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A zero-damage model for fission track annealing in zircon

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Abstract

A zircon fission track annealing model is calculated on the basis of annealing experiments from the literature with induced tracks in α -decay event damage-free zircons. Empirically derived parallel and fanning equations of this “zero-damage” model yield an excellent fit to the data, with the fanning model providing slightly better statistical parameters. A comparison between annealing models with fanning iso-annealing lines but different α -decay event damage densities reveals that annealing temperatures and closure temperatures for the estimated partial annealing zone are highest for the zero-damage model.

Compilations of existing geologic constraints on the zircon partial annealing zone on one hand and the zircon closure temperature on the other show that these constraints do not or only partly overlap with curves of proposed models for the zircon partial annealing zone and closure temperature. This is consistent with the fact that the annealing behavior of zircons from long-duration temperature evolutions is increasingly influenced by the accumulated α -decay event damage. Zircons of young age or low U content show a behavior closest to the predictions of the zero-damage model, and are in the predicted range of published models with low α -decay event damage density. For thermal events of more than 10 myr duration, however, constraints from field studies show marked differences to proposed partial annealing zone boundaries of the zero- or low-damage models.

The applicability of the zero-damage model is threefold: 1) It predicts correct closure temperatures in the case of very rapid cooling across the partial annealing zone where basically no α -decay event damage is accumulated. 2) It predicts an uppermost boundary for complete annealing of a mixture of zircon populations of different age, as found in sedimentary samples, and in this case may be used as a thermometer. 3) It represents an important reference for the establishment of a more comprehensive model of zircon fission track annealing that also includes the influence of α -decay event damage. For such a model, two different equations are discussed. However, more detailed experimental and field data are needed for a more robust annealing model that includes the influence of α -decay event damage annealing.

Introduction

Zircon is a common accessory mineral in magmatic rocks of intermediate to acid composition and their metamorphic and sedimentary counterparts. It is one of the most important storage minerals for U and Th, and has therefore been among the first and most extensively used minerals in dating of rocks of different origin. Zircon has been dated by the U-Pb method since the early fifties (Larsen et al. 1952), and was one of the first to be dated with the fission track (FT) method (Fleischer et al. 1964). Because annealing of fission tracks (FTs) in zircon commonly takes place at sub-greenschist facies conditions on a geologic time scale, this dating method has mainly been used to study late-stage cooling, together with other chronometers (e.g. Zeitler 1985; Hurford 1986), or near-surface thermal histories (e.g. Hasebe et al. 1997, 2003). For such purpose, zircons were

sampled at or below the surface in order to gain an on-site exhumation history.

Alternatively, zircon FT ages from sedimentary rocks were used in conjunction with the sedimentary age to restore the exhumation history of the provenance area, and to unravel erosion and transport patterns (e.g. Garver and Brandon 1994; Garver et al. 1999). For such application, it is imperative to understand the thermal behavior and stability of tracks in zircon in order to interpret the thermal significance of the measured FT age and track length distribution.

Similar to apatite (see e.g. Laslett et al. 1987; Gallagher 1995; Willett 1997, Ketcham et al. 1999), zircon FT ages and track length distributions have the potential to predict cooling paths. However, zircon annealing models for time-temperature modeling have not yet found the wide application as those models for apatite, in particular due to the lack of knowledge on the influence of composition and accumulated radiation damage to its annealing behavior.

Fleischer et al. (1965) published the first data on zircon FT annealing, using experiments with natural fission tracks, but only three states were distinguished: total track removal, partly faded tracks, and unaltered tracks. The established line between the experimental runs passes between unaltered and partly faded runs, and thus represents a lower boundary (with respect to temperature) of the partial annealing zone (PAZ), a transitional temperature zone between complete conservation and complete annealing of FTs. Extrapolated to geologic time scales, their prediction for the lower PAZ boundary for a 1 myr annealing time was above 350° C (Fig. 1a, the term "myr" refers to a time duration in this study, while "Ma" is used for a specific moment in time). Krishnaswami et al. (1974) used a similar classification for their experimental results, and estimated a

lower PAZ boundary at 310° C for a 1 myr annealing duration. Both results seemed at odds with geologic field studies, since zircon FT ages were systematically younger than K-Ar data on muscovite or biotite for which closure temperatures of 300 and 350 °C, respectively, were estimated under geologic conditions (e.g. Harrison et al. 1979; Hurford 1986).

Two studies on induced track lengths were published by Koul et al. (1988) and Carpéna (1992), but differ strongly from each other (Fig. 1a). Zircons with induced tracks were produced by total annealing of the natural tracks, and then inducing tracks with thermal neutrons in a reactor facility. While Koul et al. (1988) only reported their curve for total annealing (corresponding to an upper PAZ boundary), Carpéna (1992) listed all experimental runs and estimated contours for track density reduction. Figure 1a shows Carpéna's 10 and 90% contours, which were adopted to define the zircon PAZ. This estimated PAZ overlaps with the curves of Fleischer et al. (1965) and Krishnaswami et al. (1974).

More recently, Yamada et al. (1995) presented an experimental data set, which was suitable to define and test different annealing models (Fig. 1b). These authors, as well as Galbraith and Laslett (1997) who published a more refined statistical treatment on the data set considered two empirical fit equations: one corresponding to an equation with parallel and another to an equation with fanning iso-annealing lines in an Arrhenius plot. Both groups agree that the data do not clearly favor one equation over the other. Two new long-term annealing data were added by Tagami et al. (1998) and the enlarged data set fitted according to the statistical procedure of Galbraith and Laslett (1997). In those data sets, the relationship with fanning iso-annealing lines commonly provides a better fit to

the data. Figure 1b illustrates three proposed relationships, one with parallel lines, called hereafter "parallel relationship" or "parallel equation", two with fanning iso-annealing lines, called "fanning equations" (Yamada et al. 1995). The results of these equations markedly differ from each other when extrapolated to geologic time scales.

Direct comparison between experimental annealing data from different studies is complicated by the following problems: a) Sample treatment, in particular etching, is a major source of variation for fission track lengths in zircon (Amin 1988; Tagami et al. 1990; Hasebe et al. 1993), and may account for differences between experiments that otherwise included the same t-T conditions. b) Some studies report track densities, others track lengths. c) Some annealing studies are based on annealed zircons with induced tracks; others used natural zircons with varying degrees of α -decay event damage. d) A problem particular to older studies is that the zircons were not sufficiently characterized with respect to age and track density. e) Finally, there is no generally accepted definition for the zircon PAZ with respect to track density or length reduction.

In contrast to apatite (e.g. Carlson et al. 1999), zircon composition does not appear to be an important factor controlling FT annealing, but this issue needs to be studied in more detail. The influence of α -decay event damage on the annealing of fission tracks, on the other hand, has received much more attention. The damage produced by α -decay events (hereafter for simplicity called " α damage") is mainly the result of ^{238}U (and to a minor extent of ^{232}Th and ^{235}U) decaying in a multistep process to Pb and causing structural damage which affects the bulk physical properties (see e.g. Murakami et al. 1991; Ewing 1994). It includes mainly the damage produced by the recoil nucleus and to a much lesser extent by the expelled α particle (Weber et al. 1994). A single α -recoil

track is approximately 25 nm in size (depending on the single recoil energy, Palenik et al. 2003), while entire decay chains (6-8 decays) produce amorphous domains of up to 100 nm in diameter (Murakami et al. 1991), which with increasing damage density start to form percolating clusters (Salje et al. 1999) and eventually lead to complete metamictization. The α particle tracks in zircon measure 13 μm in length (Nasdala et al. 1999), which is similar to the length of fission tracks (Tagami et al. 1990). With respect to size, α -recoil tracks are much shorter than fission tracks, but by comparison of the α and fission decay constants of ^{238}U , ^{235}U and ^{232}Th , it is evident that the α decay process is more than 10^7 times more frequent than the fission decay event for ^{238}U , and that this ratio is several orders of magnitude larger for ^{235}U and ^{232}Th due to the very low fission decay constants of ^{235}U and ^{232}Th . The status of damage accumulation in zircon is determined by changes in measured macroscopic (e.g. Holland and Gottfried 1955) as well as microscopic patterns (e.g. Nasdala et al. 1995; Ríos et al. 2000; Farnan and Salje 2001; Zhang et al. 2001) and show that the crystalline-to-amorphous transition is characterized by two distinct transitions (Salje et al. 1999) and the amorphous phase shows polymerization (Farnan and Salje 2001) as well as density differences on the atomic scale (Trachenko et al. 2003).

In a study on four different zircons with natural fission track densities between 0.87 and $9.95 \cdot 10^6 \text{ cm}^{-2}$ and their annealed counterparts with induced tracks, Kasuya and Naeser (1988) were able to demonstrate that α damage-free zircons are systematically more retentive of fission tracks relative to their natural counterparts. Because of the approximately constant ratio of α decay events to fission decays, annealing behavior might be expected to correlate with spontaneous track density, but their experiments did

not show any obvious correlation. A similar behavior of track stability as a function of α damage was observed by Yamada et al. (1995).

The annealing of etchable fission tracks in zircon was shown to occur at 400-800 °C in short-term laboratory experiments (Carpéna 1992; Yamada et al. 1995; Tagami et al. 1998) and at 200-350 °C for geologic time spans (Tagami and Shimada 1996; Tagami et al. 1995a; Brandon et al. 1998; Hasebe et al. 2003). In contrast, for the annealing of α damage in zircon under laboratory and geologic conditions a variety of observations gives a very complex picture: Garver and Kamp (2002) showed that zircon color which is a result of point defects in crystalline areas is annealed during geologic time scales at reasonably low temperatures of 350-400 °C, i.e. at conditions above the FT PAZ. Short-term laboratory heating of a partially metamict zircon to temperatures up to about 700 °C only induced the removal of defects within the crystalline remnants, while epitaxial recrystallization of the amorphous part needed temperatures in excess of 700 °C (e.g. Chakoumakos et al. 1987; Zhang et al. 2000; Capitani et al. 2000; Geisler 2002). Total recovery of the crystal structure was only achieved at temperatures of 1400 to 1600 °C, with the observed decomposition into ZrO_2 and SiO_2 in heavily metamict zircons (Capitani et al. 2000). On this basis it has to be assumed that a strong reduction in a damage only takes place at temperatures in excess of those need for FT annealing.

Because FT annealing in zircon is influenced by the amount of present α damage (Kasuya and Naeser 1988; Yamada et al. 1995), the relationship between α damage and FT annealing has major implications for the interpretation of FT data. Under geologic conditions, when zircons enter the PAZ from the high temperature side at slow to moderate cooling rates, they will accumulate significant amounts of α damage before the

first retention of fission tracks. Fast cooling zircons, however, will only experience little α damage accumulation before the entrance into the FT PAZ. As a consequence, they will not have the same annealing properties, but FT retention in cooling zircons will be influenced by the individual cooling rate and the U content of each zircon grain. For very fast cooling rates, the FT retention may approach a behavior with no α damage influence and thus may be predicted by experiments on α damage-free zircons with induced tracks. Zircons entering the FT PAZ at its lower boundary will have an annealing behavior in accordance to their residence time below the PAZ (corresponding to the time of α damage accumulation) and their U content.

In this study, we present a review of all published FT annealing data on zero-damage zircons, develop a procedure to compare them across differences between the data sets and the chosen experimental approaches, and calculate a zero-damage annealing model. The term “zero-damage” refers to experiments on zircons where a total annealing of the radiation damage was achieved by heating of the zircons to temperatures of 800° C or above. These zircons are assumed to contain no radiation damage, as opposed to young natural zircons (e.g. in Yamada et al. 1995), which here are referenced as “low-damage” zircons. With the help of the zero-damage model we will be able to a) explain several field observations in various geologic settings that could not be explained by previous models, and b) develop the basis for a future model that integrates α damage as a third component affecting zircon FT annealing apart from temperature and time.

FT annealing in zero-damage zircon

Three sets of induced FT annealing data exist which supply sufficient information about the experimental conditions and the samples used (Kasuya and Naeser 1988; Carpéna 1992; Yamada et al. 1995). Kasuya and Naeser (1988) presented data on four different zircons annealed at a temperature range of 400 to 675° C, but their study only included experiments of 1h duration. Another 1h data set is provided by Yamada et al. (1995). The only study that extends to heating times other than 1h is that of Carpéna (1992) on a totally annealed Mont Blanc zircon sample. Not used for our model are data on induced FT annealing in zircon by Koul et al. (1988), since their study does not provide any annealing data apart from a line of total annealing (Fig. 1a, their Fig. 7), and by Koshimizu (1993), because his observations on differences between internal (4π) and external (2π) surfaces have raised the question of a methodical problem within this study. In the three remaining experimental studies, annealing in zircon was studied by step heating of zircon aliquots for time periods from 5 minutes to 917 hours and constant temperatures between 397 and 800° C.

A comparison of all 1h experiments reveals that these data lie close to a common curve on a L/L_o versus annealing temperature diagram (L = measured mean track length, L_o = measured initial mean track length before annealing), despite the fact that the data originate from three different labs, and etching conditions were very different (Fig. 2a). For comparison, three sets of annealing experiments at 1h from zircon samples of different age (Tagami et al. 1990; Yamada et al. 1995) show distinct differences in annealing behavior and a clear trend of decreasing track stability with increasing age, and therefore accumulated α damage (Fig. 2b), although part of the differences may be explained by differences in etching conditions (Tagami, pers. comm.). The original data

of Carpena (1992), given as track density ratios L/L_o have been converted to L/L_o using a relationship from Tagami et al. (1990). The use of the L/L_o ratio instead of absolute measured lengths provides a way to avoid differences between labs in observed maximum length. For instance, for induced tracks Kasuya and Naeser (1988) report a mean $L_o = 10.84$ (no error given¹) μm , whereas Yamada et al. (1995) report $L_o = 11.03 (\pm 0.10, 1\sigma)$ μm .

In our analysis, we used the set of measured track lengths for zero-damage zircon data from Yamada et al. (1995). Their distinction between the means of all track lengths (L_{all}) and those with an angle $>60^\circ$ to the c-axis ($L_{>60}$) is avoided for several reasons. First, the plotting of their L_{all} and $L_{>60}$ values reveals that the resulting correlation is significantly different from a 1:1 relationship (Fig. 3), but many single values and their standard deviation are not. Second, the restricted data set ($L_{>60}$) has distinctly smaller track length numbers, which leads to poorer statistics for young and U-poor zircon samples. Third, from a practical point of view, the distinction between L_{all} and $L_{>60}$ is difficult to apply to samples with sub- and anhedral zircon grains and very low track densities. Finally, similar to the behavior observed with apatite track lengths (see Ketchum et al. 1999), the relationship between the reduction of track length and the track angle to the c axis may be more complicate in zircon, requiring more detailed investigations. We therefore prefer to use a measure that is representative of the way that FTs in zircons are currently measured. Carpena (1992) observed different annealing rates as a function of zircon topology (sensu Pupin 1980). This distinction is again difficult to apply to non-euhedral zircons. Instead we seek to characterize the annealing properties of

¹ Kasuya and Naeser (1988) report "no significant difference in the initial track lengths (10.7-10.9 μm)" in

all zircons so that the results will be more relevant for current practices in zircon FT dating.

The zero-damage model

The fanning and parallel models, first developed for apatite FT dating (for a review see Ketcham et al. 1999), were examined as possible empirical annealing equations for the zircon FT system (Yamada et al. 1995; Galbraith and Laslett 1997; Tagami et al. 1998). The applied procedure is to transform L/L_o to a new variable λ ,

$$\lambda = \ln\left(1 - \frac{L}{L_o}\right) \quad (1)$$

and to define λ as the dependent variable when estimating parameters for an annealing equation. λ describes the degree of annealing as a function of the independent variables of temperature T (in Kelvins) and time t (in hours). The designation of λ as an independent variable indicates that measurement errors are largest for that variable and that least-square estimations of parameters can ignore errors in the other two variables T and t . This assumption is supported by the errors given by the different authors who claim that the accuracy in temperature is in the order of ± 2 °C, while for time the precision is in the range of ± 1 -2 s. The time precision, however, may in fact be important in short-term experiments due to the time necessary for reaching thermal equilibrium within the zircon grains.

The parallel and fanning models are defined by

their investigated zircons. This suggests a 2σ standard error of the mean (SE) of 0.1 μm .

$$\sigma = a_p + b_p \left(\frac{1}{T} \right) + c_p \ln(t) \quad (2)$$

and

$$\sigma = a_f + b_f T \ln(t) + c_f T \quad (3)$$

respectively. Each model has three parameters a , b , and c . In both cases, σ is linear with respect to a , b , and c and thus can be solved using typical weighted least square methods. Equation (2) describes a set of planes in a $\ln(t)$ - $1/T$ - space for the parallel model, and equation (3) a plane set in the $\ln(t)$ - T - space for the fanning model. For the parallel model, each iso-annealing surface is planar, whereas the fanning model has slightly curved iso-annealing surfaces, since the slope in the $\ln(t)$ direction is temperature dependent. For annealing in apatites, an alternative fanning relationship has been applied (Crowley et al. 1991, Laslett and Galbraith 1996, Ketcham et al. 1999), which allows more flexibility for the fanning point. Galbraith and Laslett (1997) and Tagami et al. (1998) have proposed more complex model equations for zircons on the basis of the maximum likelihood method and an internally consistent data set, derived from aliquots of the same material. In view of the heterogeneity of the here compiled data set, which is far from being ideal and was not produced for such purpose, we restrict ourselves to a simpler data treatment based on the equations (2) and (3) for the purpose of mathematical transparency.

From equation (1) it is evident that when L approaches L_0 (at low temperatures), σ becomes large and its variance will probably be large as well. High temperature runs where L approaches 0 will have small σ and low variances, even though some L values might be estimated from only a small number of track length measurements. This is

particularly true for the 748 and 795° C runs of Yamada et al. (1995) where $L = 0$, and for one run at 4.5 minutes and 750° C which yielded only two measurable track lengths. To account for the non-linear relationship between ρ and L , we need to calculate weighting factors for ρ to be used in our regression analysis. Galbraith and Laslett (1997) introduced such a weighting treatment for the different single data on zircon, and their method is here adopted.

If the standard error for the mean track length $SE(L)$ is known, the standard error for ρ can be estimated by

$$SE(\rho) = SE(L) \left| \frac{\partial \rho}{\partial L} \right| = \left| \frac{SE(L)}{L - L_0} \right| \quad (4)$$

This error estimation assumes that the error on L_0 is negligible, which is rectified based on the fact that the error on L_0 is small. For annealing experiments reported as track densities, we convert to track lengths using the linear relationship of Tagami et al. (1990) of

$$\left(\frac{L}{L_0} \right) = a_L + b_L \left(\frac{\rho}{\rho_0} \right) \quad (5)$$

with $a_L = 0.2$ and $b_L = 0.8$. ρ is then calculated as

$$\rho = \ln \left(1 - a_L - b_L \left(\frac{L}{L_0} \right) \right) \quad (6)$$

and a standard error approximated by

$$SE(\rho) = SE \left(\frac{\rho}{\rho_0} \right) \left(\frac{-b_L}{1 - a_L - b_L \left(\frac{L}{L_0} \right)} \right) \quad (7)$$

We use standard weighted regression analysis (e.g. Press et al. 1992) with w weighted according to $SE(.)$:

$$w = \frac{1}{SE(.)^2} \quad (8)$$

Carpéna (1992) reports standard errors for all her density data. They are only given for the restricted length measurement set $L_{<60}$ in Yamada et al. (1995). However, since there is a close relationship between $L_{>60}$ and L_{all} (Fig. 3), we use the reported standard deviations from the $L_{>60}$ values, and divide by the square root of the total number of track length measurements to get standard errors for their L_{all} . Standard errors were not visible for most of the Kasuya and Naeser (1988) data, because on their data plots the error bars of most data points are reported to be hidden behind the plotted symbols (and the original data were not available on request any more, M. Kasuya, pers. comm.). We therefore estimated the initial error bars on the basis of an empirical function between standard deviation and mean track length proposed by Galbraith and Laslett (1997) (Fig. 4). They fitted the experimental data and standard errors of Yamada et al. (1995) with a function of two straight lines, one horizontal and the other with slope b_{SD} , joined by a smooth curve:

$$SD(L) = \exp\left\{2a_{SD} + 2b_{SD}\left[(\ln(L) - \ln 9) - \sqrt{(\ln(L) - \ln 9)^2 + c_{SD}}\right]\right\} \quad (9)$$

When applied to the data set of $L_{>60}$ values from Yamada et al. (1995) and Tagami et al. (1998), we obtain the following best-fit parameters: $2a_{SE} = -0.44$, $2b_{SE} = -1.16$, $c_{SE} = 0.005$. These parameter values differ slightly from the values reported by Galbraith and Laslett (1997) due to the adding of the two new long-term annealing experiments. In Figure 4, those standard errors visible in the data plots of Kasuya and Naeser (1988) are

shown for comparison², and indicate that the estimates of standard errors for Kasuya and Naeser (1988) were indeed in the same range as those for the Yamada et al. (1995) data.

A comparison of the weighting factors indicates that those derived from track length data are generally higher than those determined from track density data. The reason is the higher precision of track length data compared to track density data. Since the weighting is based on $SE(.)$, all samples with a large difference between L and L_o are much more strongly weighted (equation (4)). Accordingly, data from low temperature and short duration runs have a weaker influence on the regression analysis because L is only slightly smaller than L_o . The only track density data that receive a stronger weighting than all track length data are those with values lower than $L/L_o = 0.25$. In this case, track length measures are few and very difficult to make resulting in large $SE(L)$ and $SE(.)$. Track density data, on the other hand, have errors in the 50% range (Carpéna, 1992), but their calculated $SE(.)$ is relatively small.

The best-fit results for zero-damage zircon are shown in Figure 5. In equation form, the parallel model is:

$$. = 9.21 - 9976 \left(\frac{1}{T} \right) + 0.222 \ln(t) \quad (10)$$

with $R^2 = 0.988$ and $.^2_r = 1.99$, and the fanning model is

$$. = -11.57 + 0.000276T \ln(t) + 0.011T \quad (11)$$

with $R^2 = 0.992$ and $.^2_r = 1.34$ (Table 1). The regression calculation used 54 data points to estimate three parameters. The low reduced $.^2_r$ indicate that the residuals are only

² The transformation of standard error $SE(r)$, as indicated in the Kasuya and Naeser (1988) figures, into the standard deviation (SD) is done by:

$$SD = SE \sqrt{n}$$

slightly larger than the estimated uncertainties $SE(.)$. In agreement with previous studies, the fanning model turns out to be slightly more consistent with the experimental data. Note that despite the fact that the zero-damage data come from three different labs, the combined data provide excellent fits. However, it has to be kept in mind that the accuracy of these fits is in part due to the facts that (a) the Kasuya and Naeser (1988) and Yamada et al. (1995) data sets on one hand and the Carpéna (1992) data set on the other have a restricted overlap with respect to annealing experiment duration (Fig. 2), and (b) the applied weighting of the data according to their measurement uncertainties produces another bias of the importance of the data sets with respect to L/L_0 .

Discussion

Comparison with previous annealing models

For comparison we have used the same procedure to analyze the annealing data for low-grade damaged zircons from Tagami et al. (1998) ($n = 27$). The parallel model gives

$$\ln(L/L_0) = 6.53 - 7248\left(\frac{1}{T}\right) + 0.204 \ln(t) \quad (12)$$

with $R^2 = 0.955$ and $\sigma_r^2 = 2.80$. The fanning model gives

$$\ln(L/L_0) = -10.77 + 0.000260T \ln(t) + 0.010T \quad (13)$$

with $R^2 = 0.966$ and $\sigma_r^2 = 2.14$. If we include other annealing experiments on damaged zircon such as those of Kasuya and Naeser (1988) or Tagami et al. (1990), regression

where n = number of track length measurements. Kasuya and Naeser (1988) report that their minimum n was more than 30. Consequently, we have used a value of $n = 31$ for all their data.

coefficients and reduced χ^2 values become worse (Table 1). Different levels of α damage and annealing behavior deteriorate the statistics of the model fit, and, interestingly, lead to relatively lower χ^2 values for the parallel model (Table 1). We conclude that the increase in density variation of α damage runs parallel to an increase in annealing behavior variation. Such variation in α damage density is common in natural zircon samples: even with a unimodal age distribution, single grains have different densities of α damage due to differences in U content and are therefore expected to show differences in their annealing behavior and closure temperature.

In Figure 6, the fanning iso-annealing contours for the zero-damage zircon model are compared to the most recent Galbraith and Laslett (1997) fitting of the Yamada et al. (1995) data, and the Tagami et al. (1998) model (thick lines). Both models refer to “low-damage” zircons, since these zircons had initial spontaneous track densities of around $4 \times 10^6 \text{ cm}^{-2}$ (Tagami et al. 1995b). The models are compared by their low-T and high-T PAZ boundaries, defined by a 10 and 90% track density reduction, respectively, as previously used by Durrani and Khan (1970) and Tagami and Dumitru (1996). The zero-damage model predicts the highest PAZ boundary temperatures, while Galbraith and Laslett (1997) are on the lower end. Fission tracks in zero-damage zircons seem to be most resistant to annealing.

Geologic constraints on the zircon PAZ

Field constraints on the zircon PAZ can be divided into three groups according whether the zircons in the investigated rocks do not show any sign of partial annealing at

a specific temperature (e.g., Tagami et al. 1995a; Tagami and Shimada 1996), they entered the PAZ without reaching its upper end (e.g., Carpéna and Caby 1984; Brandon and Vance 1992; Ito and Tanaka 1995; Wagner et al. 1997; Brandon et al. 1998; Rahn et al. 2000; Hasebe et al. 2003) or they reached complete annealing (e.g. Rahn et al. 2000). Zircons that enter the FT PAZ at its lower temperature boundary will undergo track annealing at a rate that depends on the accumulated α damage density. In sedimentary samples, fission tracks in zircons of different age and U content will have different annealing rates, and while some young or U-poor zircons still retain their provenance age at a certain temperature, old or U-rich grains start annealing their fission tracks at the same conditions. In the high-T range of the PAZ, a well-defined population of completely reset zircons may be present next to a population of only partially annealed grains. The advantage of this behavior is obvious: the presence of high-damage zircons allows that fraction to reset well before the last grains are totally reset and therefore record a geologically meaningful information (see e.g. in Brandon et al. 1998).

Several studies proposed that lower greenschist or blueschist facies conditions (i.e. temperatures up to 350° C) are needed for complete track annealing in detrital zircons (Carpéna and Caby 1984; Rahn and Brandon 1998; Rahn et al. 2000). In the Central Alps, which are known for their Neogene moderate to fast cooling rates (Hurford 1986; Hunziker et al. 1992), partially reset zircons exist up to maximum metamorphic temperatures of >300° C (Rahn et al. 2000) as constrained by fluid inclusion, vitrinite reflectance and mineral paragenesis data. Brandon et al. (1998) report zircon grain age distributions from the Olympic Subduction complex, Washington State, with populations of completely reset and only partially reset ages. For the corresponding localities,

metamorphic assemblages show pumpellyite-actinolite facies and geothermometers suggest maximum temperatures of $\sim 320^{\circ}\text{C}$ (Rahn and Brandon 1998). Ito and Tanaka (1995) report zircon fission track ages from a borehole with a bottom-hole temperature of 295°C where the zircons only underwent 46% track length reduction during a ~ 1 myr heating event. For a deep bore hole close to Vienna, Austria, Tagami et al. (1995a) observed no traces of annealing even though measured bottom temperatures of 200°C seem to have persisted over the last 5-10 myr. In a similar study on two boreholes from Japan, Hasebe et al. (2003) observed a decrease of mean track length for samples with a present borehole temperature above 205°C . The thermal conditions were estimated to have persisted for a duration of 1 myr.

A study of Carpéna and Caby (1984) presented unreset zircon ages from the Western Alps ophiolites, which contain Alpine metamorphic minerals such as lawsonite, blue amphibole, and jadeite. The authors estimated metamorphic conditions of 0.6-0.8 GPa and $300\text{-}350^{\circ}\text{C}$ for this paragenesis. From the late Triassic-early Jurassic zircon ages we would assume that these zircons would have accumulated a large density of α damage and would therefore reset at rather low temperatures. With one exception, however, all zircons show an unusually low track density. In this case, not the age, but the low U content most probably has caused a low α damage density and a high resistance to FT annealing.

The available geologic evidence for zircon PAZ boundaries from the literature is compiled in a log time versus temperature diagram (Fig. 6). All sources provide detailed information about the state of zircon annealing, and independent information about the duration of track accumulation before, and the maximum temperature and duration of the

undergone heating event. Not included are constraints from the ultra-deep borehole at the Kola Peninsula (see Tagami et al. 1998), because for these data, the thermal setting has only been estimated, mainly by assuming a constant temperature ($T = 212^{\circ}\text{C}$, measured at the bottom after drilling) for the last ~ 250 myr. The same insufficiently detailed thermal and temporal information is provided for the KTB bore hole, leading to a rejection of these data for the here presented compilation.

The temperature and time information of most of the compiled geologic examples scatters along a zone that is oblique to the modeled PAZ boundaries. The examples plot within the PAZ boundaries for short-duration heating events, but below the PAZ or its lower boundary for long-duration heating episodes. Long-duration changes in thermal conditions imply that zircons with high α damage are involved in annealing, leading to the strongest deviation from the predictions of a zero-damage annealing model. In contrast, fast changes in thermal conditions are, in general, compatible with low α damage accumulation rates in zircon, and in this case, zircons behave more according to the predictions of low damage annealing models. One interesting outlier to this general trend comes from a study with very old partially reset zircons that underwent a short-term heating event (< 1 myr, Roden et al. 1993). Independent estimates based on fluid inclusion data and conodont alteration color suggest temperatures $< 200^{\circ}\text{C}$. Other temperature indicators suggest a maximum temperature within a range of $100\text{-}200^{\circ}\text{C}$ (Roden et al., 1993). Accordingly, zircons in Roden et al. (1993) start to anneal their accumulated fission tracks below 200°C , which is much earlier as e.g. demonstrated by Rahn et al. (2000) for Alpine zircons that show no evidence of annealing in the temperature range of $180 - 230^{\circ}\text{C}$ (determined by fluid inclusion homogenization

temperatures). In this case, the α damage density of the zircons, which was accumulated according to their detrital age, determines the annealing behavior of the FTs.

Geologic evidence for the zircon FT closure temperature

The closure temperature, T_c , of the zircon FT system was estimated in a large number of geochronologic field studies, where the investigated rocks underwent monotonic cooling from temperatures above the zircon PAZ to temperatures below (e.g., Harrison et al. 1979; Zeitler 1985; Hurford 1986; Fitzgerald and Gleadow 1988; Gebauer et al. 1997; Brandon et al. 1998; Scott et al. 1998; Batt et al. 1999). Studies with fast cooling rates are of particular interest, as they produce a situation where zircons move through the PAZ in a nearly damage-free state. In this case, the FT system should most closely follow our results for zero-damage zircons. In a study on the very fast exhumation of the ultra-high pressure rocks of the Dora Maira, Western Alps, Gebauer et al. (1997) used a T_c of $290 \pm 40^\circ \text{C}$ in accordance to Tagami and Shimada (1996) and Wagner et al. (1997). On this basis, cooling rates of to 80°C per myr were estimated to have occurred subsequent to deepest burial. The FT T_c predicted from the zero-damage annealing model is 338°C , the Galbraith and Laslett (1997) model predicts $T_c = 306^\circ \text{C}$, and Tagami et al. (1998) $T_c = 312^\circ \text{C}$ (Fig. 7). In the Gebauer et al. (1997) study, the closure temperature of zircon was taken from the literature, and not constrained by geologic evidence.

Several studies determined the zircon FT closure temperature based on other geochronologic systems with neighboring closure temperatures. In those cases, the applied closure temperatures of these neighboring systems had a strong effect on the

determination of the zircon closure temperature. Commonly, such neighboring geochronologic systems are the apatite FT system and the K/Ar and Rb/Sr systems of biotite and muscovite, which are also dependent on cooling rates or the duration of a heating event (e.g. Grove and Harrison 1996; Ketchum et al. 1999). Furthermore, the Ar and Sr isotopic systems in biotite and muscovite may have higher closure temperatures than previously assumed in cases of moderate to fast cooling rates, based on comparisons with stable isotope and other thermometric data (Kirschner et al. 1996). In a geothermal field with a short-duration thermal pulse, Del Moro et al. (1982) and Villa and Puxeddu (1994) presented evidence for a closing of the K-Ar and Rb-Sr systems in biotite at > 400 °C. Estimates of the zircon closure temperature based on other isotopic systems are limited to the understanding of closure in those systems.

The only other geochronologic method that allows direct link of ages with similar temperatures is the Ar/Ar-Kfs system. We have computed available studies with a combination of Ar/Ar Kfs and zircon FT ages. Previous studies without step heating procedure showed varying relationships between Ar/Ar Kfs and zircon FT ages (e.g. Harrison et al. 1979; Zeitler 1985; Shibata et al. 1990). Step heating was, however, used by Hoisch et al. (1997), Scott et al. (1998), and Batt et al. (1999). With the help of the Ar/Ar Kfs step heating ages and the thermal history derived thereof, the closure temperature of the zircon system can be bracketed by the envelope of the modeled Kfs time-temperature path. By this procedure, Hoisch et al. (1997) estimated a zircon T_c of ~ 300 °C for a rapid cooling rate of 100 °C Ma^{-1} . Since their Kfs model's envelope turned out to have a very steep time-temperature slope in the range of the zircon FT age, this estimate has a considerable uncertainty.

Our compilation of literature data is shown in Figure 7, and compared to the calculated relations between closure temperature and cooling rate (Galbraith and Laslett 1997; Tagami et al. 1998; this study). The zero-damage model closure temperature plots approximately 25-30° C above the Galbraith and Laslett (1997) curve. It is interesting to note that the zero-damage model predictions are in the range of closure of the Ar/Ar system derived from diffusion experiments on Fe-rich biotites (Grove and Harrison, 1996).

Most zircon FT closure temperatures derived from geologic data scatter at distinctly lower values than estimated from the two zircon annealing models, and lie close to the published curve of Brandon et al. (1998). In particular for high cooling rates, however, the field data tend to shift towards the values predicted by the low-damage model of Galbraith and Laslett (1997) and Tagami et al. (1998), and might, with even faster cooling rates, approach the predictions of the zero-damage model. The latter predicts that in this case zircon FT closure would be in the temperature range of the closure of the biotite Ar/Ar system.

The applicability of the zero-damage model in the field

From our compilation it is evident that there is no direct geologic evidence for the zero-damage model, but observations are consistent with an increase of annealing temperatures with decreasing damage density. For both data sets (Figs. 6 and 7), geologic constraints for zircon FT annealing are oblique to established model predictions, and consistently move to the high-temperature side for short-duration events. In both cases,

the predictions by Galbraith and Laslett (1997) and Tagami et al. (1998) for low-damage zircons estimate high temperatures, and only seem to agree with field constraints for short-duration temperature changes. In both cases, the applicability of the zero-damage annealing model seems to be limited to cases of very fast cooling or very short thermal pulses.

Rather than being directly applicable in geologic settings the zero-damage model provides an upper boundary for the annealing rate of fission tracks in zircon. Its applicability presumably is restricted to the following cases: a) In settings of very fast cooling from very high temperatures, the zero-damage annealing model predicts a correct zircon closure temperature, when practically no α damage is accumulated before the onset of FT retention. b) In settings where mixed populations of zircon undergo partial to total resetting, the zero-damage annealing model should predict maximum temperature conditions for total annealing, and thus can be used as a thermometer and mappable isotherm, especially if sediments include a very young (e.g. volcanic) or low-U population.

The temperature difference between the low- and the zero-damage models (Fig. 6) is less than 50° C for the PAZ boundaries. A clear distinction between the different proposed models based on geologic evidence requires a high precision of the temperature estimate during a thermal pulse or metamorphic event. Most temperature-sensitive parameters used to quantify very low- to low-grade metamorphism, such as vitrinite reflectance, mineral paragenesis, chlorite and stable isotope thermometers, rarely provide a precision better than $\pm 20^\circ$ C. Therefore it might be difficult to distinguish between these different annealing models on the basis of such data. However, given the fact that

the fanning and parallel relationships differ in their long-duration predictions (at 1 to 100 myr) by up to 100 °C (Fig. 1), future emphasis should be put on the distinction between these two existing relationships on the basis of geologic field evidences.

The influence of α damage on FT annealing

Based on the proposed zero-damage model, the influence of α damage on the annealing properties can be evaluated qualitatively. For this purpose we consider the ratio \cdot_{obs}/\cdot_{pred} , corresponding to the \cdot as observed in the annealing data and \cdot as predicted by the zero-damage model. If α damage is increasing the rate of FT annealing in zircon, we expect the \cdot ratio to show values below 1 for α decay damaged zircons. Ratios are calculated for all annealing data from Tagami et al. (1998) and Kasuya and Naeser (1988), and are presented in figure 8, plotted versus the initial track densities observed in the zircons prior to the annealing experiment. The track densities here serve as a proxy for radiation damage density. Assuming that the α damage PAZ be situated at higher temperatures relative to the FT PAZ, as suggested from experimental annealing temperatures (Geisler, 2002), the initial α damage density in a zircon grain is not expected to change significantly during any annealing experiment that stops before total FT annealing. In addition to the data of Kasuya and Naeser (1988), Tagami et al. (1990), and Yamada et al. (1995), we have also added the Zaun and Wagner (1985) data to the compilation (Fig. 6). The Zaun and Wagner (1985) data are poorly constrained with respect to their published track density range, but in comparison with the other data, show the strongest difference from the zero-damage model, and the highest track densities.

The plotted data (Fig. 8) show a trend that quickly moves away from the line of equity with increasing track density, but seems to behave asymptotically towards a maximum deviation from the predictions in an α damage-free zircon at high track density. The relationship between annealing rate and α damage density ($\dot{\alpha}$) can be qualitatively estimated from existing data on natural zircons and a zero-damage zircon annealing model proposed here. A plausible empirical function for these data is

$$\dot{\alpha} = a_f + b_f T \ln(t) + c_f T + d_f \ln(\dot{\alpha}) \quad (14)$$

Such an equation has the advantage of providing a linear relationship between $\dot{\alpha}$ and the fit parameters a - d . Alternatively, an equation is proposed where the parameter b is interpreted in terms of the activation energy of the annealing process (Märk et al. 1981; Modgil and Virk 1985; Sandhu et al. 1990; Virk 1995) and changes as a function of $\dot{\alpha}$.

In this case, equation (3) is modified to

$$\dot{\alpha} = a_f + b_f(\dot{\alpha}) T \ln(t) + c_f T \quad (15)$$

or

$$\dot{\alpha} = a_f + b_f(\dot{\alpha}) [T \ln(t) + c_f T] \quad (16)$$

depending on whether we refer to a fanning model with fixed fanning point or with a fanning point drifting along the $1/T = 0$ axis (Yamada et al. 1995; Ketcham et al. 1999).

Because

$$\dot{\alpha} = \dot{\alpha}(t, T) \quad (17)$$

where t accounts for both the accumulation of α damage and the time effect in annealing, a general conclusion is that iso-annealing curves in an Arrhenius plot cannot be parallel, and the assignment of the b parameter to an activation energy, which is dependent on a

second annealing process, would also give a physical explanation on why the fanning relationship should give a better statistical fit to the data.

For the establishment of an α damage integrating model, as preliminarily outlined by equations (14)-16), much more experimental annealing data, in particular for the annealing of fission tracks under high α damage density conditions, are needed. Since there is evidence of a marked overlap of the α PAZ and the FT PAZ, the establishment of such an α damage-integrating model will have to consider the thermal and temporal brackets of α damage annealing.

Conclusions

Despite restricted use for geologic applications, the proposed zero-damage FT annealing model has important implications for understanding FT annealing in zircons. The available data for zero-damage zircons (Fig. 2a) show a remarkable consistency that cannot be found in any other comparison among the various zircon annealing experiments. Annealing experiments with zero-damage zircons are proposed as the basis for further experimental investigations. As a next step, suitable zircon samples have to be found that show the smallest possible grain to grain variation in α damage density, i.e. preferably have the same age and U content (and an average Th/U ratio, see Garver and Kamp 2002). As a counterpart to existing annealing data, experiments on FT annealing in very high-damage zircons are particularly important. Furthermore, the time-temperature relationship between FT annealing and α damage annealing has to be evaluated in more detail, e.g. by combined annealing experiments. One important step in this direction was

the establishment of α damage density quantification by Raman spectroscopy (Nasdala et al. 1995; Nasdala et al. 2001).

A compilation of geologic constraints on FT annealing in zircons reveals that none of the existing zircon FT annealing models is able to explain the range of available field evidence. Temperature conditions predicted from the zero-damage model are thought to represent an upper temperature limit for zircon FT annealing. Rather than assuming a fixed closure temperature for the zircon FT system, we have to apply a value that is dependent not only on the cooling rate but also on the U and Th content, since the annealing behavior of fission tracks in zircons is sensitive to α damage, in particular in the very low α damage density range (Fig. 8).

As an upper temperature limit for zircon annealing, the zero-damage model might represent a mappable isotherm in areas of sub-greenschist to low greenschist facies metamorphism. Since the temperatures for total resetting the FT system depend not only on the annealing duration, but also on the amount of α damage accumulated, this thermometer is also dependent on the U content and thermal history of the zircons involved. In the case of no further constraints, the zero-damage model may provide a maximum temperature value.

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Figure captions

Fig. 1 Compilation of published zircon FT PAZ boundaries in an Arrhenius plot. a) PAZ boundaries of Fleischer et al. (1965), Krishnaswami et al. (1974), Koul et al. (1988), and Carpéna (1992) (shaded area). The lines of Fleischer et al. (1965) and Krishnaswami et al. (1974) were considered to be the low T side of the PAZ. The Koul et al. (1988) line was proposed as an upper PAZ boundary. For the PAZ boundaries of Carpéna (1992), lines of 10 and 90% of track density reduction are shown. b) PAZ boundaries of the three proposed models of Yamada et al. (1995): solid line: parallel model, long-dashed line: fanning model with $T_0 = 8$, short-dashed line: fanning model with $T_0 = 8$, all boundaries are directly taken from Yamada et al. (1995), thus correspond to track length ratios (L/L_0) of 0.95 and 0.4 and track density ratios (D/D_0) of 0.94 and 0.25. Note the large differences of the models when extrapolated to geologic time scales.

Fig. 2 Comparison of 1-hour FT annealing experiments for zircons in normalized track length versus temperature diagrams: a) annealing experiments on annealed zircons with induced tracks. Filled circles: Kasuya and Naeser (1988); open circles: Yamada et al. (1995); triangle: Carpéna (1992). The two data points in brackets represent estimated values. b) annealing experiments on zircons with different levels of α damage density. Open circles as in (a), filled circles: annealing in 21 Ma zircons (track density appr. $4 \times 10^6 \text{ cm}^{-2}$) from Yamada et al. (1995), filled triangles: annealing in 69 Ma zircons (track density appr. $7 \times 10^6 \text{ cm}^{-2}$) from Tagami et al. (1990).

Fig. 3 Comparison of the mean track lengths for all orientations (L_{all}) with those of tracks at an angle $> 60^\circ$ to the crystallographic c-axis ($L_{>60}$). Data from Tagami et al. (1998) and Yamada et al. (1995). Error bars shown as 1σ . Data from zero-damage zircons are marked with open circles. The errors of the L_{all} values were estimated according to the empirical relationship in figure 4. Most mean lengths of L_{all} and $L_{>60}$ are indistinguishable from a 1:1 relationship (diagonal line) based on the displayed 68% confidence interval. The grey shaded area represents the 2σ standard deviation of a linear regression line between all L_{all} and $L_{>60}$ values ($L_{>60} = 1.029 * L_{all} - 0.381$), which is slightly but significantly different from a 1:1 relationship.

Fig. 4 Empirically derived relationship between the mean track length and its standard deviation (SD), based on all annealing data from Tagami et al. (1998) (filled circles). For the proposed regression curve, the lowermost data point, which is only on based two measured track lengths, was neglected. Open circles show the uncertainties estimated from the figures of Kasuya and Naeser (1988).

Fig. 5 Illustrated models for zero-damage zircon fission track annealing experiments. The parallel model (a) predicts a flat plane in a $-1/T - \ln(t)$ space, whereas the fanning model (b) plane has a slight curvature in a $-T - \ln(t)$ space. For the fanning model, the offset of several points below the plane is visible. These points all have very small differences between L and L_o , thus, their $SE(.)$ becomes very large, and their regression weighting factor is low.

Fig. 6 Comparison of three different zircon FT fanning annealing and geologic constraints on the zircon PAZ from the literature: solid thick lines: zero-damage

model (this study); long-dashed thick lines: Tagami et al. (1998); short-dashed thick lines: Galbraith and Laslett (1997) model. The model PAZ boundaries were calculated as 10 and 90% track density reduction lines based on the track length-density relationship of Tagami et al. (1990). Literature data: 1) Árkai et al. (1995), 2) Tagami et al. (1995a), 3) Carpéna and Caby (1984, gray area), 4) Ito and Tanaka (1995), 5) Rahn and Brandon (1998, area surrounded by dashed line), 6) Rahn et al. (2000), 7) Zaun and Wagner (1985), 8) Hasebe et al. (1997), 9) Ohmori et al. (1997), 10) Tagami and Shimada (1996), 11) Roden et al. (1993), 12) Hasebe et al. (2003). White boxes indicate conditions below the zircon FT PAZ, gray boxes conditions within the zircon FT PAZ, and one black box indicates totally reset zircons. Box boundaries are given as thick lines only where conditions are explicitly stated in the literature.

Fig. 7 Predicted closure temperatures for the case of constant cooling of zircons across the PAZ from the zero-damage (solid line), and two low-damage models (Tagami et al. (1998), long dashed line, and Galbraith and Laslett (1997), short dashed line). The predictions are compared to geologic constraints from the literature: gray line: Brandon et al. (1998); circles: constraints based on a direct comparison between Ar/Ar age spectra of Kfs (black: Scott et al. (1998), gray: Batt et al. (1999), white: Hoisch et al. (1997)); open diamond: Harrison et al. (1979), recalculated according to Brandon et al. (1998); open square: Hurford (1986); triangle: Gebauer et al. (1997); upside-down triangle: Koul et al. (1988). For comparison, the temperature range for closure of the Ar/Ar system in Fe-rich

biotite at a cooling rate of 10° C/myr from Grove and Harrison (1996) is indicated and coincides with the closure conditions of the zero-damage zircon FT model.

Fig. 8 Compilation of zero-damage zircon FT (track density = 0), and natural zircon FT experiments (Kasuya and Naeser 1988; Tagami et al. 1990; Tagami et al. 1998) and their difference from the predictions of a zero-damage model. A \cdot_{obs}/\cdot_{pred} value of 1 (horizontal line) indicates agreement with the zero-damage model. The data of Zaun and Wagner (1985) are indicated by a dashed-lined box representing their varying offset from the zero-damage model and their large variation in reported track densities (recalculated to the initial track density before annealing). The curved trend shows the predicted influence of α damage (estimated by the initial track density) on zircon FT annealing.

Tab. 1 Regression data of the different calculated models on fission track annealing.

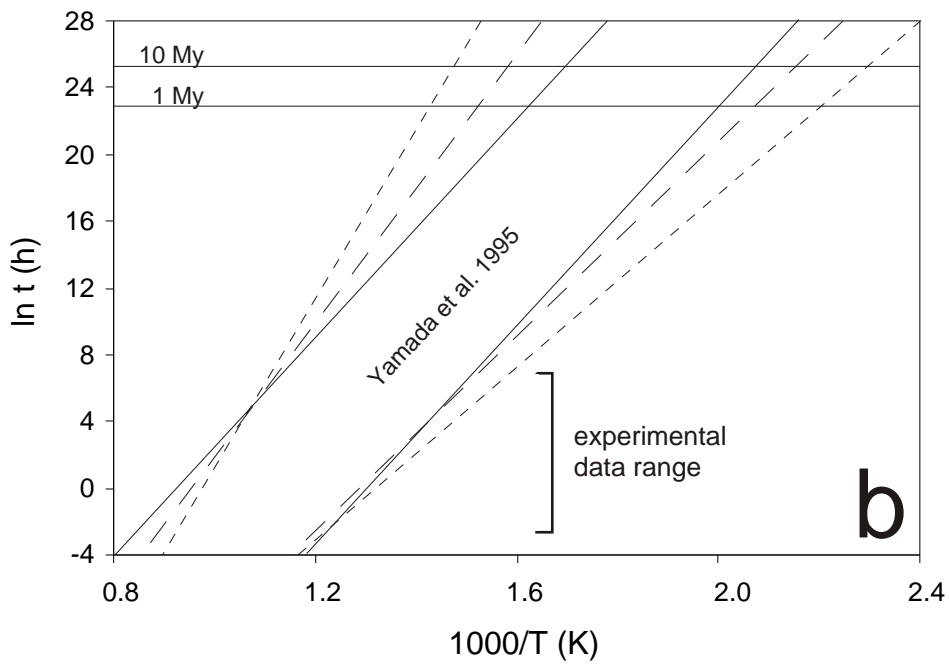
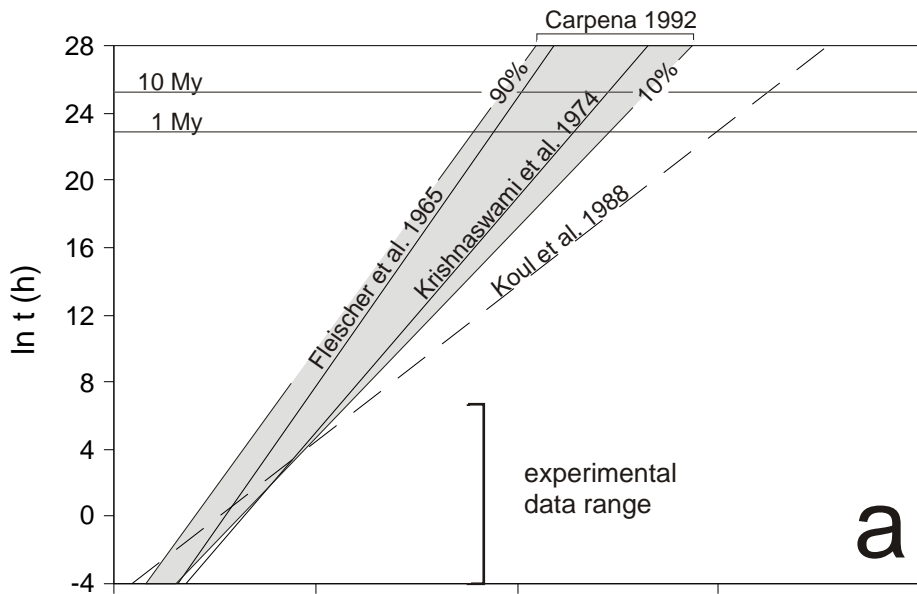
Data set	Data sources	n*	Parallel model					Fanning model				
			a [†] (±1σ)	b [†] (±1σ)	c [†] (±1σ)	R ² (±1σ)	. ² _r [‡] (±1σ)	a [†] (±1σ)	b [†] (±1σ)	c [†] (±1σ)	R ² (±1σ)	. ² _r [‡] (±1σ)
zero-damage zr	Kasuya & Naeser 1988, Yamada et al. 1995, Carpena 1992	54	9.207	-9976	0.2216	0.988	1.99	-11..57	2.755E-4	1.075E-2	0.992	1.34
			0.130	127	0.0172			0.14	0.189E-4	0.014E-2		
low-damage zr	Tagami et al. 1998	27	6.532	-7248	0.2039	0.955	2.80	-10.77	2.599E-4	1.026E-2	0.966	2.14
			0.215	192	0.0063			0.24	0.078E-4	0.027E-2		
low- to moderate- damage zr	Kasuya & Naeser 1988, Tagami et al. 1990, Tagami et al. 1998	66	6.581	-7101	0.1736	0.927	41.85	-11.41	2.472E-4	1.125E-2	0.915	48.59
			0.050	39	0.0029			0.05	0.037E-4	0.006E-2		
mixed-damage zr	Kasuya & Naeser 1988, Tagami et al. 1990, Carpena 1992, Tagami et al. 1998	120	6.221	-6855	0.1729	0.951	33.29	-9..911	2.488E-4	9.267E-3	0.938	42.50
			0.029	25	0.0028			0.031	0.034E-4	0.034E-3		

Notes:

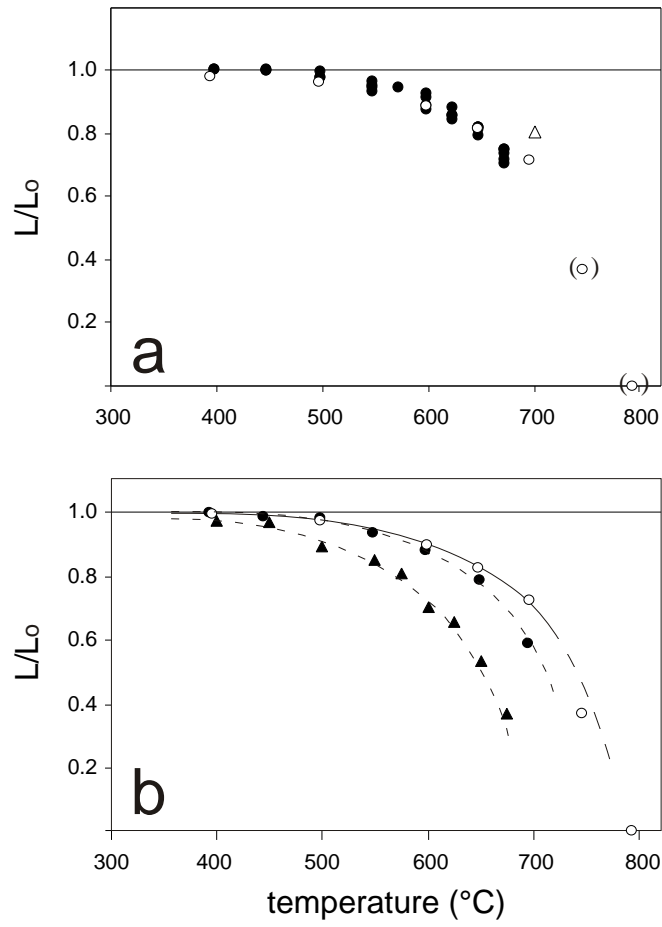
* n = number of data, not included are the measurements at ambient temperatures

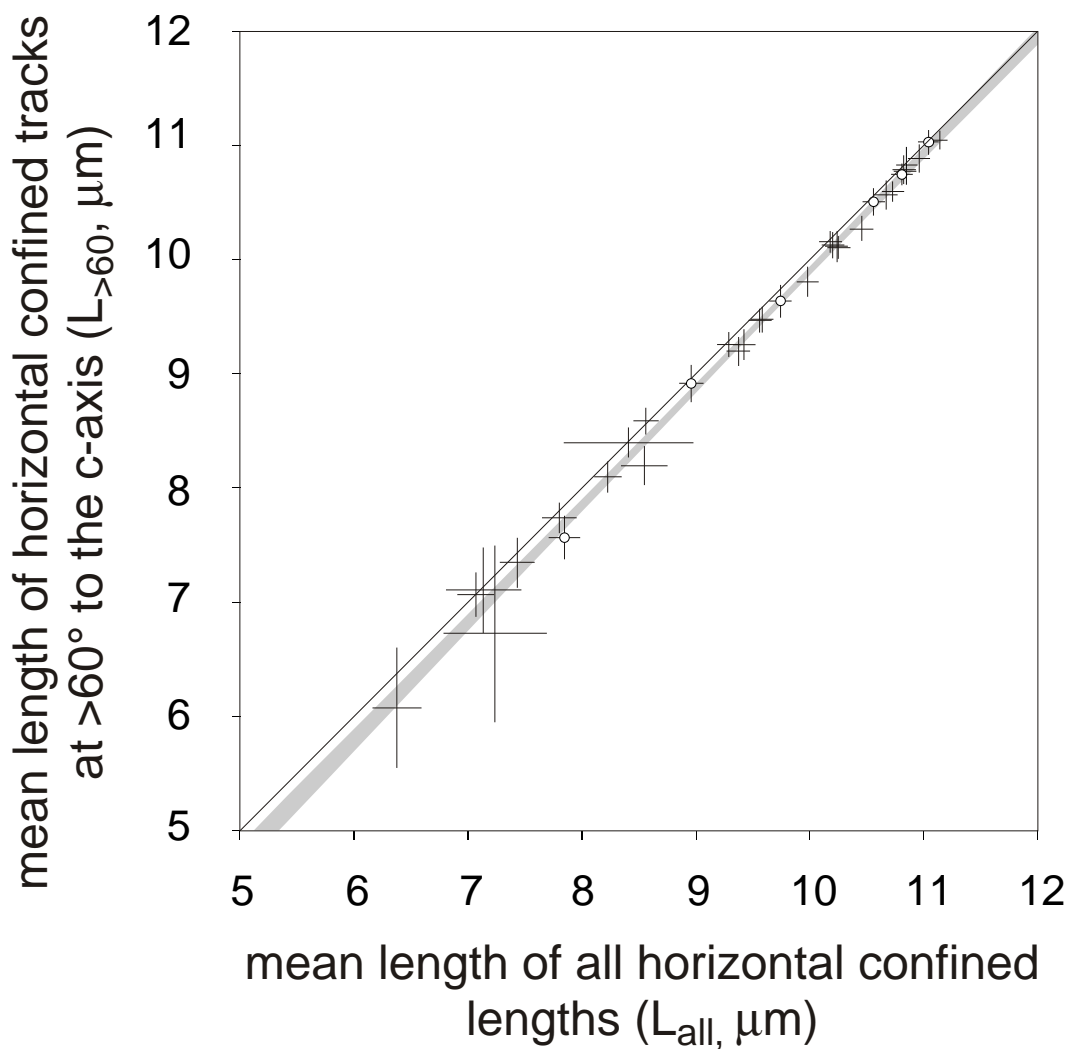
† parameters a, b, and c refer to equation 2 (parallel) or 3 (fanning) in text.

‡ .²_r = reduced chi-square, .²_r = norm²/n-3, where 3 corresponds to the number of fit parameters

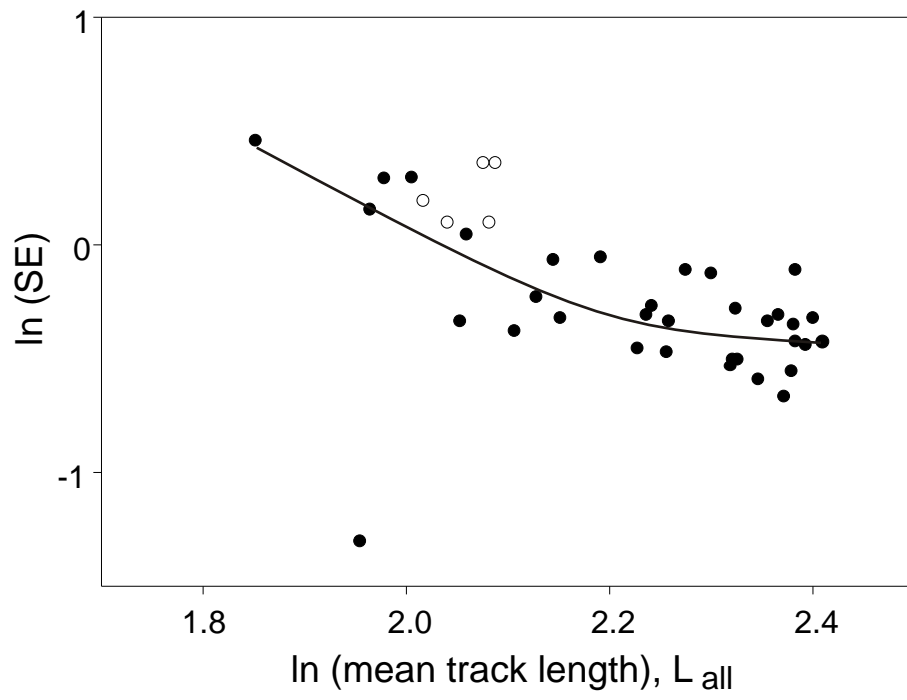


Rahn et al., Fig. 2

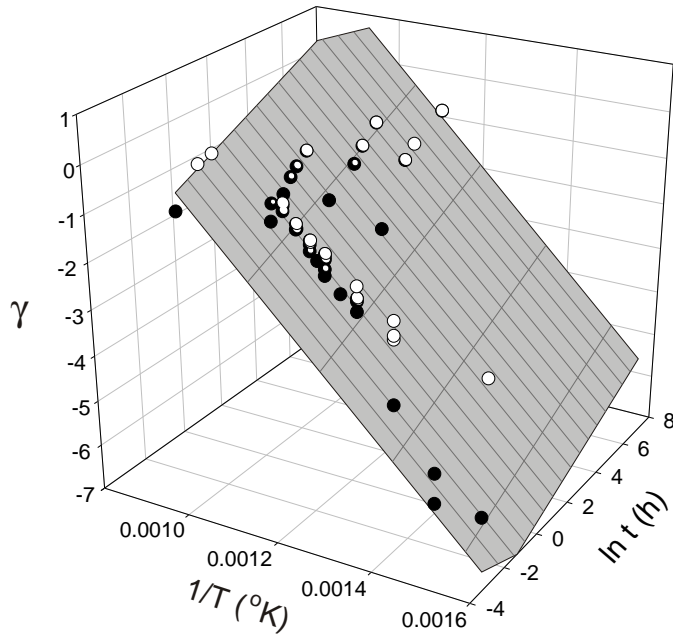




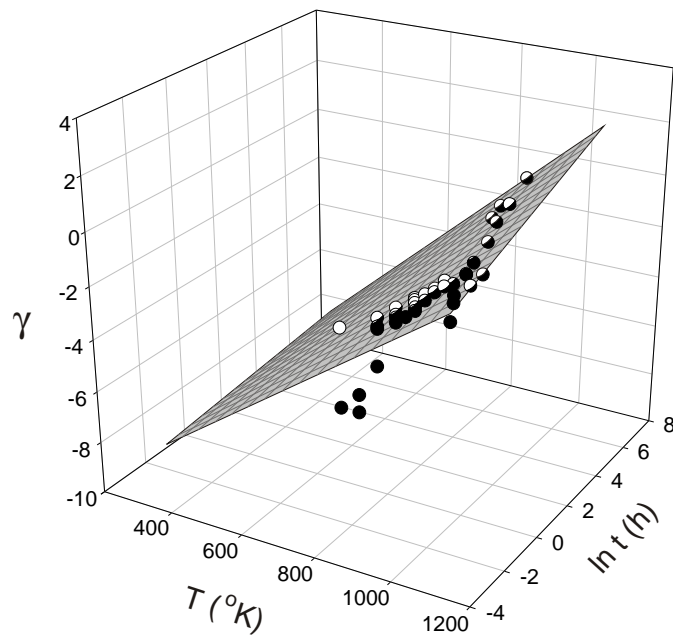
Rahn et al., Fig. 4



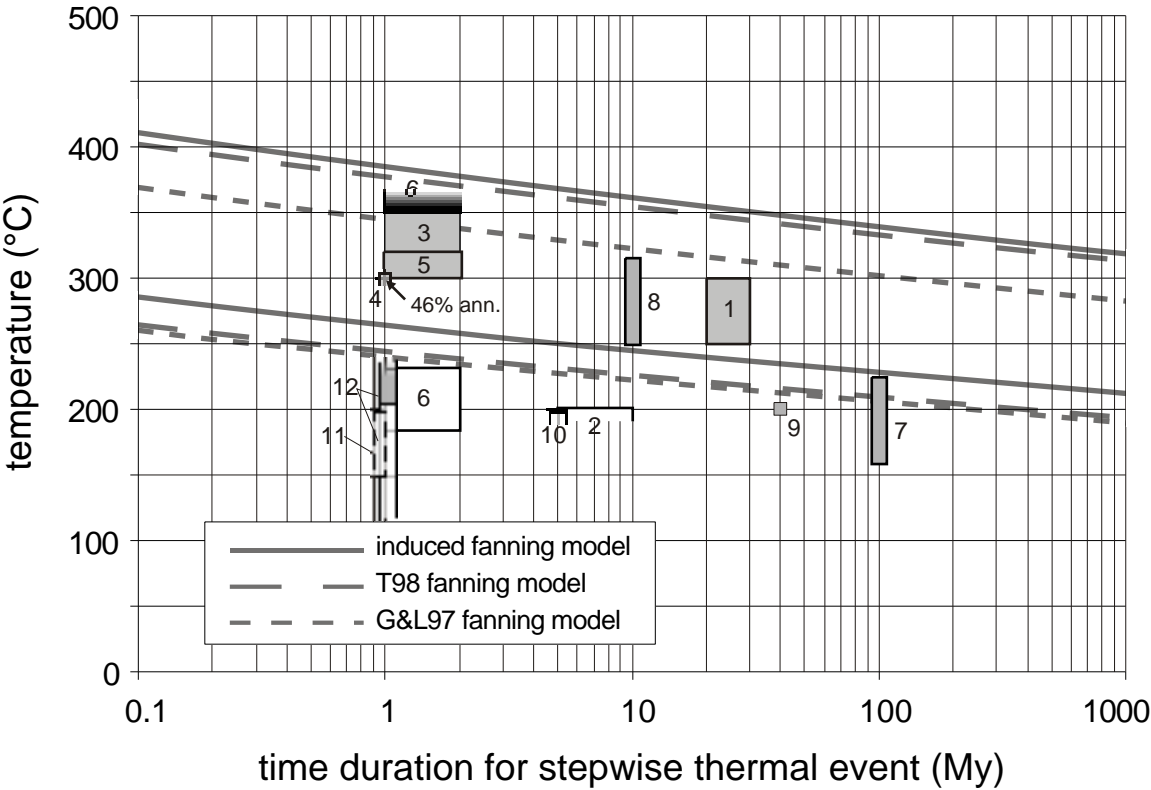
a parallel model



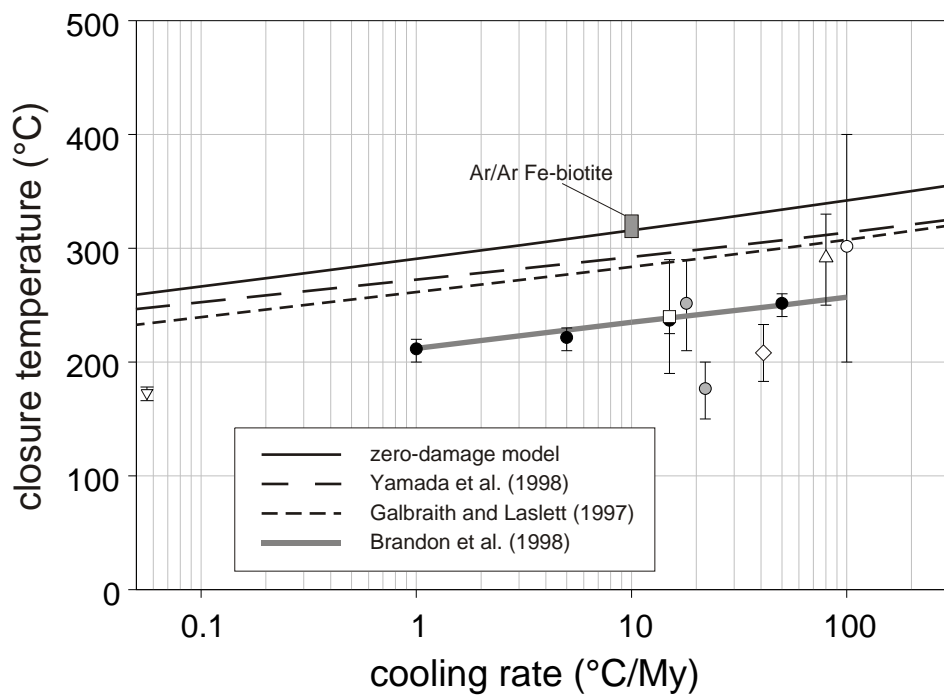
b fanning model



Rahn et al., Fig. 6



Rahn et al., Fig. 7



Rahn et al., Fig. 8

