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.

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Barbarand et al. (2003) reported results of a detailed study of the effect of apatite composition on the annealing of fission tracks in apatite, in which they investigated the reduction in mean track length as a function of temperature and time in a suite of 13 apatites, each sample being well characterised in terms of chemical composition and crystalline structure. They also investigated the linkage between composition and structure. They summarise their results through the statement (p. 131) - "This study has shown that variation in FT annealing is correlated with the apatite cell parameters, and thus is linked to crystalline structure, which, in turn, is controlled by apatite composition.", and a subsequent conclusion (p. 134) - "for any given period and temperature of heating, the degree of FT annealing shows a well-developed correlation with composition as represented by the unit-cell parameters". While accepting that the chlorine content of an apatite grain exerts the dominant compositional control on both cell parameters and annealing sensitivity, in support of previous studies, Barbarand et al. (2003) downplay the importance of this control, particularly at low levels of Cl, suggesting, for example, that rare earth elements are also important in controlling annealing rates in such samples. They also raise a number of objections to practical application of Cl content as an indicator of differential annealing response, claiming that an alternative approach is required (p. 132). On the basis of a correlation between cell parameter and etch pit size (their Figure 10b), Barbarand et al. (2003) conclude that ".. etch pit size appears a good measure of relative unit cell size and, accordingly, a feasible means of assessing annealing rate of an individual apatite grain.". Based on their experimental results, they go on to suggest (p. 135) that "…etch pit size is a valuable estimator of annealing rate of an individual apatite grain…".

These conclusions are justified by plots of data from just three annealing conditions, out of a total of 20 employed in the study. In the following, we show that systematic investigation of the results from a larger number of the annealing conditions reported by Barbarand et al. (2003) leads to a very different conclusion, namely that etch pit size is a very poor estimator of annealing properties, whereas, with one or two exceptions, annealing sensitivity shows an excellent correlation with wt% Cl. While we focus discussion on results from eight annealing temperatures for one heating interval, results from the remaining conditions studied by Barbarand et al. (2003) show the same features as those discussed here.

Figure 1 shows the relationship between mean track length and wt% Cl observed in thirteen samples after heating for ten hours at eight annealing temperatures, from the data reported by Barbarand et al. (2003). These conditions span the transition from minor annealing to total annealing in all but one of the apatite samples employed. These plots illustrate the consistent influence exerted by the chlorine content on the degree of annealing, with the mean track length increasing progressively with increasing Cl content in the data from any particular annealing treatment. As the temperature (and therefore the degree of annealing in any particular apatite sample) increases, data from the GUN sample (with a chlorine content of 1.54 wt%) plot increasingly above the main trend, such that in the sample heated at 360°C this is the sole apatite that retains any tracks. Thus, with the exception of this sample, these results highlight a clear systematic influence of wt% Cl on the degree of annealing, for apatites containing >0.1 wt% Cl (results from apatites containing less than 0.1 wt% Cl will be discussed in more detail later).

Note that while data from some temperatures (e.g. 280 and possibly 300°C) suggest a reduction of mean track length at chlorine contents beyond ~2 wt%, as suggested by Barbarand et al. (2003) and also reported by Carlson et al (1999), results from other temperatures (e.g. 320, 335 and 345°C) suggest more of a “levelling-off” or saturation in the relationship, particularly once the results from the GUN sample are identified as anomalously high. While we do not pursue this here, this aspect of the relationship between annealing rates and Cl content clearly requires further study.

In proceeding to investigate the relationship between etch pit size and annealing rates, we divide the samples into five groups on the basis of Cl content, as shown in Figure 2 which shows etch pit size plotted against wt% Cl for the thirteen apatites. Note that although the data show an overall increase in etch pit size with wt% Cl, this relationship is by no means unique. In particular, the six samples containing <0.1 wt% Cl (Group 1) show a range of etch pit sizes from 1.6 to 3.1 microns, while this upper limit is only exceeded in the remaining samples only in the three apatites containing >1.5 wt% Cl (Groups 4 and 5).

Figure 3 shows the relationship between mean track length and mean etch pit size from the data reported by Barbarand et al. (2003), for the same eight annealing temperatures for ten hour treatments as shown in Figure 1. These plots show a very poor degree of correlation between etch pit size and mean track length, for any annealing temperature. In fact, it is clear from these plots that in apatites from Groups 1, 2 and 3 (as defined in Figure 2), containing between 0 and 0.83 wt% Cl and all characterised by similar values of etch pit size around 2 microns, the mean track lengths measured in different apatites vary widely. For each temperature, data from Group 1 plot below data from Group 2, which in turn plot below Group 3, emphasising that while the variation in mean length between different samples correlates strongly with Cl content for each annealing treatment (Figure 1), it shows very little, if any, systematic relationship with etch pit size. Therefore, contrary to the conclusion reached by Barbarand et al. (2003), these results show very clearly that etch pit size provides a very poor measure of the annealing sensitivity of any particular apatite.

Returning to the question of annealing behaviour in apatites containing <0.1 wt% Cl, Figure 4 shows the results from Figure 1 plotted on a logarithmic wt% Cl scale. Again contrary to the observations of Barbarand et al. (2003), these plots suggest that even at very low levels of Cl content, the relationship between the degree of annealing (i.e. mean track length) and wt% Cl is consistent and systematic, with only results from sample MIN showing systematic departures from the main trend at values <0.1 wt% Cl. Thus, on the basis of Figures 1 and 4, we conclude that Cl content exerts a primary, systematic influence on annealing sensitivity, while as yet unrecognised second-order influences (as represented by samples MIN and GUN) also contribute some degree of scatter about this relationship. Table 1 of Barbarand et al. (2003) shows that sample MIN has the highest S content of any of the apatites studied, which might possibly contribute to the anomalously high retentivity of this apatite compared to the main dataset, but sample GUN shows no characteristics that might afford a similar explanation.

Although it is not explicit in their text, Barbarand et al. (2003) appear to conclude that the primary control on annealing rates in different apatites is the variation in crystal structure, which they suggest may be proxied by either Cl content or etch pit size (their Figure 10). However, the exact nature of the processes responsible for fission track annealing remain unknown, and there seems no *a priori* reason why Cl content, rather than crystal structure, should not exert the most direct control on annealing rates. In this case, the apparent correlations between annealing sensitivity and crystal structure (Barbarand et al., Figure 3), as well as the much weaker correlation between annealing sensitivity and etch pit size (Barbarand et al., Figure 10) would simply represent indirect correlations introduced by the mutual relationships between these parameters and wt% Cl.

To examine this point further, Figure 5 shows the relationship between mean track length and cell parameter *a* from the data reported by Barbarand et al. (2003), for the same eight annealing temperatures for ten hour treatments as shown in Figures 1, 3 and 4. Visual comparison of Figures 3, 4 and 5 is sufficient to establish that the relationships between annealing sensitivity and either wt% Cl or cell parameter *a* show generally similar levels of consistency, whereas the degree of correlation between annealing sensitivity and etch pit size is much lower. While these observations do not prove a direct influence of one parameter on the other, it remains feasible that the Cl content of an apatite does indeed exert a direct control on annealing rates, (possibly through the effect of the presence of Cl ions on diffusion rates of displaced atoms back to their original lattice sites), and that the apparent link between annealing rates and structure may be simply an indirect correlation introduced by their mutual link to Cl content.

In addition to chlorine, other elements must clearly also significantly affect annealing rates, as illustrated by the more retentive behaviour of apatites GUN and MIN compared to the overall trend in Figures 1 and 4. Carlson et al. (1999) described an experimental study of annealing kinetics in a number of different apatites, similar to that described by Barbarand et al. (2003), in which they also showed that Cl was the dominant compositional control but also reported unusual annealing sensitivities in apatites containing relatively large amounts of Sr and Mn.

But in practise, it remains to be established exactly how important such second-order effects are likely to be, in terms of routine application of apatite fission track analysis, since apatites with such unusual compositions appear to be rare in accessory or detrital grains separated from most rock types. As one illustration of this point, fission track ages in individual apatite grains from eight samples at different depths from the Fresne-1 well in the Taranaki basin (Crowhurst et al., 2002) vary systematically with wt% Cl, with only three grains out of over 200 apatite grains analysed showing a significant departure from the consistent relationship with Cl content.

The dataset presented by Crowhurst et al. (2002) highlights the unique sensitivity of wt% Cl in revealing differential annealing rates within apatites separated from individual rock samples, with data from a number of samples showing significant variation in fission track ages which correlates closely with Cl content over a range in compositions from 0.0 to 0.4 wt% Cl. The results shown here suggest that attempting to use etch pit size to resolve differential annealing behaviour in this suite of apatites would be unsuccessful, since the total range in etch pit sizes in Figure 2 corresponding to this range in wt% Cl is less than that shown by apatites containing <0.1 wt% Cl.

In conclusion, we suggest that the results reported by Barbarand et al. (2003), when investigated systematically and objectively, lead to a very different conclusion compared to that reached by the authors, namely that mean etch pit size provides a very poor estimator of the annealing sensitivity of a particular apatite species, whereas measurement of Cl content provides a reliable (and the only practicable) method of describing the differential annealing sensitivity of different apatite species.

Barbarand et al. (2003) are to be congratulated for emphasising the important and systematic influence exerted by apatite composition on the kinetics of fission track annealing, but they failed to draw attention to the practical implications of this observation. Most typical concentrates of accessory and detrital apatites derived from crystalline and sedimentary rocks contain a spread of Cl contents in the range 0.0 to at least 0.5 wt% and often as high as 1 wt%

Cl (e.g. O'Sullivan and Parrish, 1995; Argent et al, 2002; Crowhurst et al., 2002; Green, 2002; Green et al, 2002). The results presented by Barbarand et al. (2003) clearly illustrate a major differential annealing effect across this range of Cl contents, and it should therefore be clear that failure to take into account such effects within individual samples when extracting thermal history information from fission track data will produce major errors. In particular, this effectively invalidates any interpretation drawn from quantitative modelling of fission track parameters in accessory or detrital apatites using a mono-compositional annealing model such as the Laslett et al. (1987) model, commonly used in the majority of published apatite fission track studies.

References

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Figure 1: Mean track length in thirteen apatites heated at various temperatures (as shown) for 10 hours, plotted against chlorine content, taken from Barbarand et al. (2003).

Figure 2: Relationship between mean etch pit size (Dpar, in microns) and wt% Cl for thirteen apatite samples, from Barbarand et al. (2003), showing the division of samples into five groups as discussed in the text.

Figure 3: Mean track length in thirteen apatites heated at various temperatures (as shown) for 10 hours, plotted against mean etch pit size (Dpar), taken from Barbarand et al. (2003).

Figure 4: Mean track length in thirteen apatites heated at various temperatures (as shown) for 10 hours, plotted against chlorine content, taken from Barbarand et al. (2003), as in Figure 1, but with a logarithmic scale for wt% Cl. This plot highlights the systematic variation of annealing sensitivity with chlorine content even at very low values of wt% Cl.

Figure 5: Mean track length in thirteen apatites heated at various temperatures (as shown) for 10 hours, plotted against cell parameter a, taken from Barbarand et al. (2003).

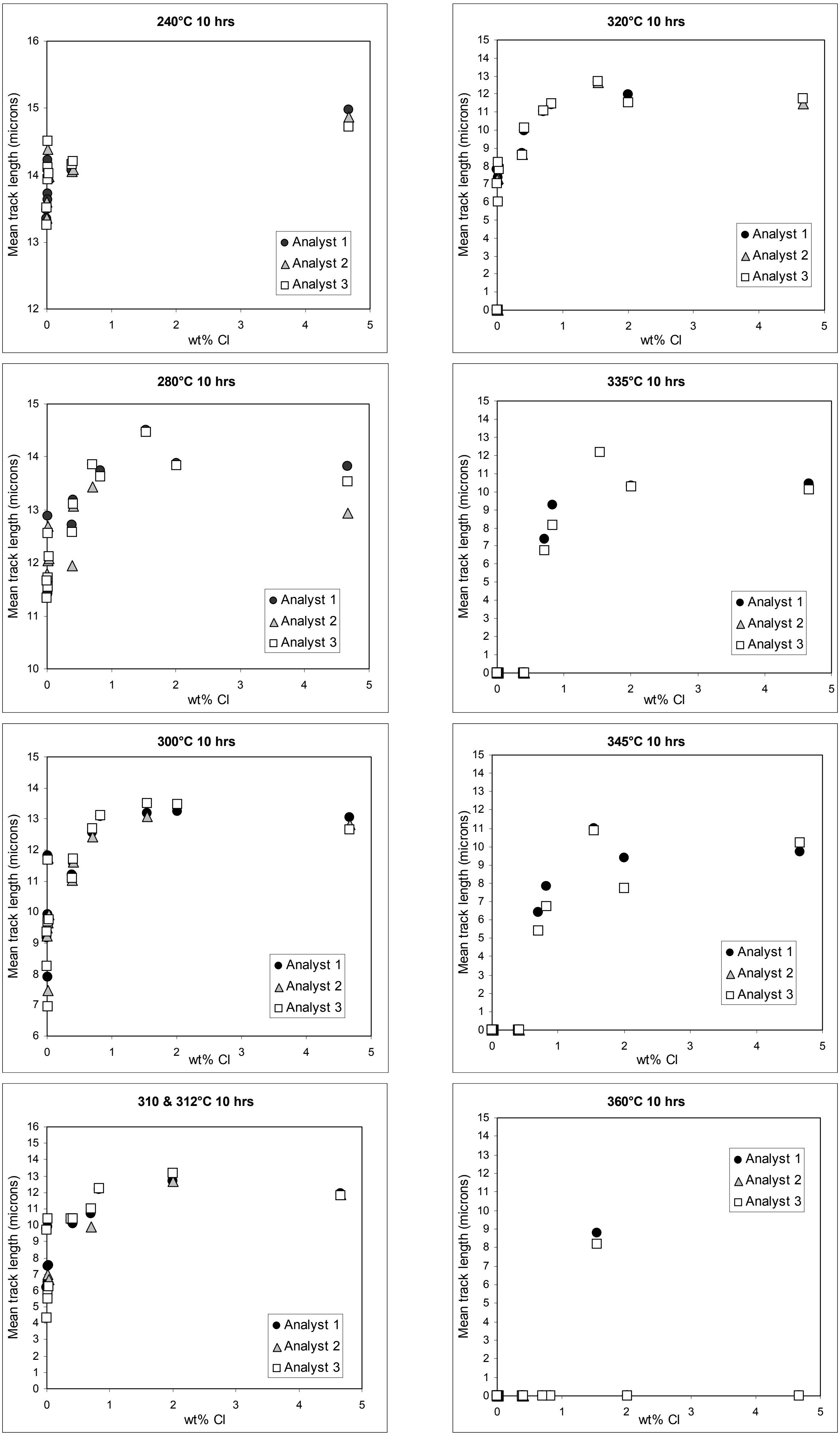
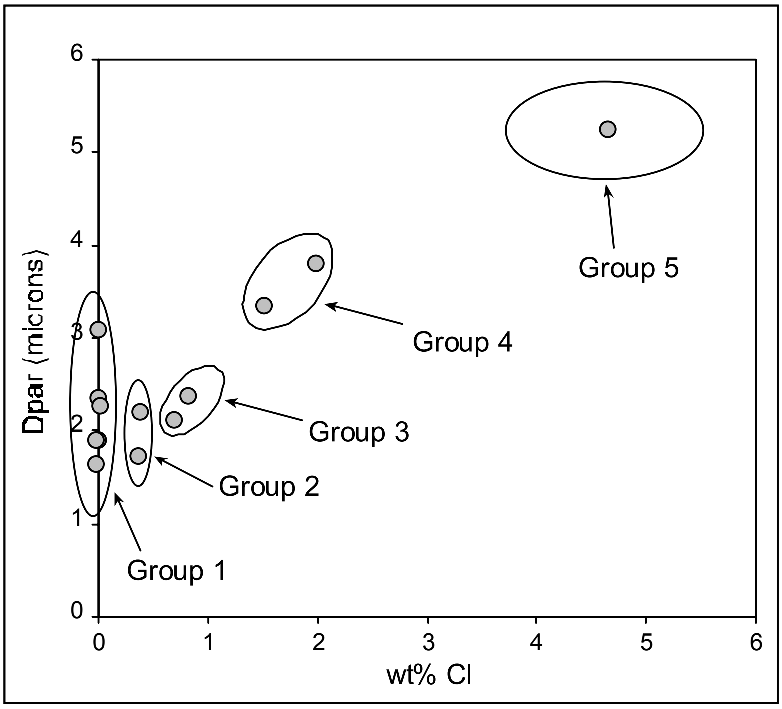

240°C 10 hrs
320°C 10 hrs
280°C 10 hrs
335°C 10 hrs
300°C 10 hrs
345°C 10 hrs
310 & 312°C 10 hrs
360°C 10 hrs
Mean track length (microns)
wt% Cl
● Analyst 1
△ Analyst 2
□ Analyst 3
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Figure 1:



Dpar (microns)
wt% Cl
0
1
2
3
4
5
6
0
1
2
3
4
5
6
Group 1
Group 2
Group 3
Group 4
Group 5

Figure 2

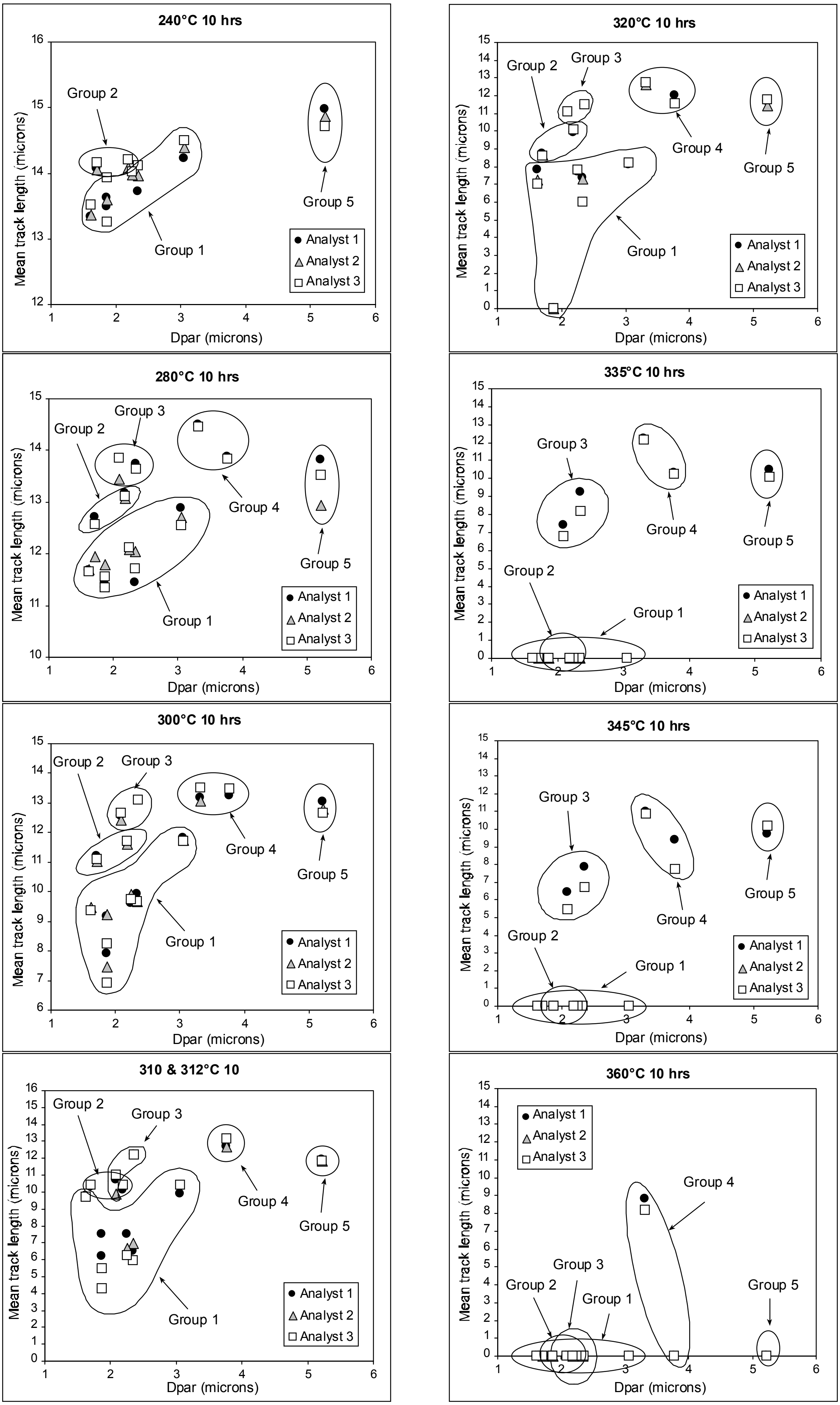

240°C 10 hrs
280°C 10 hrs
300°C 10 hrs
310 & 312°C 10
320°C 10 hrs
335°C 10 hrs
345°C 10 hrs
360°C 10 hrs
Mean track length (microns)
Dpar (microns)
Group 1
Group 2
Group 3
Group 4
Group 5
Analyst 1
Analyst 2
Analyst 3

Figure 3

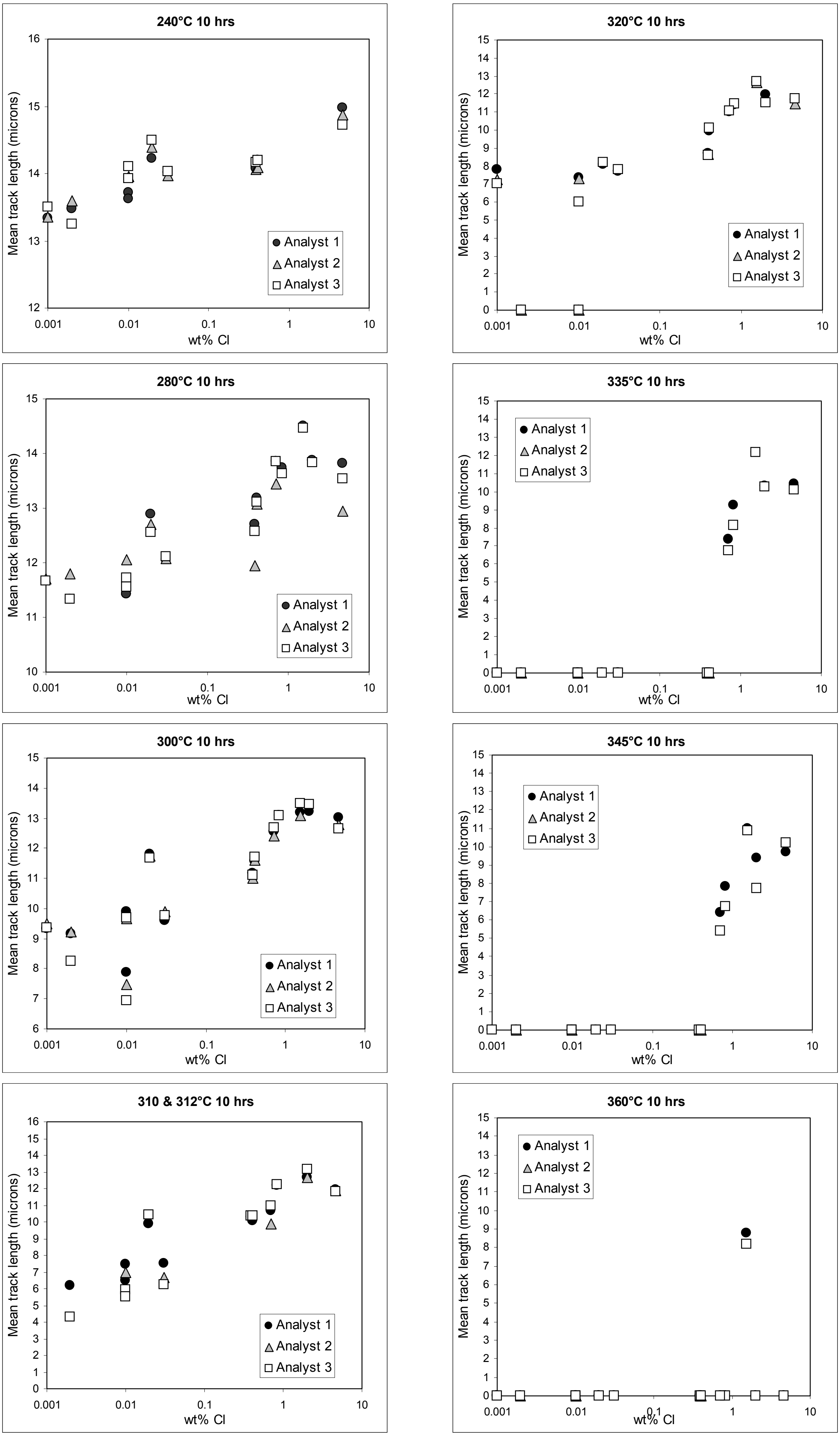

240°C 10 hrs
320°C 10 hrs
280°C 10 hrs
335°C 10 hrs
300°C 10 hrs
345°C 10 hrs
310 & 312°C 10 hrs
360°C 10 hrs
Mean track length (microns)
wt% Cl
0.001
0.01
0.1
1
10
● Analyst 1
△ Analyst 2
□ Analyst 3

Figure 4

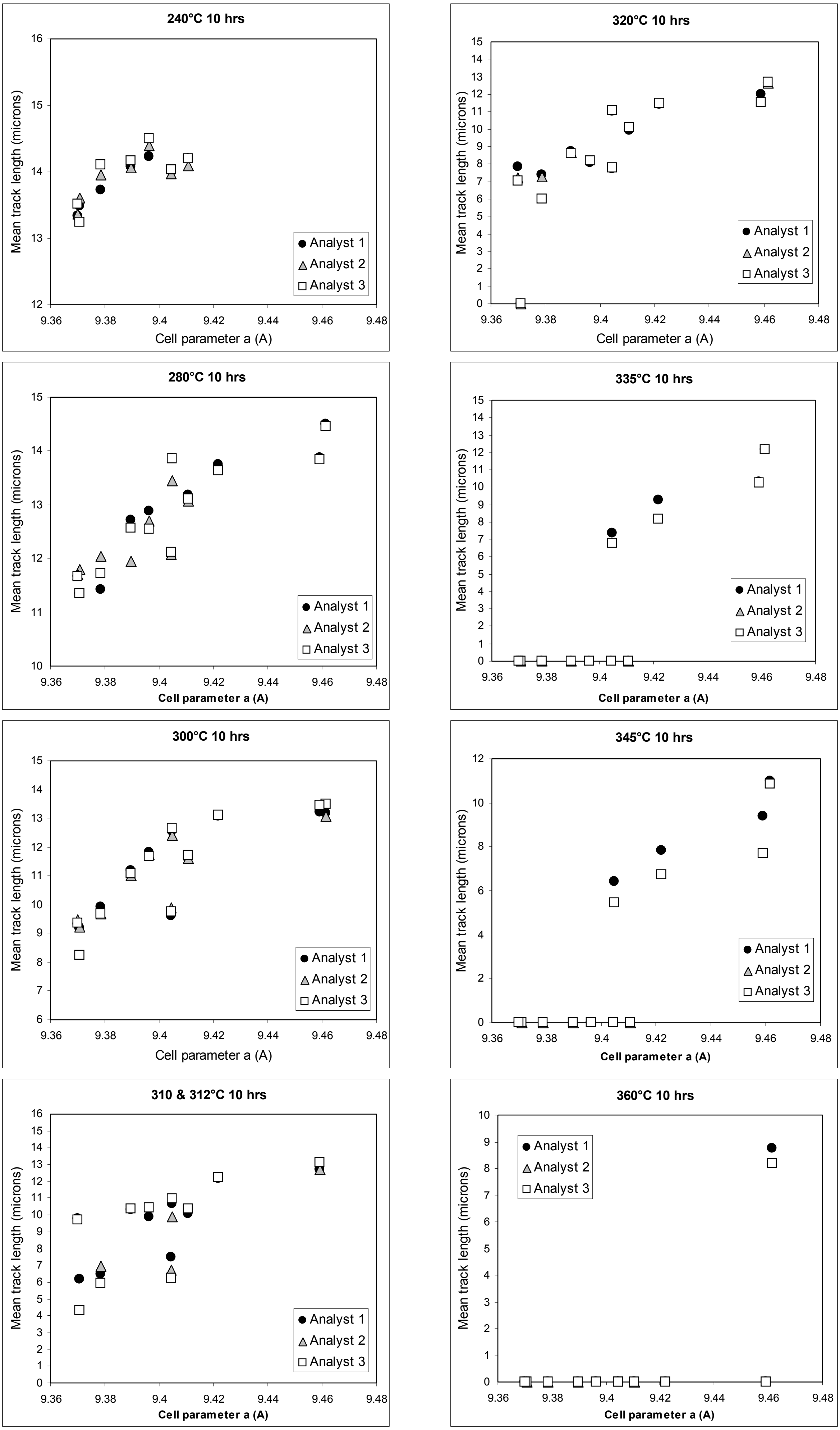

240°C 10 hrs
Mean track length (microns)
16
15
14
13
12
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
320°C 10 hrs
Mean track length (microns)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
280°C 10 hrs
Mean track length (microns)
15
14
13
12
11
10
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
335°C 10 hrs
Mean track length (microns)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
300°C 10 hrs
Mean track length (microns)
15
14
13
12
11
10
9
8
7
6
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
345°C 10 hrs
Mean track length (microns)
12
10
8
6
4
2
0
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
310 & 312°C 10 hrs
Mean track length (microns)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3
360°C 10 hrs
Mean track length (microns)
10
9
8
7
6
5
4
3
2
1
0
9.36
9.38
9.4
9.42
9.44
9.46
9.48
Cell parameter a (A)
● Analyst 1
△ Analyst 2
□ Analyst 3

Figure 5