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# Mechanisms and kinetics of apatite fission-track annealing—Reply to Kevin D. Crowley

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## INTRODUCTION

The effort in Carlson (1990) to identify the processes involved in apatite fission-track annealing represents a fundamental departure from the purely empirical approaches that preceded it because it seeks to provide a physical basis for the formulation of annealing-rate equations. Although much is still unknown about the nature of latent fission tracks and annealing mechanisms, this reply reemphasizes that the model of Carlson (1990) is solidly grounded on wholly justifiable postulates and is capable of reproducing experimental measurements—including newly published data—to a high degree of accuracy.

## RATE LAWS FOR DEFECT ELIMINATION

Too little is presently known about the defect-elimination process to make a definitive choice among possible rate laws, any one of which represents considerable idealization of a very complex natural process. I adopted in the original article the simplest formulation capable of accounting for the experimental data.

The theories of Fletcher and Brown (1953) and Waite (1957a), cited by Crowley (1993) in support of first- or second-order kinetics for defect elimination, are not applicable to the annealing of fission tracks; they treat only isolated, randomly disposed defects resulting from electron bombardment of semiconductors. The highly localized arrays of interacting defects that make up heavy-particle tracks are explicitly excluded from consideration both in the theoretical treatments (Fletcher and Brown, 1953, p. 585; Waite, 1957a, p. 463) and in their companion articles that apply the theory to Ge semiconductors (Brown et al., 1953, p. 591; Waite, 1957b, p. 472). The theoretical treatise of Gold et al. (1981) might someday provide a sophisticated alternative that is directly applicable to heavy-particle tracks, but the theory remains unconfirmed by experiment, and none of its numerous parameters can be quantified. There exists, therefore, no compelling evidence in favor of any particular rate law for defect elimination in apatite fission tracks.

One must then ask what level of complexity is justifiable in formulating annealing models. Rigorous incorporation of even a first-order rate law would require quantification of both the defect density at the core of the disrupted zone ($N_0$) and the etching-threshold value of the defect density ($N^*$). Given the impossibility at present of quantifying those values, I chose not to incorporate them as additional parameters, largely because they appear to be unnecessary: a zero-order rate law satisfies the experimental constraints to a high degree of accuracy. It appears, in fact, that the overall annealing kinetics may be relatively insensitive to the precise form of the defect-elimination rate because there is no qualitative difference in the shortening response of the system under higher order rate laws. Whereas a zero-order rate law predicts a downward shift of the radial defect distribution (RDD) without a change in shape, higher order rate laws simply predict that the RDD will flatten somewhat as it shifts down. But because positive curvature of the RDD is maintained, the predominant kinetic effect is the same, namely a rapid decrease in the rate of axial shortening with time in an isothermal anneal.

So although a zero-order formulation may be rudimentary, it is by no means physically invalid. The ability of this approach to account for a wide variety of observations and experimental measurements demonstrates that the model does not simplify the process beyond the generation of useful results.

## AGREEMENT BETWEEN MODEL PREDICTION AND EXPERIMENT

Crowley's assertion that the model of Carlson (1990) does not provide adequate fits to the laboratory data relies upon an overly optimistic assessment of the experimental uncertainty. In fact, it rests upon calculations utilizing the minimum possible value for this error. The statistical analysis he offers may therefore be misleading because the actual uncertainty in the experimental determinations of annealing rate cannot be reliably established from the data presently available.

In Crowley's analysis, the goodness of fit of a model is evaluated by comparing the residual variance of the fit to the variance of the data on track-length measurements. The variance of the data in this scheme is computed solely on the basis of the standard deviations of track-length measurements in individual (unreplicated) experiments, not upon the variation in measured lengths among several nominally identical replications of the same experiment. It is therefore an estimate merely of the error involved in the track-measurement procedure; it can be only a minimum value for the overall uncertainty in experimental determination of annealing rates. Additional uncertainties arise from the numerous vagaries of the etching process (which may contribute variations between otherwise identical experiments on the order of a micrometer or so), from variations in the bulk composition and the preannealing treatment of the experimental materials and from inaccuracy and instability in experi-

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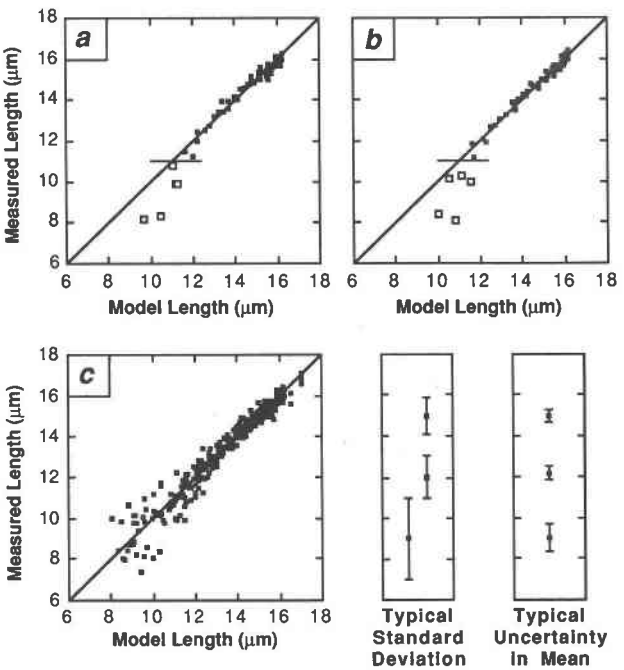


Fig. 1. Comparison of mean measured track lengths and track lengths predicted by the model of Carlson (1990). Exact correspondence between measurement and model would produce data falling on the horizontal line. Values of parameters used to produce these fits are given in the text. (**a**) Data from Crowley et al. (1991) on (low strontium) fluorapatite, compared with a model considering only an axial-shortening mechanism. Data below the short horizontal line at 11 μm (open squares) indicate the onset of track segmentation. (**b**) Data from Crowley et al. (1991) on strontian fluorapatite, compared with a model considering only an axial-shortening mechanism. Data below the short horizontal line at 11 μm (open squares) indicate the onset of track segmentation. (**c**) Composite of all published data sets: Green et al. (1986), Donelick (1988, 1991), Duddy et al. (1988), and Crowley et al. (1991). This diagram includes both the axial-shortening and track-segmentation stages of the model.

mental temperature. In determining the rate of annealing at a given time and temperature, each of these factors contributes errors over and above those associated solely with the error in measurement of track lengths in each individual case. A valid assessment of the actual experimental uncertainty will require examination of the variability found in multiple replications of experiments, replications that regenerate the entire experimental process independently from beginning to end. Until the degree of reproducibility of experimental determinations of annealing rate can be quantified in this way, statistical analyses like those presented in Crowley's discussion threaten to overinterpret the data and must be evaluated with great caution.

Nevertheless, I freely acknowledge that the fits of my model to the data are imperfect and that the presence of structure in the residuals may have significance. Although such structure is most apparent in the D88 data set, similar but less pronounced structure is present in the residuals for all data sets. This may be seen in Figure 6 of the original article and in Figure 1 of this reply: there is a slight tendency for the model to overestimate track lengths in the range $\sim 13\ \mu m < l < \sim 15\ \mu m$ and to underestimate them elsewhere. These minor discrepancies are consistent with a more Gaussian-like shape for the RDD than the power-law shape that I chose in the original formulation for its mathematical simplicity and, more pointedly, to generate the unusual terms in ln $t$ that appear in published empirical models. A Gaussian shape for the RDD assigns lower defect densities at the radially distant parts of the disrupted zone and higher densities near the radial center; a Gaussian RDD would therefore yield more rapid early annealing and slower later annealing. Thus, structure in the residuals should be diminished and the overall fit should be improved, if one were to adopt a Gaussian shape for the RDD; other possible shapes should also be considered.

After the original model appeared, Crowley et al. (1991) published additional data that invite further evaluation of the extent of agreement between experiment and model prediction. (A preprint containing these data was generously made available to me by the authors prior to its publication and while my model was under development, as acknowledged in the original article.) The data set for the low strontium fluorapatite from Crowley et al. (1991) is fit by a model using $Q = 41.1$ kcal/mol, $n = 0.151$, and $A = 2.57\ \mu m$ to the level of agreement seen in Figure 1a; the data set for the strontian fluorapatite is fit by a model using $Q = 43.2$ kcal/mol, $n = 0.137$, and $A = 3.17\ \mu m$ to the level of agreement seen in Figure 1b. The fits are comparable in quality to the fits to the earlier data sets achieved in the original article. These new data also conform to the model's predictions of the relationship between mean track length and the dispersion of the track-length distribution, as seen in Figure 2. When all five data sets that have so far been published are combined under a composite model with $Q = 44.4$ kcal/mol, $n = 0.140$, and $A = 3.48\ \mu m$, the level of agreement displayed in Figure 1c is generated. It is evident that despite increased disparities in experimental procedure and variations in composition of starting materials, excellent correspondence between model and observation remains.

## Annealing at High Temperatures

Crowley faults the model of Carlson (1990) because he believes that it predicts that etchable fission tracks are "stable at infinitely high temperatures." In fact, the model calculates that etchable tracks will persist isothermally for times longer than 1 s only at temperatures below ~700 °C; they will persist isothermally for times longer than 1 yr only at temperatures below ~275 °C. At the melting point of apatite, etchable tracks are predicted by the model to persist for merely ~10 μs. I submit that these predictions are more reasonable than an approach that completely precludes the formation of tracks above some critical temperature. After all, U atoms still decay by fission at high temperatures, and the passage of their fission

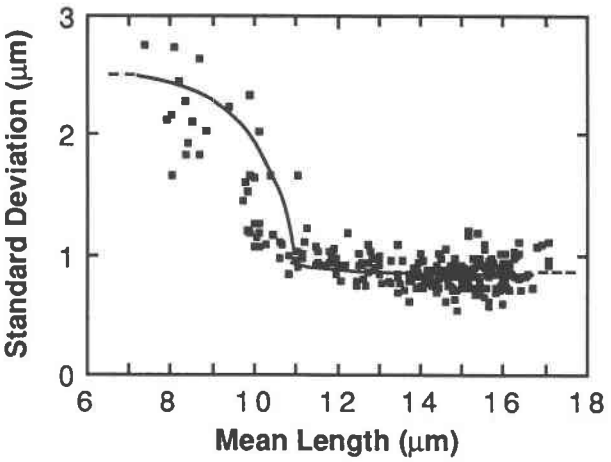


Fig. 2. Relationship between mean track length and dispersion (estimated standard deviation) of the track-length measurements. Squares are the data of Green et al. (1986), Donelick (1988, 1991), Duddy et al. (1988), and Crowley et al. (1991). Curves passing through the field of data points indicate the length-dispersion relation produced in a simulation employing the annealing model of Carlson (1990; see description therein).

fragments must still damage the crystalline structure. I therefore prefer a model that allows for generation and very rapid elimination of disrupted zones at high temperature over a proposal that denies altogether the production of a disrupted zone above some critical temperature. Contrary to Crowley's claim, Figures 1 and 2 show that the model is in excellent agreement with the observed annealing behavior of tracks in the laboratory.

As for infinitely high temperatures and temperatures that exceed the melting point of apatite, it should suffice to note that any attempt to apply any fission-track annealing model at such temperatures disregards entirely the physical mechanisms involved.

## Conclusions

The most fundamental issue still remains. Is it valid to presume that the model with the most favorable goodness-of-fit statistic is thereby superior to all others, without regard for the question of whether or not any of the adjustable parameters has physical meaning? It is here that the greatest disagreement—one that may be largely philosophical—arises between Crowley's approach and mine: I reject as shortsighted the notion that goodness of fit alone renders any empirical model scientifically more valuable than a model rooted in a physical description of the annealing process. Empirically derived equations are surely a useful means of interpolating accurately within experimentally determined limits. But deeper understanding lies in recognition of the processes involved. Because empirical approaches ignore the need for a knowledge of mechanism, all such descriptions remain purely mathematical constructs, without any solid physical foundation. This ultimately reduces them to exercises in statistics and curve fitting. An absolutely essential complement to empirical formulations is the attempt to develop models that give physical meaning to the parameters employed.

Developing a detailed physical description of fission-track annealing mechanisms is sure to be a long and difficult task. The inaugural attempt in Carlson (1990) produces good yet imperfect fits to the data, which emphasizes that the model serves only to initiate the search for an understanding of mechanism; it does not complete it. Nevertheless, the model accords well with present knowledge of the process at the atomic scale, with experiment, and with observation. The level of agreement displayed in Figures 1 and 2 of this reply, combined with the many other congruencies between prediction and observation described in the original work, simply cannot be mere coincidence. Instead, they are evidence that the model constitutes a meaningful departure point for the challenging pursuit of progressively more elaborate and more accurate physical descriptions of apatite fission-track annealing.

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