# Mechanisms and kinetics of apatite fission-track annealing—Reply to Green et al.

## WILLIAM D. CARLSON

Department of Geological Sciences, University of Texas at Austin, Austin, Texas 78712, U.S.A.

## INTRODUCTION

One issue of overriding importance deserves attention before we delve into the details of the discussion presented by Green et al. (1993). The principal purpose of my original article was to contribute to our mineralogical understanding of the atomic-scale phenomena essential to fission-track annealing. The work was emphatically not a further attempt to find those equations and parameters that replicate the experimental data with the smallest possible residuals, without regard for the form of the equations or the number or meaning of the variable parameters employed. Instead, my effort was directed at a different goal, namely to answer this question: What physical mechanisms and processes are responsible for the experimentally observed variations in annealing rate as a function of time, temperature, apatite composition, and track orientation?

The outcome was the intriguing discovery that one can begin with a set of postulates, all consistent with our present knowledge of atomic-scale phenomena, and derive from them a rate expression that matches closely the statistical best-fit models in their simpler forms (the parallel model of Laslett et al., 1987, for example). This result supports and reinforces the data-fitting efforts of Green and others because it demonstrates that the mathematical formulations they have introduced are broadly consistent with the atomic-scale phenomena most likely to govern fission-track annealing. I emphasize that the mechanistic approach does not stand in opposition to attempts to refine mathematical formulations that describe trends in the data. Instead, I view the two efforts as complementary, and I hope in the remainder of this reply to illustrate that the present discrepancies between the empirical and mechanistic approaches provide fertile grounds for further investigation.

## PURELY EMPIRICAL AND SEMIEMPIRICAL APPROACHES

At the heart of the discussion of Green et al. is the claim that the approach in Carlson (1990) "reduces to another empirical model," but this assertion is incorrect because it overlooks the absolutely essential distinction between my approach and its predecessors: in the work of Carlson (1990), explicit physical significance can be attached to every variable parameter used to quantify the rates of apatite fission-track annealing. Because each parameter has physical meaning, each can be independently measured when technology permits. This relates the model

of Carlson (1990) to physical reality in a way that is simply not possible when dealing with kinetic equations not grounded in physical mechanisms.

A brief review of the method used to develop the model in Carlson (1990) is necessary to emphasize the difference between that approach and its purely empirical predecessors to clarify those concepts that Green et al. find misleading. The analysis began (p. 1121–1122) by assessing what is known about the distribution of defects in a latent track and about the way in which they are eliminated during annealing. Reduced to essentials, the results are (1) that the defects appear, on the basis of small-angle X-ray and neutron-diffraction experiments, to be strongly concentrated near the radial center of a roughly cylindrical zone, perhaps in a radial distribution that is approximately Gaussian; (2) that the overall density of defects decreases monotonically as one moves along the axis of the track from its axial center toward each end; and (3) that the defects are eliminated in a process that requires the thermally activated repositioning of displaced atoms, so that a Boltzmann distribution of energies should govern the kinetics, leading to an exponential increase in the defect-elimination rate with increasing temperature. Every one of these concepts has a firm theoretical or observational basis, as the original article detailed. They constitute the physical foundation of the model that appears in Carlson (1990), and the contention of that article and this reply is that they are sufficient to explain the essential characteristics of the annealing process.

Having introduced these concepts as constraints, the original article next made an attempt to deduce the nature of the dominant annealing mechanisms. In the attempt, choices of specific mathematical functions must be made in order to describe quantitatively the axial and radial defect distributions and the defect-elimination rate; the hope, of course, is that some choice among the varied possibilities that are consistent with the constraints above will lead to kinetic equations consistent with experimental observation. Once this choice has been made, expressions for the annealing kinetics follow as a mathematical consequence.

So, although the general features of the physical model are firmly grounded in theory and observation, the specific axial and radial defect distributions and the defect-elimination rate employed in the original article should be considered a set of postulates, in Webster's sense of "propositions which are put forth as axiomatic; assumptions laid down or enunciated without proof." The par-

ticular mathematical functions I selected to approximate the defect distributions and the defect-elimination rate were dictated by a desire to connect my physical approach to its empirical predecessors; in making these choices, I had the specific intent of maximizing the resemblance of the resulting equations to those already in the literature. For example, a power-law RDD was introduced in lieu of a Gaussian RDD specifically to generate the curious terms in $\ln t$ that have arisen in statistical best-fit analyses. This was done explicitly to emphasize that the general model yields support for these earlier formulations. Had I chosen a Gaussian RDD instead, the resulting equations might have appeared to be more closely bound to theory and observation (and they would have yielded very similar quantitative results from qualitatively very different mathematical expressions), but the important supportive connection to the empirical approaches would have been obscured.

The crucial point was also made, however, that the actual kinetics doubtless do not obey anyone's equations precisely because the defect distributions and elimination rate are surely more complex than are any of the functions proposed as simplified analogues for them. This is the meaning of the statement from page 1123 quoted without context in the fourth paragraph of Green et al. I urge the reader to review the context of the quoted statement, provided by the paragraph preceding the one from which the quote was drawn—it emphasized that although the specific linearized geometry of a cylinder with conical tips has no theoretical or observational basis, a general shape with a decreasing defect density toward the track tips does. This fact is also highlighted by the comparison between Figure 1a (linearized geometry) and 1b (generalized geometry) in the original article; the former is a simplified representation of the latter, one that is sufficient to reproduce the essential experimental observations.

Thus in my approach the form of the annealing kinetics is determined directly from the postulates that underlie the physical model, without reference to the experimental data. This fact is the absolutely crucial difference between the model of Carlson (1990) and previous models. In the absence of independent determinations of values for the physical variables in my model, values were extracted by a best-fit procedure from the experimental data. To this extent, my approach is properly characterized as an empirical one. But the distinction between models employing kinetic parameters with and without physical meaning is profound and fundamental. This distinction could perhaps be made clear by terminology referring to the former as semiempirical and to the latter as purely empirical approaches. This emphasizes that in semiempirical approaches, the form of the equations is grounded in theory and the physical variables in them are evaluated from the experimental data, whereas in purely empirical approaches, both the form of the kinetic equations and the values of the parameters are determined from the data without reference to a physical theory.

## RESPONSES TO SPECIFIC CRITICISMS

### Alternative axial defect distributions

The mechanism sketched by Green et al. in their fifth paragraph is in fact the first possibility that I considered; upon reflection, however, I felt compelled to reject it. If the axial defect distribution has precisely the right shape, then one can indeed account for the experimental observations as they suggest, without taking into account the radial distribution of defects. But it is very difficult to justify an axial defect distribution that will produce an initial logarithmic decrease in the rate of shortening and that will also produce the subsequent marked acceleration of shortening when track lengths drop below $\sim 11$ $\mu$m. Because of the inverse relation between the rate of local annealing and the local defect density, the defect density in this alternative model must increase exponentially from the end of the latent track toward its axial center in order to generate a logarithmic reduction in rate in the initial stage of annealing; but then, in order for the annealing rate to accelerate in the later stage, the defect density in the central $\sim 11$ $\mu$m would have to drop off markedly. This contradicts directly the constraint that the defect density should be highest at the axial center of the track and fall off monotonically toward its ends.

Because of this serious inconsistency, I was led to consider the ways in which the radial defect distribution could interact with the axial defect distribution to produce track-shortening rates that initially decrease over time but accelerate in the final stages. As the original article detailed, a two-stage process involving a change in the dominant mechanism of length-reduction from axial shortening to segmentation turns out to be a natural consequence of an approximately Gaussian RDD combined with an axial defect distribution in which the axially central section of the disrupted zone has nearly uniform radius. Therefore, because of its consistency with the observational constraints on the axial and radial defect distributions, I prefer the model in the original article in which radial shrinkage of the disrupted zone produces axial shortening in the first stage of annealing, and subsequent segmentation accelerates the annealing process as the radius of the disrupted zone approaches zero.

### Empiricism in the segmentation argument

Green et al. criticized as groundless the process of fitting the segmentation parameters $l_{sg}$ and $s$ to the mean track-length data. In so doing, they overlooked the fact that a change of mechanism resulting in accelerated length reduction is an essential physical consequence of the postulated defect distributions. The kinetic theory arising from those postulates dictates an increased probability of segmentation as the radius of the disrupted zone decreases, and the fitting of a segmentation rate function to the observational data as in Figure 8 of the original article is wholly justified on that basis. Again the approach is distinctly different from a purely empirical one, because the concept (a change in mechanism) is grounded in the phys-

ical theory, and only the specific values for the segmentation parameters are extracted empirically from the experimental data.

In this instance, however, it is vital to recognize that there is in fact a wholly independent validation of the theory, to which the original article also calls attention (p. 1131): the fraction of tracks undergoing segmentation, as inferred solely from the theory and the data on mean track length, matches well the actual fraction of tracks reported to exhibit gaps in the etching experiments of Green et al. (1986, p. 248) on heavily annealed samples. If the theory were groundless, it would be an extraordinarily unlikely coincidence for the observed percentages of segmented tracks to agree with the percentages determined from the segmentation analysis.

Green et al. also claimed that the segmentation analysis predicts late-stage track-length distributions at variance with observation. This may be the expectable consequence of two simplifications invoked in the original article to render the segmentation mechanism mathematically tractable. The model proceeds from the simplifications that all tracks have equal probability of undergoing segmentation and that segmentation is equally probable at all points along the length of a partially annealed track. In reality, to the extent that shorter (partially annealed) disrupted zones have smaller radii, there should be a higher probability of segmenting those tracks that are shorter (because of their crystallographic orientation or other factors), but, to the extent that highly annealed disrupted zones preserve taper from their axial centers toward their tips, segmentation is more likely to occur near the tips of tracks, rather than at random positions along their length. Taking these factors into account would modify the predicted track-length distribution because the actual process is expected to produce one relatively long segment paired with one very short segment (which is less likely to be observed), rather than two segments of random length. Such considerations open up the possibility of refining the segmentation model by relaxing the simplifying assumptions once track-length distributions at the most advanced stages of annealing are sufficiently well characterized in the literature, if one keeps in mind the great difficulties of observational bias and accurate measurement for those tracks that lie at the short end of the length distribution.

Finally, the discussion raises the question of the relative importance of annealing anisotropy and segmentation as contributors to the increased dispersion of track lengths with decreasing mean length. There is no disagreement that anisotropy in mean length increases as mean track length decreases, but as Figure 11 of the original article demonstrated, the ratio in the amount of shortening for tracks parallel and perpendicular to the c axis remains sensibly constant down to lengths of ~11 $\mu$m. Data at shorter mean lengths are not considered because, as the measurements of Donelick (1988, 1991) clearly show, the systematic elliptical relationships among lengths of tracks in different orientations break down when

mean lengths reach ~11 $\mu$m, coincident with the marked acceleration in annealing rate and with the precipitous increase in track-length dispersion (cf. Fig. 10 of original article). I contend that all of these congruent effects arise from a single cause, namely, the onset of segmentation as a dominant mechanism of track-length reduction. The annealing simulations described in the original article, based upon the orientational dependence of rate measured by Donelick (1988, 1991), support that argument: in the absence of segmentation, the gentle increase in dispersion apparent for $l > 11$ $\mu$m continues to shorter mean lengths. That gentle increase contributes only slightly to the overall increase in dispersion for $l < 11$ $\mu$m, which arises instead principally, although not exclusively, as the consequence of segmentation. Disagreement on this point may be more apparent than real: everyone concurs that in the advanced stages of annealing, tracks at high angles to the c axis are both shorter and more likely to undergo segmentation. The two effects are clearly linked, and the original article argued (p. 1134–1135) that the linkage is explicable in terms of variable minimum track diameters for tracks in different orientations, a concept supported by the recent TEM observations of Paul and Fitzgerald (1992).

## Justification of concave-upward RDD

The statements made in the sixth paragraph of the discussion are erroneous. A concave-upward form for the RDD is not an empirical choice; that form of the RDD is required by the fact that a Gaussian radial distribution of defects provides the most satisfactory explanation of the results of small-angle X-ray and neutron-diffraction studies on charged-particle tracks.

## Discrepancies between model and experiment

The discussion calls attention to the existence of systematic variation in the misfits between the model of Carlson (1990) and the data of Green et al. (1986). For this data set, there is some tendency for the model to overestimate track lengths very slightly in the range ~11 $\mu$m $< l < $ ~15 $\mu$m and to underestimate them very slightly elsewhere. Similar structure in the residuals is also present in the fits to the two other data sets in the original article, as well as in fits to the later data of Crowley et al. (1991). Very few of these residuals, however, are larger than the uncertainties in measured track lengths, as Figure 9 in the original article emphasized. Nevertheless, this structure is plausibly understood as a consequence of simplifications introduced to quantify the RDD in the original article, and it therefore presents once again an opportunity for further refinement and improvement of the model.

The general characteristics of the annealing model will follow from any RDD that strongly concentrates defects near the radial center of the disrupted zone. But at the level of detail responsible for these small residuals, the annealing kinetics become sensitive to the precise shape that one chooses to represent the RDD. A Gaussian shape

for the RDD postulates lower defect densities at the radially distant parts of the disrupted zone than does the power-law shape, and higher densities near the radial center (cf. Fig. 4 of original article); therefore, during the axial-shortening stage ($l > \sim 11\ \mu m$), a Gaussian RDD would yield more rapid early annealing and slower late annealing than the power-law expression. Thus the fit should be expected to improve if one adopted a Gaussian shape for the RDD in place of the power-law shape used in the original article. (Recall that the power-law formulation was chosen not only for its mathematical simplicity but more pointedly to generate the peculiar terms in ln $t$ that appear in published empirical models.) Of course, as the original article pointed out (p. 1126), there is no requirement that the RDD possess either a power-law shape or a Gaussian shape, although both are apparently consistent with present knowledge gleaned from small-angle X-ray and neutron-diffraction experiments on charged-particle tracks. Instead, it is clear that, within the rather broad constraint that the RDD must strongly concentrate defects toward the radial center of the disrupted zone, one could adjust the shape of the RDD as needed to minimize the amount of structure found in the residuals. That exercise might be warranted for applications that depend upon knowing mean track lengths to within a small fraction of a micrometer, if one is convinced that the uncertainties in the experimental data are sufficiently small to ensure that the structure in the residuals is not an experimental artifact.

### Extrapolation to geological time scales

The discussion argued by analogy to the parallel model of Laslett et al. (1987) that extrapolation of the Carlson (1990) model might be deficient if judged against geological annealing data for the Otway Basin, although no direct evidence is presented to support the claim. But to judge the validity of extrapolation of any model to geological time scales, one must assign a particular thermal history to the geological annealing example against which one compares the predictions of the model. Because of the considerable uncertainties attached to assigning thermal histories, such judgments are equivocal, and we should not be surprised if different geological examples yield contradictory results. I strongly urge the fission-track community to reserve judgment on the relative extrapolative value of available annealing equations until we have had the opportunity to examine their performance in a number of carefully characterized situations in addition to the Otway Basin.

### CONCLUSIONS

The issues raised in the discussion present a challenge for theorists to generate physical models that replicate the experimental data in greater detail. This is a laudable goal, and there is reason to hope that progress will soon be made toward it. This reply calls attention to several areas in which advancements in physical models are likely to come, including refinement of the postulated shapes of RDD; inclusion of possible changes in shape of the RDD as annealing progresses; consideration of more complex axial defect distributions; and recognition of segmentation processes that are not wholly random. Each of these possibilities holds promise for decreasing the small discrepancies remaining between predicted and measured annealing rates, so I fully expect that the model of Carlson (1990) will in time be supplanted by one of greater complexity and accuracy, tied even more closely to an augmented understanding of the atomic-scale phenomena.

But at the same time, this reply should have made clear that empiricists also face important challenges, namely to justify the forms of their equations and to give meaning to the variable parameters they include. Although the discussion of Green et al. concluded with a statement of preference for their own particular set of equations, it seems to me that there is more to be gained by examining in detail the differences among the various published models and inquiring into their significance. If there are truly substantially better results to be derived from a certain set of equations having a particular form, then what is it in the physics of the process that generates those unique mathematics? Put another way, why should the kinetics of AFT annealing involve the particular terms, factors, or exponents that appear to be necessary to fit the data? Only when we can satisfactorily answer these questions will we have justification for adopting one model to the exclusion of all others.

### REFERENCES CITED

Carlson, W.D. (1990) Mechanisms and kinetics of apatite fission-track annealing. American Mineralogist, 75, 1120–1139.

Crowley, K.D., Cameron, M., and Schaefer, R.L. (1991) Experimental studies of annealing of etched fission tracks in fluorapatite. Geochimica et Cosmochimica Acta, 55, 1449–1465.

Donelick, R.A. (1988) Etchable fission track length reduction in apatite: Experimental observations, theory, and geological applications, 414 p. Ph.D. thesis, Rensselaer Polytechnic Institute, Troy, New York.

——— (1991) Crystallographic orientation dependence of mean etchable fission-track length in apatite: An empirical model and experimental observations. American Mineralogist, 76, 83–91.

Green, P.F., Duddy, I.R., Gleadow, A.J.W., Tingate, P.R., and Laslett, G.M. (1986) Thermal annealing of fission tracks in apatite. I. A qualitative description. Chemical Geology (Isotope Geoscience Section), 59, 237–253.

Green, P.F., Laslett, G.M., and Duddy, I.R. (1993) Mechanisms and kinetics of apatite fission-track annealing—Discussion. American Mineralogist, 78, 444–448.

Laslett, G.M., Green, P.F., Duddy, I.R., and Gleadow, A.J.W. (1987) Thermal annealing of fission tracks in apatite. II. A quantitative analysis. Chemical Geology (Isotope Geoscience Section), 65, 1–13.

Paul, T.A., and Fitzgerald, P.G. (1992) Transmission electron microscopic investigation of fission tracks in fluorapatite. American Mineralogist, 77, 336–344.