Author response to community comment CC1 for preprint gchron-2021-22


Green and Duddy criticize reviewer 1 for what they perceive as his downplaying of the need for compositional data for AFT studies and use this as a segue to promote their Cl-based approach to interpreting and modelling AFT data that they developed and applied as consultants at Geotrack International. Their promotion of the Cl model is an integral part of their critique of our paper and therefore we are compelled to respond. They express frustration that apatite composition is not routinely included in AFT studies but are then highly critical (community comment CC3) when an alternate method that incorporates more detailed compositional data than they use is presented. The Green and Duddy Cl model rests on two key assertions. (1) wt% Cl is the only important parameter controlling AFT annealing, and (2) other elements do not occur in significant abundance to influence annealing, both of which have been definitively refuted (see below). Unfortunately, they refuse to publish complete sample and experimental annealing data, as well as descriptions of model calibration and modelling methods in sufficient detail for other scientists to replicate their results (unlike the 1999 benchmark papers of Carlson, Donelick, and Ketcham, for example). This lack of scientific standards for transparency and reproducibility means that members of the thermochronology community may remain unconvinced of the general value of their Cl-based model.

Fortunately, their method can be evaluated by trying to apply it to sedimentary rocks of variable stratigraphic age from different tectonic settings. We have done this for numerous Phanerzoic sedimentary rocks from various regions in northern and western Canada by acquiring detailed apatite elemental data to constrain AFT interpretations. We find that both $r_{\text{Cl}}$ and Cl can define AFT kinetic populations when Cl is the only element in significant abundance or when Cl varies systematically in abundance along with other elements. In both cases, kinetic population ages show a close correspondence to population ages on radial plots that are derived from age mixture modelling. However, for more chemically heterogeneous samples that do not meet these conditions, kinetic populations can be defined using the multi-element $r_{\text{Cl}}$ parameter, but they show partial to complete overlap when plotted with respect to Cl. We have numerous samples from different areas of Canada for which a Cl-based interpretation cannot adequately describe our EDM and LA-ICPMS AFT data. Our choices were then either to: (i) abandon the data, (ii) force an unsatisfactory interpretation by assuming the Cl model was right and ignoring important features in the data that were incompatible with it (i.e., Figure 4 of Green and Duddy), or (iii) to try other data interpretation and modelling approaches. We chose the latter path and invested years in developing alternate methods that build on the results of well-documented annealing experiments and modelling approaches. We already have published examples from the Mackenzie Delta (EDM AFT data; Schneider and Issler, 2019) and Mackenzie Corridor (LA-ICPMS AFT data; Powell et al, 2020) of the Canadian Northwest Territories where $r_{\text{Cl}}$ has proven to be better suited than Cl. We are preparing to publish results for many more samples once our method paper has been published.

Everyone agrees that Cl is a common constituent of apatite that has a significant influence on thermal annealing. Figure 1 of Green and Duddy shows AFT age varying with Cl content and this pattern makes sense for apatite grains with that particular Cl-dominant composition. Figure 2 of Green and Duddy is presented and discussed in a very misleading way. We don’t understand how Green and Duddy infer that Carlson et al. (1999) and Barbarand et al. (2003) “explicitly downplayed” the importance of Cl. We take the opposite view. Their experimental data proved that Cl was insufficient to fully characterize apatite annealing behavior. They tried to accommodate the experimental data by expressing $r_{\text{Cl}}$ as a function of Cl— but they were unable to account for all the annealing data because of apatite grains with significantly different chemistry. Most of the relatively small number of apatite specimens used in the annealing experiments have variable Cl contents but low abundances of other elements and therefore they conform reasonably well to the predictions of the Cl-based $r_{\text{Cl}}$ model. Green and Duddy include these specimens in Figure 2 but they leave out key apatite specimens with high abundances of other elements that lead to different annealing behavior: HS – high OH; KP – high Sr; PC – high Mn, and TI – high Fe, Cl, OH and MIN – high OH, S, Si. Green and Duddy claim other elements show no systematic effects on annealing yet the multi-element-based $r_{\text{Cl}}$ parameter best describes the entire data set (Ketcham et al., 1999; Ketcham et al., 2007) compared to single-parameter methods. Although this is a small set of annealing data, these and other published annealing experiments (e.g.,
Ravenhurst et al., 2003; Tello et al., 2006) establish that elements other than Cl can have a significant effect on annealing, providing clear evidence that convincingly refutes assertion 1 above. Green and Duddy seem to be recommending that we ignore the science and focus on using a Cl-only scheme because we can safely omit the “few” occasional outliers that do not conform to their Cl-based model. The problem with this approach is that we do not know the true variation in apatite composition for natural samples and we never will if we don’t measure it. Apatite with variable cation and OH concentrations constitute a minor component of the specimens used for the annealing experiments but this should not be construed as being representative of their occurrence in nature. After all, no one believes that the small number of specimens used in the experiments represent the full range of apatite compositions likely to be encountered in real world situations. In fact, our analyses of thousands of naturally occurring apatite grains in our projects supports that apatite compositions do vary considerably.

Figure 3 of Green and Duddy shows another example of how Cl influences annealing. If Cl is the only element of significance for the samples in the Flaxmans-1 well then you will get the kind of population resolution that we observe using the eCl/r_{mr0} parameter. These data are similar to the Cl-dominant populations that comprise some of the specimens used in other annealing experiments (e.g., Carlson et al., 1999; Ketcham et al., 1999; Barbarand et al., 2003). Under these conditions, it is fine to use borehole and experimental annealing data to calibrate a kinetic model that applies to apatite with a Cl-dominant composition. However, it is not reasonable to assume that the composition of apatite in the Flaxmans-1 well applies to all natural apatite samples. Below is a published counterexample to the Flaxmans-1 well. The figures are from Schneider and Issler (2019) and they show EDM AFT data and results from core samples collected in a Mackenzie Delta well with temperature and thermal maturity data. This well-constrained example shows that the multi-elemental-based eCl/r_{mr0} parameter defines two kinetic populations that cannot be resolved using Cl alone. The kinetic population pooled ages closely match (within one standard deviation) the populations ages on the radial plot that are derived from age mixture modelling. Two anomalously young low retentivity grains (dark blue solid triangles) have non-stoichiometric excess F values and no associated track lengths. Such young ages are not present in other samples from this well that display two kinetic populations.

The samples are from the Paleocene-Eocene Aklak and Taglu sequences which have remarkably uniform properties across the basin. The lower retentivity population (red symbols) is similar to other fluorapatites in nature with an eCl value of ~0.05 apfu. The more retentive older population (purple symbols) has high and variable amounts of Fe, Na, Mg, Ce, OH and Cl and it has an eCl of ~0.20 apfu. Six core samples were collected from this well and they show a consistent decrease in kinetic-population ages with increasing temperature and thermal maturity down the borehole.
The less annealed, higher retentivity population shows more variability in population age that is likely related to variability in provenance.

Independent AFTINV thermal models were run for each sample, yielding a coherent set of thermal histories (exponential mean histories are shown in the figure) that are compatible with geological constraints and the known very rapid burial rates in this deltaic succession. This published example provides additional evidence that assertion 2 of Green and Duddy is not supported and that elements beyond Cl occur in natural samples and they influence AFT annealing.

Green and Duddy contend that compositional outliers are rare and they use their Figure 4 to support their claim. This claim needs to be scrutinized in the context of how their analyses are undertaken. Their example (and other published examples by them) show that they measure approximately 25 age grains which is typical of many EDM AFT applications. This number of age grains may be adequate for single age populations but our experience shows that this is generally inadequate to properly characterize single-grain age distributions for the Phanerzoic multikinetic AFT samples that we have examined. Our recommendation is that 40 age grains are needed but, based on processing separate sample aliquots, even more may be necessary if three or more populations are present. It is not a surprise to us that they observe “rare” outliers if ages are undersampled. Also, as discussed in the reply to reviewer 2, unconscious bias related to EDM AFT age measurement may be a contributing factor to the apparent low frequency of “outliers.” This can neither be proven nor disproven if populations are undersampled and the true variation in age is unknown.

We know that Cl is a common and important element that influences annealing so, if we believe the Cl-based model to be correct, it should be possible to select a subset of grains that “confirm” this. Green and Duddy seemingly only measure wt % Cl and therefore do not have the information to properly assess apatite composition and ensure that it conforms to their assumptions. We believe that the lack of elemental data and undersampling of age grains creates the potential for confirmation bias where the model is assumed to be correct, so there is no need for further investigation. Therefore, alternative methods involving newer technologies that yield results that are inconsistent with the Cl-only model are viewed with suspicion. This conviction seems to be well summarized in the statement by Green and Duddy, “We find it amusing to contrast the negative attitude to compositional analysis evident in Ketcham’s review with the willingness of many thermochronology labs to invest in expensive new machines to measure uranium for fission track studies by laser ablation, and to measure U-Th/He ages, when these methods are far from proven and have been shown to provide misleading results in many cases.” We believe that science advances when new technologies are adopted and that challenges to conventional ways of thinking are a normal part of scientific endeavors.
References cited:


