

Reply on CC5

Richard A. Ketcham (Referee)

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-RC3>, 2021

Comment on discussion contributions by Green, Duddy, and Issler

In comment CC1, Green and Duddy have chosen to interpret a statement I made in a very particular way, which was inconsistent with my other comments in this review, and my other work in AFT thermochronology. I share the reviewers' frustration with the lack of uptake of the community concerning acquiring kinetic data to help with their quantitative interpretation of their fission-track results. The way I chose to phrase this in my review derives from many individual conversations with fission trackers, about their resistance to acquiring compositional data. Access to a good electron probe, with an operator that is familiar with the vagaries of analyzing apatite, and the additional money to pay for it, do not come easy for many fission-track labs that are under-resourced. For people in that circumstance, I hesitate to try to bully them into it, as it's a significant expense and trouble which may in fact turn up that compositional variation was insignificant for a given study. Trying a carrot rather than stick approach, I often advise that they should at least look for variation in Dpar (which will vary if Cl varies) and failure to pass chi-squared as signs that a sample will benefit from more work, and certainly not shove it into a thermal history inversion program. Admittedly, the carrot has not worked wonders either, which is why I welcome this contribution from Issler and coworkers to provide more well-documented examples of the advantages of getting the additional data.

Concerning the other point made in CC1, it's simply inaccurate to say that my previous work has "downplayed the importance of Cl." All experimental work to date document that it's a dominant influence, but the data also clearly show that other factors can influence annealing as well; it's simply a question of how often a given variant is encountered. Table 4 in Carlson et al. (1999) provides some idea, based on one set of EMP analyses from a handful of studies. It will be good to have more data sets to add to this one, and I look forward to Duddy and Green's upcoming contribution on this front. In any event, the implication of this table is that Cl enrichment is indeed much more common than cation substitutions in sufficient degree to affect annealing, though there remains insufficient data to be confident about just what a sufficient degree is

Although one should be careful in putting too much stock in a single apatite, an important one in the Carlson et al. (1999) data set is Tioga (TI), which has only a modest amount of Cl (0.85 wt. %, or 0.24 apfu), but is among the most resistant analyzed, far beyond apatites with similar or greater Cl content. Based on the limited data, it's unclear whether

this annealing resistance can be attributed to its fairly low but present FeO and MnO content (0.12 and 0.07 apfu, respectively), or its high OH content (0.96 apfu), as other indications in the Carlson et al. (1999) data set point to mixing on the anion site being more important than simple Cl content; near-end-member Cl-apatite B3 is much less annealing-resistant than near-ternary F-Cl-OH apatite B2. There have been occasional studies that have found OH to be influential (Indrelid and Terken, 2000), and so an interesting question remains whether this factor is important – one which certainly requires more data.

Both this study, and associated ones by the Canadian group (e.g., Powell et al., 2018) seem to point to OH as being important, but there are also FeO analyses approaching the values observed in TI apatite. One improvement the authors might consider is providing some indication of the relative influence of OH and cations for these samples, at least as approximated by the r_{m0} equation; maybe as simple as calculating r_{m0} from cations alone and OH alone and Cl alone, to give a ballpark estimate, and maybe a closer analysis would allow them to suss out some more insights.

Concerning the quality of the EMP data brought up by Duddy in CC3, this is indeed a concern that merits more attention and discussion by the authors. One thing concerning their EMP totals is that it appears that they do not add in the OH inferred from stoichiometry, as allowed in the spreadsheet provided by Ketcham (2015). Including this factor will push many analyses back over the 98% limit. The systematic bias between the Ca and P site can also be a result of using the wrong number of oxygens to normalize, so that should be double-checked (I could not work out which apatites in the open file report corresponded to which ones in the data table for P013-12, so a more reliable mapping between those would also be good). Once these things are seen to, a frank assessment of the quality of the EMP data is certainly in order. However, I don't think perfection is necessary for this to be a useful contribution; if someone wants to add a grain of salt because of poor totals, they are entitled to do so. If FeO is present, or F+Cl is absent (indicating a substantial OH content), poor totals will probably not affect that too much.

Concerning the 101%-98% criterion set forth by Duddy and Green, it can be difficult to achieve in apatite, or it can be achieved spuriously, depending on what elements one analyzes for and how one sets up one's calibration. Looking in particular at the rare earth elements, they are often present, but only a few are characteristically analyzed for with the EMP (Ce, La, maybe Sm and/or Nd); however, because they are heavy, and there are so many of them that generally travel together, it doesn't take much in terms of atoms per formula unit to affect totals. HREE's are almost never analyzed for with EMP, and are usually depleted compared to LREE's, but not always, as shown by the increasing number of LA-ICPMS analyses. Neglecting REE's by omission during calibration may provide better apparent totals, but an incomplete picture. Anion stoichiometry (i.e. not having excess F+Cl) is also an important quality for evaluating EMP data, given the mobility of F under the electron beam (Stormer et al., 1993), which in turn is affected by the crystallographic orientation of the grain.

References cited

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

Indrelid, S. L. and Terken, J. M. J.: Constraints on the thermal history of the interior basins of the Sultanate of Oman using apatite fission track analysis (AFTA), 9th International Conference on Fission Track Dating and Thermochronology, Lorne, Australia 2000.

Ketcham, R. A.: Technical Note: Calculation of stoichiometry from EMP data for apatite and other phases with mixing on monovalent anion sites, *Am. Mineral.*, 100, 1620-1623, 10.2138/am-2015-5171, 2015.

Powell, J. W., Schneider, D. A., and Issler, D. R.: Application of multi-kinetic apatite fission track and (U-Th)/He thermochronology to source rock thermal history: a case study from the Mackenzie Plain, NWT, Canada, *Basin Res.*, 30, 497-512, 10.1111/bre.12233, 2018.

Stormer, J. C. J., Pierson, M. L., and Tacker, R. C.: Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis, *Am. Mineral.*, 78, 641-648, 1993.

Richard Ketcham, 20 October 2021