Estimation of radiation damage in titanites using Raman spectroscopy

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Abstract

Recent studies have shown that α-damage in titanite influences He diffusivity and thus the closure temperature of the (U-Th)/He system in titanite. We compare different methods for measuring the α-dose in titanite by Raman spectroscopy. Raman spectra of randomly oriented titanite fragments from the Archean Karelian domain in eastern Finland along with some well-studied young titanites and U-Pb standard reference materials were analyzed and related to the concentration of α-emitting elements (U and Th) that generated damage in the respective grains. Automated curve-fitting was performed by the IFORS software and different curve-fitting protocols were tested and compared.

The Raman bands at 424 and 465 cm⁻¹ show a good correlation of full-width at half maximum (FWHM) and position with the α-dose. However, these bands are not always present because titanite is highly anisotropic implying that Raman spectra are sensitive to orientation. The intensity-weighted mean FWHM (iw-FWHM) of all Raman bands of a spectrum proves to be the most robust measure of the α-dose. A simplified fitting approach considering 15 peaks is sufficient to describe the accumulated α-dose. For α-doses below 5 × 10¹⁴α/g the iw-FWHM is independent of α-dose and ranges from 25 to 50 cm⁻¹. Above this value the iw-FWHM increases linearly with increasing α-dose up to 3 × 10¹⁶α/g. The linear correlation can be described as iw-FWHM[cm⁻¹] = 39(±1.2)[cm⁻¹] + 3.84(±0.61, -0.26) × 10⁻¹⁷[cm⁻¹/(α/g)] × α-dose[α/g]. The approach provides a pre-selection method to optimize the range of α-doses of titanite crystals to be dated by (U-Th)/He thermochronology.

Keywords: Titanite, (U-Th)/He, metamictization, radiation damage, α-dose, Raman spectroscopy, thermochronology

Introduction

Low-temperature thermochronology is a widely applied tool for deciphering thermal histories of cratonic areas, especially when sedimentary successions constraining the timing of subsidence and exhumation are missing. In contrast to zircon that has commonly effective uranium content (eU = U_{ppm} + 0.235TH_{ppm}) of ≥300 ppm (up to 5000 ppm), titanite usually has lower eU contents in the range of 10–500 ppm and is thus less subjected to metamictization. Moreover, titanite is common in intermediate to mafic rocks where zircon is typically absent.

The closure temperature (T_c) of the (U-Th)/He thermochronometers is influenced by the composition and crystalline state of the dated crystals. Among all influencing parameters, metamictization is the dominant one (Flowers 2009; Orme et al. 2016; Johnson et al. 2017). The influence of metamictization on the T_c values of the most widely used minerals, zircon and apatite, has been intensively investigated (Shuster et al. 2006; Flowers et al. 2009; Gautheiron et al. 2009; Guenthner et al. 2013; Orme et al. 2016). In contrast, its influence on the titanite (U-Th)/He thermochronometer (THe) has been reported only recently (Baughman et al. 2017; Guenthner et al. 2017). These studies show that with increasing α-dose the T_c of the THe system drops to a significantly lower value. Unfortunately, several aspects of the THe system remain unclear (Reiners and Farley 1999; Stockli and Farley 2004; Cherniak and Watson 2011). Titanite has been discussed as host material for nuclear waste (Weber et al. 1998; Stefanovsky et al. 2004; Lumpkin 2006) and various studies focus on the effects of radiation damage in this mineral (Bismayer et al. 2010; Salje et al. 2011; Beirau et al. 2016).

The α-dose of zircon can be estimated from the width of its main Raman band at approximately 1000–1008 cm⁻¹ (Zhang et al. 2000; Nasdala et al. 2001; Palenik et al. 2003; Nasdala et al. 2004). Therefore, Raman spectroscopy offers a quick, non-destructive method for selecting grains for zircon (U-Th)/He (ZHe) thermochronology according to their α-dose (e.g., Ault et al. 2018). For titanite, as for zircon, metamictization affects the Raman spectrum by broadening and shifting the position of several bands (Salje et al. 1993; Meyer et al. 1996; Zhang and Salje 2003; Bismayer et al. 2010; Beirau et al. 2012; Zhang et al. 2013). However, Raman spectroscopy of titanite is more complicated when compared to zircon because of (1) strong anisotropy, (2) higher amount of Raman bands, and (3) adjacent Raman bands often overlap in highly metamict titanite grains (e.g., Beirau et al. 2012; Zhang et al. 2013). Moreover, titanite crystals usually have irregular shapes. Therefore mineral fragments without crystal faces are typically used for THe dating, which makes the crystallographic orientation of the grains difficult.