Geochronology Discuss., referee comment RC1
https://doi.org/10.5194/gchron-2022-23-RC1, 2022

Comment on gchron-2022-23

Alexis Ault (Referee)

Referee comment on "Origin of Great Unconformity Obscured by Thermochronometric Uncertainty" by Matthew Fox et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2022-23-RC1, 2022

gchron-2022-23 review: Fox et al.

The manuscript "Origin of Great Unconformity obscured by thermochronometric uncertainty" by Fox et al. presents numerical models of uncertainty of He diffusion kinetic parameters from an undamaged zircon and zircon N17 (of Guenthner et al., 2013). Specifically, they consider uncertainties in the frequency factor (D0) and activation energy (Ea) for these two end-member grains, which co-vary, and they use ZRDAAM (Guenthner) with their updated kinetics for these two grains to predict zircon (U-Th)/He (zircon He) thermochronometry dates for an example deep time thermal (tT) history.

This contribution drives at a timely and important topic – the utility, and potential limitations, of zircon He thermochronometry to resolve deep time thermal histories. As the authors point out, zircon He data has been used to evaluate the timing and magnitude of erosion during the creation of the Great Unconformity, with data patterns being used to discriminate between glacial, tectonic, and geodynamic mechanisms for unroofing. However, uncertainty in He diffusion kinetic parameters, which are a function of radiation damage accumulation and annealing, have not previously been considered before and I appreciate the authors tackling this here. As the authors show with their suite of numerical models: the effect of these uncertainties is magnified in long time scales (i.e., deep time) and dispersion in a zircon He date for a given eU value and deep time tT history can be >>> 100 Ma. This suggests that, in the absence of additional diffusion experiments on zircon grains over a spectrum of effective damage, it may not be possible to resolve cooling during say the Sturtian and Marinoan glaciations, or doing a specific Neoproterozoic time period.

I think that this manuscript is suitable for *Geochronology* pending moderate revisions. There are elements of the manuscript that I think should and can be expanded and clarified prior to acceptance for publication:

First, the authors center their analysis on only two end-member zircon grains. One grain, “z”, is sometimes called a minimally damaged grain and elsewhere called an undamaged grain or a “low” grain. As Guenthner et al. (2013) shows, these are different. What is the source of the data for the low/undamaged grain? This is never stated in the text and should be added. (see comment below about Figure 1).

Second, and more importantly, it is not clear how the authors are taking accounting for uncertainties in intermediate or even high damage zircon grains (N17 is effectively an amorphous grain; Guenthner et al., 2013). The authors state (152-153) that they are focused on end member grains and imply their approach is an improvement on the extrapolations between high and low damage levels in Guenthner et al. (2013) (152-157). Regardless of whether the low damage end member is zero damage or Mud Tank kinetics, what happens *in between* the low damage and N17 is, I think, critical. What about moderately-damaged to high damage grains: how do the predicted versus observed diffusivities vary for RB140, BR231, M127, and G3? (Guenthner et al., 2013)? Note that Guenthner et al. (2013) presents data for slabs of the crystals cut parallel and orthogonal to the C axis for each grain. Related to this, looking at figure 3, I found myself wondering if D0 and Ea are correlated in the same way in moderate to high damage zircon grains, and do these correlations align with Guenthner et al. (2013), as they do for the low damage “z” grain?

The reason why this additional analysis I think matters is because the evolution of effective damage and resulting He diffusivity is complex as the authors point out (126-128). Diffusivity initially decreases from an undamaged/low damage grain to a moderate damage grain, but diffusivity then dramatically increases from a moderate to an amorphous grain. In figure 4, the greatest spread in dates when taking into account the variation in grain “z” and N17 uncertainties occurs in the range of moderate to high damage grains (1000-1500 ppm eU). If only endmembers are being considered, how are uncertainties in diffusion kinetics between these two endmembers being accounted for or propagated through a tT history? This was not clear to me.

I think the authors can address these questions in two ways: I encourage the authors to perform the same calculations that they perform on an undamaged/low damage grain and N17 on additional grains, mentioned in the paragraph above, and expand figure 2. I think showing how the D0 and Ea values compare with Guenthner et al. (2013) will be useful for the community. It was interesting to see how their models reproduced N17, but not for the un/low damage grain. At the very least, the authors should expand the text to explain how they are interpolating between un/low damage and the amorphous grain when propagating model uncertainties across a range of eU – I apologize, I could not follow how this was done with the information provided.

Third, Figure 1 would benefit from more information. Adding these details will help the reader follow the discussion in the text and also help if additional analyses are added:

-Please label each of the Arrhenius relationships for the different diffusion experiments – perhaps using different symbols and colors. I think these figures could be enlarged as well. I found myself flipping back to the original data of Guenthner et al. (2013) to identify N17 and I could not figure out the low or undamaged grain.

-I would make the trend lines a darker grey or perhaps thicker – it is hard to see them. Enlarging the figures (perhaps single column?) would help.

Additional edits and comments:

12-13: I would rephrase this topic sentence, as it is confusing as written. Perhaps something like "Thermochronology provides a unique perspective on the timing and magnitude of erosion during the generation of unconformities."

17: I do not think However is needed at the beginning of this sentence.

23: I would add "… as a function of radiation damage *accumulation and annealing*." At the end of this sentence.

25: "less well resolved" – during what time interval?

26 and 320-322: "calibration with natural laboratories" – Calibrating zircon He diffusion kinetics from natural samples that experienced deep time thermal histories is challenging, right? Because it is precisely during those long tT histories where issues such as U-Th zonation will be exacerbated. And so if you chose to advocate for an empirical approach, I would add a cautionary note that provided U-Th zonation can be quantified in analyzed grains (which is hard, right? because grains that are consumed for zircon He analyses are not available for detailed LA-ICPMS zonation investigation. And LA-ICPMS zircon He analyses also have uncertainties that would need to be taken into account in this modeling approach).

33: I would omit Keller et al., 2019, as this Great Unconformity study does not include zircon He thermochronometry data, which is the subject of the sentence.

36: I believe this is 1300 to 200 million years of missing time.

38: Here I think you could cite other papers besides McDannell et al., 2022 such as those that you site in 33 plus others, minus Keller et al., 2019.

38-40: Although I do not think you want to wade into this with this paper, I would rephrase this because the modeling approaches described in McDannell et al. (2022) reflect only one approach to this problem as I understand it.

95: “variability in radiation damage annealing parameters” – do you mean “diffusion kinetic parameters”? Although D0 and Ea depend on the effective radiation damage (i.e., accumulated and annealed damage), the work presented here does not evaluate damage annealing specifically as this phrase implies.

210: Useful to call-up the inset in Figure 4.

Figure 4: Please add tick marks for x and y axis values.

229: Grain size = equivalent spherical radius? Or?

244-245: These are incredibly precise numbers – is this level of precision warranted here? And how much does it matter?

238-256: I think this analysis would be useful for grains like RB140, BR231, M127, or G3!

Alexis K. Ault

Department of Geosciences

Utah State University