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

P. W. Reiners K. A. Farley

Division of Geological & Planetary Sciences, MS 100-23, California Institute of Technology, Pasadena, CA, USA, 91125

Recent developments in the (U+Th)/He-dating method of apatite demonstrate the potential of this method to record cooling histories of rocks through low temperatures and to constrain rates of a variety of near-surface geologic processes (e.g. Wolf *et al.*, 1996a,b; Farley *et al.*, 1996). In an effort to expand the (U+Th)/He-dating method to other minerals and ranges of closure-temperatures we have been investigating the use of the method for, and characteristics of He-diffusion in, titanite (sphene).

He-diffusion in sphene

We have performed a series of temperature-cycled,

incremental step-heating experiments on sphenes from a variety of geologic environments and cooling rates, measuring ⁴He abundances in each extraction step using ³He isotope dilution and quadropole mass-spectrometry. These experiments indicate that sphene has a greater retentivity for He than apatite, and suggest two discernible trends of slightly different slopes in a plot of $\ln(D/a^2) vs 10^4/T$. He-diffusivity in initial low-temperature (330–450°C) extractions (prior to heating above approximately 490°C) is slightly higher than in extractions following heating above higher temperatures. Following relatively high-temperature heatingsteps, step-heating extractions show good linear



MH-10 Sphene, Chain of Ponds Pluton, Maine

FIG. 1. Example of cycled step-heating diffusion experiment on MH-10 sphene (sample provided courtesy of M. Heizler). Initial low-temperature extractions indicate higher He-diffusivity than successive extractions. Following high-temperature heating-steps, all further extractions show a highly linear correlation between $\ln(D/a^2)$ and reciprocal temperature, yielding a closure temperature of about 195°C.

correlation in a $ln(D/a^2)$ vs $10^4/T$ plot (Fig. 1), yielding a closure temperature of about $190-210^{\circ}C$ for a cooling rate of $10^{\circ}C/Ma$ (compared with 75°C for apatite). These characteristics are observed for a range of sphene grain sizes. This behaviour may indicate more than one diffusion domain for He in sphene, whereby some fraction of the total He resides in a relatively less-retentive domain and is extracted at relatively low temperatures. If a closure-temperature of about 190-210°C is applicable, it would provide useful thermochronometric age constraints comparable to ages from K-feldspar-⁴⁰Ar/³⁹Ar, as well as zircon-fission-track, methods.

Sphene (U+Th)/He ages

(U+Th)/He dating of sphene is somewhat simpler than that of apatite, both because its higher U and Th concentrations allow dating of single crystals or crystal fragments, and because larger crystal sizes reduce or obviate the need for corrections for alpha ejections from crystals (Farley *et al.*, 1996). Quantitative He extraction from sphene is accomplished by heating the sample to approximately $1150-1190^{\circ}$ C, and ⁴He abundances are measured using either quadropole (with ³He isotope dilution), or sector mass-spectrometry. Sphene crystals are then retrieved, spiked with a ²³⁰Th and ²³⁵U solution, and dissolved in hot HCl + HF; U and Th abundances are measured using isotope-ratio ICP-MS measurements.

(U+Th)/He-ages of five quickly-cooled sphenes from the Fish Canyon Tuff, Colorado, range from 27.6 to 32.0 Ma (mean = 29.5 Ma, estimated uncertainty = 2.3 Ma), in good agreement with the accepted age of 27.8 Ma. Five sphenes from the Chain of Ponds pluton, Maine (samples MH-10 and MH-42), used by Lovera *et al.* (1989) for determining the multiple diffusion-domain character of K-feldspars, yield ages of 200-244 Ma (mean = 223 Ma, estimated uncertainty = 17.8 Ma). If these ages represent cooling through about $190-210^{\circ}$ C, this implies a slower cooling history for the pluton than previously interpreted from 40 Ar/³⁹Ar-dates of amphibole, biotite, and K-feldspar (Heizler *et al.*, 1988). These ages are consistent with 40 Ar/³⁹Ar-dates implied by some of the smallest domain-size Ar-fractions in K-feldspar however, which were interpreted as unreliable age-indicators by Lovera *et al.* (1989). More work on the He-diffusion characteristics of sphene and more sphene (U+Th)/He-dates from the pluton are required before these results can be fully interpreted.

We are also working on sphene (U+Th)/He ages from a suite of granitic samples from the Gold Butte Block, a tilted Proterozoic crustal section representing about 17 km of palaeo-crustal depth. Sphene He-dates will provide useful comparisons to previous apatite fission-track dates from the section (Fitzgerald *et al.*, 1991), and should indicate the usefulness of this method for dating slowly-cooled rocks in uplifted crustal blocks.

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