

**Comment on:**

Issler, D.R., McDannell, K.T., O’Sullivan, P.B. and Lane, L.S., in review. Simulating sedimentary burial cycles – Part 2: Elemental-based multikinetic apatite fission-track interpretation and modelling techniques illustrated using examples from northern Yukon.

MS No.: gchron-2021-22

**Summary**

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  $\text{rmr}_0$  over chlorine (wt%) as a kinetic control on apatite fission track annealing. Because of these problems the subsequent thermal history modelling has no basis.

**EMPA data.**

Of the 92 apatite compositions reported for Devonian outcrop sample LHA003, 59 (~64%) have a total outside the 98-101 wt% range generally regarded as defining acceptable totals (as low as 82.4%). Poor EMPA analyses are alluded to when discussing sample PO13-12 (lines 336-340), but the scale of the issue was not mentioned. Further, Issler et al. violate their own workflow Step 7, in Lines 105-110:

*“Step 7 involves assessing the interpretation by considering all available data in the context of measurement uncertainty and missing information. The goal here is to try to use all the available data except for obviously poor analyses.”*

The majority of the EMPA data for LHA003 are clearly “*obviously poor*” and are thus unsuitable both for determining structural formulae and subsequently  $\text{rmr}_0$  and eCl for defining kinetic populations.

The structural formulae calculations for LHA003 presented in Table D.2 (“assets link”; Issler et al., 2021) were apparently made using a non-standard procedure, markedly different to that described in Ketcham (2015), for example, which was used by the authors for sample PO13-12. It appears that the calculations for LHA003 have been made by assuming a stoichiometric ratio for the Ca and P sites, whereas the raw data show that most analyses have very low totals and the analyses are clearly not stoichiometric (Figure 1). Even though we show that most analyses for LHA003 are unsuitable for structural formula calculation, we have followed the authors in doing this, but using the same methods as they used for sample PO13-12, to demonstrate the effect that the poor totals have on subsequent calculations.

The relationship between EMPA total and the ratio (in apfu) of the Ca to P sites (stoichiometric ratio ~1.67) is shown in Figure 1. The obvious correlation between decreasing total and increasingly non-stoichiometric B/A ratio (i.e. Ca site/P site) provides a strong indication that there is a serious problem with the EMPA analyses with unequal effects on different elements. The potential effect on the reported Cl and F values cannot be determined. In other words, these analyses cannot be simply normalised to 100% and used to estimate the structural formula, as may have been done to produce the data listed in Table D.2.

We contend that the values of  $\text{rmr}_0$  and eCl determined from most of these apatite analyses are inaccurate and unfit for purpose. This is confirmed with plots of these parameters in Figure 2, where increasingly lower totals correlate with lower  $\text{rmr}_0$  and higher eCl values.

Poor totals will have a direct influence, for example, on the calculation of OH which is determined by difference, and this will feed through to  $\text{rmr}_0$ .

Thus, we see no justification for the conclusion stated in lines 344-345:

*“The Devonian outcrop sample is of high quality with 39 single grain ages and 202 track lengths that clearly define two robust kinetic populations in eCl-space (Fig. 5a, b).”*

It follows that relationships shown in Figure 5 of Issler et al. cannot be relied upon as showing the  $\text{rmr}_0$  is a useful discriminator of AFT annealing behavior.

Is the EMPA data for Permian cuttings sample PO13-12 any better?

Thirty four of 78 EMPA analyses for PO13-12 (~44%) are less than 98% (as low as ~93.8%) and while the data set appears to be of higher quality than that presented for LHA003 (i.e. totals do not get extremely low), a similar trend been EMPA total and B/A ratio is displayed (Figure 3) with resulting question marks over the calculated  $\text{rmr}_0$  and eCl values.

We conclude that the values of  $\text{rmr}_0$  and eCl calculated by Issler et al for sample PO13-12 cannot be used to accurately characterize the properties of individual apatite grains and cannot therefore provide a reliable discrimination of differential AFT annealing.

Why are the EMPA analyses so poor and how can it be done better?

The analytical strategy described by the authors in Figure 1 of Issler et al appears to be the main reason their EMPA analyses are so poor, with probing relegated to the last step in the chain, despite apparently being aware of the problems resulting from this workflow for at least a decade (results for LHA003 were produced in 2011).

We are currently undertaking a research study investigating the usefulness of  $\text{rmr}_0$  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.

We achieved this high quality data by simply carrying out EMPA after FT ages and lengths were measured and prior to ablation. In this way we were able to analyse the same area in which spontaneous tracks were measured and to put the ablation spot at the same location, avoiding the problems encountered in the MS under review.

### **LAICPMS AFT Data**

The complete raw LAICPMS data for the two samples described in this study are not provided, only a reduced data summary available under the assets link (AFT\_age\_Tables B.1 and B.2 and AFT\_length\_Tables C.1 and C.2; Issler et al 2021). Note that key details such as the single ablation spot size (16  $\mu\text{m}$ ) and depth (16 to 18  $\mu\text{m}$ ), laser conditions, etc. are not provided in the MS (but can be found in Issler et al., 2021). In addition, the “primary” zeta value quoted is not enough by itself for calculating the AFT ages from the tabulated results.

The data for sample PO13-12 shows evidence for significant U-zoning in many grains although no mention is made of this in the paper under review. Two versions of uranium magnitude are tabulated: 1) the  $^{238}\text{U}/^{43}\text{Ca}$  ratio used to determine the FT age and 2) U (ppm). These values are not equivalent, as apparently the former is a depth-weighted mean value and the latter a simple average over the full ablation depth (16-18  $\mu\text{m}$ ). A plot of one against the other for sample PO13-12 provided in Figure 4 reveals what we consider to be clear

evidence for U-zoning, with some grains showing extreme excursions from the one to one line. The possible effect of this zoning on the AFT ages and the trends with chemical composition should be discussed. From the unreviewed online assets link (Issler et al., 2021) high U ppm values are attributed to the presence of high U inclusions, but we feel U-zoning is more likely.

One important corollary of this observation is that the U, Th and Sm ppm values listed for these samples should not be used to calculate, for example, eU as a proxy for radiation damage, as they do not refer to the same sample volume. Some comments on the tabulated U, Th and Sm values are provided in Issler et al. (2021) to the effect that they are not absolute measurements due to changes in the U/Ca ratio between analytical sessions, referencing Cogne et al. (2020). In fact, Cogne et al. (2020) recommend against even reporting U ppm values (and presumably also Th and Sm) determined by LAICPMS as they are not accurate. This is a stark reminder that the generally increased precision of U-determination by LAICPMS over EDM is at the expense of accuracy. Here it is important to note that Seiler et al. (2013) found that U-determination by LAICPMS were systematically low at values less than ~5 ppm, while our own experience suggests this limit is at best 10 ppm. This leads to AFT ages which are too old, a major reason for the additional dispersion in LAICPMS AFT ages compared to EDM (e.g. Ketcham et al. 2018).

We are also concerned with additional unaccounted inaccuracies introduced by assuming that each of the analysed apatites are stoichiometric, with 53.454 wt% CaO assumed (McDannell et al 2019) in order to determine the U concentration of the ablated volume and calculate the AFT age. Considering only acceptable EMPA totals for both samples, CaO values in nearly all grains exceed this level (see Elemental wt% Oxide Tables in Issler et al, 2021).

We have some other concerns with the LAICPMS data integrity. For example, three grains from PO13-12, the two youngest and the oldest are rejected from the data set before assessment against eCl, on the grounds of poor U-analysis? (Table B.1). The oldest grain was also rejected from sample LHA003 on the same grounds.

The reader is entitled to ask why these should be regarded as poor U-determination, while the rest are considered OK. In this respect we note that in an earlier paper involving most of the same authors that attempts to resuscitate the concept of radiation enhanced annealing (McDannell et al., 2019) such data appear to have been accepted without question. Other grains have  $rmr_0$  compositions that do not accord with the defined age populations and these are arbitrarily assigned to another population without adequate explanation (Lines 330-340). The same arbitrary reassignment was not carried out in relation to evaluating age trends with Cl apfu which the authors regard as inferior to  $rmr_0$ .

Further comments on this aspect of the MS are beyond the scope of this comment, but these examples highlight one of the major shortcomings of LAICPMS compared to EDM. With EDM the user has a permanent record of the U-distribution and magnitude in the mica detector and any anomalies can be checked and evaluated. With LAICPMS the evidence of U-distribution is difficult to obtain as the area ablated is generally much smaller than the area in which spontaneous tracks are measured (as applies to most grains in this study) and the ablation destroys the sample. We agree with reviewer Karl Lang that the supposed advantages of LAICPMS over EDM are overstated.

### **$rmr_0$ calculations**

The authors prefer the use of the  $rmr_0$  relationship of Carlson et al (1999) over the updated

version of Ketcham et al (2007) on the grounds that “it resolves kinetic populations better (less grain overlap) for the samples we have studied” (Line 212).

It is worthwhile to review the two relationships for  $rmr_0$ .

1) Carlson et al (1999), equation 6:

$$rmr_0 = [0.027 + 0.431 \text{ ABS(Cl} - 1) + 0.107 \text{ ABS(OH} - 1) - 1.01 \text{ Mn} - 2.67 \text{ Fe} - 0.144 \text{ Others}]^{0.25}.$$

The “others” term refers only to the total (in apfu) of the cations measured in the original Carlson et al (1999) data set that substituted for Ca: Sr, Ce, La and Na.

We concur with the warning of Carlson et al (1999): Quote:

“The relative magnitudes of the coefficients can be used together with the data in Table 4 to estimate the relative significance of each of these compositional variables. However, in the absence of any physical understanding of why compositional variations impede or enhance annealing, we have little confidence that it can be used meaningfully to predict the annealing behavior of apatites not included in the experiments. For example, the effect of Fe concentration is determined entirely by the annealing behavior of a single extremely Fe-rich apatite. Nonetheless, these data appear to suggest that substituents for Ca tend to reduce rates of annealing, and that annealing kinetics depend upon the degree of mixing on the halogen site, in some still-concealed and probably complex way.”

It is unclear whether the  $rmr_0$  calculations in the paper under review conform to the original equation. Ti, Zr, Al, As, Y, Sm, Nd, Mg, Ba and K were additionally measured for sample LHA003 and Mg and Y, not measured by Carlson et al (op.cit.), were additionally measured in PO13-12 but it is not stated whether any of these elements have been used to determine “others” for  $rmr_0$ . We have a suspicion that some may have been included since our own calculations of  $rmr_0$  from these data (following the authors and ignoring the low EMPA totals) are a little different to those in the MS. Most are not greatly different, but in two grains with >2wt% Cl, our calculations give negative pre-power values, preventing calculation of  $rmr_0$  and thus eCl, whereas finite values are listed for these grains in Supplementary Table S2 and are shown in the plots.

2) Ketcham et al. (2007), equation 11:

$$rmr_0 = [-0.0495 - (0.0348 \times F) + 0.3528 \text{ ABS(Cl} - 1) + 0.0701 \text{ ABS(OH} - 1) - (0.8592 \times \text{Mn}) - (1.2252 \times \text{Fe}) - (0.1721 \times \text{Others})]^{0.1433}.$$

We concur with the further warning regarding use of  $rmr_0$  of Ketcham et al (2007): Quote:

“Others is the sum of all other cation substituents aside from Mn and Fe. The relative magnitudes of the coefficients are broadly similar to those obtained by Carlson et al. (1999, Eq. 6), with the main difference being to de-emphasize Mn and OH. Attempts to fit different sets and combinations of compositional variables were less successful. The relationship between measured and estimated  $rmr_0$  is shown in Figure 7; most estimates are within 0.02 of the correct figure, which translates into a roughly 5 to 10 °C uncertainty in closure temperature. However, we reiterate here the warning of Carlson et al. (1999) that this approach should only be used with caution, as the cation-based terms are poorly constrained and are likely to be oversimplified and have nonlinear effects. Furthermore, there is no physical basis for the form of Equation 11, and a different form could result in a more confident basis for extrapolation.”

Issler et al. dismiss these warnings (Lines 555-561) and proceed without regard to the limited constraints on chemical composition available in the original Carlson et al (1999) annealing data set, for which no follow-up studies that might confirm or otherwise the importance of elements other than Cl have been undertaken in almost the last 2 decades.

A summary of the range of elements (apfu) in each sample is provided in Issler et al. (Table 3). We think it noteworthy that no element that is significant to the  $\text{rnr}_0$  calculation is particularly abundant. Fe and Mn do not exceed 0.1 and 0.11 apfu ( $\sim 0.41$  and  $0.5$  wt%), respectively, in either sample while SrO is  $< 1.8$ wt%. No other cation exceeds 1 wt% oxide. SO<sub>3</sub> reaches no higher than 1.2 wt% in PO13-12, but this element is not included in  $\text{rnr}_0$ . SiO<sub>2</sub> reaches 1.17wt% in HA003, but again this element is not a part of  $\text{rnr}_0$ . These values are very much less than measured in the single high Fe, Mn and Sr apatites in the Carlson et al. (1999) data set.

### What is controlling $\text{rnr}_0$ in the two samples?

The major control on  $\text{rnr}_0$  is clearly the chlorine content above all other elements, as shown by a plot of wt% chlorine versus  $\text{rnr}_0$  for PO13-12 and LHA003 provided in Figure 5.

This observation accords with the observation of Barbarand et al. (2003) , Quote:

“for samples with  $\text{Cl} > 0.1$  apfu ( $\sim 0.35$  wt%), Cl is the dominant control on track annealing, effectively masking any effect from Ce or other REE substitutions. The presence of large numbers of cations substituted for Ca exhibits some correlation with the annealing properties of F-apatites (Crowley et al., 1991; Carlson et al., 1999). In our study, little information about how Sr, Mn and Fe control mean track length was forthcoming because of the low concentrations of the elements in our samples (see Table 1). Seemingly very high concentrations are required to modify apatite track annealing properties; in the studies cited above, samples with 4.44 wt.% of SrO (Crowley et al., 1991), 7.04 wt.% of Mn and 9.15 wt.% of SrO (Carlson et al., 1999) were considered. For most apatites where Sr, Mn and Fe concentrations are low, the effect of these elements may be safely ignored”.

So why do the apatites in LHA003 have  $\text{rnr}_0$  values that range down to 0.31 (in our calculations this value is also incorrect – see above) if none of the measured elements are outside the typical range of ‘normal’ apatite? The answer is that Cl is having the dominant effect (Figure 5) and major excursions from the trend probably reflect the low quality of the EMPA analyses.

### **Multikinetic annealing**

We have investigated the effect of apatite composition of AFT annealing since the early 1980s and have incorporated the chlorine content in our work since for over 30 years. Despite the overwhelming evidence of the importance of Cl (e.g. Green and Duddy, 2012), we are bemused at the reluctance of the community to take it on board. While we support Issler et al. in attempting to promote the use of apatite composition, we believe their attempt is misguided, and that the approach of collecting “complete” compositional data and calculating  $\text{rnr}_0$  is unnecessary. Simpler and better results can be achieved by determination of chlorine alone. The paper in review falls far short in demonstrating that  $\text{rnr}_0$  is superior to Cl (wt%) alone.

### Further comments for the benefit of the authors

Should the authors decide to continue with trying to demonstrate that  $r_{mr_0}$  is useful as a measure of annealing, we suggest that this can never be achieved with the analysis of further outcrop samples or well samples of the type used in this study (and apparently in a upcoming analysis of 50 further similar samples).

The only rigorous strategy is to use core samples from deep wells that *are currently at maximum temperatures at the present-day* (e.g. like those for the Flaxmans-1 well - Green and Duddy, 2012 – see also Geochron CC1 reply on RC1), or to subject outcrop samples to laboratory annealing. For example, sample LHA003 would be a good candidate for an annealing experiment, where both induced and spontaneous tracks could be used with a specific aim at investigating potential compositional controls in apatite with  $<0.4\text{wt}\%$  Cl. Such a controlled experiment, and accurate EMPA analyses, would overcome the major shortcomings evident in the paper under review.

Further, the approach employed by Issler et al in defining age populations and then applying an arbitrary compositional boundary is backwards. If apatite composition is important, it is important in all samples, regardless of the range of AFT ages. Compositional boundaries should be defined based on the annealing kinetics of known compositions, and the ages in each group should be compared with model ages to derive a common thermal history. In our approach we have derived individual kinetic descriptions for chlorine (wt%) compositional groups at 0.1 wt% intervals up to 3 wt%. Typical quartzose-arkosic samples have Cl between 0 and  $\sim 0.6$  wt% (6 compositional groups) while volcanogenic sandstones range up to  $\sim 3$  wt% (30 groups) (e.g. Figures 18, 16 and others in Green and Duddy, 2013). Such an approach enables tighter constraints on maximum paleotemperature and time of cooling than available from assuming composition, or using an average value for a wide range of compositions as employed in the MS under review

In developing a more detailed understanding of compositional influences on FT annealing, cuttings samples should be avoided due to potential down hole or drilling additive contamination.

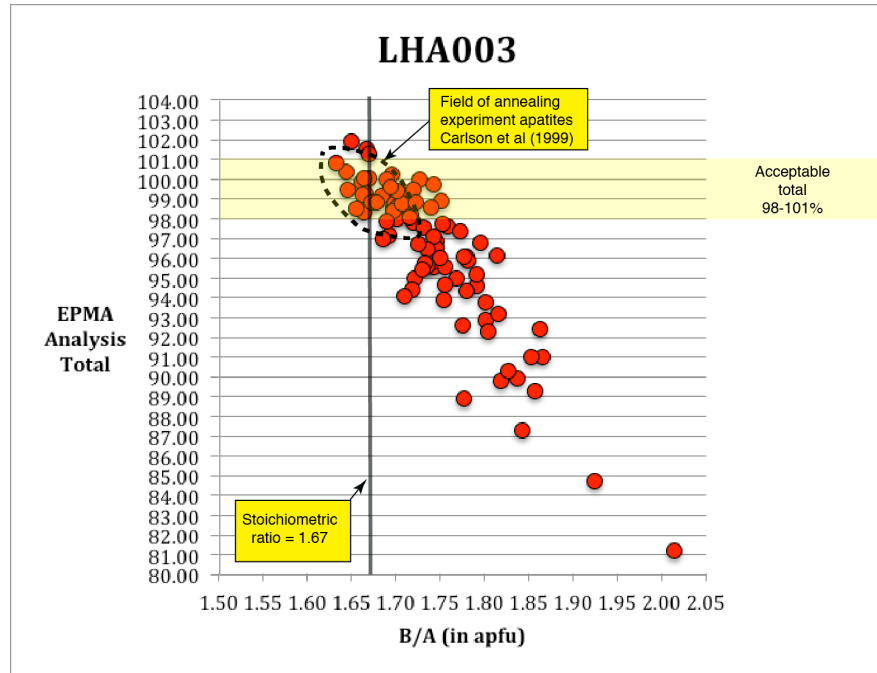
We also suggest that LAICPMS U analyses are avoided due to the current uncertainties surrounding the accuracy of U-determinations (Seiler et al 2013; Cogne et al 2020; Duddy and Green, in prep).

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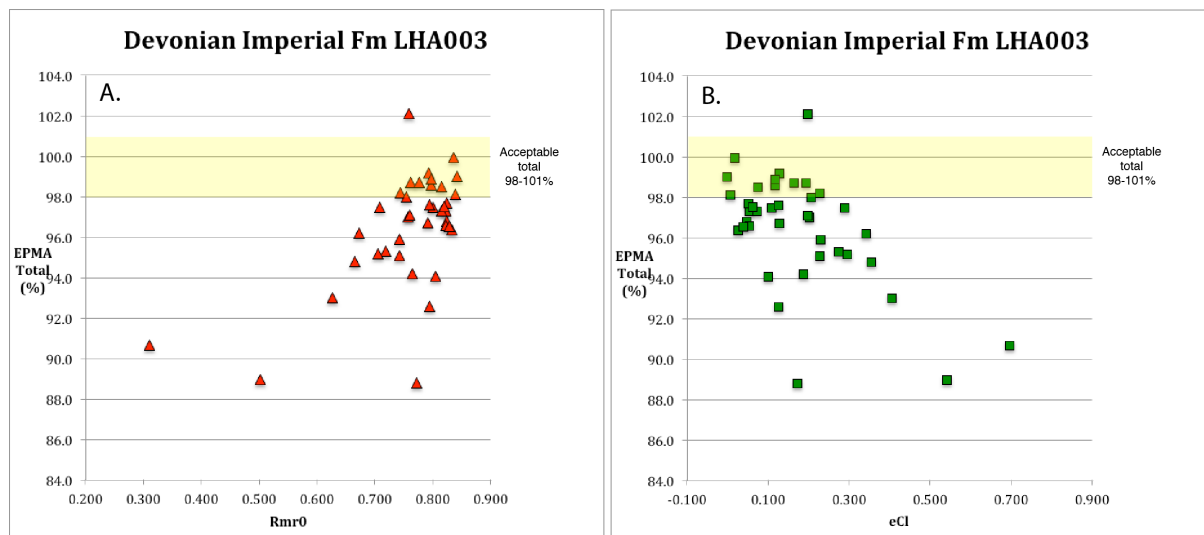
October 15<sup>th</sup> 2021

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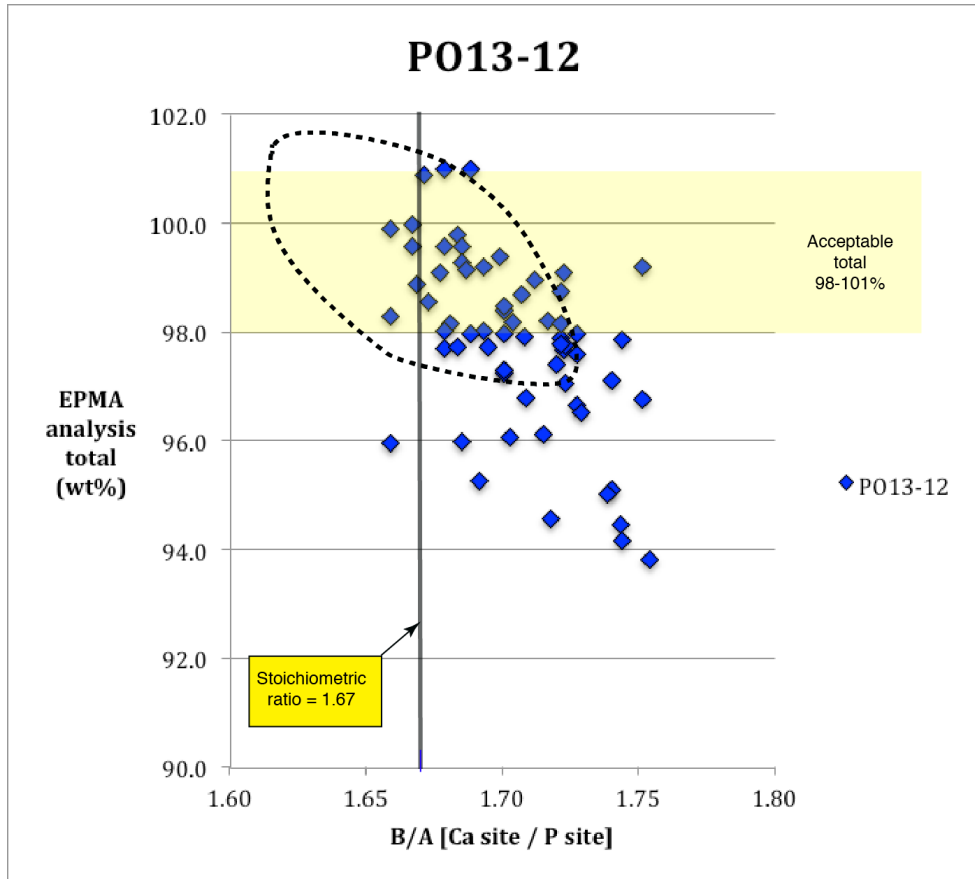
**Figure 1:** Sample LHA003 apatite EMPA analysis total versus Ca site:P site ratio (B/A apfu). 59 of 92 analyses (64%) are outside the acceptable range. The strong correlation between low total and increasingly non-stoichiometric B/A ratio (i.e. Ca site/P site) is in stark contrast to the apatites used by Carlson et al (1999) to define  $rmr_0$ . (Note that the apatites used in annealing experiments by Barbarand et al 2003) fall in similar field to those from Carlson et al., 1999).



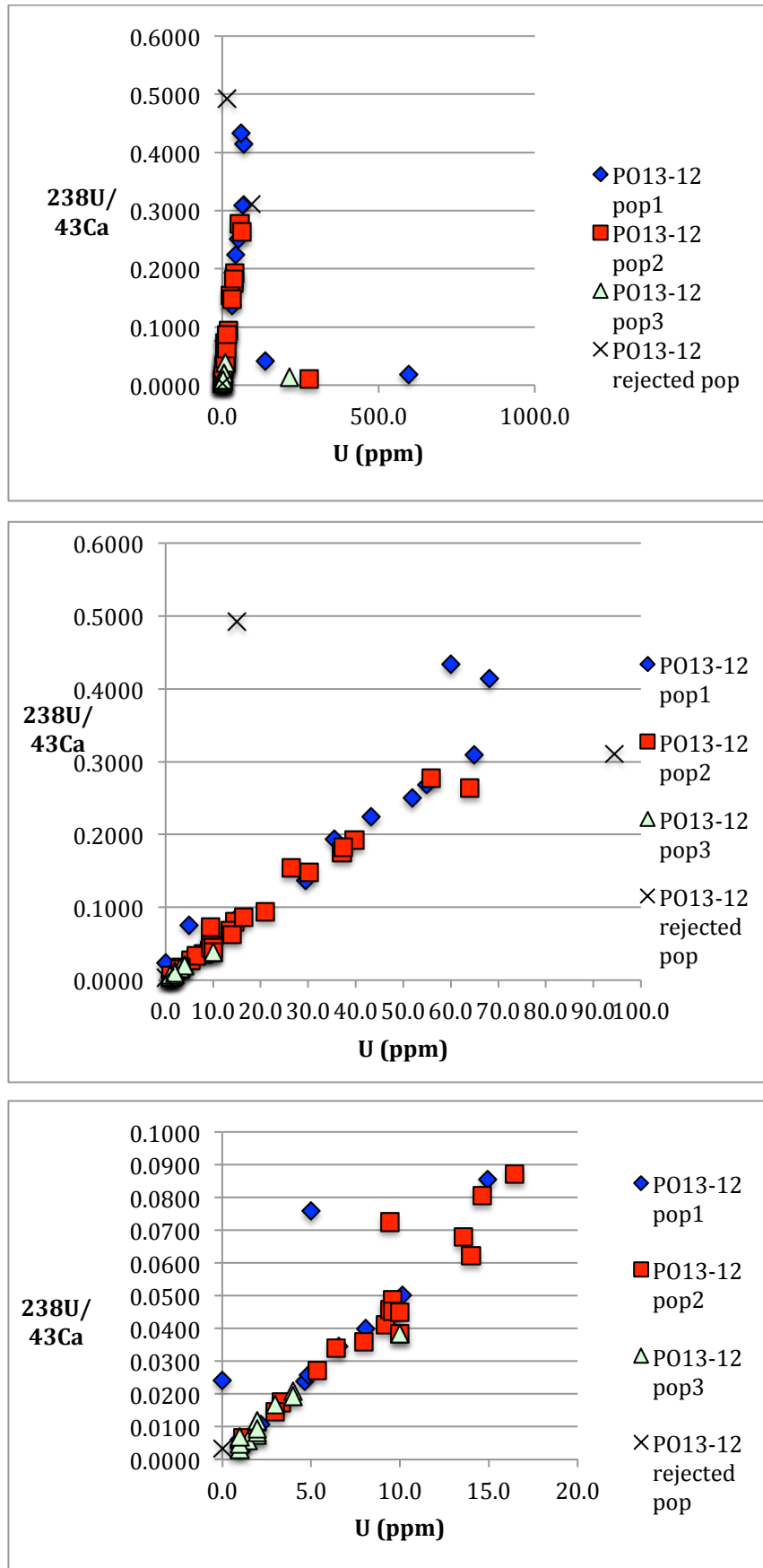
**Figure 2:** Sample LHA003 apatite EMPA analysis total versus  $Rmr_0$  and  $eCl$ .

The clear trend of decreasing  $rmr_0$  (A.) and increasing  $eCl$  (B.) with decreasing EMPA total shows that the differences in fission track retentivity interpreted by the authors from these parameters is likely an artifact of the poor quality EMPA data and provides a strong indication that values of  $rmr_0$  and  $eCl$  determined from most of these apatite are inaccurate, and unfit for purpose (also see Figure 3).

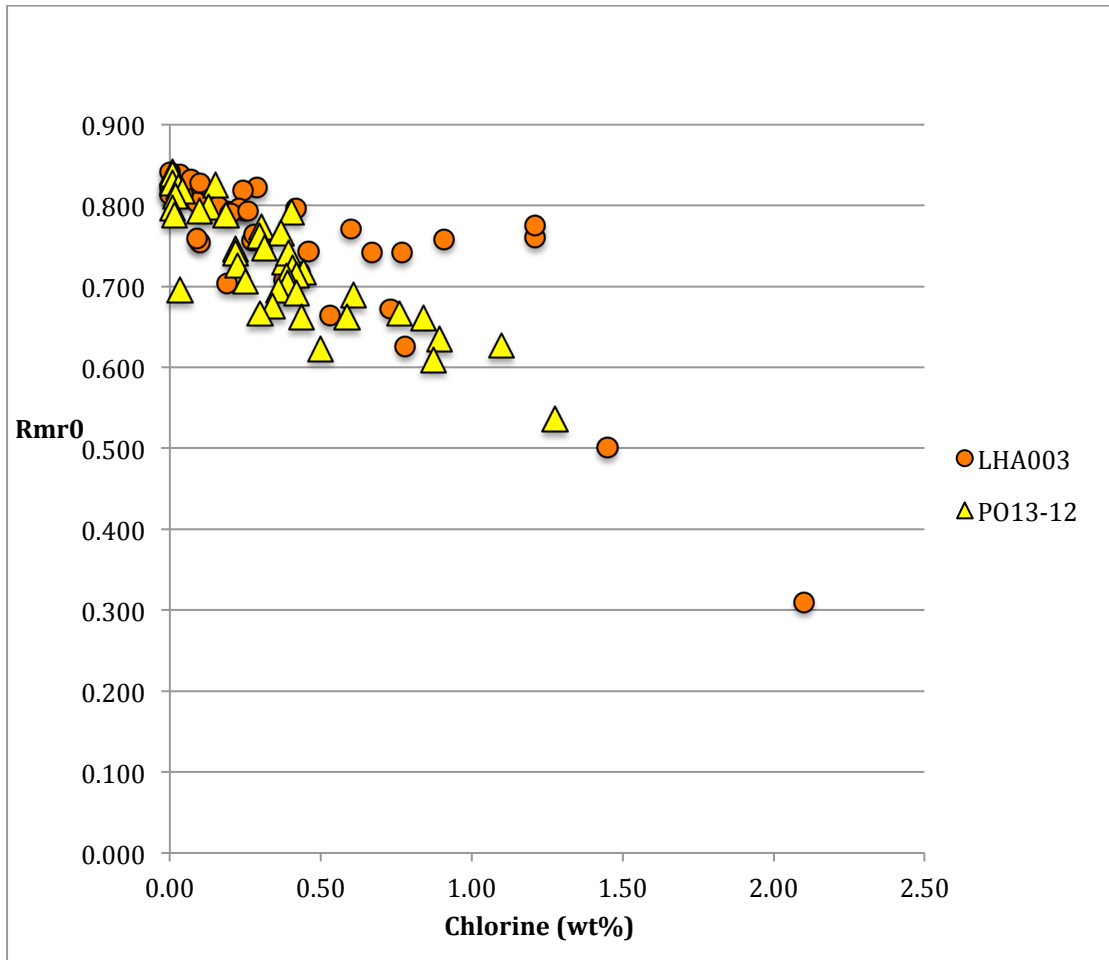




**Figure 3:** Sample P013-12 apatite EMPA analysis total versus Ca site:P site ratio (B/A apfu). ~44% of EMPA totals are outside the acceptable range. The strong correlation between low total and increasingly non-stoichiometric B/A ratio observed for sample LHA003 is less stark for this sample, but still evident. Dashed field is the range of values for the apatites used by Carlson et al (1999) to define  $\text{rnr}_0$ .



**Figure 4:** Sample PO13-12  $^{238}\text{U}/^{43}\text{Ca}$  ratio versus U (ppm) at three scales. Major excursions from a 1:1 trend at all U levels strongly suggests U-zoning.



**Figure 5:** A strong correlation is seen between Chlorine wt% and  $rmr_0$  indicating that variation in  $rmr_0$  largely results from variation in chlorine content (values taken from Tables D1, D2 and Elemental oxide data tables of Issler et al, 2021).

Major excursions from the general trend, especially for sample LHA003, are attributed to the very poor EMPA analyses for this sample.