Helium diffusion and (U–Th)/He thermochronometry of titanite

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Abstract—We have explored the diffusivity characteristics of radiogenic He in titanite (sphene) and have developed analytical techniques for (U–Th)/He dating of this mineral. Results of incremental He outgassing experiments performed on titanites from a variety of geological environments suggest a thermally activated volume diffusion mechanism with an activation energy of 44.6 ± 3.4 (2σ) kcal/mol and a frequency factor of ~60 cm²/s. Diffusivity is highly linearly correlated with the inverse square of the grain size, indicating that the He diffusion domain in titanite is the crystal itself. For typical titanite grains of 200- to 800-μm minimum dimension, the He closure temperature is in the range 191 to 218°C (for a cooling rate of 10°C/Myr). There is no indication in the titanites we studied that radiation damage plays a major role in He diffusion. (U–Th)/He ages of titanites from quickly cooled rocks yield ages (with ~5–8% 1σ reproducibility) that are concordant with known ages, and (U–Th)/He ages of titanites from slowly cooled rocks are consistent with independently established cooling paths, supporting the closure temperature estimates. These experiments suggest that titanite (U–Th)/He ages may be useful for constraining cooling histories at temperatures near the lower limit of those accessed by feldspar ⁴⁰Ar/³⁹Ar dating but higher than apatite fission track or (U-Th)/He dating. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Recent development of analytical techniques for apatite (U–Th)/He dating (Zeitler et al., 1987; Lippolt et al., 1994; Wolf et al., 1996; Farley et al., 1996) and practical demonstration of its usefulness as a low temperature (~75°C) thermochronometer (Wolf et al., 1997; House et al., 1997; Spotila et al., 1998; House et al., 1998) suggest that (U–Th)/He thermochronometry of other minerals may be feasible. The relatively high U and Th concentrations and the common occurrence of titanite (sphene, CaTiSiO₅) in crustal rocks motivated us to examine the He diffusivity characteristics of this mineral.

Early attempts to date titanates by using ⁴⁰He ingrowth yielded inconsistent results, similar to those obtained on other minerals and whole rocks (e.g., references in Harper, 1973; Wolf et al., 1996). Most calculated ages were younger than expected from geologic constraints (Strutt, 1911; Larsen and Keevil, 1942; Keevil et al., 1944), an observation attributed to high He diffusivity either inherent to the normal structure and composition of the mineral or due to radiation damage. Hurley (1952; 1954) and Hurley and Fairbairn (1953) documented inverse correlations between estimated radiation dosage (from U and Th content and an assumed age) and “helium retention” (fraction of He present relative to that expected from the assumed age) for both zircon and titanite. They interpreted the correlations as evidence for a strong influence of radiation damage on He diffusivity. Damon and Kulp (1957) presented similar results for zircon, although they noted that radiation dosage alone could not explain all of their observations. Given the weak age constraints available at the time, the potential for annealing of radiation damage at high temperature, and most importantly the high probability that some samples have been at sufficiently high temperatures to cause diffusive He loss well after crystallization, the usefulness of titanite (U–Th)/He dating has not yet been convincingly determined.

Here we report (1) the diffusion characteristics of He in titanite, determined from experiments on specimens from a variety of geologic environments, that indicate a closure temperature of ~200°C (for a cooling rate of 10°C/Myr), and (2) age determinations from both quickly and slowly cooled titanites of a variety of ages. In addition, we report an important grain size control on helium diffusivity with implications for dating of crystals of different sizes, as well as crystal fragments.

2. SAMPLES

To assess natural variability and potential influences of cooling rate and host rock age on He age and diffusion characteristics, we performed experiments on titanites from several different settings. Relatively quickly cooled titanites were obtained from Mount Dromedary, Australia (MD) and the Fish Canyon tuff, Colorado (FCT), erupted at 98.7 ± 1.1 and 27.8 ± 0.7 Ma, respectively (Green, 1985; McDougall and Wellman, 1976; Williams et al., 1982; Boesen and Joplin, 1972; Hurford and Hammerschmidt, 1985; Carpén and Mailhé, 1987). Slowly cooled samples include titanites from the Devonian intrusive age ~375 Ma) Chain of Ponds pluton, Maine (MH-10; Heizler et al., 1988; Lovera et al., 1989), Cretaceous (U–Pb age ~104 Ma) Dinkey Creek Pluton in the Sierra Nevada batholith (MH96–6; Stern et al., 1981), Proterozoic (U–Pb age ~1.45 Ga) Gold Butte Granite, NE (GB; Silver et al., 1977; Fitzgerald et al., 1991; Fryxell et al., 1992), and late Proterozoic or early Paleozoic amphibolite near Arkaroola (ARK), in southern Australia (B. Kohn, personal communication).

Electron microprobe analyses of titanites from Mount Dromedary, Fish Canyon tuff, and Chain of Ponds pluton show similar compositions, with minor (1–5%) FeO and Al₂O₃ con-
Fig. 1. Arrhenius plots and step-heating schedules for titanite diffusion experiments. The fraction of He released during the step-heating experiments ranged from 9 to 52% of the total He in each sample, with most samples yielding between 11 and 22% of the total. (A) Fish Canyon Tuff, Colorado. Error bars shown for $10^4/\text{T}$ represent estimated thermocouple accuracy during each step ($\pm 3^\circ$). (B) Chain of Ponds Pluton, Maine. (C) Mt. Dromedary, Australia. MDBIG consists of several large ($\sim$300 by 800 $\mu$m) euhedral titanites, and MDPOW is a partly powdered sample, consisting of a range of grain sizes, from $\sim$10 to 150 $\mu$m. (D) MH96–6, Dinkey Creek pluton, Sierra Nevada, CA. Four different fractions of crushed and sieved titanites are shown for MH96–6. The sample labeled $\sim$250 $\mu$m consists of two large ($\sim$250 by 800 $\mu$m) euhedral titanites. (E) MH96–6, spherical titanite grains $\sim$250 to 350 $\mu$m in diameter, ground against an abrasive surface in air-circulating tumbler. (F) Gold Butte, NV. (G) Arkaroola, Australia: unknown cooling rate, late Proterozoic to early Paleozoic (B. Kohn, personal communication). (H) Example of diffusion data from sized MH96–6 samples, in which initial up-temperature steps have been removed to yield linear correlations for calculation of $E_a$, $D_0/a^2$, and $T_c$ (Table 1).
Fig. 1a.

1E. MH96-6 spheres

\[ \ln(D/a^2) \]

-13
-17
-21
-25

-13
-17
-21
-25

MB96-6 sph: \( T_C = 180^\circ C \)

- \( T_C = 193^\circ C \)

- \( T_C = 204^\circ C \)

1F. Gold Butte

\[ 10^4/T \]

-13
-17
-21
-25

-13
-17
-21
-25

1G. Arkaroola 74-140\( \mu \)

\[ \ln(D/a^2) \]

-13
-17
-21
-25

-13
-17
-21
-25

\( T_C = 188^\circ C \)

- \( T_C = 175^\circ C \)

- \( T_C = 196^\circ C \)

1H. MH96-6, filtered data

\[ 10^4/T \]

-13
-17
-21
-25

-13
-17
-21
-25

\( T_C = 188^\circ C \)

- \( T_C = 200^\circ C \)

- \( T_C = 203^\circ C \)
tents. Some grains from these rocks also contain rare inclusions of apatite, calcite, zircon, K-feldspar, xenotime, and rutile. Nearly all Fish Canyon tuff titanites contain abundant small (∼5–40μm) apatite inclusions. All grains (except those from Fish Canyon tuff) containing visible microscopic inclusions were eliminated from aliquots used for dating and diffusion experiments. Relative U and Th contents in titanite and apatite suggest that the minor apatite inclusions in Fish Canyon Tuff samples should have little effect on age determinations or measured diffusion characteristics.

3. He DIFFUSION IN TITANITE

3.1. Diffusion Methods

Accurate interpretation of dates obtained from any isotopic dating system requires a detailed understanding of the mobility characteristics of the parent and daughter isotopes as a function of temperature. Because He diffusivity is many orders of magnitude faster than that of U and Th, He dating requires careful characterization of He diffusivity. We have measured He diffusion characteristics in titanite at relatively low temperatures (330–500°C), with high precision and accuracy for both temperature and fraction of He released, by using a specially designed experimental apparatus (Farley et al., 1999). Our incremental outgassing procedure involved step-heating of 0.1–1.0 mg of titanite wrapped in Cu foil and suspended in a vacuum chamber. The sample was heated by radiation from a light bulb projected through a sapphire window, and temperature was monitored by a thermocouple in direct contact with the sample. Several thermally activated pill getters (SAES ST 707) in a chamber adjacent to the samples scavenged reactive gas (H₂, CO₂, H₂O) released from the sample at higher temperatures to minimize heat loss to the chamber walls. Estimated accuracy of the temperature measurements in each step is ±3°C, based on stated thermocouple characteristics; within-run temperature stability during each step is better than ±1°C.

Individual heating steps ranged from 30 min for gas-rich samples at high temperatures to 600 min for gas-poor samples at low temperatures. Heating, gas processing, and measurement in each multi-step experiment were fully automated, running between 35 and 45 steps over 5 to 7 days. All experiments were cycled (i.e., included step sequences of both increasing and decreasing temperature). Most experiments had step sequences that first increased in temperature, then decreased, then increased again; many cycled from low to high temperature several more times (Fig. 1). Run-up and cool-down times between steps were <1–2 min and are insignificant for diffusivity measurements compared with the isothermal holding times.

4He released from the sample in each step was measured by a quadrupole mass spectrometer, using 3He isotope dilution. He blanks were determined throughout the temperature range of our experiments and showed no time or temperature dependence; cold blanks were checked prior to each run and a typical blank of 0.02 ncc of 4He (≤0.05% of typical 4He released at 500°C) was subtracted from each step. Average 1σ reproducibility of 4He standards comparable in size to the sample extractions is better than 1%.

Diffusivity calculations require knowledge of cumulative fraction of He released in each step, so the final step of each experiment was total fusion of the grains. Because our diffusion apparatus cannot achieve temperatures greater than ~800°C, we used a resistively heated furnace and measured the residual He content on a MAP 215–50 mass spectrometer by peak height and comparison to standards (for details see Wolf et al., 1996). No 3He above blank was measured in any of the total fusion steps.

For consistency with previous work on noble gas diffusivity, our calculations of diffusivity (D/a², Fechtig and Kalbitzer, 1966) and closure temperature (Tc, Dodson, 1973) assume spherical geometry of diffusion domains. As we show below, this is not strictly valid for He diffusion in titanite. However, assumptions of spherical, plane-sheet, or cubic geometries (using equations of Harrison and McDougall, 1988, table 5.1, modified for step-wise He-loss) do not affect calculated activation energies or closure temperatures significantly (<1 kcal/mol, and <10°C, respectively).

3.2. Diffusion Results

Figure 1 shows heating schedules and Arrhenius plots for the titanite diffusion experiments. The most important feature of the data in Figure 1 is that, with the exception of initial low temperature steps, in every instance the diffusion data for each sample lie on a well defined line on an Arrhenius plot, with D/a² decreasing with reciprocal temperature. Using only the linear segments of these data by removing initial low temperature steps that deviate more than 0.25 ln-units from a best-fit line to the rest of the data (typically <15% of the steps) yields excellent linear correlations (R² > 0.996). As described below, we believe that the first few steps of these runs do not accurately reflect He diffusivity from the bulk titanite but rather are an artifact associated with the surfaces of the grains and an additional effect we describe below. Thus, we use the linear portions of these experiments to calculate activation energies Eₐ, frequency factors Dᵢ₀/a² and closure temperatures Tc, for each sample (Table 1). As suggested by the similar slopes in Figure 1, there is little variation in Eₐ among samples (41.7–46.6 kcal/mol, with an average of 44.6 ± 3.4 (2σ) kcal/mol).

In contrast to relatively constant activation energy, there is a wide variation in Dᵢ₀/a² among samples (Fig. 1). Specifically, samples with smaller grain size, including MDPOW (with grains ranging from <38 to ~150 μm in size) and the finer sieve fractions of sample MH96–6, show consistently higher Dᵢ₀/a² than other samples (Fig. 1, c and d; Table 1).

We note three types of deviation from linear behavior in the plots of Figure 1:

- Positive deviations from linearity occur in the first few low temperature steps of most sample runs. Two of the three experiments with reversed heating schedules (those that start with three high temperature steps and then drop to low temperature) show much less of this high diffusivity deviation in their low temperature steps (MH-10B and MDB, Fig. 1, b and c).
- In contrast to these positive deviations from linearity, the two largest grain-size splits of MH96–6 (Fig. 1d) yield lower diffusivities in the first few steps than later steps at the same temperature.
Although titanite from Gold Butte, NV has similar He diffusivity characteristics to samples from other localities, it shows slightly more scatter in Arrenius plots, with anomalously high diffusivity in several parts of the run (Fig. 1f).

3.3. Diffusion Discussion

With the exception of the initial low temperature steps, the strong linear correlations on Arrenius plots (Fig. 1) are consistent with He loss from titanite by thermally activated volume diffusion, with an activation energy of \( \approx 44.6 \pm 3.4 \) \( (2\sigma) \) kcal/mol. In addition, \( D/\alpha^2 \) is clearly related to grain size. In the following discussion, we elaborate on the significance of these observations for (U–Th)/He thermochronometry.

3.3.1. Effect of grain size

The four MH96–6 sieve fractions illustrate the effect of grain size on \( D/\alpha^2 \) (Fig. 1h). Although \( E_a \) is relatively constant for each fraction (44–47 kcal/mol), \( D/\alpha^2 \) varies over more than two orders of magnitude, with higher \( D/\alpha^2 \) corresponding to smaller grain size fractions. To test the hypothesis that diffusion domain size (\( \alpha \)) scales with grain size, we assigned approximate effective grain radii (\( r \)) to each sieve fraction and plotted \( D/\alpha^2 \) vs. \( 1/r^2 \) for several temperatures (Fig. 2). We assumed that the effective radii \( r_a \) of the \(<38 \mu \text{m}, 43–74 \mu \text{m}, 74–140 \mu \text{m}, \text{and BIG fractions were} \) 16, 43, 74, and 125 \( \mu \text{m} \), respectively (one-half the mesh opening for the smallest grain size, the smallest mesh opening for intermediate size fractions, and approximately one-half the short axis of the individual crystals in the BIG fraction). High linear correlations between \( D/\alpha^2 \) and \( 1/r^2 \)(\( R^2>0.999 \)) and intercepts near zero (\( 10^{-8}–10^{-9} \)) for all temperatures (Fig. 2) indicate that the diffusion domain length scale (\( \alpha \)) of titanite is equivalent to grain size (\( r \)), and sub-grain-size diffusion domains are absent (at least after the initial low temperature steps, as discussed below). Contrary to initial observations (Wolf et al., 1996), we have also observed grain size and diffusion domain equivalency for He loss from apatite (Farley et al., 1998). Assuming that these approximate \( r \)'s represent \( \alpha \)'s in the MH96–6 experiments yields an average diffusivity at infinite temperature (\( D_0 \)) for He in titanite of \( \approx 59 \text{ cm}^2/\text{s} \). Uncertainty in the actual effective grain size of each split, however (which we have heuristically assumed as above), causes large uncertainty in the average \( D_0 \) and this estimate is probably only accurate within an order of magnitude. Combining this \( D_0 \) value with the average \( E_a \) of the MH96–6 experiments (45.7 kcal/mol), we predict diffusivities (\( D/\alpha^2 \)) that agree very well with observed diffusivities for all temperatures and steps of the MH96–6 experiments (excluding the initial up-temperature steps, as discussed below) (Fig. 2).

Both the estimated average value of \( D_0 \) (59 \text{cm}^2/\text{s}) from the MH96–6 experiments and the average value of \( E_a \) (44.6 kcal/mol) from all our titanite experiments are intermediate between values for He diffusion in olivine (\( D_0 = 2.2 \times 10^5 \text{ cm}^2/\text{s}, E_a = 120 \text{ kcal/mol} \); Hart, 1984) and basaltic glass (\( D_0 = 0.07 \text{ cm}^2/\text{s}, E_a = 19.9 \text{ kcal/mol} \); Kurz and Jenkins, 1981).

3.3.2. Closure temperature

Because \( T_c \) is a function of diffusion domain size (Dodson, 1973), our results indicate that the He closure temperature in titanite will be a function of crystal size. By using the average \( E_a \) of all our titanite experiments and average estimated \( D_0 \) of the MH96–6 experiments, we can directly estimate the influence of crystal size (approximated as radius \( a \), of an ideally spherical crystal) on closure temperature (Fig. 3). Figure 3 shows that the variation in \( T_c \) is \( \approx 11–15^\circ \text{C} \) for titanite grain size variations over a factor of two (e.g., change in a from 12.5 \( \mu \text{m} \) to 25 \( \mu \text{m} \) causes change in \( T_c \) from 162°C to 173°C; change in \( a \) from 200 \( \mu \text{m} \) to 400 \( \mu \text{m} \) causes change in \( T_c \) from 211°C to 226°C). Typical whole titanite crystals from igneous rocks that we have examined are \( \approx 300 \mu \text{m} \) by 800 \( \mu \text{m} \) in perpendicular smallest and largest dimensions, respectively. If natural titanite crystal sizes vary by a factor of two around this size range, slowly cooled crystals (\( \approx 1^\circ \text{C/Myr} \)) from the same rock could vary in (U–Th)/He age by as much as 10–15 Myr.
3.3.3. High diffusivity in initial low temperature steps

The anomalously high diffusivity in initial low temperature steps of many of the diffusion experiments (Fig. 1) is not consistent with simple volume diffusion from a single domain size. This behavior is probably not a consequence of assuming an inappropriate diffusion domain geometry, as models using plane sheet and cubic geometries show the same pattern as the spherical assumption shown in Figure 1.

Titanite undergoes a rapid, reversible phase transition at 223°C from space group $P2_1/a$ to $A2/a$, in which the Ti atom in the TiO$_6$ octahedron moves approximately 0.10 Å from one corner of the octahedron to the center (Taylor and Brown, 1976). As all of our heating steps were performed at 330°C or higher, it may be argued that He diffusivity below 223°C is different than predicted by our experiments. If for some reason diffusivity below 223°C were extremely high (much higher than predicted by extrapolation from higher temperature), some significant fraction of He could be released at temperatures below 223°C during the short time (5–10 min) between extraction steps that the sample resides at low temperature and the extracted gas is processed and measured. As the fraction of gas released from the sample is low in the low temperature steps, this effect might be sufficiently significant to explain the deviation from linearity in these steps (although it should also be observed in later low temperature steps as well). To test this possibility, we performed a diffusion experiment on an additional split of MH96–6 (grain size 43–74 μm) in which the temperature between each step was held at 250°C to prevent the phase transition from occurring. The Arrhenius plot and diffusion characteristics of this split were not noticeably different from the normal experiment and showed almost exactly the same degree of initial low temperature deviation from linearity. We conclude that the initial low temperature diffusivity deviations are not due to the 223°C phase transition.

Another potential explanation for the initial low temperature deviations is the presence of multiple diffusion domains, such as observed during Ar release from K-feldspar (Lovera et al., 1989). The transition from the initial anomalously high diffusivity steps to those lying on the best-fit line occurs gradually rather than by discrete steps. This behavior is unlike Ar release from most K-feldspars, where discrete steps in diffusivity occur as individual domains are depleted of their Ar (Lovera et al., 1989). Plots of the deviation from linear behavior [$\ln\left(\frac{D}{a^2}\right)$] vs. total fraction of He released (similar to Lovera et al.’s log($r/r_0$) plots) show considerable variability among samples even from the same rock (Fig. 4). Thus, there is no evidence for a finite number of domains of varying $a$ with fixed He contents.

The initial low temperature deviations and the decreasing $D/a^2$ in low temperature isothermal repetitions (Fig. 1, b and c) are qualitatively similar to effects observed in rare K-feldspar crystals that have been attributed to a range of (rather than several discrete) domain sizes (Lovera et al., 1997). It is possible that the anomalously high He diffusivity in initial low temperature steps can be interpreted in a similar way. If each sample consists of a range of domain sizes of equal He concentration, the bulk diffusion characteristics should reflect a mass-weighted average of the diffusion characteristics of all domains. As Figure 1h suggests, trends corresponding to diffusion from small domains (which in this case correspond to small grains) will be parallel to, but have higher intercepts than, trends corresponding to diffusion from large domains. However, because the equations for $D/a^2$ depend on cumulative gas fraction released in each step (which represents the sum over all
domains), if He in small domains is exhausted before He in large domains, \( D_0/a^2 \) will decrease during the experiment, causing anomalously shallow slopes on Arrhenius plots.

Figure 5 shows synthetic diffusion data for combinations of model titanite grains with identical \( E_a \) and \( D_0 \) (from the four MH96–6 samples in Fig. 1d) but varying \( a \)'s (domain, or grain, sizes) and relative fractions. These models show that a very small fraction (<1%) of domains with very small size (radii \( \sim 0.1 \mu m \)) will modify the initial, low temperature steps of a diffusion experiment in a way that reproduces the main features of the Arrhenius plots and \( \ln(D/a^2) - \ln(D/a^2)'0 \) plots (Figs. 1, 4, and 5). This is because the small domains release a relatively large amount of He in the initial low temperature steps but are exhausted of all their He within the first few steps, whereas large domains are far from exhaustion. Because of the gradual, continuous decrease in \( D_0/a^2 \) in the initial low temperature steps (Fig. 1), there is no reason to conclude that the titanite grains consist of populations of discrete domains either 100 or 0.1 \( \mu m \) (or anywhere in between) in size. But these models do suggest the presence of a range of effective domain sizes in each sample, with at least some small fraction less \( \sim 0.1 \mu m \) in effective radius. This is necessary so that He-exhaustion of some domains begins at even the first low temperature step, causing decreasing \( D_0/a^2 \) in the initial steps.

Because most of our samples (except for the size-sorted MH96–6 and MDPOW samples) consisted of several independently picked grains that were rinsed in alcohol to remove small particles, it is unlikely any very small grains that could represent small domains were actually present in any sample. Instead, we favor the interpretation that the small domains

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**Figure 3.** Closure temperature \( T_c \) (equation 23 of Dodson [1973]) versus effective grain radius \( a \). Solid lines are curves calculated by using average \( E_a \) and \( D_0 \) derived from four crushed and sieved MH96–6 titanite diffusion experiments. Sized samples of MH96–6 fall almost directly on the \( dT/dt = 10^\circ C/Myr \) trend because these samples were used to calculate the average \( E_a \) and \( D_0 \) used for calculating the trends.

**Figure 4.** Extent of deviation from linearity vs. cumulative fraction of He released in diffusion experiments for five MH96–6 samples (the four sized splits and the abraded [spherical] grains in Fig. 1d and e). The extent of deviation from linearity is \( \ln(D/a^2) - \ln(D/a^2)'0 \), where \( \ln(D/a^2)'0 \) is the \( \ln(D/a^2) \) that would be expected in the case of a perfectly linear correlation (assumed to be the best fit trend through data from which initial low temperature steps with anomalously high-diffusivity have been removed). This parameter is similar to \( \log(r/r_0) \) introduced by Lovera et al. (1991). All samples show diffusivity for the lowest cumulative gas fraction released that is higher than diffusivity for the higher cumulative fractions. Samples with larger grain size (especially MH96–6BIG and MH96–6.74–140 \( \mu m \)) also show a transient effect of lower diffusivity following the initially higher diffusivity, interpreted as indicating the presence of rounded He profiles in the crystals. All samples have slightly different curves, and none show step-like transitions suggestive of discrete domains. The fine black line labeled “Model…” represents the curve for the synthetic diffusion data in Figure 5c, suggesting that these patterns can be explained by the presence of a small mass fraction (0.5%) of a small domain size (\( \sim 0.1 \mu m \)) in titanite.
Several of these experiments, however, still show some degree of anomalously high diffusivity in the first low temperature steps, especially FCTB and MH-10B. Trends between the initial high temperature steps and the subsequent low temperature steps for these samples have lower slopes than trends through later steps, which cannot be explained simply by a range of domain sizes. This suggests that another phenomenon also may contribute to anomalously high diffusivity at low temperature in cases in which low temperature steps immediately follow high temperature steps. Very similar effects (anomalously high diffusivity at low temperature immediately following high temperature steps) also have been observed in He diffusion from apatite (K. A. Farley, unpublished data), and work is ongoing to determine their cause.

Small domains with effective radii of 0.1 to 1.0 \( \mu m \) within or on the surface of titanite crystals will have closure temperatures of \(-90\) to \(120^\circ C\) (Fig. 2), so it is possible that these domains affect the bulk closure temperature of a titanite crystal. The modeling shown in Figures 4 and 5, however, illustrates that only a small fraction (<1%) of He residing in small domains (~0.1 \( \mu m \)) can explain the diffusion characteristics of most of the titanites examined in this study. Thus, they would have very little effect on the bulk closure temperature. The multi-domain modeling and reversed heating schedule results permit the possibility of larger domains (up to \(-5\mu m\)) and a range of sizes in some samples for which the deviation from linearity in initial low temperature steps is the most extreme (e.g., MH-10 in Fig. 1b). Even in this case, however, our modeling of the extent of deviation from linearity in the initial low temperature steps

![Fig. 5. Synthetic diffusion data for models of mixtures of titanite grains of different domain sizes, but identical \( E_r \) and \( D_r \) (from four sized fractions of MH96–6; Fig. 1d). Synthetic step-heating schedule is the same as for FCTA (Fig. 1a). Each grey line corresponds to an ideal diffusion trend for an individual grain size fraction. Black circles and solid line between them are modeled diffusion data for binary mixtures of two distinct grain sizes, 100 \( \mu m \) and 25 \( \mu m \), 100 \( \mu m \) and 1.0 \( \mu m \), and 100 \( \mu m \) and 0.1 \( \mu m \), in proportions of 95.5:4.5 and 99.5:0.5. Only models with 0.1-\( \mu m \) grain sizes reproduce the initial low temperature diffusivity phenomena observed in Figure 1, and only a very small fraction of these grains is required (C). This small grain size is required because it loses more than \(-90\)% of its He in the first one or two steps, leading to the distinct curvature in the trends in the initial low temperature steps. Our data show no evidence for the presence of discrete diffusion domains, as in the case of Ar in K-feldspar, because the exhaustion of He from small effective grain sizes appears to be gradual, and not occur in steps, as shown in E. We cannot rule out the existence of a range of diffusion domain sizes internal to each crystal, rather than microscale surface irregularities such as cracks, as an explanation for these phenomena. However, because the diffusion data in each case conform to a single linear trend after \(-1–5\)% (up to 10–20% in a few cases) of the total He is released, these portions of the grain do not contain a large enough fraction of the total He (0.5% to approximately 4% for MH-10, Fig. 1b) to appreciably change the bulk closure temperature of the grain.

represents microscale cracks and/or irregularities on the surfaces of larger grains. That these features would have to be less than \(-1–10 \mu m\) is supported by our diffusion experiment on MH96–6 titanite grains ground (by tumbling against an abrasive surface) into 250-\( \mu m \) diameter spheres (Fig. 1e). These titanite grains lacked any geometric irregularities on the scale of \(-10–20 \mu m\) but did contain abundant surface cracks and scratches giving the spheres a frosted appearance. These coarsely abraded spherical titanites showed enhanced deviation from linearity in the initial steps compared to other MH96–6 samples (Figs. 1 and 3), suggesting that cracks and scratches are responsible. Because these grains were spherical on the 100- to 200-\( \mu m \) scale, this observation also rules out the possibility that the initial low temperature deviations are simply an artifact of incorrectly assuming spherical macro-scale geometry.

The suggestion that microscopic surface irregularities act as small domains is also supported, at least in part, by the diffusion experiments with reversed heating schedules (those that begin with high temperature steps and then drop to low temperature). Our modeling of mixtures of large and small domains suggests that the initial high temperature steps should strongly outgas the small domains, reducing or eliminating the high diffusivity deviation at low temperature. Two of the three experiments (MH-10B and MDB in Fig. 1, b and c) do indeed show such reduction, suggesting that most of the He in the small domains is exhausted in the initial high temperature steps. Several of these experiments, however, still show some degree...
constrains the total fraction of He in very small domains (0.1–1 μm) to less than ~4%. The presence of slightly larger domains of order 10 to 25 μm in some samples is difficult to rule out because they may not be exhausted at any stage of the experiment. However, the consistent scaling of grain size and \( D/a^2 \) in the MH96–6 samples suggests that, if present, these domains are volumetrically insignificant compared with physical grain size. In addition, intermediate-sized domains of 10–25 μm would have closure temperatures (160–175°C) closer to that of the whole crystal, so their potential influence on bulk closure temperature would be much less than that of very small domains.

Lastly, it is unknown whether the surface features we envision are even present in natural titanite crystals in cooling rocks. They may instead be created by crushing or separation procedures as part of sample preparation, in which case their diffusion characteristics would be irrelevant to natural He diffusion characteristics and He ages.

3.3.4. Low diffusivity in initial steps

In contrast to most other samples, the two largest grain-size aliquots of MH96–6 (BIG: 250 μm by 800 μm euhedral crystals, and 74–140 μm: grains ranging from 74 to 140 μm) exhibit anomalously low diffusivity in the initial steps. With higher temperature steps, the slopes of the trends in the Arrhenius plot steepen, and after the highest temperature extraction, higher temperature steps, the slopes of the trends in the Arrhenius plots for these samples (Fig. 4). In most samples, \([\ln(D/a^2) - \ln(D/a^2)_{\text{initial}}]\) levels off at values near zero after several percent He extracted, but in these samples \([\ln(D/a^2) - \ln(D/a^2)_{\text{initial}}]\) declines quickly to values below zero \((-0.75 \text{ to } -0.22)\) before increasing to and leveling off near zero.

Lovera et al. (1997) observed a similar initial low diffusivity phenomenon for Ar diffusion from K-feldspars and attributed it to inhomogeneous Ar distribution in the sample. Also, Farley et al. (1998) observed this effect for He diffusion from apatite, suggesting that it arises from diffusion-induced rounding of the He concentration profile within the crystals. Such an effect could be caused by slow cooling or long holding periods at temperatures near the closure temperature, or both. Alternatively, the He profile could also be rounded simply by the effects of alpha ejection, which results in lower He concentration in the outer 15–20 μm of the crystals. These effects should be observed in samples that include a large fraction of original crystal surfaces. Modeling an inhomogeneous starting distribution of He using the numerical model of Wolf et al. (1998) coupled with a synthetic step heating experiment predicts qualitatively the same effect whether caused by diffusive loss or alpha ejection. Either explanation is consistent with the observation that the euhedral crystal sample shows the effect most strongly (most or all of the exposed grain surfaces are crystal surfaces), whereas it is less pronounced or absent in smaller grain sizes (which possess fractured surfaces representing former crystal interiors).

3.3.5. Radiation damage and He diffusion

Previous studies have concluded that alpha-decay damage in zircon and titanite with ages in the range 300 to 1000 Ma significantly decreases He retention, thus potentially compromising the reliability of \((U-\text{Th})/\text{He}\) dating of these phases (Hurley, 1952; 1954; Hurley and Fairbairn, 1953; Damon and Kulp, 1957). Cherniak (1993) also provided evidence of the effect of radiation damage on diffusivity in titanite, observing that Pb ion implantation (with energy similar to alpha recoil energy) into titanite at 600°C causes increases in Pb diffusion rates of about two orders of magnitude and a decrease in activation energy by about a factor of four. Above 800°C, these effects were not evident, suggesting rapid annealing of radiation damage at higher temperatures. Natural titanites with U and Th concentrations of approximately 400–800 ppm and ages of ~1 Ga (radiation dosages of \(\sim2 - 4 \times 10^{15} \text{ a/mg titanite}\)) show up to 30% metamictization (Vance and Metson, 1985; Chrosch et al., 1998), which could be expected to strongly affect diffusion properties. These studies also demonstrated significant annealing and recrystallization on hour timescales at temperatures above ~500°C. It is unclear what combination of timescales and temperatures are required to anneal radiation damage under geologic conditions, but the partial annealing zone of titanite fission tracks (on geologic timescales) between ~265–310°C (Coyle and Wagner, 1998) provides a possible constraint.

Typical titanites that we have examined from batholithic rocks have significantly lower U and Th (50–300 ppm) than samples used for radiation damage studies. Nonetheless, we attempted to address the possibility of radiation damage effects on He diffusion by performing diffusion experiments on titanites from Proterozoic (Gold Butte Granite, 1.45 Ga [Silver et al., 1977]), and late Proterozoic to early Paleozoic (Arkaroola, exact age unknown) host rocks. Because Gold Butte, NV represents a >14-km thick exhumed section of Proterozoic crust (Fitzgerald et al., 1991; Fryxell et al., 1992), titanites from the 1.45-Ga granite in the block provide an opportunity to examine the potential effect of temperature on radiation damage annealing. Titanites from Gold Butte show a very systematic gradation in color with respect to paleolevel in the block: those from the deepest end (estimated temperature of 330°C prior to Miocene exhumation) are light yellow, whereas crystals toward the paleosurface of the block (estimated pre-exhumation temperature of 85°C) are increasingly darker brown. The systematic color change from paleobottom to paleotop of the block may reflect the influence of temperature on annealing the coloration effects of radiation.

Diffusion experiments on Gold Butte titanites from both ends of the block show \(E_a\) and \(D/a^2\) that are similar to other samples (GB4, GB18 in Table 1); however, Arrhenius trends for Gold Butte titanite show more scatter (Fig. 1f), with several slightly anomalous diffusivity steps, especially at high temperature. Arkaroola titanite is darker brown than any other sample, but diffusion characteristics are not significantly different from those of other titanites (Table 1), except for one anomalously high diffusivity step at high temperature (Fig. 1g). It is possible that the greater scatter in the Gold Butte trends, as well as the high diffusivity step in the Arkaroola sample, reflect radiation damage effects such as might be expected for outgassing of He-rich pockets in damage zones. If these samples are radiation-damaged, however, the agreement of \(E_a\) and \(D/a^2\) with other samples suggests that at least this extent of damage has not seriously affected their He diffusion characteristics. None-
The most important results of these diffusion experiments for the potential of (U–Th)/He dating are: (1) He diffusion from titanite from a variety of geologic environments indicates a closure temperature for the (U–Th)/He system of ~200°C for a cooling rate of 10°C/Myr. (2) Because titanite diffusion domain size equals physical grain size, there is a small dependence of \( T_c \) on crystal size. For typical titanites we estimate that a factor of two size difference results in a \( T_c \) difference of ~11 to 15°C. (3) Titanite shows diffusion characteristics that suggest the presence of secondary and very small domain size(s) probably associated with surface irregularities. These domains should have low \( T_c \) (90–120°C); however, modeling suggests that they probably contain <1% of the He in the bulk grain and thus should not affect the bulk \( T_c \) significantly.

4. AGE DETERMINATIONS

4.1. Methods

Titanite grains were separated from whole rocks by standard crushing and mineral separation procedures using a jaw crushe, sieving, and magnetic fluid (Magstream) separation. In contrast to typical preservation of euhedral crystal morphologies of apatite and zircon by these procedures, most titanite grains recovered from our separations were irregular, blocky fragments of larger crystals. All dated grains were immersed in appropriate index refractive oil and examined under high power microscopy. For typical titanites we estimate that a factor of two size difference results in a \( T_c \) difference of ~11 to 15°C. For typical titanites we estimate that a factor of two size difference results in a \( T_c \) difference of ~11 to 15°C.

4.2. Age Determination Results

4.2.1. Quickly cooled samples

Table 2 and Figure 6 show (U–Th)/He ages of Fish Canyon Tuff and Mt. Dromedary titanites. Ages of samples from which He was extracted by resistance heating or LiBO2 flux-melting are 95.4 ± 6.0 (1σ) Ma for Mt. Dromedary and 30.1 ± 1.0 (1σ) Ma for Fish Canyon Tuff. These are in reasonable agreement with K/Ar, \(^{40}\)Ar/\(^{39}\)Ar, and fission-track ages determined from other phases in these rocks. K-Ar and Rb-Sr ages of various minerals in the Mt. Dromedary intrusion yield a weighted mean age of 98.7 ± 1.1 Ma (Green, 1985; McDougall and Wellman, 1976; Williams et al., 1982). Accepted \(^{40}\)Ar/\(^{39}\)Ar ages for the Fish Canyon Tuff are 27.8 ± 0.2 Ma (Hurford and Hammerschmidt, 1985), while fission track ages are 26.8 ± 4.2 Ma for apatites and 27.9 ± 2.2 Ma for zircons (Carpéna and Mailhé, 1987).

Figure 6 illustrates that, although He extraction by resistance heating or LiBO2 fusion provides reasonable ages, He extraction by laser-fusion does not. Most laser-fused samples showed U loss, presumably by volatilization, which yielded low U/Th ratios and high ages. In an attempt to minimize this effect, we reduced laser power to <0.1 W for some samples, but this resulted in incomplete outgassing. The result was U/Th ratios that agree with those determined by other methods but anomalously young ages. Because of these problems, we were not
able to identify a robust laser-extraction technique for (U–Th)/He dating of titanite.

4.2.2. Slowly cooled samples

Slowly cooled samples provide an opportunity to compare the laboratory-determined He closure temperature of titanite with thermochronometric constraints from other systems. (U–Th)/He ages of titanites from the Chain of Ponds pluton in Maine range from 206 to 234 Ma for sample MH-10 and 213 to 267 Ma for sample MH-42 (Table 2). Figure 6 shows the cooling curve determined for the Chain of Ponds pluton from 40 Ar/39 Ar dates of hornblende, biotite, and K-feldspar (Lovera et al., 1989; Heizler et al., 1988). Lovera et al. (1989) showed that K-feldspars from this pluton contain three to four diffusion domains with distinct closure temperatures, so that each feldspar defines a unique cooling curve. As a whole, these data suggest that between ~200 and 250°C, the cooling rate of the pluton was ~1°C/Myr. Extrapolation of this cooling rate, combined with the activation energy of 43.1 kcal/mol determined for MH-10 titanite (Fig. 1; Table 1), and 


dy of 2.62 \times 10^5 s^{-1} (D_y from MH96–6 samples and assumed a of 150 µm), yields a closure temperature of 163°C. (U–Th)/He ages for this temperature are in reasonable agreement with the overall Chain of Ponds cooling curve (Fig. 7).

4.3. Discussion of Age Determination Results

4.3.1. Comparison with geochronologic and thermochronologic constraints

The reasonable agreement of (U–Th)/He ages (for resistance-heated and LiBO$_2$-fused samples) of titanites from Fish Canyon tuff and Mt. Dromedary with known K/Ar, 40 Ar/39 Ar,
and fission-track ages demonstrates the accuracy of titanite He-dating for quickly cooled samples. The inverse correlation between U/Th and age and the wide range in U/Th for titanites fused by laser suggest that U is volatilized from titanite (or titanite glass) during laser fusion under vacuum.

Our determination of relatively low closure temperature (200°C) for He in titanite indicates that (U–Th)/He dating of this mineral can provide useful constraints for cooling through a temperature region accessed by few other techniques. The broad agreement of titanite ages from the Chain of Ponds pluton with predictions of the cooling curve deduced from 40Ar/39Ar dating of multi-domain K-feldspars suggests that our determination of relatively low closure temperature is applicable in nature and that the method has potential application in constraining cooling rates of slowly cooled rocks. However, although the titanite He ages are consistent with the pluton cooling curve, there is a relatively large range of He ages for titanites from individual rocks (SD = 14 Myr, or 6% of the average age, for MH-10 and 27 Myr, or 11%, for MH-42). Part of this range may represent the effects of $T_c$, variation caused by variations in the original sizes of the grains analyzed. However, crystal size cannot explain all of the age range for each sample. Assuming an $E_v$ of 44.6 kcal/mol, $D_o$ of 59 cm²/s, and a cooling rate of 1°C/Myr, two titanite crystals with effective crystal sizes (assumed to represent the radius of the short axis of the crystal) of 75 μm and 150 μm would show a 12-Myr difference, only 86% and 44% of the MH-10 and MH-42 SD, respectively. Another potential sources of age variability are inaccuracies associated with alpha-ejection or dating of fragments of crystals with rounded He concentration profiles, as discussed below.

4.3.2. Inhomogeneous He distribution

A potential source of error in titanite (U–Th)/He dating is the possibility of inhomogeneous He distributions arising from: (1) alpha ejection from the outer 20 μm (weighted average of U– and Th-series alpha-stopping distances in titanite) of a crystal (Farley et al., 1996); or (2) diffusive loss of He from crystals held for a large fraction of their history near the closure temperature.

The effect of long alpha-stopping distances on (U–Th)/He ages has been modeled for various geometries by Farley et al. (1996). In the case of apatite, measurement of the dimensions of the largely euhedral crystals permits effective modeling and correction for He lost by ejection. However, in our experience, most titanite grains recovered from sample crushing and mineral separation processes are irregular fragments of larger crystals, which prohibits simple geometric characterization of the original grain. Fortunately, titanite crystals are typically much larger than apatite crystals, commonly 300 to 800 μm in shortest and longest axes of a wedge-like form. We can estimate the potential magnitude of alpha ejection effects on titanite He dates by assuming as a worst case that alpha ejection from a 300 × 800 μm titanite is equivalent to that in a sphere with a radius of one-half of the minimum axis dimension (150μm). Such a sphere will retain 90% of the alphas generated within it and thus yield an age 90% of the true age (Farley et al., 1996). This is illustrated in Figure 8a, which shows He content as a function of radial position in a (model spherical) crystal 150 μm in radius, normalized to the He content of the whole crystal. This is also equivalent to the apparent (U–Th)/He age, normalized to the apparent whole crystal age (90% of the true crystal age, due to alpha ejection). The He content of the interior 130 μm of the crystal, which has retained all its alphas, is approximately 10% higher than the He content of the bulk crystal; therefore, it would yield an age equal to the true age of the whole crystal. It may be possible to remove the outer 20 μm of crystals by abrasion in an attempt to date crystal interiors (as suggested by Farley et al., 1996), although any rounding of the He profile caused by diffusive loss (as discussed below) or by intragrain U or Th heterogeneity would produce age errors in this case.

The outer 20 μm of the crystal contains significantly less He than the bulk crystal; thus, dating of grain fragments from the outer 20 μm would clearly lead to erroneously young ages (Fig. 8a). Given that the titanite grains we analyze are typically 300 μm in minimum dimension, however, this is not likely to be a problem. Similarly, all of the grains we have dated thus far are fragments of larger grains with some surfaces that were once interior portions of the original crystal that have experienced no alpha ejection. Thus, the fraction of He lost by alpha ejection is almost certainly <10%. Additionally, we have calculated alpha effects for a sphere of 150-μm radius, but titanite crystals also possess a longer dimension, typically 800 μm in length, further reducing expected alpha ejection effects on crystal age.

Although we have not treated the effects of alpha ejection for these samples, the above considerations suggest that the preferred material for titanite (U–Th)/He dating would be either whole euhedral crystals, for which an ejection correction may be determined and applied, or a completely unfaceted and formerly internal fragment of a grain for which no correction
would be needed. In any case, as suggested above, the agreement between our uncorrected ages for titanites from Fish Canyon tuff and Mt. Dromedary with known Ar-dates suggests that corrections for alpha ejection do not exceed ~8%.

An additional and more problematic difficulty arising from dating crystal fragments is the possibility of inhomogeneous He distributions (rounded He concentration profiles) arising from diffusive He loss. In quickly cooled grains with uniform U and Th abundances, He concentration will be constant and fragments from any region (except those within 20 µm of the rim, due to alpha-ejection) should yield correct (U–Th)/He ages. However, thermal histories involving a large fraction of time near the closure temperature will result in crystals with rounded He concentration profiles. In this case, arbitrary fragments of a crystal may not yield the true age of the whole crystal, and fragments near the edge or core may yield ages that are too young and too old, respectively.

To evaluate the importance of this phenomenon, we modeled the radial distribution of (U–Th)/He ages of spherical titanite grains with 150 µm radius for several different thermal histories using the numerical models of Farley et al. (1996) and Wolf et al. (1998). Figure 8, b and c show normalized He content (and ages normalized to apparent whole crystal ages) as a function of radial position in the crystal. In these models, we have assumed an activation energy of 44.6 kcal/mol (the average $E_a$ of all diffusion experiments) and $D_0/\alpha^2$ of 2.62 × 10$^{-5}$ (average $D_0$ of MH96–6, with $\alpha = 150$ µm), yielding a $T_c$ of 200°C. These models also include the effects of alpha ejection, as in Fig. 8a, so that the retained He is 90% of the total He produced within the crystal (apparent whole crystal age is 90% of the true crystal age).

The strongest rounding of the He age profile due to diffusive He loss occurs when the crystal is held near its closure temperature for long periods of time (Fig. 8b). In this case, interior portions of crystals held for 100 Myr can be 260% of the bulk crystal age, whereas exterior portions could yield near zero ages. Actual crystal fragments would represent an integrated age over some portion of each profile, however, so that this age contrast would be less (e.g., the interior and exterior halves of the crystal representing the worst-case profile in Fig. 7b would be ~220% and 71% of the bulk crystal age, respectively). Nonetheless, crystals recently derived from extended stays at regions near 200°C can have quite heterogeneous He distributions that could produce (at least small, <150 µm) crystal fragments with large age variations.

Fortunately, because the total He content of crystals held near their closure temperature is quite low, subsequently holding the crystal at relatively low temperatures for even short periods of time reduces the core-to-rim He content (and age) contrast considerably. For the case shown in Figure 8b, exposure at the earth’s surface for 100 Myr flattens the He profile to one nearly indistinguishable from the instantaneous cooling case (He content of the interior of the crystal is only 16% higher than the He in the bulk crystal, and the age of the interior of the crystal is only 6% older than the true crystal age).

Figure 8 also shows He profiles for two contrasting thermal histories corresponding to those estimated for the Chain of Ponds pluton (sample MH-10) and the lower part of the Gold Butte block (sample GB4). These thermal histories generate He contents in the crystal interiors that are only 4 to 8% higher...
than they are in the instantaneous cooling case. Thus, as a worst case scenario, dating only the innermost portions of these crystals, would yield ages 4 to 8% older than the true crystal ages.

The probability of inadvertently dating only core or rim fragments may be reduced if multiple grains are selected for each aliquot. Alternatively, whole, euhedral crystals could be selected for dating when samples are suspected to have undergone slow-cooling near the closure temperature. As most of the Chain of Ponds Pluton samples that we dated consisted of 1–2 irregular blocky fragments, it is possible that some of the large range in He ages for these samples are the product of this phenomenon.

5. CONCLUSIONS

He diffusion in titanite is dominated by thermally activated volume diffusion that yields a closure temperature for the (U–Th)/He system of \( \sim 200 \pm 10^\circ \text{C} \) for titanite crystals of typical size and a cooling rate of 10°C/Myr. We identify no obvious variability in, or controls on, the diffusion characteristics of titanite, other than a strong correlation between \( D_t/a^2 \) and grain size. The effective diffusion domain size for He in titanite is equivalent to the physical grain size, so closure temperature is slightly dependent on crystal size. Anomalous diffusion characteristics of titanite in early low temperature diffusion steps suggest the presence of microscale (≈0.1 μm) features such as cracks or surface irregularities that act as very small diffusion domains. These features contain a small proportion of He however, so their influence on bulk closure temperature is negligible.

(U–Th)/He dating of titanite provides ages in agreement with known ages and proposed cooling histories from several localities and supports the closure temperature determined in diffusion experiments. Large crystal size, high U and Th concentrations, systematic and regular diffusion characteristics, and agreement of ages with known standards suggest that (U–Th)/He dating of titanite is a potentially reliable low temperature thermochronometer for constraining cooling histories at temperatures near the lower limit of those accessed by feldspar \( ^{40}\text{Ar}/^{39}\text{Ar} \) dating but higher than apatite fission track or (U–Th)/He dating.

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