

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 approach with the ^{204}Pb -based correction method should be equivalent to that outlined in my manuscript, although the math, at least in UcomPbine, is not exactly the same (if I understand correctly the IgorPro language in UcomPbine file that I have). This similarity escaped my attention before, partly because the ^{207}Pb -based correction method is used more widely, but I can mention it in the revised manuscript. Another notable similarity, is that with the $^{40}\text{Ar}/^{39}\text{Ar}$ method: division by factor k in Eq. 21, 24, 26 and 28 is similar to multiplication by factor J in the $^{40}\text{Ar}/^{39}\text{Ar}$ method.

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.

One of the reasons why I selected “short communication” as the article type is that I did not want to go into these details. I am not the best person to advise on this subject, and I also do not have time to thoroughly review relevant literature in the near future. However, I can show how to propagate the uncertainties related to the mass fractionation correction to the date uncertainties. Unfortunately, I currently do not have any real-world data to assess the importance of this. According to my brief tests with synthetic data, % level of uncertainty for the mass fractionation correction factor are needed to have a significant impact on the date uncertainty, which seems to be unrealistically high.

Notably, it is possible to completely ignore the mass and fractionation correction if (i) the primary standard is sufficiently heterogeneous in terms of the parent to daughter isotope ratio, (ii) there is no significant instrument drift so that multiple primary standard measurements can be used to calculate k , (iii) only isotope ratios measured during one session of LA-ICP-MS analyses enter the equations to calculate the date of the unknown, (iv) the date of the unknown is calculated as a multi-spot isochron date. In these circumstances, the slope b_s of the line fitted through the standard data can be used to calculate the factor k and its uncertainty:

$$k = \frac{b_s}{e^{\lambda t} - 1}; \sigma_k^2 = \sigma_{b_s}^2 \left(\frac{k}{b_s}\right)^2 + \sigma_t^2 \left(\frac{-\lambda k}{1 - e^{-\lambda t}}\right)^2 + \sigma_\lambda^2 \left(\frac{-tk}{1 - e^{-\lambda t}}\right)^2 + 2\sigma_{\lambda,t} \left(\frac{t\lambda k^2}{(1 - e^{-\lambda t})^2}\right).$$

The righthand side of the first of the above equations can be substituted for k_{av} in Eq. 24 from the manuscript (the one needed to calculate the date of the unknown):

$$T_{isochron} = \frac{\ln\left(\frac{b}{b_s}(e^{\lambda t} - 1) + 1\right)}{\lambda}.$$

Considering that mass fractionation has the effect of multiplying both b and b_s by the same constant, the above equation indicates that it can be completely ignored (this constant will be cancelled out). The uncertainty of thereby calculated date can be estimated using Eq. 25 from the manuscript with appropriate substitutions for k_{av} and $\sigma_{k_{av}}$. Note that the only parameter that is needed to characterise the primary standard in the described scenario is its date, and its use would be analogous to the use of the neutron flux monitors in the $^{40}\text{Ar}/^{39}\text{Ar}$ method.

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.

I can show how to propagate the uncertainties associated with the mass fractionation correction to the date uncertainties. Additionally, the date uncertainty can be affected by the isobaric interference corrections. However, these effects would be specific for each method and setup, and therefore I cannot derive generic formulas. In theory, the addition of these two sources of uncertainty to the revised equations from my reply to Pieter Vermeesch's review should provide means to estimate the full external uncertainties in a way that is generally consistent with Horstwood et al. (2016). The way Horstwood et al. (2016) proposed to account for the excess uncertainties that become evident from the repeated analyses of secondary standards is, in my understanding, an ad hoc protocol for what to do, if the chosen approach to estimate the full external uncertainties demonstrably did not work. This problem goes beyond the scope of my work, and I suggest that I will simply refer readers 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):

Most U-Pb applications that I am aware of use the ^{207}Pb -based correction method. I mention in the introduction that this method is similar. The ^{204}Pb -based method is equivalent to that outlined in my manuscript, but I cannot easily recall any studies that employ it to use common-Pb bearing standards (except for Chew et al., 2014, where it is one of the methods), and I certainly have not seen any studies that explain how to propagate uncertainties when using it. I can highlight the similarity in the revised manuscript. Zack and Hogmalm (2016) do something similar to what I describe in the manuscript, which I mention in the introduction. Simpson et al. (2021) do correct sample data for common Hf before correcting thereby calculated $^{176}\text{Hf}/^{176}\text{Lu}$ ratios for elemental fractionation. However, with some adjustments, these two corrections could be done in the reverse order. Overall, I am missing the point of the above paragraph.

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 (for example, due to instrument instability). The idea was to show that factors to correct for elemental fraction can be calculated from individual analyses, revealing any instrument drift over analytical sessions. I can clarify this in the revised manuscript.

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 think that my introduction already makes a fair overview of previous work, and the only missing point is that about the similarity with the ^{204}Pb -based correction method applied to primary standards in U-Pb applications of LA-ICP-MS. I do not think that a short communication needs to make a thorough review of every aspect of LA-ICP-MS data treatment, and I was hoping to avoid this by choosing this article type. I also think that the intended readership will have a general knowledge of how to treat LA-ICP-MS data. I do not agree that a more detailed description of a workflow for data treatment is prerequisite. I presume that the comment requests to do something similar to Horstwood et al. (2016). However, I do not fully agree with that paper to just copy the outline, and I would like to avoid engaging in lengthy discussions and arguments that may arise during the review (hence I chose “short communication” as the article type). There is no error in my figure 1. I can adjust equations to include the uncertainties that are associated with the mass fractionation correction (see below).

How to propagate the uncertainty related to the mass fractionation correction the date uncertainty in the normal isochron space

Say the true value y is obtained by multiplying the measured value y_m by the constant l :

$$y = y_m l .$$

The uncertainty of y can be calculated as follows:

$$\sigma_y^2 = \sigma_{y_m}^2 l^2 + \sigma_l^2 y_m^2 ,$$

where the first term provides the internal uncertainty, while the entire equation provides the external uncertainty. The entire Equation 4 from the manuscript should be used to calculate the external uncertainties of individual estimates for k , while their internal uncertainties should be calculated by using the first three terms and substituting $\sigma_{x_{int}}$ and $\sigma_{y_{int}}$ for σ_x and σ_y . The uncertainty of the averaged value k_{av} can be calculated by adding the term c to Eq. 14 from the manuscript:

$$c = \frac{\sigma_l^2}{N^2 l^2 (e^{\lambda t} - 1)^2} \left(\frac{y_1}{x_1} + \dots + \frac{y_N}{x_N} \right)^2 .$$

The uncertainty of the spot date can be calculated by adding the term d to Eq. 22 from the manuscript (the full external uncertainties σ_{x_u} and σ_{y_u} should be used in that equation):

$$d = 2 \frac{\sigma_i^2}{l^2} y_u \left(k_{av} + \frac{Y_o}{(e^{\lambda t} - 1)} \left(\frac{1}{Nx_1} + \dots + \frac{1}{Nx_N} \right) \right) \frac{y_{ou} - y_u}{k_{av} \lambda^2 (y_u - y_{ou} + k_{av} x_u)^2}.$$

The uncertainty of the multi-spot isochron date can be calculated by adding the term f to Eq. 25 from the manuscript (the internal uncertainties $\sigma_{x_{u_{int}}}$ and $\sigma_{y_{u_{int}}}$ should be used to calculate the uncertainty σ_b that should be plugged into this equation):

$$f = 2 \frac{\sigma_i^2}{l^2} \frac{b^2}{\lambda^2 (b + k_{av})^2} \left(-1 - \frac{2Y_o}{k_{av}(e^{\lambda t} - 1)} \left(\frac{1}{Nx_1} + \dots + \frac{1}{Nx_N} \right) \right).$$