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Comment on gchron-2022-4

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Referee comment on "An algorithm for U–Pb geochronology by secondary ion mass spectrometry" by Pieter Vermeesch, Geochronology Discuss., https://doi.org/10.5194/gchron-2022-4-RC2, 2022

This is a well written, well organized, clear and easy to follow presentation of issues in SIMS data reduction. I agree entirely with the sentiments expressed in the opening paragraph of comment RC1 and thus will not repeat them here.

I approached this review as a manager of a SHRIMP ion probe laboratory and thus someone with a hands-on perspective of dealing with SIMS data in a geological research setting. While this paper shines a light on issues that have been known by parts of the community for some time and provides a novel method of addressing these, at the current level of development the simplex data reduction protocol is not practical even with the limited functionality that the author is upfront about. To be clear, my reservations about simplex as a *tool* does NOT indicate reservations regarding the publication of this manuscript and the concepts therein. This is an excellent manuscript that introduces the geochronology community to a novel method of data reduction. As my concerns mainly relate to user needs within simplex (as opposed to the mathematics) I hope that by flagging these it may lead to changes that will engage the geochronology community to enhance the uptake, utility and ensure community-wide rigorous testing of this approach with a wide variety of "real-world" datasets in all their imperfect glory.

I will give a couple of examples below of my experience trying to use simplex (both online and through the R GUI) that I hope illustrate overarching issues with the current structure that limit the utility of simplex.

I had quite a bit of difficulty importing in new files. I was unable to get a .pd file to properly load (online or using the R GUI). When I attempted to load a .pd file I got a cryptic error message, then the numbers in the table in section 2 (Drift) changed but they did not correspond to the actual data and the spot names under Aliquots did not change from the test file. Clearly the file did not load properly (and some parts of the previously loaded dataset persisted) but given the opaqueness of the interface I have no idea what the problem was. I think it was partly related to the fact that there doesn't seem to be a way to "clear" the existing data out of the algorithm and start from scratch. Relatedly,

there is no record of what data file is being processed. Better tracking of what is being processed (and how it is being processed - for example when defining the reference materials) key to making this a useful tool because ultimately the data for a given rock sample stands alone but needs to be linked to its data reduction metadata (but not necessarily to other unknown samples in that analytical session. A single JSON output is impractical in that regard).

I had better luck loading a .op file but even then the behaviour was inconsistent. Part of this inconsistency is due to the fact that some (most?) interfaces seem to require a "refresh" of some sort (e.g. press "Plot" again after excluding a scan in Drift) to redo the calculations. This also means that things get out of sync. If you advance to a different aliquot in DRIFT, the plots don't advance, but there is no label on the plots to indicate which aliquot is being displayed. These are just two examples of instances where the algorithm as currently structured does not meet the needs of geochronologists working in SIMS labs producing data and then interpreted ages. Reproducibility and even more importantly, traceabilitity, in the data reduction package is crucial and this needs to be considered and baked into every step of any new process.

This manuscript is an excellent first step in starting to addresses the mathematical challenges of dealing with mass spectrometer data, while acknowledging that a great deal of work is still required to translate this contribution from better handling of mass spec counts all the way to geological interpretations of ages. In order to bring the geochronological community along this journey (which I am assuming is one of the reasons for this paper) I think that this manuscript would benefit from a more explicit presentation of what simplex CAN do (today) and CANNOT do (today). Given that this is a first step in a long path toward usability (and while I appreciate that not all the benefits of the covariance matrices can currently be accomplished) I think many readers from the geochronology community would like to see a comparison of the previous approaches (squid or NordSIM spreadsheet) and simplex as a first demonstration of its utility.

Specific comments/Technical corrections

Line 75, while things like negative lower limits of confidence intervals are physically impossible, the "reliability of analytical uncertainty assigned to dates…." is best addressed by systematic long term evaluations of laboratory data, including by inter-laboratory comparison work not just by working in compositional space. I suggest the last sentence of this paragraph be removed.

Line 86 – inconsistent use of "standard" "reference material" and "reference standard" throughout the manuscript. Suggest use of "reference material" throughout particularly because of the ambiguous meaning of "standard" (e.g. standard error as statistical term or as the uncertainty of a reference material). If this change is made use abbreviation RM as subscript when needed in equations eg. L102, 105.

Caption Figure 1 – "calibration error" should be calibration uncertainty

108. Here you refer to "samples" when you really mean "aliquots". Later on you refer to "within-spot" drift or other uncertainties, for consistency of usage/clarity for the reader I suggest you refer to these as "analytical spot".

Line 129 consider illustrating Table 1 data in a ternary diagram prior to mapping to Euclidean space (data points on Figure 2 perhaps?).

Line 150 – here "inter-sample" should be "inter-spot", as "inter-sample" to most people will signify 2 different ROCK samples, not analyses/aliquots/spots

Line 164 – typo "black" instead of "blank"

Section 7 "Zeros" – consider merging with the blanks section, they are two parts of the same problem and I find the current breakdown into two sections jarring. Since section 7 is so brief, I am not even very clear why it is needed.

Sections 8 and 9 – as a SIMS mass spectrometrist/geochronologist and not a statistician I am searching for points of familiarity, which up to this point I am largely able to do. You lose me here in these sections. More direct explanation of the steps in traditional data reduction that replaced by this approach and then how these values get used/incorporated into ratios would be helpful. Part of the difficulty in following is that is the traditional data reduction approach the deadtime correction happens first, but in the paper "Deadtime" follows the section about "Dealing with count data" which seems counterintuitive.

Line 250 states that mass-dependent fractionation is commonly ignored. It has been established from long term reproducibility studies that this is not true, and some labs do not ignore it (e.g. GA uses OG1 and the Geological survey of Canada uses 1242, see Davis et al. 2019). This paper doesn't propose that this algorithm (or more broadly approaching SIMS geochronology data as compositional) will solve all issues related to data processing of SIMS data, however a number of issues such as this are glossed over as secondary concerns. This is an example one of my general statements about this paper, where in an attempt to address some of problems related to the data reduction (sections 2-4, 6, 7) others that are known in real-world SIMS data are minimized (e.g. blanks greater than 204, or overcounts in 204).

Line 283, refer to it as Temora2 throughout the manuscript (not just in the parentheses this one time) as that is its name.

Line 293 refer to mass spec “cycles”, elsewhere “sweeps”. I prefer cycle, but either is fine as long as consistent (including axis labels of figure 5)

Line 301, not negative, positive

Line 302 “207” superscript in error

Line 302 Again I’m trying to map this to the usual approach of secondary beam normalization of SHRIMP data. Is this treatment instead of SBM norm or before/after? I think in lieu but I don’t understand how this might be affected by drift in the primary beam intensity which might either enhance or minimize the depth/oxygen availability effect illustrated in this diagram. For example if over the time of the analysis the primary beam intensity decreases then increases, the within-spot drift may be is U-shaped, not linear and thus a single slope regression applied to each cycle isn’t appropriate.

Line 307 – the strict enforcement of a positive value for 204-b doesn’t reflect the real-life behaviour of ion-counted data and could indicate a real problem with the analytical setup. I am concerned that this approach “hides” a real problem.

Line 312 – insert “within-spot” when referring to fractionation here for clarity.

Caption 5 – since side a is blank and drift corrected (eg. Pb204 – b/Pb206 - b), are the converted counts shown in part b also blank corrected (in which case the vertical axis should be labelled Pb204 – b, Pb206 – b etc)

Line 328 – edit text to “Figure 7 applies the Pb/U calibration (Equation 23) to 91500….” Makes it easier for the reader to know “Equation 23” does without having to go back to check.

Line 330 – again “inter-sample” when should be inter-spot (reminder to rationalize this usage throughout)

Line 331 – figure 7 uses Temora2 as the reference material and 91500 as the sample. Figure 8 uses 91500 as the reference material and Temora2 as the sample. Both of these materials are commonly used as RM’s and so switching their usage back and forth is tricky for the reader. Perhaps there is one but I don’t see any reason why Figure 8 can’t be recast with Temora2 as the RM which would streamline things.

Figure 7 caption – specify “using Temora2 as the reference material” at the end of the first sentence.

Line 368 – I’m not sure what is meant by “In contrast with existing data reduction protocols, the new algorithm simultaneously processes all the aliquots in an analytical sequence.” Please clarify.

Line 381 – While I appreciate that not all the benefits of the covariance matrices can currently be accomplished, it would be great to see a comparison of results between the previous approaches and this one one using the provided datasets.

Davis, W.J., Pestaj, T., Rayner, N., McNicoll, V.M., 2019. Long-term reproducibility of 207Pb/206Pb age at the GSC SHRIMP lab based on the GSC Archean reference zircon z1242. Geological Survey of Canada, Scientific Presentation 111, 1 poster, https://doi.org/10.4095/321203