Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 205 (2017) 50–64

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Influence of radiation damage on titanite He diffusion kinetics

Jaclyn S. Baughman [a,*], Rebecca M. Flowers [a], James R. Metcalf [a], Taufeeq Dhansay [b]

[a] Dept. of Geological Sciences, University of Colorado, Boulder, CO 80309, USA
[b] South African Council for Geoscience, Pretoria 0184, South Africa

Received 9 May 2016; accepted in revised form 28 January 2017; Available online 9 February 2017

Abstract

Titanite is a common U-Th bearing accessory mineral that previous study suggested has a (U-Th)/He closure temperature (T_c) of 210–175 °C. Although it has been recognized that radiation damage influences the He retentivity of apatite and zircon, this effect has not been documented in titanite. We acquired 51 THe analyses from 11 Archean basement samples across the Kaapvaal craton, South Africa. The THe dates range from ~20 to 1200 Ma and are negatively correlated with their ~10–970 ppm span of effective uranium concentration (eU). Raman spectra acquired for 4 of these samples display peak broadening with increasing eU. ^{4}He diffusion experiments on the same 4 samples suggest T_c values that vary by ~175 °C. Estimated alpha dose versus T_c for our results and published THe diffusion data document T_c values of ~150–210 °C at alpha doses $<50 \times 10^{16}$ α/g, with a sharp decrease in He retentivity above this threshold. This damage-diffusivity pattern is similar to zircon, but the damage level at which the reduction in retentivity occurs appears to be lower for titanite. Because titanite typically has substantially lower eU than zircon, for the same protracted thermal history THe dates are likely to record higher temperature portions of the history than zircon (U–Th)/He dates. The results demonstrate that THe dating can access a much larger temperature range and potentially be used to decipher more detailed time–temperature paths than previously thought.

Keywords: (U–Th)/He thermochronology; Titanite; Radiation damage; Zircon; Kaapvaal craton

1. INTRODUCTION

(U–Th)/He thermochronometry is a powerful tool for deciphering thermal histories and therefore is applied to help understand diverse temperature-dependent processes. The vast majority of published (U–Th)/He studies have focused on just two minerals, apatite and zircon. Radiation damage can cause the closure temperatures of these two phases to vary by 10's of °C (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013). The recognition of this phenomenon has expanded the temperature range that can be deciphered using these two minerals alone (e.g. Flowers et al., 2007, 2009; Flowers, 2009; Ault et al., 2013; Guenthner et al., 2014; Orme et al., 2016). Better understanding the extent to which radiation damage affects the He retentivity of other U–Th rich accessory minerals may open new opportunities to further exploit this phenomenon to improve thermal history interpretation.

Like apatite and zircon, titanite is a relatively common U- and Th-bearing accessory phase in igneous and metamorphic rocks. Titanite is regularly used as a U–Pb chronometer (e.g. Corfu, 1988; Cherniak, 1993; Schoene and Bowring, 2007), geochemical tracer (e.g. von Blanckenburg, 1992; Cherniak, 2015) and geothermometer (e.g. Hayden et al., 2008; Kohn and Corrie, 2011). However, only a handful of studies have applied it as a He thermochronometer (Reiners et al., 2000; Pik et al., 2003; Duebendorfer et al., 2010; Bauer et al., 2016). (U–Th)/He

* Corresponding author.
E-mail address: jaclyn.baughman@colorado.edu (J.S. Baughman).

http://dx.doi.org/10.1016/j.gca.2017.01.049
0016-7037/

dating and ^{4}He diffusion experiments on titanites from different geologic settings previously documented grain-size dependent He closure temperatures from 210 to 175 °C (Reiners and Farley, 1999). This finding was corroborated with (U–Th)/He data and diffusion experiments on titanites from the well-studied KTB borehole (Stockli and Farley, 2004). ^{4}He/^{3}He outgassing and implantation studies also supported this conclusion (Shuster et al., 2004; Cherniak and Watson, 2011), and further showed that titanite He diffusion is isotropic (Cherniak and Watson, 2011). Although an early He dating study of titanite had suggested that radiation damage enhanced He diffusivity in highly damaged crystals (Hurley, 1954), the later work did not observe a radiation damage effect. However, the recognition that radiation damage influences apatite and zircon retentivity suggests that its role in titanite He diffusion kinetics should be re-examined.

Here we present (U–Th)/He, Raman, heating experiment, and ^{4}He diffusion experiment data for titanite from basement samples across the Kaapvaal craton in South Africa (Fig. 1a). The initial goal of our study was to use THe dating to decipher the ~200 °C cooling history of the region, but our results instead documented the strong influence of radiation damage on the THe thermochronometer. We combine our results with previously published THe kinetic data to evaluate the titanite radiation damage-He diffusivity relationship, and compare this pattern with that of the zircon (U–Th)/He (ZHe) system.

2. BACKGROUND

2.1. (U–Th)/He thermochronology

(U–Th)/He thermochronology takes advantage of the radioactive decay of uranium and thorium to lead. These decay chains include several episodes of alpha decay that release a ^{4}He nucleus. A mineral's He diffusivity is not only a function of crystal lattice structure, but also of grain size (e.g., Reiners and Farley, 1999; Farley, 2000), U and Th distribution (e.g., Hourigan et al., 2005; Farley et al., 2011; Ault and Flowers, 2012), and to a large extent (in at least some minerals) accumulated radiation damage (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013).

Radiation damage has been shown to affect He retentivity and therefore the temperature sensitivity of apatite and zircon. For samples that experienced the same thermal history, the effective uranium concentration (eU, [U] + 0.235 [Th]; Shuster et al., 2006; Flowers et al., 2007) can be used as a proxy for accumulated radiation damage because grains with higher eU will experience greater self-irradiation than grains with lower eU. In apatite, radiation damage accumulation increases the mineral closure temperature (Shuster et al., 2006; Flowers et al., 2009), which can manifest as a positive correlation between date and eU for samples that experienced protracted thermal histories (Shuster et al., 2006; Flowers et al., 2009; Flowers, 2009). In zircon, damage accumulation initially increases the He closure temperature from ~140 to 220 °C, until a damage percolation threshold at an alpha dose of $\sim 150 \times 10^{16}$ α/g is reached, at which point He retentivity decreases and the closure temperature is reduced (Guenthner et al., 2013; Ketcham et al., 2013). This effect can cause a positive correlation between ZHe date and eU at low damage levels, and a negative date-eU correlation at damage levels greater than the percolation threshold, depending on the thermal history (e.g. Guenthner et al., 2014; Orme et al., 2016). Radiation damage can be annealed at high temperatures, reversing the effects of damage accumulation on He diffusivity (e.g., Shuster and Farley, 2009; Flowers et al., 2009; Gautheron et al., 2009; Guenthner et al., 2013). Understanding both damage accumulation and annealing systematics is therefore important for interpreting (U–Th)/He data.

Additional considerations in (U–Th)/He date calculation and data interpretation include alpha-ejection corrections and U–Th zonation. During alpha decay of U and Th, He atoms can travel up to 20 μm, requiring a geometric correction for He lost from the crystal lattice due to alpha-ejection (Farley et al., 1996). Parent isotope zonation influences the alpha-ejection correction and ^{4}He concentration gradient, and may lead to variable intracrystalline damage and He retentivity (e.g., Hourigan et al., 2005; Farley et al., 2011; Ault and Flowers, 2012; Johnstone et al., 2013). U–Th zoning may also produce a heterogeneous distribution of He, which can cause apparent non-Arrhenius diffusive behavior (e.g., Farley et al., 2011).

2.2. Raman spectroscopy and titanite characterization

Raman spectroscopy uses a laser to irradiate a small area and induce inelastic or "Raman" scattering of the monochromatic laser light. The measured Raman scattering is used to identify the chemistry and bond strength of the sample. Raman spectroscopy is routinely employed to quantitatively evaluate radiation damage in zircon by measuring the width and/or position of a major peak that broadens and shifts with increasing damage due to changing bond strength (e.g., Nasdala et al., 2001; Palenik et al., 2003). In contrast, the approach is more qualitative for titanite. With increasing structural damage, the major titanite Raman peaks undergo spectral broadening, frequency shifts, and merging, making it more difficult to quantitatively assess the effect of damage using a single peak (Beirau et al., 2012; Zhang et al., 2013).

Backscattered electrons (BSE) consist of high energy electrons that reflect off of the sample as a function of atomic number. High atomic numbers, or denser material, backscatter electrons more strongly than less dense material. Studies have taken advantage of this phenomenon and used BSE imaging to identify titanite REE zonation, which commonly is correlated with titanite U–Th zonation (e.g., Aleinikoff et al., 2002).

2.3. Geologic setting

The Kaapvaal craton of southern Africa is an archetypal Archean craton bounded by Proterozoic mobile belts (Fig. 1). Younger terranes were accreted during the Neoproterozoic Pan-African and Paleozoic Cape orogenies.