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Comment on egusphere-2022-299

Ryan Ickert (Referee)

Referee comment on "Calculation of uncertainty in the (U–Th)□/□He system" by Peter E. Martin et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-299-RC2, 2022

Review of "Calculation of Uncertainty in the (U-Th)/He System" for Geochronology, by Martin et al.

This review is by Ryan Ickert (Purdue University)

This manuscript presents an algorithm for determining U-Th-Sm/He dates in accessory minerals and then derives uncertainty propagation equations for them, combining uncertainties in measurements of nuclide amounts and geometric correction factors. They also introduce a Monte Carlo method and compare the two. These algorithms are implemented in a python package hosted on zenodo.

A consistent set of uncertainty propagation equations for the community is a welcome addition to the literature, although it is unlikely that it will strongly affect science derived from the measurements due to pervasive overdispersion.

I've had the opportunity to read the review by Pieter Vermeesch prior to writing this, and that saves me a lot of time writing my review because I came to basically the same conclusions as him. I don't think it's necessary for me to state specifically on which points I agree, but one that affects the manuscript substantially is the suggestion to cut down the length. I agree that section five can be completely removed. I don't think it's necessary for the authors to include log functions to the analytical solutions, but I agree that it would be a superior technique.

What I think would be very useful is a comparison of before/after of typical analyses from the authors lab. A few representative datasets would be just fine. I think this would be of great value in showing readers whether this approach changes assigned uncertainties in any substantial way. Maybe it doesn't, but that's not necessarily a bad thing.

I think it's a missed opportunity somewhat to not assess the accuracy of assigned uncertainties in the U-Th-Sm, and the He analyses. I appreciate that the authors have carved the manuscript such that this is "out of scope" (which is their prerogative), but the brief comment that tracers are often added by pipetting (without discussing the implications of adding a spike isotope using a technique with such a high variability) suggests to me that the radionuclide measurements may be underestimated. Not to mention that the treatment of under/over spiking and blank subtraction (to name a couple), in my experience, are dealt with in a highly variable way by different people in the U-Th-Sm/He community. I guess that leaves space for the next paper!

I have a few shorter comments below:

L9: What quantities are ^{4}He and "radionuclide" here. Are they amounts, concentrations….? Please briefly define F_T in the abstract for a non-specialist, particularly because it's referred to as particularly important later in the abstract.

L11: Is this relative or absolute uncertainty?

L15: Again, is this concentration?

L15: What is the confidence level for these estimates? 95%? 2sigma?

L34: I assume that by "kinetic" the authors mean diffusion kinetics.

L76: "ppm" is, in general, ambiguous and best practice is that it should be avoided. I appreciate that there is an implicit convention in some geochemical subfields that it refers only to μg/g, but it is not always the case and there is no disadvantage to being explicit and using the SI-consistent μg/g.

L80: "sector" should say "magnetic sector"

L81: The technique is called "isotope dilution" not "isotope spike".

L82: I'm not sure what "ratioed mass spectrometric measurements" are?

L103-104: It's not clear to me that this is true. For example, if a mixed U-Th-Sm tracer is used and the mass of spike solution is relatively small (which is usually the case), the uncertainty in the amount of spike added (which propagates directly onto the amount of U, Th, and Sm calculated) will be relatively large and since the tracer is added as a mixture, that component will be highly correlated. It takes special care to get weighing errors to less than 1%, and with small amounts of spike they can easily be in the 5-10% range. When pipetting without weighing (which is what is implied here) the problem can be much worse. Pipetting consistency can vary, for sure, but for 25 μl the relative standard deviation on masses dispensed can be 3-5%, which translates directly to a 3-5% uncertainty on the measured quantities. This seems like it should be large enough to matter?

L117: 2-9% in what? The Ft correction or the final date? And is this a bias (e.g., the technical definition of "error") or additional uncertainty on the date?

L131: Here and elsewhere the word "variance" is used. It's unclear as to whether this is referring to a moment of the gaussian distribution or as a casual synonym for uncertainty or data scatter.

L366: A Th/U (by mass) ratio of 1.25 is *not* typical of zircon, it is unusually high. Looking at the georoc database of zircon compositions, after doing some data culling, the median value is about 0.6 (mean = 0.8). That sounds much more realistic to me than 1.25.

L420: This statement should be justified or referenced, or else removed. It sounds a little bit like it is underestimating the math and stats skills of typical geochronologists.