Mechanisms and kinetics of apatite fission-track annealing—Discussion

Kevin D. Crowley

Department of Geology, Miami University, Oxford, OH 45056, U.S.A.

Carlson (1990) presented a kinetic model for annealing of fission tracks in apatite that is based on atomic-scale mechanisms. This discussion addresses the validity of this model in view of generally accepted principles of annealing kinetics and model fitting and testing. Specifically, this discussion will show that Carlson's model is not a valid kinetic description of annealing because (1) the annealing mechanism is physically invalid; (2) the model does not provide adequate fits to laboratory data, and it does not provide as good a fit to laboratory data as previously published empirical models; and (3) the model does not provide reasonable predictions when extrapolated outside the range of the data.

PHYSICALLY INVALID MECHANISMS FOR DEFECT ELIMINATION

Carlson suggested (p. 1121, 1122, 1125) that the kinetics of topotactic mineral transformations can be applied to defect elimination in fission tracks. They cannot. Topotactic transformation is a zero-order process: its rate depends primarily on temperature and is independent of the concentration of reactants in the volume. The rate of defect elimination, on the other hand, depends on the density of reactants in the mineral volume.

Although zero-order kinetics have been demonstrated for certain types of surface reactions (e.g., Noggle, 1989), they do not apply to volume reactions like defect elimination. In fact, the application of zero-order kinetics to defect elimination leads to some rather implausible predictions, for example, that elimination can occur in the absence of defects.

Work published during the past four decades (e.g., Fletcher and Brown, 1953; Waite, 1957; Gold et al., 1981), which was neither cited nor discussed by Carlson, demonstrated that defect elimination involves higher order kinetics. Fletcher and Brown (1953) and Waite (1957) showed that defect elimination is governed by first-order or second-order kinetics, depending on initial defect distribution. Gold et al. (1981) invoked a multiple first-order process in recognition that not all defects in the damage zone are identical.

The rate of defect elimination must be a function of defect concentration; that is, the order of the process must be greater than zero. Consequently, Carlson's Equation 2 and the annealing model from which it is derived (his Eqs. 4, 5) are physically invalid. Although it could be argued that a model based on zero-order kinetics is a useful empirical description of annealing, such a model does not provide a realistic physical description of the annealing process, as Carlson suggests in his paper.

INADEQUATE FITS TO LABORATORY DATA

Carlson's statement that "the model . . . reproduces the kinetics of AFT length reduction in laboratory experiments with an accuracy equal to the precision with which the experimental measurements can be made" (p. 1122) is demonstrably untrue, as could have been shown, had basic statistical analyses been performed. The model does not fit either the Green et al. (1986) or Donelick (1988) data sets (hereafter denoted G86 and D88, respectively) within the precision of the measurements and, in fact, the model provides a poor fit to the D88 data.

Model fits can be quantitatively assessed using established goodness-of-fit statistics, as illustrated below for the axial shortening component of Carlson's model. Carlson's Equation 5, which applies to isothermal anneals of tracks having lengths greater than 11 μm, can be rearranged to give

$$g(r; \alpha = 0, \beta = 1) = \log(1 - r)$$
$$= C_0 + C_1 \log(Tt) + C_2 T^{-1} \quad (1)$$

where $g(r; \alpha, \beta)$ is a Box and Cox (1964) transformation used by Laslett et al. (1987) in their annealing models, and where $r = l_{as}/l_0$, $C_0 = \log(A/l_0) + n\log(k/h)$, $C_1 = n$ and $C_2 = -nQ/R$. The symbols l_{as}, l_0, A, n, k, h, Q, R, t, and T are defined in Carlson's Table 1.

The goodness-of-fit of Equation 1 to the G86 and D88 data sets can be assessed by comparing the residual variances of the fits, calculated in the conventional manner, to the variance of the data, which can be calculated using the delta method (e.g., Elandt-Johnson and Johnson, 1980). Residual variances for fits of Equation 1 to the G86 and D88 data are estimated to be 0.0277 and 0.0254, respectively. The variances of the G86 and D88 data are estimated to be 0.0240 and 0.0065, respectively, from the delta method. The residual variance is about 15% greater than the variance of the G86 data and is almost 400% greater than the variance of the D88 data. The especially poor fit of Equation 1 to the D88 data is confirmed by the presence of structure in the residual plot (Fig. 1). Clearly, Carlson's model does not fit the data within precision of the measurements, nor does it provide the quality of fit expected for an accurate kinetic description of annealing.

Carlson's model is deficient even as an empirical description of annealing because it does not provide as good a fit to the data as previously published empirical models. This can be illustrated by comparing the fit of the axial shortening component of the proposed model (Eq. 1) to fits of previously published models. Equation 1 can be

nested within a mathematical super model:

$$g(r; \alpha, \beta) = C_0 + C_1 \log(Tt) + C_2T^{-1} + C_3 \ln t \\ + C_4T \ln t + C_5T \qquad (2)$$

Equation 1 can be obtained from Equation 2 when $\alpha = 0$, $\beta = 1$ and $C_3 = C_4 = C_5 = 0$. Nested within this super model are several previously published empirical annealing models:

$$g(r; \alpha = 0, \beta = 1) = C_0 + C_3 \ln t + C_2T^{-1} \qquad (3)$$

$$g(r; \alpha, \beta) = C_0 + C_3 \ln t + C_2T^{-1} \qquad (4)$$

$$g(r; \alpha, \beta) = C_0 + C_4T \ln t + C_5T \qquad (5)$$

which are, respectively, the parallel model of Green et al. (1985), the parallel model of Laslett et al. (1987), and the fanning model of Laslett et al. (1987).

The parameters α, β, $C_0, \ldots, C_5$ can be estimated from the isothermal annealing data sets (G86, D88) by maximizing the log likelihood function (e.g., Box and Cox, 1964, their Eq. 7). The significance of fits to the various models can be determined using the likelihood ratio test (Gilchrist, 1984), which takes into account the different number of adjustable parameters in the equations.

Likelihood ratio tests reveal that the fanning model of Laslett et al. (1987) (Eq. 5, above) provides a significantly better fit to the G86 annealing data than the axial shortening component of Carlson's kinetic model (Eq. 1) (likelihood ratio = 24.0 with 2 degrees of freedom, which is significant at the 1% level). None of the previously published models, including the axial component of Carlson's model (Eq. 1 of this discussion), provides acceptable fits to the D88 data compared with the super model (Eq. 2).

In his reply to this discussion, Carlson fits his model to the two data sets published by Crowley et al. (1991), concluding that the "fits are comparable in quality to the fits to the earlier data sets achieved in the original article." However, likelihood ratio tests show that the fanning model (Eq. 5) provides a significantly better fit to both data sets compared to the axial shortening component of Carlson's model (likelihood ratio = 18.6 for the fluorine apatite data, which is significant at the 1% level; likelihood ratio = 104 for strontium fluorine apatite data, which is significant at the 0.1% level of significance). Thus the fits of Carlson's model to the data of Crowley et al. (1991) show discrepancies as great as those in the fits to the data in his original article.

In the section titled "Comparison to the fanning model" (p. 1137), Carlson states that the fanning Arrhenius plot "which results from modifications required to fit the data at lengths less than ∼11 μm, probably reflects a change in the predominant mechanism of length reduction for short tracks. . . ." The preceding analysis demonstrates that, to the contrary, fanning is inherent, at least in the G86 and Crowley et al. (1991) data sets, for $l >$
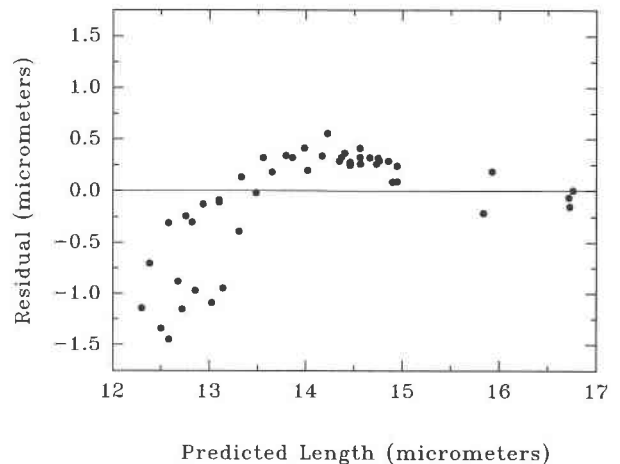

Fig. 1. Residual plot for fit of Eq. 1 to the isothermal annealing data (for $l_{as} > 11$ μm) of Donelick (1988).

11 μm, where, according to Carlson's analysis, axial shortening predominates.

UNREASONABLE PREDICTIONS WHEN EXTRAPOLATED OUTSIDE THE RANGE OF THE DATA

One characteristic of a good theory or model is its capacity for producing testable predictions. One testable prediction of Carlson's model is track-annealing behavior at high temperatures. This is best illustrated by examining the axial shortening component of the model (Eq. 1, above) in the context of the Arrhenius diagram, in which fading contours that represent fixed values of r (= l/l_0, where l is mean track length) are plotted in $1/T - \ln t$ space.

Figure 2 shows the Arrhenius diagram derived from the fit of Equation 1 to the G86 data for $l = l_{as} > 11$ μm. The fading contours are parallel and linear. One prediction of this geometry is that etchable tracks (i.e., the cylindrical features revealed by chemical etching that are conventionally identified as fission tracks, which should not be confused with latent or unetched fission tracks) are stable at infinitely high temperatures. This geometry predicts that etchable tracks exist above the melting and boiling points of apatite; indeed, this geometry predicts that etchable tracks exist in high-temperature plasmas, where latent tracks would not be expected to form. This predicted behavior is physically absurd and is at variance with the observed annealing behavior of etchable tracks in the laboratory, which are known to be unstable at temperatures exceeding a few hundred degrees Celsius.

It seems reasonable to suggest that the only physically reasonable Arrhenius geometry is the fanning plot, in which the fading contours intersect and terminate at a single point at high temperatures. This termination represents the limit of stability of etchable tracks (but not necessarily latent tracks) in apatite. Indeed, as shown above, the fanning plot provides a significantly better fit to the G86 data than the Carlson model.
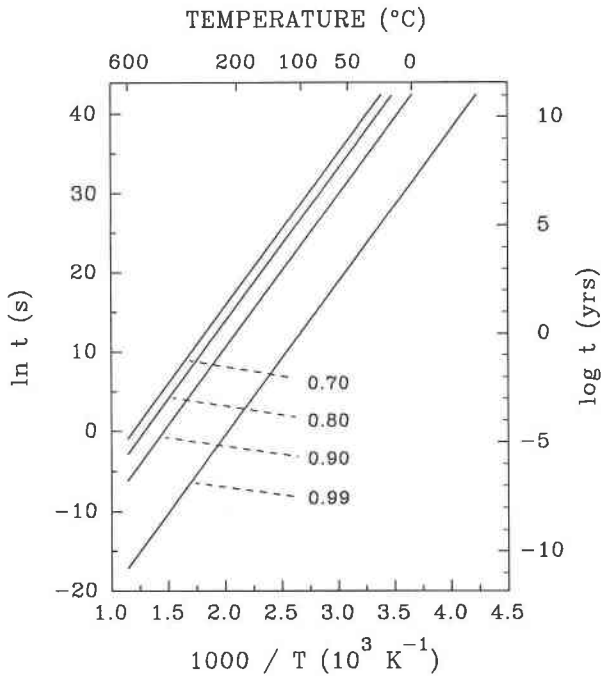
Fig. 2. Arrhenius diagram derived from the fit of Eq. 1 to the isothermal annealing data (for $l_{as} > 11$ μm) of Green et al. (1986). The fading contours are labeled with values of normalized mean length (r).

CONCLUSIONS

A mathematical model is a valid physical description of annealing if and only if it is based on realistic atomic-scale processes. Carson's model is not. Rather, it is based on the zero-order kinetics of topotactic transformations, and such kinetics do not apply to defect elimination. Carlson's model is inconsistent with observation, as shown by its implausible behavior at high temperatures.

I agree completely with the premise of Carlson's paper: namely, that efforts should be made to develop physical models that can be more confidently extrapolated to geo-logical time and temperature conditions. However, it is essential that such models have a realistic physical underpinning. I submit that an empirical model that provides a good fit to laboratory data is better than a physical model that does not and that is based on incorrect kinetic processes.

REFERENCES CITED

Box, G.E.P., and Cox, D.R. (1964) An analysis of transformations. Journal of the Royal Statistical Society, Series B, 26, 211–252.
Carlson, William 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. Ph.D. thesis, Rensselaer Polytechnic Institute, Troy, New York.
Elandt-Johnson, R.C., and Johnson, N.L. (1980) Survival models and data analysis, 457 p. Wiley, New York.
Fletcher, R.C., and Brown, W.L. (1953) Annealing of bombardment damage in a diamond-type lattice: Theoretical. Physical Review, 92, 585–590.
Gilchrist, W. (1984) Statistical modelling, 339 p. Wiley, New York.
Gold, R., Roberts, J.H., and Ruddy, F.H. (1981) Annealing phenomena in solid state track recorders. Nuclear Tracks, 5, 253–264.
Green, P.F., Duddy, I.R., Gleadow, A.J.W., Tingate, P.R., and Laslett, G.M. (1985) Fission-track annealing in apatite: Track length measurements and the form of the Arrhenius plot. Nuclear Tracks, 10, 323–328.
——— (1986) Thermal annealing of fission tracks in apatite. I. A qualitative description. Chemical Geology, 59, 237–253.
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, 65, 1–13.
Noggle, J.H. (1989) Physical chemistry. Scott, Foresman, Boston.
Waite, T.R. (1957) Theoretical treatment of the kinetics of diffusion-limited reactions. Physical Review, 107, 463–470.