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Mechanisms and kinetics of apatite fission-track annealing—Discussion

PAUL F. GREEN, GEOFF M. LASLETT, IAN R. DUDDY
Geotrack International Pty Ltd., P.O. Box 4120, Melbourne University, Victoria 3052, Australia

Carlson (1990) proposed a model to describe the kinetics of fission-track annealing in apatite and claimed that "because this kinetic model is based on explicit physical mechanisms, extrapolations of annealing rates to the lower temperatures and longer time scales required for the interpretation of natural fission-track length distributions can be made with greater confidence than is the case for purely empirical relationships fitted to the experimental annealing data" (Carlson, 1990: abstract, final paragraph).

However, Carlson's approach actually reduces to another empirical model fitted to laboratory annealing data, designed with the specific and sole purpose of accounting for the observed temperature and time dependence of annealing. As such, Carlson's model is inherently no more reliable for the interpretation of natural data than other empirical models. In fact, Carlson's model does not give a good fit to experimental data, and its extrapolations are inconsistent with established controls on geological annealing rates.

The basis of Carlson's model is a description of the atomic-scale defect structure of an unannealed fission track in apatite, consisting of a "cylindrical zone of disruption ~11 μm long, with a width *w* of a few tens of ångströms," which is "terminated by two conical tips, each ~2.5 μm in length." During annealing the track is assumed to shrink radially inwards, resulting in a reduction in track length for geometrical reasons. When the radial shrinkage has resulted in the tapering ends being reduced to near-zero length, the track is reduced to a linear defect, which then undergoes segmentation caused by the appearance of gaps.

This design is not adopted from any a priori evidence of the nature of the latent track structure, but solely to explain aspects of fission-track behavior observed during annealing, specifically the dominant process of shrinking of tracks from their ends and the appearance in the final stages of annealing of gaps in individual tracks (Green et al., 1986). Carlson commented (p. 1123) that ". . . the particular geometry . . . has no direct basis in theory or observation," and is ". . . a simplification, one that is shown in this article to be capable of reproducing the essential features of the annealing process. . . ." Thus, Carlson's model is not designed on the basis of physical evidence but is specified on purely empirical grounds. In fact, the model does not accurately explain the detail of the observed annealing behavior reported by Green et al. (1986). Patterns of confined track length observed in progressive etching of a severely annealed sample in Figure 7 of Green et al. (1986) show that gaps appear mainly in tracks at high angles to the **c** axis (~45° or more), and that these tracks have a maximum length decreasing from ~8 to ~3 μm as the angle to the **c** axis increases to 90°.

Carlson's concept is not the only way that the shrinkage of tracks from their ends and gapping within tracks can be envisaged to occur. Considerations of track formation as summarized by Fleischer et al. (1975) suggest a model in which track etchability is controlled only by the extent to which the density of damage within the track region is greater than some threshold level. Fission fragments generally produce their highest damage density in the initial portion of their trajectory, with the degree of damage decreasing as the fission fragment penetrates increasing thicknesses of matter. Therefore the profile of damage along a fission track will be highest at the center and will fall progressively toward each end. As annealing reduces the density of damage remaining within the track core, less of the track will remain etchable, and tracks will appear to shrink from each end. Anisotropy in annealing rates will produce different maximum etchable lengths at given angles to the **c** axis. Gaps in etchability within individual tracks might result either from random fluctuations in damage density, possibly accentuated by annealing, or by some fission fragments forming with energies above the "Bragg peak" of the energy-loss curve so that the annealed damage profile might contain a natural break when reduced to near-threshold levels. Such a model would qualitatively account for all facets of the observed annealing behavior of fission tracks in apatite, but it is impossible to quantify at present because of the absence of basic data on damage densities, etchability thresholds, and the quantitative effects of annealing.

At each step in the construction of Carlson's model, his methods are dominated by empirical choices. To justify a "concave-upward" form for the radial defect distribution within individual tracks, Carlson invoked an assumption (p. 1124) that "the defect-elimination rate at fixed temperature is constant and uniform throughout the crystal." This assumption is invoked, not for any fundamental physical reasons, but solely to produce a dependence of track length on annealing time that matches that observed in experimental data. It is also important to note that there is no evidence of any link between the radius of the track and the etchable length, although this forms the keystone of Carlson's model.

Carlson introduced kinetic control to his model through his Equation 2, which relates the defect elimination rate to temperature through the usual form of the Boltzmann relationship. To convert this to a relationship linking reduction in track length, temperature, and time, it was necessary for Carlson to assume a form for the initial radial defect distribution (RDD). Again, there is no a priori evidence as to the form of this distribution, and Carlson used an empirical relationship derived from laboratory annealing data to obtain a suitable form for the initial RDD.

Carlson identified a linear relationship between the logarithm of the amount of shortening, Δl, and the logarithm of the annealing time, Δt, as shown in his Figure 3, and from this derived a form for the RDD that is consistent with that relationship. Carlson then reported a final kinetic equation to describe his model (his Eq. 5, with annealing time now written as t):

$$l_{as} = l_0 - A\left(\frac{kT}{h}\right)^n \exp\frac{-nQ}{RT} t^n. \tag{1}$$

Carlson argued (p. 1121) that this equation was derived directly from the physical model and later claimed that this equation was then verified against laboratory data by showing that they fit the above equation. However, this claim is misleading, as it is clear that Equation 1 (above) is simply an empirical relationship among length reduction, temperature, and time, derived directly from the laboratory annealing data through the relationship inferred from Carlson's Figure 3. This becomes clearer if we rewrite annealing time as Δt and recast Equation 1 as

$$\Delta l = B_1 \exp\frac{B_2}{T}(\Delta t)^n \tag{2}$$

where $\Delta l = l_0 - l_{as}$; $B_1 = A(kT/h)^n$ and $B_2 = -nQ/R$. Note that T in B_1 can be regarded as constant between ~100 and 300 °C, as explained by Carlson on page 1136. Equation 2 can then be written as

$$\ln \Delta l = C_0 + C_1 \ln \Delta t + \frac{C_2}{T} \tag{3}$$

which embodies the relationship in Carlson's Figure 3.

This relationship is the sole reason for the adoption by Carlson of his Equation 5 (Eq. 1, above) to invoke kinetic control in his model, and his model is therefore just as empirical as all previous attempts to describe relationships among degree of annealing (either track length or density reduction), annealing temperature, and time.

According to Carlson, his Equation 5 describes laboratory annealing data for lengths greater than ~11 μm, whereas below this length the dominant length-reduction process changes to one of segmentation, which produces a rapid decrease in length to zero. Carlson readily adapted his model to allow for this process by an analysis that is cast in terms of the probability of segmentation (his Eqs. 11–13). However this analysis (p. 1129–1131) essentially amounts to fitting a function to the dispersion of the data from Equation 5 at lengths <11 μm and then correcting values of length predicted using Equation 5 for this "misfit." It is therefore not surprising that the final values of length predicted by this procedure agree with the laboratory data, because this is exactly what the analysis is designed to achieve. The section on verification of the kinetic model for segmentation (p. 1131–1132) is entirely misleading. The agreement between observed and modeled length shown in Figure 9 provides no verification of this aspect of the model, showing only that Carlson's Equations 11–13 are internally consistent.

Evidence against Carlson's segmentation model comes from consideration of the form of track length distributions resulting from the model, which show a peak at $\sim l_{sg}$ and a flat tail to shorter lengths, since segmentation is assumed to occur with equal probability at all points along the track. This form of distribution is in clear conflict with those typically observed in heavily annealed apatite (e.g., Green et al., 1986).

A further illustration of the empirical nature of Carlson's model comes on page 1131. A value of 12 μm is adopted for the length of the cylindrical zone, rather than the value of 11 μm initially specified, because experimental annealing data give a better fit with the higher value.

On page 1136, Carlson introduced a comparison between his mechanistic model and previous empirical models and aimed to demonstrate that his kinetic equations "include the empirical parallel model of Laslett et al. (1987) as a special case." This should not be at all surprising. The original parallel model of Laslett et al. (1987), as also originally presented by Green et al. (1985), was derived by searching for empirical relationships among length reduction and annealing temperature and time. In doing so, we restricted the temperature and time terms to those involving ln t and $1/T$, as is normal in this type of analysis, because these reflect the usual type of kinetic control. We also identified the linear relationship between ln Δl and ln Δt shown in Carlson's Figure 3, which forms the basis of the introduction of kinetic control. Green et al. (1985) reported this equation in the form

$$\ln(1 - l/l_0) = A_2(T) + B_2 \ln t. \tag{4}$$

By defining an explicit form for the temperature dependence of A_2, the parallel model was obtained in its original form. Thus both Carlson's model and our parallel model were designed by equally empirical procedures on the basis of this observed relationship in the laboratory data.

Carlson (p. 1137) compared his model with our fanning model, and stated that the fanning model was introduced "in an attempt to refine [the] parallel model to produce a better fit to experimental data in the range $r' < 0.65$ ($l < \sim 11$ μm)." This statement is incorrect. In Laslett et al. (1987), we introduced the parallel and fanning Arrhenius plot models as rival options to describe the data shown in Figure 1 of that paper. We then proceeded to show that, whereas the parallel model gives quite a good fit to the data, the fanning model gives a better fit.

The key point here is that the fanning model gives a better fit for all values of length, not just those less than ≈11 μm. Thus the fanning is not an artifact introduced

TABLE 1. Estimates of Arrhenius plot parameters, with standard errors

Param.	Est.	Std. error	Param.	Est.	Std. error	Param.	Est.	Std. error
c_1	0.2165	0.0187						
a_1	5.342	0.635	b_1	−5018.0	459.0	B_1	23184.0	1258.0
a_2	4.659	0.661	b_2	−4660.0	451.0	B_2	21530.0	1418.0
a_3	4.010	0.606	b_3	−4332.0	391.0	B_3	20012.0	1101.0
a_4	3.393	0.400	b_4	−3979.0	263.0	B_4	18384.0	674.0

by the overlap of two competing processes but is inherent in the kinetics of annealing. To demonstrate this point, we first fit a parallel model to the data from the 72 annealing experiments of Green et al. (1986), thus obtaining Equation 14 of Laslett et al. (1987):

$$\ln(1 - r) = 3.87 + 0.219(\ln t - 19270/T) \quad (5)$$

where r is the fitted length reduction of tracks heated at temperature T for time t. We then use this equation to define conditions of temperature and time, which divide the data into four groups, and fit a parallel model separately to each group. If the overall model (Eq. 5, above) is correct, the four models should agree with each other and with Equation 5. Not only do we discover significant disagreement, but the pattern of departure is distinctive. The group boundaries are chosen to have about the same numbers in each, thus Group 1: $r < 0.7$; Group 2: $0.7 \leq r < 0.8$; Group 3: $0.8 \leq r < 0.9$; and Group 4: $0.9 \leq r$. We then fit parallel models separately to each group, by fitting (by linear regression) the model

$$\ln(1 - r_i) = c_1 \ln t_i + \sum_{g=1}^{4} \delta_{ig}a_g + \sum_{g=1}^{4} \delta_{ig}b_g/T_i + \epsilon_i \quad (6)$$

for $i = 1$–72, where r_i is the observed length reduction in experiment i, a_g, b_g, $g = 1$–4, and c_1 are nine unknown constants

$$\delta_{ig} = \begin{cases} 1 & \text{if experiment } i \text{ belongs to group } g \\ 0 & \text{otherwise} \end{cases}$$

and $\{\epsilon_i = 1\text{–}72\}$ are independent errors with mean 0 and variance σ^2.

The variance σ^2 encompasses errors in r_i caused by several sources of variation: the natural variability of lengths of fission tracks, slight variations in etching strength of acid or the temperature of the etchant, observer effects, and a variety of more subtle effects as discussed, for example, by Galbraith et al. (1990). (This exploratory model is physically imperfect, in that some crossing over of contour lines is possible in the vicinity of group boundaries. We took this approach in order to stabilize the estimation of σ^2 by maximizing the residual degrees of freedom.) The Arrhenius plot slope B_g for each group was estimated as $B_g = -b_g/c_1$; results are summarized in Table 1. Standard errors for B_1–B_4 were obtained by invoking the standard formula for the error of a ratio. The estimated slopes suggest a monotonic change with length reduction r. Laslett et al. (1987) proposed the common origin model as one simple model that captured this monotonic trend.

Statistically, testing for $H_0{:}b_1 = b_2 = b_3 = b_4$ (and hence $B_1 = B_2 = B_3 = B_4$; i.e., a parallel model) against the general alternative $H_1{:}b_g$ unequal within Equation 6, above, leads to rejection of the null hypothesis H_0 at the 0.8% level. Testing for $H_0{:}b_2 = b_3 = b_4$ leads to rejection of the hypothesis only at the 9.2% level. Thus, an alternative interpretation might be that a parallel model applies for $r > 0.7$ (that is, for lengths >11.2 μm), with evidence for fanning only provided by heavily annealed data (lengths <11.2 μm). However, if we replace the general alternative by the specific alternative $H_1{:}b_g$ changes linearly with g ($b_2 = b_3 + \Delta$, $b_4 = b_3 - \Delta$), the test for H_0: $b_2 = b_3 = b_4$ is significant at the 2.8% level, instead of the 9.2% level. Thus the fanning appears to be inherent in the data at all lengths, not only <11 μm.

We can further examine Carlson's claims by applying his model for lengths ≥ 11 μm to the data of Green et al. (1986). Figure 1a shows a plot of residuals vs. fitted values for Carlson's model with $n = 0.206$, $A = 1.81$, $Q = 40.6$ (from Carlson's Table 2). If his model and parameters are adequate, this scatterplot would be flat (with mean 0) from 16 to 11 μm, and would then increase to shorter lengths because of the increasing incidence of gaps. However, a distinctive quadratic style trend is seen, and the model clearly does not give a good fit for any range of lengths.

The same problem can be seen in Carlson's Figures 6, 7, and 8, where distinct curvature is present within the trend of the data in all three figures. Such plots are not recommended for the assessment of fit because of their capacity to disguise areas of poor fit. Figure 1b is much more sensitive: it shows the sign of Carlson's residuals on an Arrhenius plot. Most of the residuals between the 11 and 15 μm contour lines are negative, indicating a very poor fit.

The final test of the validity of rival models lies in extrapolation to geological time scales. Green et al. (1989) showed that extrapolation of the Laslett et al. (1987) fanning model gives predictions that are consistent with geological annealing data in a series of samples from the Otway Basin (southeast Australia). Laslett et al. (1987) compared the extrapolation of the parallel and fanning models and showed that the parallel model predicted greater degrees of annealing in geological conditions than those predicted by the fanning model. Thus the fanning model not only fits laboratory data better than the parallel model but also gives much better agreement in geological conditions. Because Carlson's model for mean lengths >11 μm is essentially identical to the parallel model, his model will be equally deficient.

There are also numerous errors and misunderstandings evident in Carlson's discussion, particularly on the subject of the equivalent time concept (Goswami et al., 1984) employed by Duddy et al. (1988) to account for variable temperature annealing of fission tracks in apatite. Carlson stated (p. 1137) that "variable-temperature histories have been treated in earlier work by invoking the concept of equivalent time. . . . This difficulty does not arise in the case of the present model. . . ." However, use of equivalent time constitutes no difficulty. It simply assumes that at any time, the rate of annealing is determined only by the amount of annealing that has already occurred and the prevailing temperature. Prior history, i.e., the temperature-time conditions that produced the present degree of annealing, is assumed to have no effect. Similar assumptions are implicit in integrating any differential kinetic equation through variable temperature-time histories, as for instance in the use of Carlson's Equation 4 and its variants.

Carlson also commented that "in the context of this physical model, it becomes evident that the successive recalculations of equivalent time employed by Duddy et al. (1988) to treat nonisothermal annealing are in fact a coarse approximation to a numerical evaluation of the time-temperature integral that appears in Equation 4." In fact, a complete discussion of this point is given in the appendix to Duddy et al. (1988). There it is shown that length reductions calculated by equivalent time and by the time-temperature integral (A-7) are identical for parallel models, in which the differential form of the length reduction equation is separable. For fanning models in which the differential form is not separable, the integration may need to be done numerically, and Duddy et al. (1988) explained that their approach constituted one such numerical method, with several advantages over rival methods. The approximation is in no sense coarse, as Carlson states. Indeed, Duddy et al. (1988) stressed that it gives exact answers for stepped temperature histories.

On page 1135, Carlson apparently did not appreciate that length bias (Laslett et al., 1982) is a fundamental geometrical property of all tracks of different length, which must always be accounted for.

On page 1136, Carlson states that the abrupt increase in the standard deviation of the track length distribution during annealing as mean lengths are reduced below ~11 μm cannot be ascribed, even in part, to the effects of annealing anisotropy, contrary to the conclusions of Green et al. (1986). Galbraith and Laslett (1988, Section 6b and Fig. 5) examined this issue quantitatively using data from two different annealing experiments and concluded that the observed annealing anisotropy can account almost completely for the observed relationship between the standard deviation of the track length distribution and the mean track length.

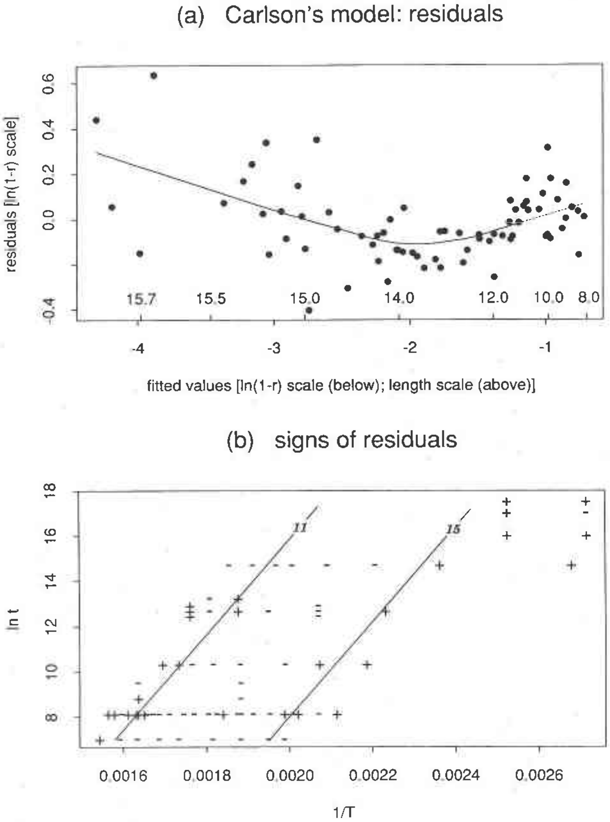

Fig. 1. Residuals from Carlson's model applied to the laboratory annealing data of Green et al. (1986); (**a**) residuals against fitted values: the trend is highlighted by Cleveland's (1979) robust scatterplot smoother, displayed as a solid line at lengths >11 μm, and as a dotted line otherwise; (**b**) signs of residuals in Arrhenius plot, with contours for length reduction to 15 and 11 μm predicted from Carlson's model.

Carlson's statement is without foundation because no independent knowledge exists of the inherent form of the anisotropic annealing function. Inspection of the plots of confined track length against angle to the *c* axis such as those in Green et al. (1986) clearly show that anisotropy increases as the mean track length decreases. Parameterization of the length-angle data also shows this clearly (Galbraith et al, 1990, their Eq. 9), as does Carlson's Figure 11.

Carlson (p. 1136) also claimed that, compared with the initial variation in track lengths and the continuous production of tracks through time, anisotropy of annealing is comparatively unimportant in affecting the form of natural track length distributions. However, Green et al. (1989) demonstrated that the continuous production of tracks through time is relatively unimportant in this regard, the dominant factors being variation of temperature through time and the increase in the spread of lengths with increasing degree of annealing, which as noted above is due in large part to the anisotropy of annealing.

In summary, we submit that Carlson's model is as empirical as any other model for the kinetic response of fission-track annealing in apatite. Despite claims that his kinetic model is derived from a physical model for track damage and that it is verified by testing against laboratory data, it is clear that the model is derived directly from laboratory data using an empirical approach similar to that employed in all previous treatments. Physical or mechanistic aspects of Carlson's model contribute no independent kinetic control.

Carlson's model does not give a good empirical fit to laboratory data and does not give accurate extrapolations. In contrast, the fanning model of Laslett et al. (1987) not only fits laboratory data (for all values of track length), but also gives extrapolations to geological conditions that are consistent with observations (Green et al., 1989). Therefore we recommend against the use of Carlson's model for thermal history interpretation of AFTA data, and of those currently available we regard the Laslett et al. (1987) model as the most appropriate to describe all facets of fission-track annealing in apatite.

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