Author response to community comment for preprint gchron-2021-22

Issler, D. R., McDannell, K. T., O'Sullivan, P. B., and Lane, L. S.: Simulating sedimentary burial cycles – Part 2: Elemental-based multikinetic apatite fission-track interpretation and modelling techniques illustrated using examples from northern Yukon, Geochronology Discuss. [preprint], https://doi.org/10.5194/gchron-2021-22, in review, 2021.

We appreciate that Ian Duddy and Paul Green of Geotrack Intl. took the time to comment on our manuscript in review with GChron (doi: 10.5194/gchron-2021-22). The relationship between apatite composition and annealing is elegantly but incompletely captured by the single kinetic parameter r_{mr0}—we were fully transparent about this in our manuscript (lines 548–561 and 650–653). To simply dismiss this complexity as immaterial rather than to investigate it further (when in an obvious position to do so), is in our mind a disservice to the thermochronological community. While Carlson et al. (1999) cautioned the reader on use of the r_{mr0} parameter outside of the examined apatite compositional range, this does not mean it should be disregarded entirely, as implied by Green and Duddy. It is therefore not surprising that the Geotrack authors "concur" with the cautionary statements in Carlson et al. (1999) and Ketcham et al. (2007) regarding r_{mr0}.

The initial Green and Duddy comment (https://doi.org/10.5194/gchron-2021-22-CC1) on R. Ketcham's review (https://doi.org/10.5194/gchron-2021-22-RC1) was not meant to address our manuscript under consideration, but to defend what they view as their methods (using only Cl content). We would ask, what are the motivations of the authors for making these claims? While we commend them for being pioneers in AFT methodology, they operate outside the sphere of academic research and benefit from marketing their in-house methods and data interpretations. Have the *details* of the Geotrack "multi-compositional" kinetic model, whose results are illustrated in Green and Duddy (2012) undergone formal peer review? The kinetic models in the aforementioned papers have met this condition.

Duddy asks (https://doi.org/10.5194/gchron-2021-22-CC3) *"what is controlling r_{mr0} in the two* [Issler et al.] *samples?"*—then answers that it is *clearly* chlorine content. We would respond by saying that Cl is unquestionably significant and is a key element in the r_{mr0} relation. It is obvious in our figures 4 and 5 that Cl is a dominant element and we do not deny the importance of Cl for track annealing. It is also evident that our interpreted kinetic populations overlap when considering only Cl, and better population definition occurs with r_{mr0} (kinetic populations also align with radial plot mixture modelling age peaks). The Geotrack authors rely on an ad hoc approach where apatite grains are binned by Cl (wt%), which will not work if a sample contains heterogenous apatite compositions. We assert that because the AFT method is rooted in population statistics—if a sample is revealed to contain grains of different 'true' ages—that kinetic populations should have some quantitative basis relative to such component ages. This was conceptually discussed in Galbraith and Green (1990), among other publications and is a powerful tool used in many geochronological applications.

We demonstrated that *both* measured Cl and D_{par} are inadequate for multikinetic interpretation (in our samples), so why do Green and Duddy only take issue with Cl? The answer may be that the kinetic parameter D_{par} is low precision and often has poor resolving power for distinguishing kinetic populations and Green and Duddy agree with this statement (our Figs. 2, 4, and 5 and Green et al., 2005 comment on Barbarand et al., 2003; Green and Duddy, 2012; their Fig. 8). So why is Cl any different than D_{par} in the results we discuss? Does Cl always work well for every sample? It will if Cl really is the only element in abundance. It can 'appear' to work if significant elements covary systematically with Cl. In other cases, where different elements are important, a Cl-only based framework could lead authors to dismiss data that do not conform to the expected trend as outliers. Imposing an interpretation framework onto which the data must conform is untenable. If the results of many annealing experiments show that elements other than Cl affect track retentivity, then the relationships exist—regardless of elemental preference or other yet unexplained phenomena that complicate the annealing dependence on apatite composition. These relationships are not negated just because the Geotrack authors prefer Cl. This is confirmation bias that disagrees with empirical evidence. We believe the multikinetic results of Carlson et al. (1999), Barbarand et al. (2003), and Ketcham et al. (2007) were compelling, albeit complicated, and should have led to a flourish of further AFT research into apatite composition/annealing, just like what was done with Cl in the late 1980s. This did not happen.

In their own published work, they show arbitrary designation of grains as "likely outliers" (as an example Fig. 4 of Green comment, https://doi.org/10.5194/gchron-2021-22-CC1). To quote Duddy, "The reader is entitled to ask why these [outliers] should be regarded as poor?" —this label does little to appease the reader or impart any confidence in this purported designation. Green and Duddy can assert that elements other than Cl are trivial, or argue about nuance (i.e., specific elemental abundance thresholds for annealing or lack of a physical mechanism to explain other elemental effects on annealing behavior) because this fits their preconceptions and there are conveniently no definitive studies to prove otherwise.

Duddy in his comment summarizes with: *"Serious problems with the quality of the EMPA and LAICPMS AFT data used in this paper irrevocably compromise the conclusions concerning the use and superiority of rmr0 over chlorine (wt%) as a kinetic control on apatite fission track annealing. Because of these problems the subsequent thermal history modelling has no basis".* We find this statement interesting, considering that our data and figures clearly show trends that are not refuted by their discussion. In a literature survey of (only) the last 21 years, we cannot find a single instance of a peer-reviewed publication that contains all raw fission track or electron probe data produced by Geotrack. We leave open the rare possibility that we may be wrong in this appraisal but consider it unlikely given that the authors can claim data as proprietary without undergoing public scrutiny. Only reporting summary tables of AFT central ages, binned track length information, and single (or a range of) wt% chlorine values are in no way transparent for data quality assessment, adequate for high-quality peer review standards, and are certainly not reproducible. In addition, we can find no strong, available evidence for a positive assessment of, or comment on, any new fission-track research in the last 21 years either.

The chief focus on the electron microprobe (EPMA) data in Duddy's comment CC3 delves into minutiae to distract from the important matter at hand regarding the application of multikinetic AFT for thermal history analysis. Low elemental wt% totals can occur for a variety of reasons, namely grain damage from laser ablation, mount polish issues, electron beam damage during analysis, or the inability to fit good spots on small grains—but also from simply neglecting to measure an abundant element in the apatite. We made no claim that our data were perfect—of course, the preferred scenario is to have 100% elemental totals and ideal stoichiometric apatite—but real data are often messy and complex. All of the information necessary to evaluate EPMA data quality are in the assets included with the paper and low totals are flagged. Low totals or the absolute accuracy of the halogen measurements have little effect on the AFT data interpretations that involve *relative* annealing characteristics. We have other Imperial Fm. examples where elemental totals are ~97–101% with the same data patterns that are present in the LHA003 Imperial Fm. sample in our paper (Figure 1, see below). Suppose we have a sample that contains apatite with 0.0 wt% Cl but elevated concentrations of Fe, Mn, or Sr (elements that clearly enhance retentivity, e.g., Crowley et al., 1990; Carlson et al., 1999; Barbarand et al., 2003; Ravenhurst et al., 2003; Ketcham et al., 2007)—would the Geotrack authors be underestimating the retentivity of their sample by only considering Cl and would it matter for thermal history analysis? The discounting of elements where there is clear empirical evidence for the enhancement of FT retentivity would seem to be a gross oversight.

Duddy stated in his comment: *"We are currently undertaking a research study investigating the usefulness of rmr0 and LAICPMS for AFT U-determination and as part of this study we produced 1057 full EMPA analyses on apatite. Of these analyses, only 4, or <0.4 %, fell outside the range of acceptable totals noted above. This should be the norm for any apatite EMPA study."* Making this statement is meaningless without verifiable proof (i.e., data) and a full description of the microprobe analytical conditions, standards used, accuracy/precision of measurements, etc. We provided our data and analytical information openly, in support of our manuscript that is in a public forum and under consideration for publication in a peer-reviewed journal. We would ask, do Green and Duddy measure only Cl, and if so, what do the probe data and stoichiometry of their apatites look like? We do not know the answers to these questions because no complete data are made available or published.

The Geotrack authors also call into question the LAICPMS method, specifically the $^{238}U/^{43}Ca$ ratio and the reported U (ppm) in our AFT dataset. The mention of these details is an attempt at misdirection and has little bearing on the manuscript being evaluated. The U (or Th, Sm values in ppm) are reported in the supplementary data tables for completeness only—and are a simple ablation pit average—and nothing more, as we have previously mentioned in email correspondence with Duddy and Green and which they recounted in their comment CC3. As Duddy states *"These values are not equivalent"* —we know that. U (ppm) is not used for age calculation or data interpretation of any kind. Duddy discusses deviation of U and U/Ca values from a 1:1 line and shows plots of this in his Fig. 4. The fact that the U (ppm) and U/Ca value do not fall on a 1:1 line *could* indicate the presence of U zoning—or it could simply mean that the U (ppm) value averaged across the ablation-pit depth is not representative of the down-pit weighted U/Ca value that is used for age determination (e.g., hitting small inclusions with the laser)—one reason why the U (ppm) value is not used. We agree with the recommendation by Cogné and Gallagher (2021) that only U/Ca should be assessed for single-grain AFT ages. Effective uranium (i.e., eU) was only utilized in McDannell et al. (2019)

to facilitate comparison with apatite (U–Th)/He data (He reporting convention is U, Th, and Sm, or eU in ppm) and due to the non-intuitive nature of U/Ca values. The use of U/Ca values instead of eU in McDannell et al. (2019) only strengthens the discussed negative age-U trends for most examples. Regardless of these points, their lengthy discussion of eU is both incorrect and irrelevant to the current manuscript. Furthermore, all the required information to calculate AFT ages is available in the manuscript and accompanying (peer-reviewed) documents.

In their numerous publications and paper comments, the Geotrack authors frequently refer to apatite annealing behavior in Otway Basin of Australia, or specifically the Flaxmans-1 borehole (see comments and figures presented in CC1 and CC3 supplements). While we acknowledge that the data from Otway Basin were, and remain, integral results that helped to establish many of the empirical relationships between track annealing and apatite composition—in no way does this mean that the Otway Basin relationships are the universal rule for kinetic behavior and therefore should be applied to all natural apatites. On the contrary, applying a kinetic model based on a single locality or limited data (while better than nothing) could potentially be a hazardous assumption for assessing other apatites that do not adhere to the expected model. We could easily foresee said results being cast aside and considered “outliers.” The Carlson et al. (1999), Barbarand et al. (2003), and Ketcham et al. (2007), work should be commended for considering a broad range of apatite species that are undoubtedly encountered in nature. The need for geological calibration is necessary to make reliable thermal history predictions, but those predictions are only as robust as the calibration data.

While the Geotrack authors may rely on their “experience” and “beliefs,” in what can only be interpreted as attempts to impede any developments or advances in thermochronological research, we hold no such views and prefer to evaluate work based on data and modelling approaches that are available for public examination and peer review. To disregard this and proceed otherwise is not adhering to the rigours of the established scientific process, it is simply the manufacture of incensed prose disguised as objective criticism.

—Dale Issler, Kalin McDannell, Paul O’Sullivan, and Larry Lane

References

Barbarand, J., Carter, A., Wood, I. and Hurford, T.: Compositional and structural control of fission-track annealing in apatite, Chem. Geol., 198(1–2), 107–137, doi:10.1016/S0009-2541(02)00424-2, 2003.

Carlson, W. D., Donelick, R. A. and Ketcham, R. A.: Variability of apatite fission-track annealing kinetics: I. Experimental results, Am. Mineral., 84(9), 1213–1223, doi:10.2138/am-1999-0901, 1999.

Cogné, N. and Gallagher, K.: Some comments on the effect of uranium zonation on fission track dating by LA-ICP-MS, Chem. Geol., 573, 120226, doi:10.1016/j.chemgeo.2021.120226, 2021.

Crowley, K. D., Cameron, M. and McPherson, B. J.: Annealing of etchable fission-track damage in F-, OH-, Cl- and Sr-apatite. 1. Systematics and preliminary interpretations, Nucl. Tracks Radiat. Meas., 17(3), 409–410, doi:10.1016/1359-0189(90)90066-7, 1990.

Duddy, I.: Community comment on "Simulating sedimentary burial cycles – Part 2: Elemental-based multikinetic apatite fission-track interpretation and modelling techniques illustrated using examples from northern Yukon" by Dale R. Issler et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-22-CC3, 2021

Galbraith, R. F. and Green, P. F.: Estimating the component ages in a finite mixture, Int. J. Radiat. Appl. Instrumentation. Part D. Nucl. Tracks Radiat. Meas., 17(3), 197–206, doi:10.1016/1359-0189(90)90035-V, 1990.

Green, P. F.: Community comment on "Simulating sedimentary burial cycles – Part 2: Elemental-based multikinetic apatite fission-track interpretation and modelling techniques illustrated using examples from northern Yukon" by Dale R. Issler et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-22-CC1, 2021

Green, P. F., Duddy, I. R. and Hegarty, K. A.: Comment on “Compositional and structural control of fission track annealing in apatite” by J. Barbarand, A. Carter, I. Wood and A.J. Hurford, Chemical Geology, 198 (2003) 107-137, Chem. Geol., 214(3–4), 351–358, doi:10.1016/j.chemgeo.2004.10.010, 2005.

Green, P. F., and Duddy, I. R.: Thermal history reconstruction in sedimentary basins using apatite fission-track analysis and related techniques. Analyzing the thermal history of sedimentary basins: Methods and case studies, 103, 65-104, 2012.

Issler, D. R., McDannell, K. T., O’Sullivan, P. B. and Lane, L. S.: Simulating sedimentary burial cycles – Part 2: Elemental-based multikinetic apatite fission-track interpretation and modelling techniques illustrated using examples from northern Yukon, Geochronol. Discuss., 1–37, doi:10.5194/gchron-2021-22, 2021.

Ketcham, R. A.: Referee comment on "Simulating sedimentary burial cycles – Part 2: Elemental-based multikinetic apatite fission-track interpretation and modelling techniques illustrated using examples from northern Yukon" by Dale R. Issler et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-22-RC1, 2021.

Ketcham, R. A., Carter, A., Donelick, R. A., Barbarand, J. and Hurford, A. J.: Improved modeling of fission-track annealing in apatite, Am. Mineral., 92(5–6), 799–810, doi:10.2138/am.2007.2281, 2007.

McDannell, K. T., Issler, D. R. and O’Sullivan, P. B.: Radiation-enhanced fission track annealing revisited and consequences for apatite thermochronometry, Geochim. Cosmochim. Acta, 252, 213–239, doi:10.1016/j.gca.2019.03.006, 2019.

Ravenhurst, C. E., Roden-Tice, M. K. and Miller, D. S.: Thermal annealing of fission tracks in fluorapatite, chlorapatite, manganoanapatite, and Durango apatite: Experimental results, Can. J. Earth Sci., 40(7), 995–1007, doi:10.1139/e03-032, 2003.

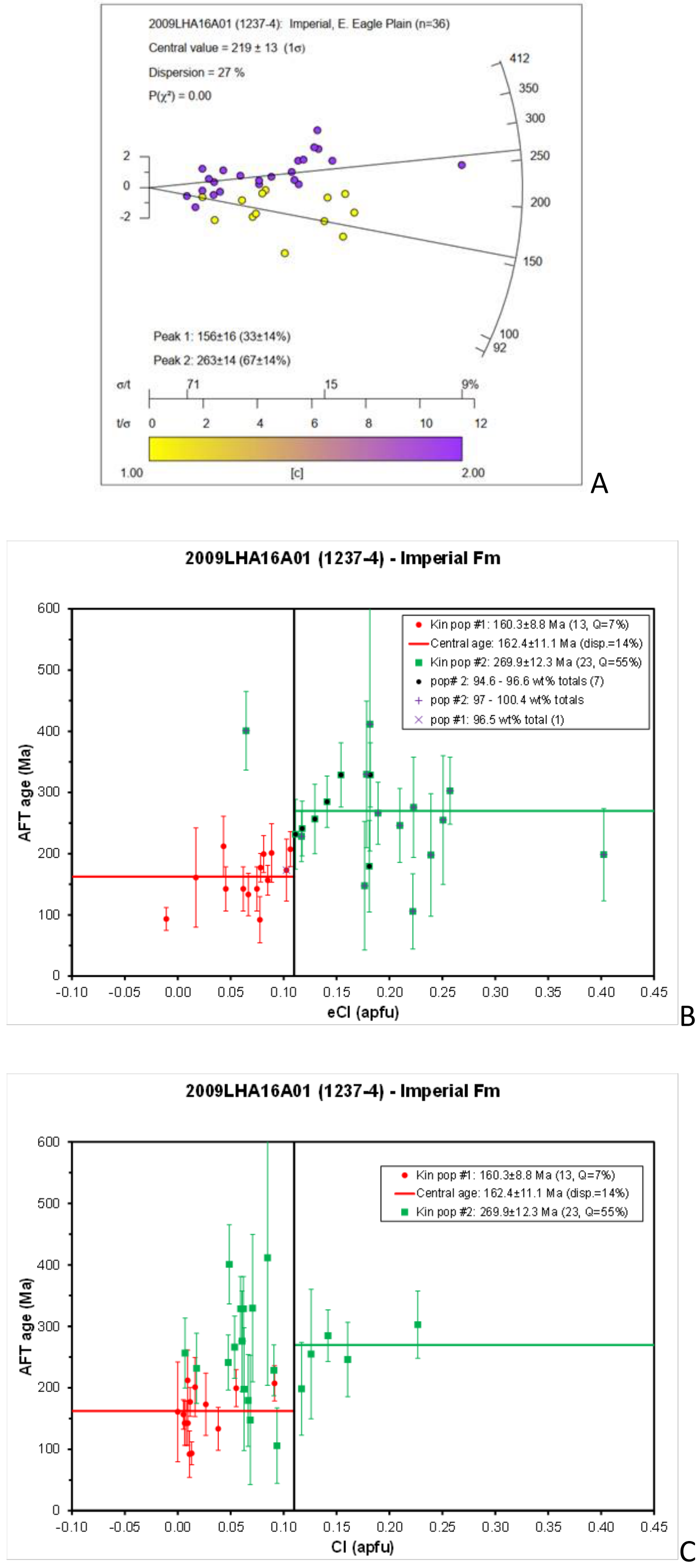

Figure 1: Imperial Formation multikinetic AFT sample, same unit as sample LHA003 in the gchron-2021-22 manuscript from northern Canada. **(A)** Radial plot showing two mixture model age peaks. **(B)** Multikinetic interpretation using r_{mr0} or eCl (apfu), where the two populations agree with model age peaks. Only the pooled age is shown for pop. 2 because of low age dispersion (4%). Symbol overlays show EPMA wt % totals. All pop. 1 totals are 100% unless otherwise noted. Population 2 shows some variation between ~95–100%. There is no clear relationship between probe grain total wt % and eCl. **(C)** multikinetic populations using Cl only, showing complete population overlap. Q = X^2 probability.