

Dear Prof. Rubatto,

Thank you for handling my manuscript and providing thoughtful comments and suggestions. I have introduced some considerable changes to address the received comments:

- 1) Equations for normal and inverse isochron spaces were put in separate sections to facilitate reading and understanding, and notation was made more consistent.
- 2) Revised equations account for the uncertainty related to the mass fraction correction.
- 3) All arithmetic means are replaced with weighted means.
- 4) Intermediate steps were introduced that show how to calculate corrected compositions of unknowns with associated internal and external uncertainties. Hopefully, this will make it easier to understand how to apply these equations and prepare data tables for publication.
- 5) An approach to combine data from multiple analytical sessions to calculate a single isochron data was outlined.
- 6) The revised manuscript includes a better way to estimate the covariance between the age of the primary standard and its initial isotopic composition.
- 7) The revised manuscript mentions the approach with the ^{204}Pb -based correction, cites one more non-U-Pb study that used a heterogeneous material to correct for elemental fractionation, and provides a citation for using 2 non-radiogenic isotopes to monitor mass dependent fractionation.
- 8) The work of Horstwood et al. (2016) was cited.
- 9) My affiliations and funding information were updated.

Kind regards,

Daniil

Daniela Rubatto

Dear Dr Popov

Thanks for providing replies to the comments of the referees.

Regarding the comment of Vermeesch, I accept that you will add to the paper your equation for calculating systematic uncertainties. Additionally, you could however mention that an alternative strategy would be that of Maximum Likelihood with reference to Ludwig work.

The revised manuscript includes equations that were modified in accordance with my previous reply and also mentions this alternative strategy with the reference to Pieter Vermeesch's review.

Regarding the comment on Referee 1:

- I agree that a short communication may have a lean introduction, but acknowledgement to previous studies is still due, even if without much discussion. Thus please add additional reference in the introduction for the common Pb correction strategies.

The revised manuscript has the reference to the ^{204}Pb -based correction method.

- Please add to your manuscript the explanation of how to propagate the uncertainties related to the mass fractionation correction.

The revised manuscript shows how to do this.

- The application of your method to “real world data” is recommended as it will improve understanding and strengthen the paper. The absence of real world data is surely not a difficult hurdle to overcome given that you are in a department where LA-ICPMS geochronology is well established. Contacting authors that have published LA-ICPMS dataset for Rb-Sr would be an alternative. I suggest you at least give it a try.

According to my tests with synthetic data, it should work. I have already left that department and exist in a very unstable situation that precludes any kind of collaboration to get hands on real-world data in the near future.

- Adding a workflow to follow for the correct implementation of your method and calculation of uncertainties is more critical and highly recommended. This is yes a short technical communication, but if you want others to adopt and properly use your method, a workflow give will go a long way in making it more accessible. Such a workflow requires not much discussion, particularly if adapted from Horstwood et al. 2016.

I rearranged formulas into two subsections (2.1 and 2.3), introduced some simplifications and intermediate steps and provided more detailed explanations, so it should be easier to follow the manuscript and use it as an outline for a workflow. I placed a reference to Horstwood et al. (2016) in subsection 2.3.

- Please clarify the meaning of figure 1 to avoid any miss interpretation. I have an additional comment for Fig. 1a. The line between age on Concordia and initial Pb on the Y-axis should not be named “Discordia” as this term is conventionally used for the line on the Wetherill Concordia plots that joins two radiogenic ratios. For the TW diagram I suggest to use “regression”. I am looking forward to receive the revised version of your manuscript. Kind regards Daniela Rubatto

The revised figure caption provides more clarity. I changed ‘discordias’ to ‘isochrons’, which is what those lines essentially represent.

Pieter Vermeesch

I have derived appropriate formulas, which now have been incorporated in Eq. (8 and 8’). The introductory part of section 2 now includes a reference to the discussion of the maximum likelihood method in Pieter Vermeesch’s review.

Anonymous reviewer

This short communication is a technique-based manuscript, useful for those performing LA-ICPMS dating for systems other than U-Pb—that is, those with only one parent/daughter—that also have variable parent and daughter concentrations. It includes a standardization technique for correcting raw parent/daughter ratios, subject to elemental fractionation by laser ablation, transport, ionization efficiency, etc.. The general idea, as follows, is no different than correction of LA-ICPMS U-Pb data, which has been explored by many of the authors referenced within: 1) correct for mass bias of the daughter ratio (can be done a number of ways, including the use of a non-matrixed matched RM (reference material), via solution, or internal standardization of a non-U-Pb system) and correct all RMs and unknowns accordingly; 2) assume concordance for the RM and correct the parent/daughter ratio, such that the age matches its accepted value. This is a relatively straightforward correction that has been explained many times over, primarily for U-Pb. As such, this communication seems a touch superfluous, as a single isotopic geochronometer is simpler than the U-Pb system, but nevertheless is rarely mentioned and therefore warrants more discussion, especially in the light of recent developments in LA-ICP dating techniques (e.g., Zack and Hogmalm, 2016 and Simpson et al., 2021).

In my experience, the best example of standardization of elemental fractionation of common-daughter-bearing minerals is that in Chew et al., 2014, and I shall thus refer to it often below; though the Chew et al. study discusses the U-Pb system, it does so on a system-by-system basis, that is, it

corrects $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios using any of the other isotopes of the daughter product of the system (i.e., ^{204}Pb , ^{207}Pb , ^{208}Pb for $^{206}\text{Pb}/^{238}\text{U}$ and ^{204}Pb , ^{206}Pb , ^{208}Pb for $^{207}\text{Pb}/^{235}\text{U}$). As an example, one can look at Fig. 2E, in which each parent/daughter ratio has been corrected using a non-radiogenic daughter (^{204}Pb); the math by which to do this should be identical to the math by which to correct any spot analysis for any radioisotopic system - that is, it should be identical to Equation 21 in this manuscript. Nevertheless, it is not spelled out in this paper at least, that the calculation for U-Pb applies the same way for other isotopic systems such as Rb-Sr, Sm-Nd, Lu-Hf etc., which is presumably why the author has endeavored to write this short communication.

[The revised manuscript cites the approach with the \$^{204}\text{Pb}\$ -based correction.](#)

What the Chew et al. study doesn't explain as well is how to correct the mass bias for the ratio of the daughter isotopes (e.g., $^{207}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, etc.). Unfortunately, that is also mostly missing from this manuscript, which should be revised to state how this can/should be done in a clear and concise manner; for non-U-Pb LA-ICPMS geochronology—Rb/Sr, Sm/Nd, Lu/Hf—the mass fractionation (Y-axis value) can be calculated internally, unlike for U-Pb, which has no two non-radiogenic isotopes (however this internal standardization is rarely done - this needs discussion). The analytical uncertainty in this correction is likely to be in the 10's low 100's of ppm ($\ll 1\%$) and for intents and purposes, can be considered negligible when calculating age uncertainties, however, the actual uncertainty of the measurement—because of interferences and matrix effects, for example—is likely to be much larger.

[The revised manuscript cites a paper that uses the suggested approach to calculate factors for the mass fractionation correction. It also shows how to account for the uncertainties in these correction factors. I think that this is sufficient for a “short communication” that is intended for those who are in a position to use the equations from it.](#)

On this note, these excess uncertainties are not included in the equations herein, as far as I can tell, and in many cases, these types of uncertainties are likely to be the biggest cause of the actual uncertainty of the measurement. One of the seminal papers in uncertainty propagation for LA-ICPMS dating is that of Horstwood et al., 2016, in which they explain how the reproducibility of measurements can easily overwhelm the instrument analytical uncertainty. In that paper, without equations, they give their best practices for data reduction workflow, which include propagating excess uncertainty (different than external uncertainty). This is a critical step in reporting ages and uncertainties in all LA-ICPMS derived data and cannot be ignored in the current manuscript.

The revised manuscript mentions this problem and refers to Horstwood et al. (2016) to see their recommendations.

The main aspect of this paper that is relevant, and has not been discussed in great detail, is the correction of parent/daughter ratios and consequent age calculation using a standard isochron method, that is, a graph in which both axes have a non-radiogenic, non-radioactive daughter isotope as the denominator (or numerator on the Y-axis in an inverse diagram; this is opposed to a Tera-Wasserburg diagram, for example, which uses radiogenic daughters on both axes). Again, the correction of the ratios for each axis (ratio) of this diagram have been described in numerous publications (primarily for U-Pb, but see Zack and Hogmalm, 2016 and Simpson et al., 2021, and furthermore there is no difference in the correction method between that and non-U-Pb geochronometers), but few 1) demonstrate visually the uncorrected vs. corrected data, or 2) give the equations for uncertainties for each parameter. Point 1) is easy enough to do on one's own to get a visual representation of the 2-step correction for each ratio, and is analogous to the correction of U-Pb on a TW diagram as shown in Chew et al., 2014, Fig. A1. As noted above, this figure is missing the daughter-ratio correction, and would be more appropriate shown below, but this time in a single-system isochron diagram (analogous to Fig 1b in the submitted manuscript):

The revised manuscript mentions the approach with the ^{204}Pb -based correction method. The work of Zack and Hogmalm (2016) was cited in the submitted version, and this citation remained in the revised manuscript. I have found and cited one more study that utilises a similar approach.

I did not cite Simpson et al. (2021). They do correct sample data for common Hf before correcting thereby calculated $^{176}\text{Hf}_i/^{176}\text{Lu}$ ratios for elemental fractionation, however, with some adjustments, these two corrections could be done in the reverse order.

Note that the figures in the current manuscript are either misleading or wrong. Given that there is little discussion about the correction of the y-axis, my impression is that it is the latter; the plots do not accurately represent theoretical data, as data of the same age, whether real or synthetic, should be isochronous, whether corrected for elemental fractionation or not. Given that the math for generating such apparent and corrected isochrons is trivial, it is worrisome that the plots in Figure 1 are incorrectly represented.

Each of these figures shows two data points that are assumed to be corrected for mass dependent fractionation and have different elemental fractionation factors (e.g. due to instrument instability). The idea was to show that factors to correct for elemental fractionation can be calculated from individual analyses, revealing any instrument drift over analytical sessions. The revised figure caption explains this.

In conclusion, for this manuscript to merit publication, it must first contain a broader background of previous work, and a better description of the workflow to correcting measured ratios, both for elemental fractionation (including differences fractionation down-hole which is completely missing). Second, it needs a better description of all possible sources of uncertainty and how and when they should be properly propagated. Third, any figure must accurately represent real-world data.

I rearranged equations from the previous version, added some additional ones and provided more explanations to facilitate the implementation of the proposed approach. I think that this is sufficient for intended readership of my “short communication”.