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A helium-based model for the effects of radiation damage annealing on helium diffusion kinetics in apatite

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ABSTRACT

Widely used to study surface processes and the development of topography through geologic time, (U–Th)/He thermochronometry in apatite depends on a quantitative description of the kinetics of ^{4}He diffusion across a range of temperatures, timescales, and geologic scenarios. Empirical observations demonstrate that He diffusivity in apatite is not solely a function of temperature, but also depends on damage to the crystal structure from radioactive decay processes. Commonly-used models accounting for the influence of thermal annealing of radiation damage on He diffusivity assume the net effects evolve in proportion to the rate of fission track annealing, although the majority of radiation damage results from α-recoil. While existing models adequately quantify the net effects of damage annealing in many geologic scenarios, experimental work suggests different annealing rates for the two damage types. Here, we introduce an alpha-damage annealing model (ADAM) that is independent of fission track annealing kinetics, and directly quantifies the influence of thermal annealing on He diffusivity in apatite. We present an empirical fit to diffusion kinetics data and incorporate this fit into a model that tracks the competing effects of radiation damage accumulation and annealing on He diffusivity in apatite through geologic time. Using time–temperature paths to illustrate differences between models, we highlight the influence of damage annealing on data interpretation. In certain, but not all, geologic scenarios, the interpretation of low-temperature thermochronometric data can be strongly influenced by which model of radiation damage annealing is assumed. In particular, geologic scenarios involving 1–2 km of sedimentary burial are especially sensitive to the assumed rate of annealing and its influence on He diffusivity. In cases such as basement rocks in Grand Canyon and the Canadian Shield, (U–Th)/He ages predicted from the ADAM can differ by hundreds of Ma from those predicted by other models for a given thermal path involving extended residence between ~40–80 °C.

1. Introduction

Over the past two decades, (U–Th)/He thermochronometry in apatite has been widely used to study surface processes and topography development through geologic time (e.g., Reiners and Brandon, 2006). Because the diffusion of He in apatite is sensitive to temperatures found in the uppermost few kilometers of Earth's crust, the production and diffusion of radiogenic ^{4}He via α-decay of radioactive nuclides (i.e. along the U- and Th-series decay chains) can be used to quantify the timing, rates, and spatial patterns of exhumation over typically >0.1 million year (Ma) timescales (e.g., Farley, 2002). A quantitative description of the diffusion kinetics of ^{4}He in apatite is required for accurate interpretation of (U–Th)/He data. Complexity in the kinetic function has been revealed by empirical observations that He diffusivity in apatite is not solely a function of temperature, but may also evolve as a function of damage to the apatite crystal structure resulting from α-recoil and fission events (Shuster et al., 2006; Flowers et al., 2009; Shuster and Farley, 2009; Gautheron et al., 2009). Damage from α-recoil has recently been mapped in zircon (Valley et al., 2014), revealing small pockets of damage capable of trapping He (Shuster et al., 2006; Flowers et al., 2009; Shuster and Farley, 2009; Gautheron et al., 2009) and other elements. The radiation damage content in a crystal will increase as a function of time, at a rate proportional to parent nuclide concentration, but will also decrease in response to thermal heating (Shuster and Farley, 2009). The effects of thermal annealing of radiation damage and its influence on He diffusivity complicates the

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problem of quantifying ^{4}He diffusivity through time, as the diffusivity at any point in time will be influenced by the sample's prior thermal path. A quantitative understanding of the competing effects of radiation damage accumulation and annealing is necessary to accurately model and interpret the results of all (U–Th)/He thermochronometric data, but especially in scenarios involving reheating over geologic time (e.g., due to sedimentary burial).

Previous treatments of the accumulation and annealing of radiation damage in apatite have recently been challenged by observations in certain geologic scenarios, demonstrating the important influence of the assumed rate of annealing on (U–Th)/He data interpretation (e.g., Fox and Shuster, 2014). Existing models, now commonly used to interpret (U–Th)/He data, make the fundamental assumption that the net effects of radiation damage in apatite, which primarily result from α-recoil damage, can be quantified using empirical models of apatite fission track (AFT) annealing (Flowers et al., 2009; Gautheron et al., 2009). This assumption – that fission tracks and α-recoil damage anneal, and in response control He diffusivity, at the same rate – adequately describes the effects of annealing in many geologic scenarios. However, measurements of optical properties suggest that annealing rates of damage resulting from α-recoil and fission events in apatite likely differ (Ritter and Märk, 1986). In the event that fission tracks are less resistant to annealing than α-recoil damage, perhaps a function of damage geometry or size, the previous diffusion models would overpredict the rate of damage annealing and underpredict the (U–Th)/He age.

Here, we present a new alpha-damage annealing model (ADAM) that quantifies the influence of thermal annealing on He diffusivity without relying on the assumption that α-recoil damage anneals at a rate that is ultimately tied to the annealing of fission tracks. The ADAM instead quantifies the effects of annealing with empirical relationships calibrated by experimentally-controlled damage annealing and He diffusion kinetics data, thus providing an internally consistent and more direct relationship between α-recoil damage annealing and He diffusivity. We present an empirical fit to data of Shuster and Farley (2009), which quantify the resulting effects of annealing temperature and duration on He diffusivity. By assuming these experimental results are extrapolatable to longer times and lower temperatures, we incorporate the calibrated functions into a numerical model that tracks the competing effects of radiation damage accumulation and annealing on He diffusivity in apatite; we show evolutions of radiation damage, diffusion kinetics, and the (U–Th)/He age through geologic time. We compare the results of this new model framework with existing models (Farley, 2000; Flowers et al., 2009) and demonstrate that in certain, but not all, geologic scenarios, the interpretation of low-temperature thermochronometric data can be strongly influenced by the assumed model of radiation damage annealing.

2. A new framework for quantifying the effects of annealing

Predicting (U–Th)/He ages for a given apatite sample requires specifying the diffusivity of He as it evolves through geologic time and temperature (Farley, 2002; Shuster et al., 2006; Shuster and Farley, 2009; Flowers et al., 2009; Gautheron et al., 2009). As in previous treatments of this problem, the ADAM calculates the production and diffusion of ^{4}He in a finite crystal domain based on the grain size, U and Th concentrations, temperature, and the damage concentration in the crystal. The ADAM assumes the accumulation of radiation damage causes He diffusivity to decrease, following empirical relationships calibrated in Shuster and Farley (2009), Flowers et al. (2009). However, unlike other models, the ADAM assumes that the annealing of damage from spontaneous fission events and damage from α-recoil do not necessarily occur at the same rate, or even a scaleable rate. Experimental work measuring the effects of thermal annealing conditions in apatite found large differences based on the type of radiation damage (i.e. fission track versus α-recoil), quantified by optical properties (Ritter and Märk, 1986). We calibrate the annealing portion of the ADAM using experimentally-determined diffusion kinetics data (Shuster and Farley, 2009). Employing an empirical fit to diffusion data produces a simpler, more direct relationship between damage concentration and He diffusion, and – importantly – restores independence between models, and thus interpretations, of (U–Th)/He and fission track systems in apatite.

The experiments of Shuster and Farley (2009) systematically measure changes in He diffusivity by varying the annealing temperature and duration in Durango apatite; these data provide the basis for our empirical fits integrated into the ADAM. Shuster and Farley (2009) present diffusivity or closure temperature (Dodson, 1973), both derivative quantities of activation energy (E_a) and the pre-exponential term (D_0/a^2) in the Arrhenius relation for diffusivity. Here, we use the reported values of E_a and $\ln(D_0/a^2)$ in Table 2 of that work. Because we are interested in how diffusion kinetics parameters change in response to annealing conditions, the results are expressed as differences between the measured E_a and $\ln(D_0/a^2)$ values in the suite of annealed samples and the sample with no preheating. Fig. 1 shows the (Shuster and Farley, 2009) results in this form, plotting the systematic changes in E_a (ΔE_a) in Fig. 1A and the changes in $\ln(D_0/a^2)$ ($\Delta\ln(D_0/a^2)$) in Fig. 1B.

Based on previously published results (Shuster et al., 2006; Shuster and Farley, 2009; Flowers et al., 2009), we sought a mathematical expression to relate temperature, heating duration, and diffusion kinetics with two goals. First, the expression needed to reach maximum and minimum values at low and high temperatures, respectively. That is, no change to diffusion kinetics occurs at very low temperatures, and above some combination of duration and sufficiently high temperature, the parameters reach values characteristic of a fully annealed (or damage-free) crystal: 122.3 kJ/mol for E_a and 9.733 for $\ln(D_0/a^2)$ (Flowers et al., 2009). Second, we required the ΔE_a and $\Delta\ln(D_0/a^2)$ to depend on both temperature and duration. We thus chose an empirical relationship between annealing temperature, annealing duration, and diffusion kinetics that both adequately describes the available experimental data, and predicts the expected behavior at very low and very high temperatures. We adapted a functional form previously used to quantify similar effects in damage annealing (Laslett et al., 1987), and use two expressions that describe resulting changes in He diffusion kinetics directly: one for ΔE_a and one for $\Delta\ln(D_0/a^2)$:

$$\ln\left[-\ln\left(\frac{\Delta E_a}{c_3\_E_a}-1\right)\right]=c_1\_E_a+\ln(t)+c_2\_E_a*T^{-1} \quad (1)$$

$$\ln\left[-\ln\left(\frac{\Delta\ln D_0/a^2}{c_3\_D_0}-1\right)\right]=c_1\_D_0+\ln(t)+c_2\_D_0*T^{-1} \quad (2)$$

where t is duration of thermal annealing at temperature T, c_1 and c_2 (for E_a and D_0) are empirically fit parameters, and $c_3\_E_a$ and $c_3\_D_0$ are calculated values, described below.

To quantify the best-fitting set of parameters for Equations (1) and (2), we conducted a systematic search of parameter combinations. The tested values for $c_1\_E_a$ and $c_1\_D_0$ range from 55 to 65 and the values for $c_2\_E_a$ and $c_2\_D_0$ range from −25000 to −19000, with both ranges divided into 101 linearly-spaced values. These ranges were selected to encompass combinations of fits that plot near the data and complete the search at an informative resolution. The quantities $c_3\_E_a$ and $c_3\_D_0$ are not fitted values, but rather the differences between the observed values of E_a (141 kJ/mol) and $\ln(D_0/a^2)$ (14.23) for natural (i.e., non-annealed) Durango apatite (Shuster and Farley, 2009; Fig. 1) and the assumed

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