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Comment on gchron-2021-37

Anonymous Referee #1

Referee comment on "Short communication: On the potential use of materials with heterogeneously distributed parent and daughter isotopes as primary standards for non-U–Pb geochronological applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)" by Daniil V. Popov, Geochronology Discuss., https://doi.org/10.5194/gchron-2021-37-RC1, 2022

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 it's 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 206Pb/238U and 207Pb/235U ratios using any of the other isotopes of the daughter product of the system (i.e., 204¬Pb, 207¬Pb, 208Pb for 206Pb/238U and 204¬Pb, 206¬Pb, 208Pb for 207Pb/235U). 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 is 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.
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., 207Pb/206¬Pb, 207Pb/204¬Pb, 87Sr/86¬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 (<<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.

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 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):

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.

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.