss, discordance, and common Pb amount and composition that would have an implication for the model. Moreover, as precision increases so a natural outcome of this will be a non-gaussian distribution, the point where this non-gaussian distribution appearance breaks down would be a function of the growth duration of a population of zircon which is highly magma (size, temperature, cooling rate, chemistry, etc) dependent. A more sophisticated realisation of what zircon growth is, would benefit this work (there are several new mineral equilibrium model papers that deal with zircon growth rates that clearly are relevant in this regard). It is highly simplistic, without any caveats, to assume zircon growth is instantaneous – there are many environments where prolonged zircon growth has been demonstrated and these sorts of environments are entirely unsuited to a model assumption of a normal distribution.

Overlooked published similar population-based approaches in geochronology:

The work makes quite a few claims of novelty. While aspects of the proposed model are indeed new, there is quite a body of existing work that uses ostensibly, very similar, to similar, to quite similar approaches to understand: 1/ the most likely timing of radiogenic-Pb loss, 2/ mixing between different compositional domains and 3/ common Pb correction.

Specifically, the comparison between a model distribution and a measured U-Pb distribution has in fact been frequently previously utilized and a recognition of this foundation to the present study clearly required to provide context to this work and demonstrate the advance it makes.

The following works are only those I am aware of, but they may provide some useful context from which the current model appears developed. It is odd they are not considered and implies some limitation in the survey of existing literature relevant to this work.

Pb loss modelling

1/ Morris et al., 2015, Lithosphere, 138-143; Kirkland et al., 2017, GR, v. 52, 39-47; Kirkland et al., 2020, GR, v. 77, 223-237. There are probably other publications from this research group that use distribution comparison techniques to understand Pb loss as well.

Of note here is that the similarity test for the model distribution to the measured distribution is essentially the same as this work proposes. Surely, this should be acknowledged. The major difference in these works and the current approach is that they used the observed concordant distribution in the model whereas the approach proposed in this work is to compare the age distribution to theoretical distributions.

Unmixing

2/ Olierook et al., 2021, GR, v. 92, 102-112.

A similar approach in some regards to address the potential of mixing between different zircon domains. It also uses a comparison between a reconstructed (e.g. model) distribution and a known distribution.

Common Pb correction

3/ Andersen 2002, CG, v. 192, 59-79.

The common Pb correction approach of Andersen uses some of the same concepts.

The proposed procedure would be able to provide more geological insight if the various distributions (gamma, Weibull, lognormal, uniform, half normal, pareto etc) compared to the data were firmly rooted in some dominant geological process. Specifically, the discussion of the distribution shapes relative to geological processes needs to be significantly enhanced. For example, even simple end member distributions can be linked to likely geological processes; radiogenic-Pb loss / uranium gain / Pb gain / U loss, discrete or episodic, common Pb gain, heterogeneous common Pb, recent Pb loss, ancient Pb loss. In short, more geological context is required for the patterns that are compared to the measured data.

Specific points

Abstract: the authors claim that Pb loss in natural samples has not been well characterized. I would dispute this, the simplest measure of this process (discordance) is the primary filter essentially every U-Pb geochronology work uses, there are numerous works considering the process of radiogenic-Pb loss from the pioneering work of Silver, Pigeon, Krough, Black etc, the field of U-Pb geochronology has been focused around addressing open system processes (just consider the formulation of the concordia and Tera-Wasserburg diagrams even). So is it really "not well characterized"? However, is radiogenic-Pb loss **difficult** to characterise, absolutely it **can** be, depending on the measurement precision (which itself can be a function of age). This latter aspect is worth focusing on, to indicate where the proposed modelling approach may have benefits.

Line 26>. Very limited referencing to U-Pb geochronology concepts that appear to favour a specific author. Suggest providing a more balance and historically accurate list of references that recognises the contributions to the field.

Line 34. Inaccurate statement, depending on when radiogenic Pb loss has occurred (and the measurement precision) and the degree of radiogenic Pb loss (e.g. if complete) data may not be off the concordia curve.

Section 5.3 has specifically been addressed in other works (using a similar more tailored approach) it seems highly unusual that this context isn't provided here.

Also, the proposed approach for DZ seems incomplete as it is unclear what the purpose of this modelling is for; is it to better understand the primary crystallization ages, the timing of Pb loss, or the degree of mixing between different age components in any distribution? Furthermore, the proposition is somewhat cryptic and certainly difficult to apply to a detrital situation. I really don't see the contribution this paragraph of text makes to the overall presentation.

A major assumption of this work is that radiogenic-Pb loss is an impediment to understanding. Yet the reality is that tracking open system processes is possible with radiogenic-Pb loss and depending on the geological question posed, a very useful way of gaining otherwise difficult to access geological information. Moreover, the whole point of insitu dating is to characterize the full range of (texturally / geochemically defined) age components thus providing an understanding of the full range of geological processes a sample may have undergone. CA work clearly has its place but it is inevitable that such approach is removing some element of geological information in favour of another. The text is strongly one sided in its appraisal of CA and its merits or otherwise.

The discussion of strategies for future data collection needs to be very specific about what the aim of any data collection is; is it to date igneous crystallization, metamorphism, fluid mediated recrystallization, overprinting thermal events? What? Such fundamental information is necessary first before the strategy can be evaluated for the proposed purpose because such underlying geological question would affect everything from required temporal resolution to the most likely manifestation of radiogenic-Pb loss. Simply arguing for greater number of analyses to better characterise apparent age distributions seems a rather weak suggestion. The more dominant age components (be they detrital or caused by radiogenic-Pb loss) will be more likely to be sampled (assuming random sampling) for any n selected. This aspect appears to be overlooked but the statistics in some of the DZ work of Anderson and others demonstrate this point.

It is incorrect to appeal to increasing precision alone to identify radiogenic-Pb loss. The natural extension of this argument ends, rather, with being able to identify the timeframes of which zircon itself grows; there are plenty of zircon growth models about based on modified equilibrium pseudosections that demonstrate zircon has variably prolonged growth intervals in certain environments. Again, the geological environment that the strategy is proposed for needs to be much better presented (e.g. rapid volcanic crystallization).

Furthermore, it would seem useful to consider the model in the context of thermochronology considerations where timing through closure temperature is of relevance (e.g. growth within a magma chamber versus explosive removal from that chamber).

The reality is that strategies should be developed that integrate geochemical parameters of the zircon to better understand the growth or modification process the U-Pb systematics have been potentially affected by. Considering the age distribution alone seems a simplistic and potentially highly misleading approach given the numerous cofounding variables that could give rise to the same distribution.