Author response to reviewer comment RC3 for preprint gChron-2021-22


Reviewer 1 (Rich Ketcham) has made useful suggestions on trying to assess the relative effects of OH, Cl and cations on annealing kinetics. We have already dealt with the effect of Cl alone in our response (comment AC4) to the comment CC3 of Duddy and Green but include some results here for reference. It is useful to examine the importance of OH on eCl/r_{m0} values because, in the early stages of our study, we collected LA-ICPMS elemental data and had problems resolving kinetic populations. F could not be measured accurately using LA-ICPMS and therefore OH could not be calculated. The effect of neglecting OH is to decrease eCl values (increase r_{m0}) in ways that lead to population overlap. This is illustrated in the figures 1 and 2 below where we set OH values equal to zero and recalculated eCl/r_{m0} values to simulate the effect of using LA-ICPMS elemental data.

Figure 1 shows various plots of AFT ages and lengths versus eCl (A and B), eCl excluding OH (C and D), and Cl alone (E and F) for the Devonian LHA003 AFT sample. AFT single grain ages are well resolved into two age populations using eCl values derived from r_{m0} values calculated using multi-elemental data with the Carlson et al. (1999) r_{m0} equation. The age populations closely match those derived from independent age mixture modelling as shown in preprint gChron-2021-22. Figure 1C and 1D show the same plots but exclude OH from the r_{m0} calculations. This is analogous to the results we have for samples with LA-ICPMS elemental data that lack the Fe measurements required for estimating OH values. Both kinetic populations show a shift to lower eCl values (compare Figure 1C with 1A and 1D with 1B) but the change is larger for kinetic population two which has grains with the highest OH content (see table in author reply AC4), causing some grains to overlap with population one. The average eCl values for kinetic populations one and two are 0.03 apfu and 0.20 apfu, respectively, for the complete elemental data (Figure 1A and 1B), and 0.01 apfu and 0.15 apfu for eCl values excluding OH (Figure 1C and 1D). Thus, population two shifts to lower eCl values by 0.05 apfu on average although individual values can decrease by > 0.1 apfu. The effect is smaller for population one (~0.02 apfu decrease on average) with some eCl values becoming negative. For comparison, populations one and two overlap when the AFT data are plotted with respect to Cl alone (Figures 1E and 1F).

OH is clearly important but so are other elements, especially Fe, which has a larger effect than other cations on calculated r_{m0} values. Fe is common in many Phanerozoic AFT sedimentary samples that we have examined from northern and western Canada. The LHA003 sample has quite a few grains with Fe contents in the range of 0.04–0.07 apfu and this can increase eCl values significantly as observed for apatite grains with high Fe and low Cl values. This is illustrated in the table below which shows elemental data (apfu) for apatite grains with good elemental totals. Cation abundances ≥ ~0.04 apfu are highlighted in blue, Fe values ≤ ~0.02 apfu and Cl values ≤ 0.1 apfu are highlighted in yellow, and OH values > 0.5 apfu are highlighted in green. Both Cl and eCl values ≥ 0.1 apfu are highlighted in green. It is difficult to isolate the contribution of each element to calculated eCl values, but it is clear from equation 6 of Carlson et al. (1999) that Fe has approximately double the effect of other cations. Fe concentrations in the range of 0.4 to 0.6 apfu increase eCl relative to Cl in apatite grains with relatively low Cl and OH contents (age grains 2, 19; length grains 5, 35, 36, 39 and 51). High OH also increases eCl values (age grains 30, 31, 39; length grain 34, 40). The effects are modulated by the addition of other elements (age grains 33, 35, 37; length grains 5, 6, 45 and 51). Age grain 32 has low Cl and OH, and high Na and Mn which increase eCl by 0.07 relative to Cl (with a small contribution from Fe as well). These results suggest that Fe has the strongest effect on track retentivity at a given apfu value with very significant contributions from OH due to its high abundance in many grains. Figure 2A and 2B show a significant reduction in eCl values for LHA003 when Fe is excluded from the r_{m0} calculations. Average eCl decreases by ~0.05 apfu and >0.1 apfu for populations one and two, respectively, resulting in population overlap. The reduction in eCl values is less if Mn and other cations are excluded from the r_{m0} calculations but Fe is retained (Figure 2C and 2D) – average eCl values decrease by ~0.02 and ~0.03-0.04 apfu for populations one and two. Even though the effect is smaller, neglecting other cations can still contribute to population overlap.
Figure 1. AFT ages (A) and lengths (B) versus eCl derived from Carlson et al. (1999) $r_{rec}$ equation using multi-elemental data for sample LHA003. AFT ages (C) and lengths (D) versus eCl derived from Carlson et al. (1999) $r_{rec}$ equation using multi-elemental data without OH to simulate ICPMS elemental data (F not measured). AFT ages (E) and lengths (F) versus measured Cl. Kinetic populations are best resolved using eCl (A and B). Excluding OH contributes to population overlap (C and D) whereas Cl alone cannot resolve different kinetic populations (E and F).
Figure 2. AFT ages (A) and lengths (B) versus eCl derived from Carlson et al. (1999) \( r_{\text{eq}} \) equation using multi-elemental data excluding Fe for sample LHA003. AFT ages (C) and lengths (D) versus eCl derived from Carlson et al. (1999) \( r_{\text{eq}} \) equation using multi-elemental data without Mn and other cations (but including Fe). Kinetic populations are best resolved using eCl with full elemental data (see Figure 1A and 1B). Excluding Fe decreases eCl values significantly and contributes to population overlap (A and B). Excluding Mn and other cations has a smaller effect but still contributes to population overlap (C and D).
Figure 3 shows the same plots as Figure 1 but for the Permian P013-12 AFT sample. Again, we see that kinetic populations are best resolved using eCl values calculated using the full suite of elemental data (Figure 3A and 3B) but that excluding OH decreases eCl values and contributes to population overlap (Figure 3C and 3D). For this example, the average eCl values for population one, two and three, respectively, are 0.05, 0.24 and 0.37 apfu when using the full elemental data (Figure 3A and 3B). If OH is excluded, there is a reduction in corresponding average eCl values to 0.02, 0.17 and 0.28 apfu. The higher retentivity populations with higher OH values have the largest reduction in average eCl values (kinetic population three average eCl is reduced by 0.09 apfu)—similar to the LHA003 sample. Also, kinetic populations show significant overlap if the AFT data are plotted with respect to Cl alone (Figure 3E and 3F). It is clear that the effect of omitting OH in the calculations will depend on the composition of the samples being studied. For low OH samples, LA-ICPMS elemental data can resolve kinetic populations. However, most of the multikinetic samples that we have investigated have variable OH content and therefore we had to acquire EPMA data for many of our samples with LA-ICPMS elemental data so we could better interpret and model the AFT data. From the above discussion, it is clear that elements other than Cl can have a strong effect on track retentivity and use of Cl alone can bias interpretations and model results. In our experience, chemical heterogeneity is the norm for sedimentary samples that contain multikinetic AFT populations.

Figures 4 and 5 show comparisons of eCl values calculated using the Carlson et al. (1999) and Ketcham et al. (2007) \( r_{\text{mr0}} \) equations for the LHA003 and P013-12 samples, respectively. Figure 4A and 4B show AFT ages and lengths plotted with respect to eCl derived from the Carlson et al. (1999) equation with Figure 4C and 4D showing the results for the Ketcham et al. (2007) equation. Both sets of results are very similar for the LHA003 sample with the Ketcham et al. (2007) equation producing slightly more population overlap with a shift to slightly higher average eCl values for both populations. Average eCl values for populations one and two shift to 0.05 and 0.23 apfu from 0.03 and 0.20 when using the Ketcham et al. (2007) equation. There is more population overlap when the Ketcham et al. (2007) equation is used for sample P013-12 (Figure 5). In general, the Ketcham et al. (2007) equation produces a wider range of eCl values than the Carlson et al. (1999) equation (eCl values both increase and decrease). The average eCl value remains unchanged for kinetic population one (0.05 apfu) but it increases to 0.27 and 0.43 apfu from 0.24 and 0.37 apfu for populations two and three when the Ketcham et al. (2007) equation is used. This is probably because the Ketcham et al. (2007) equation is weighted more heavily towards Cl than the Carlson et al. (1999) equation. The Ketcham et al. (2007) equation uses the combined data from Carlson et al. (1999) and Barbarand et al. (2003) and the apatite specimens used by Barbarand et al. (2003) are dominated by Cl. Alternatively, potential incompatibilities between the Carlson et al. (1999) and Barbarand et al. (2003) datasets may contribute to the differences in calculated \( r_{\text{mr0}} \) values. However, similar annealing temperatures can occur when using different \( r_{\text{mr0}} \) values in these models because they were calibrated differently. Either of these \( r_{\text{mr0}} \) relations may be used but we believe that the Carlson et al. (1999) equation does a better job of resolving kinetic populations for our samples.

Reviewers 1 states, “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.” We discuss this extensively in our reply (AC4) to community comment CC3 and show that the purported trends in eCl values with elemental wt% totals do not exist when the data are examined in detail. Almost all of the eCl values with lower elemental totals are in the same range as those with totals between 97–100 wt% and independently measured high Dpar values confirm the population assignments based on the elemental data. The data with the good elemental totals show the largest deviation from the predictions of the Cl-only model. The reviewer is correct that OH is not included in the elemental totals in the raw elemental data tables for both samples nor is it included with the apfu values for sample LHA003 which were provided by AtoZ Inc. However, OH wt% values are incorporated in the elemental totals that are included with the elemental apfu data for sample P013-12 because this is a routine output of our software, Probecal. As mentioned in our reply (AC4), apfu values were recalculated for LHA003 using Probecal and they give virtually identical results to those provided by AtoZ Inc. (see table in reply AC4). We agree with the reviewer on the various potential causes for lower totals and would add that ideal totals will not be possible for all grains in a sample that has small apatite grains. Before EPMA analysis, grains need to be processed and etched for AFT measurement. Even without Cf-irradiation, it may not be possible to find a “clean” measurement area that avoid tracks, fractures and other imperfections on very small grains and this has been observed for some of our samples analysed using EDM. Therefore, although the majority of our samples have good totals, some samples will have suboptimal totals for smaller grains. Simply skipping over small grains in order to get only good elemental totals will contribute to age-selection bias.
Figure 3. AFT ages (A) and lengths (B) versus eCl derived from Carlson et al. (1999) \( r_{\text{ins}} \) equation using multi-elemental data for sample P013-12. AFT ages (C) and lengths (D) versus eCl derived from Carlson et al. (1999) \( r_{\text{ins}} \) equation using multi-elemental data without OH to simulate ICPMS elemental data (E not measured). AFT ages (E) and lengths (F) versus measured CI. Kinetic populations are best resolved using eCl (A and B). Excluding OH (C and D) or using CI alone (E and F) contributes to significant population overlap.
Reviewer 1 “could not work out which apatites in the open file report corresponded to which ones in the data table for P013-12” and requested “a more reliable mapping between those.” Sample P013-12 was processed in two separate aliquots in an effort to increase the number of AFT ages and lengths. As a result, elemental data were acquired at different stages and are listed in order of the date of acquisition on three separate worksheets in the raw elemental data file (see dates on worksheet tabs). Age and length grains are identified in the first column of each worksheet and grain number is given in the fourth column. The first worksheet (May 20, 2015) has elemental data for twelve age grains and nine length grains (numbers 1 to 24) and this corresponds to series A listed in the AFT age, length and elemental apfu tables in the GSC Open File 8821 data report. The second worksheet (October 9, 2016) has element data for 33 age grains (grain numbers 1 to 40) and the third worksheet (February 26, 2017) has elemental data for 16 length grains. The data in worksheets two and three correspond to series B data in the AFT age, length and elemental apfu tables in the data report. Data are presented in this exact order in the elemental apfu table in the report with labels A and B added to the grain numbers. These data were sorted into kinetic populations in the AFT age and length tables, and sorted by eCl value, so the grain numbers are no longer in sequence.
Figure 5. AFT ages (A) and lengths (B) versus eCl derived from Carlson et al. (1999) $r_{ref}$ equation using multi-elemental data for sample P013-12. AFT ages (C) and lengths (D) versus eCl derived from Ketcham et al. (2007) $r_{ref}$ equation using multi-elemental data. For this example, the Ketcham et al. (2007) $r_{ref}$ equation produces more population overlap than the Carlson et al. (1999) equation.
References


