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Dear Editor,

We are re-submitting a manuscript (gchron-2023-6) entitled "**Modeling apparent Pb loss in zircon U-Pb geochronology**" to *Geochronology*. This manuscript provides a novel mathematical framework for deconvolving the influence of Pb loss, or other processes that cause negative Pb*/U offsets, on zircon U-Pb date distributions. We believe that this revised manuscript has been substantially improved following incorporation of feedback by two anonymous reviewers. We have provided both a clean and tracked-changes version of our manuscript. We also provide a document with responses to each reviewer comment. The list below outlines some of the more significant changes that stem from reviewer feedback:

- Modeling Pb*/U ratios instead of calculated U-Pb ages (Reviewer 1)
- Clarifying issues related to the timing of Pb loss and incorporating the timing of Pb loss as an adjustable parameter in the model (Reviewer 1)
- Adding statements that address potential bias from common Pb overcorrection (Reviewers 1 and 2)
- Clarifying the novelty/aim of this work and putting in better context with previous studies, including additional citations (Reviewer 2)
- Many additional changes to the text that reflect comments and suggestions from both reviewers

In addition, this revised manuscript incorporates edits that stem from a virtual meeting with associate editor Pieter Vermeesch, including incorporating the logit-normal distribution as the preferred parameterization of *g(t)* and simplifying and shortening the manuscript (e.g., moving Figure 3 to supplemental and removing the discussion related to detrital samples). We have also explored the possibility of modeling Pb loss through the lens of optimal transport modeling, as suggested. Preliminary analysis has shown some promise, but we have reached a conclusion with Alex Lipp that this approach is likely outside of the scope of what can be accomplished in this paper as more analysis is needed.

We believe that this study would be of wide interest to the readership of *Geochronology*, particularly to the *in-situ* U-Pb geochronological community. We have included supporting data, and code is available via a GitHub repository. We thank you for your consideration of our revision.

Sincerely,

Glenn R. Sharman*, Matthew A. Malkowski

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Responses to Reviewers

Our responses are shown in **red, bold text**

Reviewer 1

The fundamental concept underlying this contribution by Sharman and Malkowski -- that observed U-Pb ages can be considered as a convolution an a true age distribution (i.e., a distribution representing analytical uncertainty around the true mean age of the analyzed material) with a distribution representing Pb-loss -- is certainly reasonable, though the form of these distributions may vary widely. The analytical age distribution of a single analysis in the absence of Pb-loss is frequently assumed to be Gaussian, so this is a reasonable assumption; the distribution of Pb-loss is at present much less well understood. To better understand this latter distribution, the authors start with independent (arguably Pb-loss-free, CA or non U-Pb) ages for ten Phanerozoic samples, and convolve each with different potential Pb-loss distributions to see which best reproduces the observed non-CA U-Pb distribution. While I have a number of questions and suggestions, overall this is a worthwhile contribution.

The authors represent Pb-loss as a negative percentage offset from the true crystallization age. This is fine mathematically for the purposes of modelling Pb loss in a single decay system, but perhaps it is worth emphasizing that

1) this is not equivalent to the percent of Pb lost, and

2) this percentage age difference will not generally be the same for the 206Pb/238U and 207Pb/235U ages, and for each system will depend on both the time of Pb-loss as well as actual amount of Pb lost

In this context, how do the authors propose to deal with the fact that different "Pb-loss" proportional age distributions must be convolved for the 206Pb/238U and 207Pb/235U systems? Would it be possible to consider instead a convolution between a Gaussian distribution representing the isotopic ratios at the time of Pb-loss and a distribution representing the actual amount of Pb lost? This would allow the same convolution or deconvolution to apply to both systems simultaneously (and even in principle 208Pb/232Th).

Our Response: In our revision we now apply our mathematical framework to Pb*/U ratios instead of calculated ages. Figures, tables, and the text have been revised accordingly. We now clarify that the modeling approach may be applied to both ^{206}Pb*/^{238}U and ^{207}Pb*/^{235}U. We also clarify in the text (Part 3 of Section 5.1) that *g(t)* will underestimate the true magnitude of ancient Pb loss if present-day Pb*/U ratios are used. We now add the ability in the code to specify the timing of Pb loss as an adjustable parameter.

One other issue arising from the fact that Pb-loss happens in terms of atoms rather than ages is that of common Pb corrections. In CA-ID-TIMS, common Pb from inclusions is generally thought to be removed by CA, so only a lab blank subtraction is performed. However, in in-situ analyses some form of common Pb correction is commonplace; this may have secondary consequences in the case that a sample is also discordant (e.g., discussion in Andersen et al. 2019, which you currently cite in the context of the general problem of Pb-loss in in-situ datasets). Fully dealing with this may be outside the scope of the current paper, but perhaps bears some consideration.

Our Response: We now include a statement relating to common Pb corrections in Part 1 of Section 5.1. Given that this topic has been extensively discussed in other publications (e.g., Anderson et al., 2019), we don't think that a fuller treatment of the topic is necessary in this article. However, we agree that this and other complexities related to the U-Pb system should be considered carefully when applying the modeling framework presented herein.

One other conceptual concern involves the form of the distributions chosen to represent Pb-loss; a number of parametric distributions are tested, and all are better than no correction (with Weibull performing best), it seems possible that the true distribution of Pb-loss may diverge from any of these (i.e., be a combination of multiple distributions, or nonparametric). Ideally, it might be possible to invert for the true form of the Pb-loss distribution.. have the authors considered if a deconvolution / inverse approach is feasible? Absent that, is there perhaps any underlying quantitative or intuitive rationale to explain the relative success of the Weibull distribution?

Our Response: Part 2 of Section 5.1 now explicitly mentions some of the benefits and drawbacks of parametric modeling and that our approach should be viewed in the context of exploratory modeling. We agree that development of a nonparametric approach to estimating *g(t)* would be an improvement. However, nonparametric approaches benefit from high data density (i.e., high-*n* samples), which currently available samples do not have.

We have also greatly simplified the number of parametrizations of *g(t)* that are presented in the manuscript. We now present just one type of continuous probability distribution, the logit-normal distribution, and explore how this distribution can accommodate different scenarios of Pb loss in Section 3.1. We also include a new figure (Figure 4) that explores this concept.

A few other more minor notes:

While the authors do provide several nice illustrations of convolution, one point which may be worth noting to help make the concept more intuitive to nonspecialists may be that convolving distributions is equivalent to adding random variables -- so for example convolving an exponential Pb-loss distribution with a Gaussian analytical distribution yields a third distribution which is the same one you would draw from by drawing a random variable (i.e., a random age) from the Gaussian and another from the Exponential and adding them together.

Our Response: We added a sentence to Section 2 that explicitly makes this point.

Another point which bears some note: while both CA-ID-TIMS U-Pb ages and Ar/Ar ages are likely to avoid the influence of Pb-loss, daughter loss is not unheard of in the Ar/Ar system. How analogous is the HF leaching sometimes conducted by Ar labs to CA? Is this equally effective in eliminating daughter loss?

Our Response: Although this paper is focused on the U-Pb system, we see some parallels with loss of daughter product in other geochronological systems. However, we are hesitant to make this connection as neither of us have expertise in the Ar-Ar system.

I was glad to see that the authors provided their full code via a persistent DOI (in this case, Zenodo), in line with best practices. The supplementary video illustrating convolution was a fun addition.

Reviewer 2

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).

Our Response: We now include additional citations to key sources. We also include additional statements in the Introduction that clarify the relationship of this work to previous study on the general topic of Pb loss.

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.

Our Response: Please refer to Point #2 in our "Response to Reviewer 2's comments on manuscript gchron-2023-6" dated June 7, 2023.

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.

Our Response: We have added a citation to Pidgeon et al. (1966) and added "exposure to hydrothermal alteration" as a mechanism of Pb loss in the Introduction.

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.

Our Response: We have revised the text to better explain that our assumption of a Gaussian distribution relates to random variability in repeated measurements about the true isotopic value. To support this, we now cite Schoene et al. (2013) who state: "…random uncertainties vary in an unpredictable manner, usually with an assumed Gaussian distribution, and include analytical uncertainties in isotope ratio mass spectrometry." We have rewritten Part 4 of Section 5.1 to further clarify that our approach assumes no geologic variation in the true crystallization age, which is a simplification as even autocrystic zircon crystallize over 10^3-10^4 yr timescales.

Complexities related to common Pb corrections are now considered in Part 1 of Section 5.1.

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.

Our Response: We now cite several of the suggested references in the revised manuscript. However, we contend that the relevance of some of these references to our study is overstated (Point #1 in our "Response to Reviewer 2's comments on manuscript gchron-2023-6" dated June 7, 2023.). For example, although Olierook et al. (2021) provide a useful approach for analyzing rim-core mixtures, this approach uses an unmixing paradigm which is distinct from the approach of mathematical convolution used in our article. Thus, while the approach used by Olierook et al. (2021) permits analysis of individual U-Pb dates (i.e., estimation of a core age with uncertainty), our approach is not applicable to individual U-Pb dates (i.e., we are unable to resolve the amount of Pb loss any given analysis has experienced) and instead relies upon analysis of Pb*/U distributions.

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.

Our Response: We now specify that we are referring to "Pb loss distributions", versus "Pb loss" more generally. Although there has been a long history of study of open system behavior in the U-Pb system, this article is narrowly focused on a method for estimating apparent Pb loss *distributions*, which we contend is a novel contribution.

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.

Our Response: We now cite Davis et al. (2003), which includes a discussion of the history of U-Pb geochronology in zircon. We have removed two Schoene references to avoid over-citing any given author.

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.

Our Response: We have deleted this sentence.

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.

Our Response: We have removed the section relating to modeling detrital samples in the revised manuscript.

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.

Our Response: We appreciate the perspective provided here that 'noise' to someone might be the 'signal' to someone else. We now include a statement in the Introduction that mentions the geologic information that Pb loss events can provide (citing Morris et al., 2015 and Kirkland et al., 2017). Even though the motivation for this work stems from the issue of incorrectly interpreting crystallization ages from Pb loss perturbed Pb*/U dates, particularly for Mesozoic and younger zircon, the approach used provides quantification of Pb loss distributions which could be of use to those who are interested in the Pb loss event itself.

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.

Our Response: We have deleted the sections 'Detrital and other multi-modal samples' and 'Strategies for future data collection'.

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).

Our Response: Part 4 of Section 5.1 now includes statements related to timescales of zircon growth in magmatic systems

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.

Our Response: We believe that considerations that relate to thermochronology are likely outside of the scope of this manuscript, which has a very specific focus and aim.