Response to Reviewer 1's comments on manuscript gchron-2023-6 "Modeling apparent Pb loss in zircon U-Pb geochronology"

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Reviewer #1 provided a thoughtful review of our manuscript that highlighted several ways in which our modeling framework could be improved. Below, we explore how we will implement Reviewer #1's suggestions in a future revision, with ***bold, italic text*** highlighting specific changes that we intend to make. We also provide the Reviewer #1's comments below with line numbers, which we reference in our response.

In our original submission, we represented apparent Pb loss as a negative percentage offset from the true crystallization age. Although Reviewer #1 noted that this is mathematically expedient (lines 14-15), they made several worthy suggestions for improving the modeling framework. We see these suggestions as having several inter-connected elements, which we will consider in sequence below.

First, Reviewer #1 pointed out that negative percent offset from the true crystallization age, which is what we modeled, is not equivalent to the percent of Pb lost (line 16). This is a fair point and one that stems from both (1) the non-linear relationship of $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ over time (Fig. 1) and (2) the fact that the relationship between % age offset and % Pb lost is dependent on the timing of when Pb is lost.

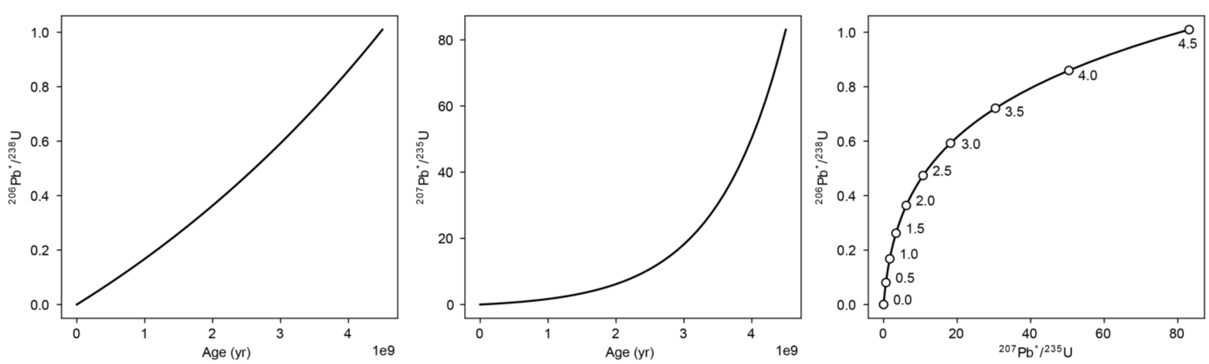

Figure 1. The relationship between age and isotopic ratios in the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ systems.

To understand the first point above, we plotted the relationship between % age decrease and % of Pb loss (at present-day) for zircon crystals of three ages 10, 100, and 1000 Ma for both the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ systems (Fig. 2). As Reviewer #1 suggested, the relationship is not exactly linear. However, the relationship is very close to linear for the $^{206}Pb/^{238}U$ system and for younger crystals in both systems. For example, if a 500 Ma zircon crystal loses 50% of its Pb at present-day, its $^{206}Pb/^{238}U$ age would decrease by 49.0% and its $^{207}Pb/^{235}U$ age would decrease by 43.9%. This effect is less pronounced for younger crystals; 50% Pb loss in a 100 Ma zircon would produce a 49.8% reduction in $^{206}Pb/^{238}U$ age and a 48.8% reduction in $^{207}Pb/^{235}U$ age. Fig. 2

illustrates that the discrepancy is lower for small or large amounts of Pb loss (i.e., the difference is greatest ~50% Pb loss).

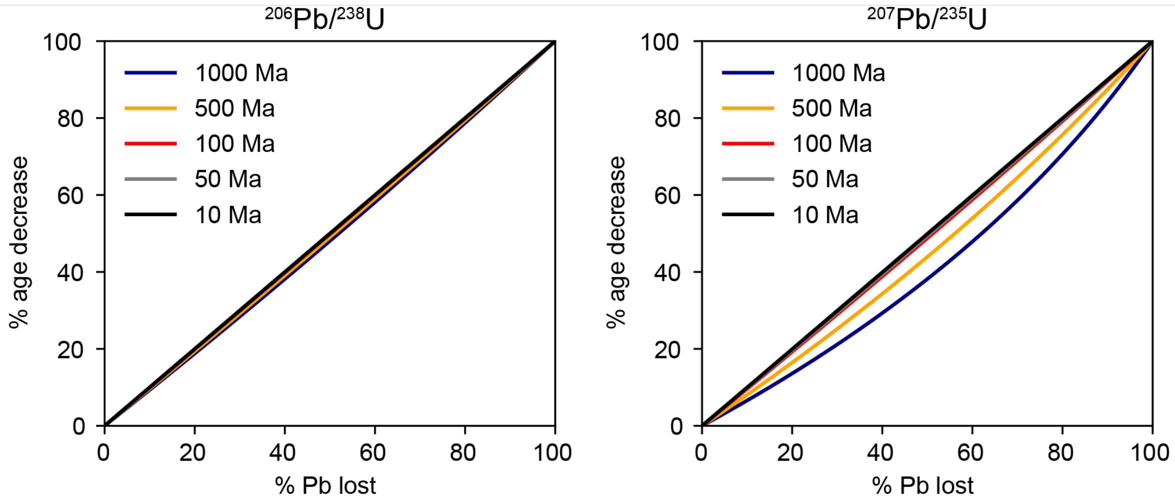

Figure 2. Relationship between relative age decrease and % recent Pb loss.

To address this issue, ***we will change the modeling framework to use isotopic ratios as input data instead of calculated ages***. Figure 3 illustrates that we achieve similar results using either approach for sample 284-2. This is to be expected as the relationship between % age decrease and % Pb loss is approximately linear for young samples and modest amounts of Pb loss in the $^{206}Pb/^{238}U$ system (Fig. 2). Regardless, we believe that this change will allow the modeling framework to be more accurate and flexible. In our revision, we will ***revise all tables and figures*** after implementing the new modeling approach.

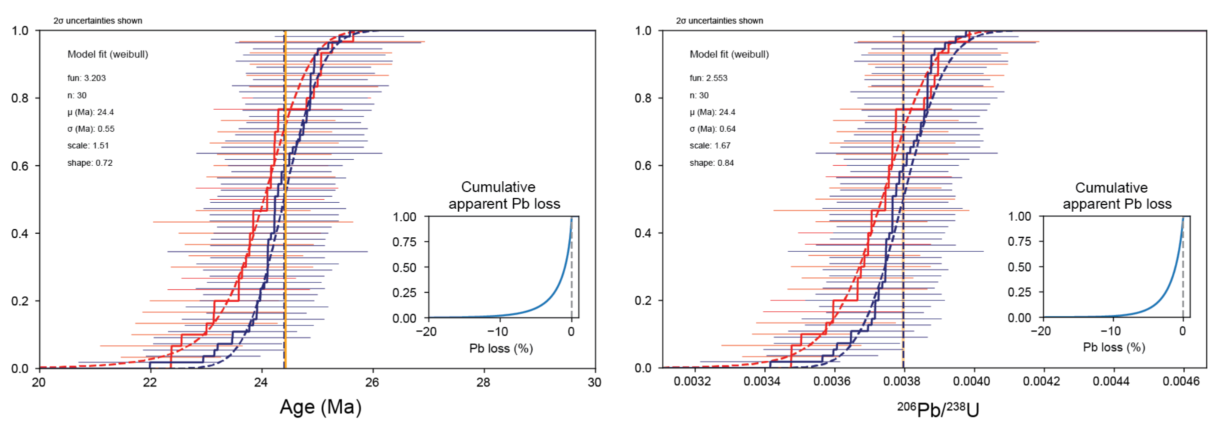

Figure 3. Comparison of modeling apparent Pb loss as a function of $^{206}Pb/^{238}U$ age (left) versus $^{206}Pb/^{238}U$ ratio (right) for sample 248-2 (von Quadt et al., 2014). Using isotopic ratios as input into the model yields a similar result.

The second point above relates to the timing of Pb loss (lines 17-26). In our original submission we did not discuss the timing of Pb loss, but rather focused on the magnitude of age offset as a proxy for amount of Pb lost. However, in doing so we failed to clearly articulate an important point that Reviewer #1 raises: % reduction in age (or isotopic ratio) can only be directly related to % Pb loss if the Pb loss event occurred recently.

We explore this idea through a thought experiment of three 100 Ma zircon crystals that experienced Pb loss at different times: 10% after 100 Myr (present-day), 20% after 50 Myr, and 40% after 25 Myr (Fig. 4). All three zircon crystals yield similar $^{206}Pb/^{238}U$ ratios (~0.01406, or ~90 Ma) despite the magnitude of actual Pb loss being very different (Fig. 4). Because the shape of Concordia is nearly linear between 0 and 100 Ma, all three zircon crystals move along similar pathways.

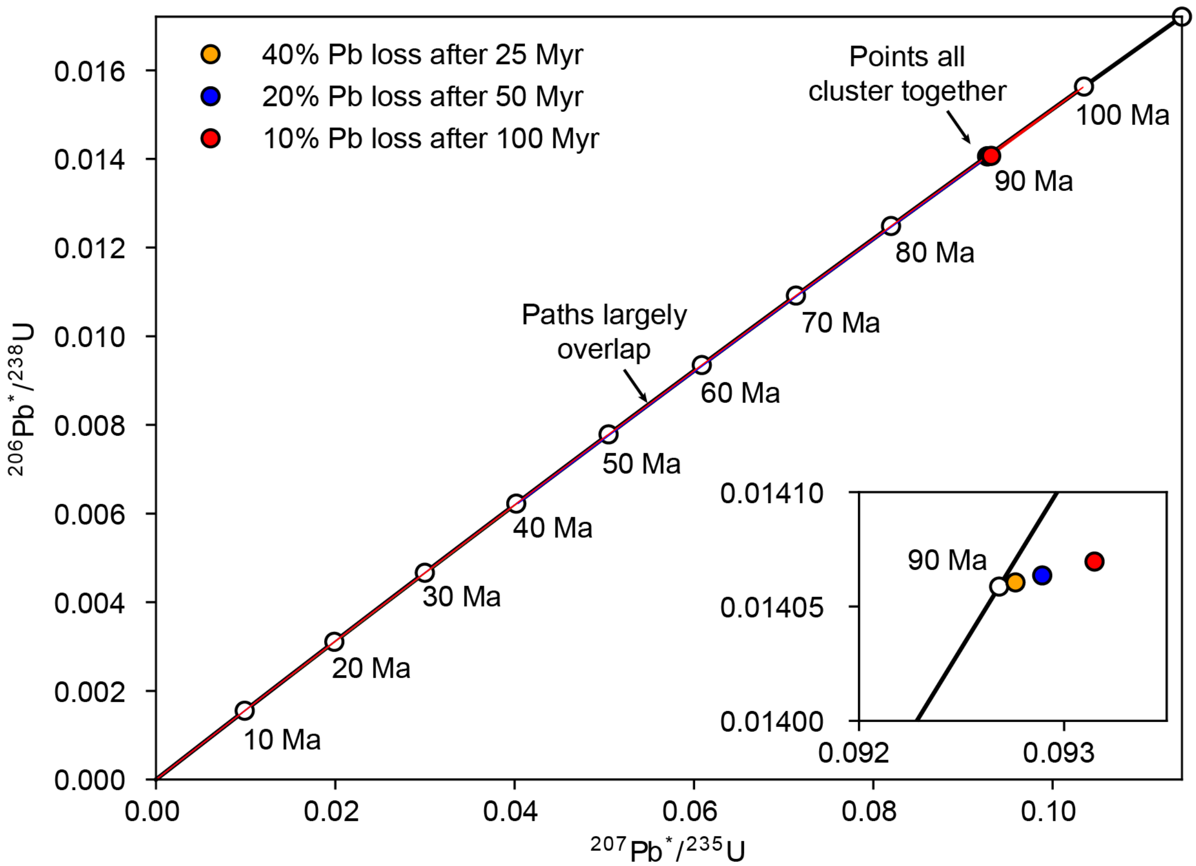

Figure 4. Illustration of how similar $^{206}Pb/^{238}U$ can be obtained by different Pb loss histories. Due to the approximately linear shape of Concordia for young analyses, there is relatively little discordance despite highly contrasting Pb loss histories.

One way of handling this issue in a revision would be to ***better articulate that the % apparent Pb loss reflects the cumulative amount of Pb lost over the history of the zircon crystal, and that this value could be thought of as a 'minimum' because a greater amount of Pb loss in the past would be required to achieve the same reduction in final $^{206}Pb/^{238}U$ ratio*** (Fig. 4). For instance, a 10% reduction in Pb after 100 Myr (present-day) is approximately equivalent to a 20% reduction after 50 Myr in the example provided in Figure 4.

Another way of handling this issue in a revision would be to ***incorporate the timing of Pb loss as an adjustable parameter in the model***. Reviewer #1 specifically asks "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?" (lines 22-24). This is indeed possible by adding an additional step: adjusting isotopic ratios backwards in time to the specified timing of the Pb loss event prior to applying the modeling framework to the adjusted data. We have tested this approach and found it to be effective if the timing of the Pb loss event is known. ***We plan on including this flexibility in the revised model.*** Although it was not the goal of the paper to model the timing of Pb loss, there are a number of existing approaches that have been developed for this purpose (including several highlighted by Reviewer #2, e.g., Kirkland et al., 2017). We note that Keller (2023) also recently proposed a Bayesian approach to assessing the timing of Pb loss in *Geochronogy Discussions* (https://doi.org/10.5194/gchron-2023-9). Such an approach could be potentially used to constrain the timing of Pb loss as input into our model.

However, we are skeptical that adding the ability to specify the timing of Pb loss will be useful in practice for the samples modeled in this study and for Phanerozoic zircon more generally. This is because it is challenging to determine the timing of Pb loss in "young" (i.e., < several 100 Ma) crystals for several reasons: (1) the shape of the $^{206}Pb/^{238}U$ vs $^{207}Pb/^{235}U$ Concordia line is close to linear and thus discordance as a consequence of Pb loss is minimal, (2) $^{207}Pb/^{235}U$ dates are typically low precision for *in-situ* U-Pb analyses, and (3) amounts of apparent Pb loss measured in the samples we model is relatively low (typically <10%). All of these factors together will likely make it challenging to accurately determine the timing of Pb loss. As briefly discussed in our original submission, these factors also contribute to cryptic Pb loss being challenging to identify, in general, on the basis of comparing the $^{206}Pb/^{238}U$ vs $^{207}Pb/^{235}U$ systems.

Figure 4 illustrates this point; despite vastly different Pb loss histories, all four zircon crystals plot on approximately the same location on the Concordia diagram. Regardless, we will aim for **our revised manuscript to include a discussion of the effects of the timing of Pb loss and allow users the flexibility of modeling % Pb loss in context of when it occurred in the zircon's history.**

This change will also allow Pb loss to be modeled in the $^{207}Pb/^{235}U$ (and theoretically $^{208}Pb/^{232}Th$) systems. In practice we are skeptical that modeling $^{207}Pb/^{235}U$ will be as successful as in the $^{206}Pb/^{238}U$ system due to higher uncertainty in $^{207}Pb/^{235}U$ dates. Regardless, we anticipate that the revised modeling framework will allow the flexibility for modeling all three Pb-based decay chains.

Reviewer #1 makes several additional suggestions, which we summarize below.

1. Consider the effects of a common Pb correction (lines 27-34). ***We will add discussion text that considers the potential influence of common Pb corrections***. See also Reviewer #2s comment. We suspect that a full exploration of this topic may be outside the scope of this manuscript, but we agree that this topic warrants discussion.
2. Directly inverting the Pb loss signal from the data (lines 35-42). This is a good suggestion and one that we have attempted to do. However, we have so far been unsuccessful in directly deconvolving the Pb loss distribution (e.g., we have experimented with scipy.signal functions). This may be in part due to a high degree of noise in our datasets, which are comprised of relatively few analyses. Ultimately, neither of us have expertise in signal

processing and would likely need to involve a collaborator. We think that this would be a worthy follow-up manuscript should the approach prove successful.

3. Make it clearer that convolution is essentially adding random variables together (lines 44-50). ***We will add text to clarify that convolution is equivalent to the sum of random variables.*** We intended to communicate this point with the “Z = X + Y” notation at the top of Figure 1. However, clearly this point did not come across in the paper and we can do a better job communicating it. As an aside, we started this project by adding random numbers together, and only realized later than this process can be described by mathematical convolution. So, the suggestion here is well taken.
4. Consider whether “HF leaching sometimes conducted by Ar labs [is comparable to] to CA” in U-Pb. Neither of us have expertise in Ar-Ar geochronology. However, we will ***look into this suggestion and consider adding statements that expand the applicability of the modeling framework, if appropriate***. For example, it’s a worthwhile question of whether the U-Pb focused approach that we describe might be exported to other radiogenic systems.

References

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.

Keller, C.B.: Technical Note: Pb-loss-aware eruption/deposition age estimation. Geochronology Discussions [preprint], https://doi.org/10.5194/gchron-2023-9, in review, 2023.

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.

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).

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.

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?

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.

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?

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.