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 × 10⁻⁶α/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 × 10⁻⁴α/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 = Uppm +0.235T 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 (Tc) 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 Tc values of the most widely used minerals, zircon and apatite, has been intensively investigated (Shuster et al. 2006; Flowers et al. 2009; Gautier and Orme 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 Tc 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.

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So far, no advanced diffusion model exists for titanite that takes radiation damage into consideration. As a consequence, THe ages measured on highly damaged grains are more difficult to interpret than THe ages of slightly damaged grains. Therefore, the routine application of THe thermochronology requires an easy-to-use, orientation independent method for damage estimation and selection of the crystals to be dated.

This study compares different approaches considering single peaks as well as the entire Raman spectrum for quantifying the α-dose in titanite. We present coupled Raman, εU, and THe data of titanite from the Archean Karelian domain in Fennoscandia. The area has been tectonically stable since the Svecofennian orogeny (ca. 1.92–1.80 Ga) (Kähkönen 2005; Lahtinen et al. 2005; Heller et al., in preparation) and since then all samples have experienced the same thermal history. To cover a broad range of α-doses, measurements of younger titanite samples and titanite reference materials with known age and simple cooling histories complement the data set. The main goal of this study is to establish a quick (and non-destructive) method for estimating the α-dose from the titanite Raman spectrum. We demonstrate that characterization of the entire Raman spectrum can be used as a robust estimator independent of grain orientation and evaluation method.

BACKGROUND

Crystal structure and metamictization of titanite

Titanite, CaTi(SiO₄)₂(O,OH,F), also called spherne, is a monoclinic nesosilicate. Zig-zag chains of corner-sharing TiO₆ octahedra are cross-linked by isolated SiO₄-tetrahedra, building a framework. This (TiOSiO₄)₂-framework contains large cavities that enclose sevenfold-coordinated Ca atoms (Speer and Gibbs 1976). Through lattice substitutions, titanite can incorporate significant amounts of rare earth elements (REE), U, Th, Sr, Y, Mn, and Pb at the sevenfold Ca sites and at the octahedral Ti sites (Higgins and Ribbe 1976; Tiepolo et al. 2002; Xu et al. 2015) and may also concentrate significant amounts of HFSEs, such as Nb, Ta, Zr, and W, on the octahedral Ti site (Groat et al. 1985; Lucassen et al. 2011).

The consecutive radioactive decay of U and Th atoms induces metamictization in titanite crystals (Zhang and Salje 2003; Beirau et al. 2010; Bismayer et al. 2010; Beirau et al. 2012, 2014, 2016; Zhang et al. 2013). In metamict titanites, both crystalline and amorphous domains coexist (Hawthorne et al. 1991; Lumpkin et al. 1991). Hawthorne et al. (1991) and Farges (1997) suggest that metamictization leads to disordering around the Ti positions and a partial reduction of the Ti coordination down to five and/or four. This further disturbs the Ti-O-Ti intra-chain linkages (Beirau et al. 2012), triggering an anisotropic response of the titanite lattice. This means that the plane containing Si-O-Ti-O bond closed contours is less susceptible to a self-accumulation of defects as compared to the perpendicular planes, which contain chains of Ti-O bonds (Beirau et al. 2012).

Raman spectroscopy of titanite

Several studies have applied Raman spectroscopy to titanite (Salje et al. 1993; Meyer et al. 1996; Zhang and Salje 2003; Bismayer et al. 2010; Beirau et al. 2012; Zhang et al. 2013). Titanite is an anisotropic phase, exhibiting Raman spectra strongly dependent on the crystallographic orientation. Up to 40 different Raman bands have been reported for natural titanite samples (Zhang et al. 2013), whereas other authors (Salje et al. 1993) reported only up to 30 bands. The increasing degree of metamictization (Fig. 1) changes the Raman spectrum by broadening bands, shifting their frequency, decreasing the overall intensity and appearance of additional bands (Zhang et al. 2013). As result of metamictization, weakening of the bands at 163, 252, 466, 544, and 605 cm⁻¹ (see Fig. 1), appearance of new bands at 574 and 643 cm⁻¹, shifting of bands from 993 to 978 cm⁻¹, 1017 to 1008 cm⁻¹, and 643 to 675 cm⁻¹, and appearance of a shoulder at 650 cm⁻¹ have been documented (Zhang et al. 2013).

For estimating the degree of metamictization, Zhang et al. (2013) proposed to use the 605 cm⁻¹ peak as it gets broader, shifts toward 612 cm⁻¹, and becomes increasingly asymmetric. Beirau et al. (2012) suggested estimating the degree of metamictization from the full-width at half maximum (FWHM) of the 465 cm⁻¹ band, which arises from the SiO₄-bending mode (Heyns et al.

![FIGURE 1](image-url)
metamorphism based on dating of monazite growth. During the Lapland-Savo orogenic phase of the Paleoproterozoic Svecofennian orogeny, thick, east-verging nappes were emplaced on the Archean basement of eastern Finland and temperatures in the Ilomantsi greenstone belt reached 400–500 °C as indicated by partial reset of hornblende K-Ar ages (Kontinen et al. 1992) and Pb isotope exchange studies (Hall and Heilimo 2009). Biotite K-Ar, as well as biotite and muscovite Ar-Ar ages suggest cooling below ~350–300 °C at ~1.8 Ga (Kontinen et al. 1992; Molnár et al. 2016).

The later orogenies and accretionary events that occurred in Fennoscandia, such as the Gothian (1.64–1.52 Ga) and the Telemarkian accretion (1.52–1.48 Ga), the Hallandian and Danopolitan orogenies (1.47–1.42 Ga), and the Sveconorwegian orogeny (1.14–0.90 Ga) (Bingen et al. 2008) affected mainly the southwestern margin of Fennoscandia and were of little and poorly understood impact for eastern Finland. The lack of sedimentary record makes the reconstruction of the post-Svecofennian thermal evolution difficult (Kohonen 2005). A kaolinite deposit at Virtasalmi, ~200 km WSW of the Ilomantsi greenstone belt, indicates surface exposure of the Svecofennian crystalline basement during the Mesoproterozoic at ~1.18 Ga (Sarapää 1996). Late Neoproterozoic, in Fennoscandia referred to as Vendian, and Cambrian sediments are common further south in Estonia. The extent of this unconformity and sediment coverage toward north (e.g., Finland) is not clear and has been a matter of discussion (Puura et al. 1996; Larson et al. 1999; Siaupa et al. 2006).

Thermochronologic data from eastern Finland comprise of a wide range of Neoproterozoic and early Paleozoic apatite fission track (AFT) and apatite (U-Th)/He (AHe) ages (Lehtovaara 1976; Lorencak 2003; Murrell 2003; Murrell and Andriessen 2004; Kohn et al. 2009). In combination with new ZHe, THe, and AHe data (Heller et al. in preparation) they indicate that the Ilomantsi greenstone belt experienced slow cooling since the Svecofennian orogeny and that temperatures did not exceed 100 °C for the last 1.0 Ga.

For calculation of radiation damage densities the duration of α-damage accumulation has to be estimated. However, neither the thermal history of the samples in the time interval of 1.8–1.5 Ga (see below) nor the temperature range of α-damage annealing are well defined. While it is a common praxis to estimate that annealing of α-damage occurs at similar temperatures as annealing of fission tracks (Baughman et al. 2017 for titanite and Pidgeon 2014 for zircon), experiments by Gleadow (1978) indicate that α-damage annealing of titanites occurs mainly in the lower part of the titanite fission track partial annealing zone (TPAZ). For the TPAZ different estimates exist (197 °C, Naeser and Forbes 1976; 260 ± 20 °C, Gleadow and Lovering 1978; 250 ± 50 °C, Gleadow and Brooks 1979; 240 ± 40 °C, Harrison et al. 1979; 275 ± 25 °C, Fitzgerald and Gleadow 1988; 275 ± 25 °C, Kohn et al. 1993; 265–310 °C, Coyle and Wagner 1998). Studies including thermal annealing experiments (Bismayer et al. 2010; Beirau et al. 2012; Salje et al. 2012) indicate that α-damage annealing is a complex process occurring over a temperature range; while recovery of point defect is possible at lower temperatures (T < 300 °C), relevant recrystallization of amorphous areas happens only at T > 320 °C. However, note that temperature estimates
from thermal annealing experiments are often too high as they do not include geological timescales.

In our case, the onset of $\alpha$-damage accumulation can be bracketed to 1.5–1.8 Ga. The upper limit is given by the ~1.8 Ga biotite and muscovite K-Ar and Ar-Ar ages (Kontinen et al. 1992; Molnár et al. 2016). Note that Kohn et al. (1993) report that K-Ar ages are always greater or equal to titanite fission track ages. The lower bracket is given by the oldest THe ages (~1.5 Ga) of our samples, which in our case of typical grains sizes and slow cooling correspond to temperatures of ~180 °C.

The time interval from 1.5–1.8 Ga thus corresponds to a temperature drop from ~300 to ~180 °C, the onset of $\alpha$-damage accumulation lies somewhere in between. Assuming that post-metamorphic cooling was faster in the beginning and then slowed down we decided to calculate with 1.7 Gy as damage accumulation duration. However, due to the uncertainties involved, we also present the results for 1.8, 1.6, and 1.5 Gy accumulation duration and discuss the respective error below.

The sample set with relatively high damage densities from the Ilomantsi belt was complemented by some well-studied titanites (partly reference materials for U-Pb geochronology) of considerably lower $\alpha$-doses (Table 2).
**Methods**

**Sample preparation**

The mineral separation has been performed at the Geological Survey of Finland. The samples were crushed, sieved, and titanite fractions were separated by density and magnetic methods. For single grain analysis, inclusion-free titanite fragments from the 63–200 μm sieve fractions were handpicked. Two to five aliquots of 19 different samples from Finland were chosen. For the polished mineral grain mounts, nine Finnish samples as well as six low-damage samples were mounted in epoxy resin disks, ground, and diamond-polished.

**Raman spectroscopy**

Raman measurements were done on (1) unmounted crystal fragments and (2) polished grain mounts. The measurements were performed with a Horiba XPLora Plus system equipped with a 532 nm excitation laser (25 mW maximum output power) and an Olympus BX41 microscope, which is coupled to a 200 mm focal length spectrograph with a four-grating turret. The system has a Multi-Pinned-Phase (MPP) open-electrode CCD detector with a precision of ±1 pixel. Using 532 nm excitation laser, the crystals were degassed in a high vacuum setup using an infrared laser. A Ti-Zr getter at 450 °C during the re-extraction was done to check the complete degassing of the crystal fragment. For the He measurement, the crystals were degassed in a high vacuum setup using an infrared laser. A Ti-Zr getter at 450 °C during the re-extraction was done to check the complete degassing of the crystal fragment.

**Table 1.** Locality, lithology, and emplacement age of the studied titanite-bearing formations from Finland

<table>
<thead>
<tr>
<th>Sample</th>
<th>YK1-north</th>
<th>Location</th>
<th>Rock type</th>
<th>Zircon U-Pb Age [Ma] (±2σ)</th>
<th>Titanite U-Pb Age [Ma] (±2σ)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0050</td>
<td>6953820</td>
<td>Ilomantsi</td>
<td>Granodiorite (sanukitoid)</td>
<td>2728 (7)</td>
<td>2707 (10)</td>
<td>Vaasjoki et al. (1993); Heilimo et al. (2011)</td>
</tr>
<tr>
<td>A0284</td>
<td>6973076</td>
<td>Lehtovaara Ilomantsi</td>
<td>Granodiorite</td>
<td>2752 (4)</td>
<td>2705 (10)</td>
<td>Sorjenen-Ward and Claoué-Long (1993); Vaasjoki et al. (1993)</td>
</tr>
<tr>
<td>A0301</td>
<td>696216</td>
<td>Vehkavaara Ilomantsi</td>
<td>Porphyry (felsic, dike)</td>
<td>2755 (4)</td>
<td>2720 (10)</td>
<td>Vaasjoki et al. (1993); Huhma et al. (2012a)</td>
</tr>
<tr>
<td>A0338</td>
<td>696716</td>
<td>Vehkavaara Ilomantsi</td>
<td>Porphyry (felsic, dike)</td>
<td>2747 (15)</td>
<td>2747 (15)</td>
<td>Vaasjoki et al. (1993)</td>
</tr>
<tr>
<td>A0339</td>
<td>683951</td>
<td>Silvevaara Ilomantsi</td>
<td>Granodiorite (porphyritic)</td>
<td>2658 (10)</td>
<td>Vaasjoki et al. (1993)</td>
<td></td>
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<tr>
<td>A0804</td>
<td>6982475</td>
<td>Luokonlahti Kaavi</td>
<td>Granite</td>
<td>2756 (6)</td>
<td>Vaasjoki et al. (1993)</td>
<td></td>
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<tr>
<td>A0951</td>
<td>6940674</td>
<td>Paaonvaara Ilomantsi</td>
<td>Granite</td>
<td>2702 (5)</td>
<td>Halla (2002); Mikkola et al. (2013)</td>
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</tr>
<tr>
<td>A1078</td>
<td>6953174</td>
<td>Oinassalmi Ilomantsi</td>
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<td>Vaasjoki et al. (1993); Heilimo et al. (2011)</td>
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<td>6974229</td>
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<td>Vaasjoki et al. (1993)</td>
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<tr>
<td>A1340</td>
<td>7003399</td>
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<td>Diorite</td>
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<td>Pajaluhtil Niisla</td>
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<td>Huhma et al. (2012a)</td>
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<td>Huhma et al. (2012a)</td>
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<td>7027497</td>
<td>Emorvaara</td>
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<td>Huhma et al. (2012b)</td>
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<td>Vaasjoki et al. (1993); Heilimo et al. (2011)</td>
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<td>A1964</td>
<td>7021049</td>
<td>Kiti</td>
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<td>Vilvuaara</td>
<td>Granodiorite</td>
<td>2751 (4)</td>
<td>Vaasjoki et al. (1993)</td>
<td></td>
</tr>
</tbody>
</table>

* Finnish national grid.  
* WR Sm-Nd age.

**Determinations of the concentration of α-emitting elements and the U-Th/He ages**

**Unmounted titanite crystal fragments.** For U and Th concentration measurements (U-Th)/He age determination clear, inclusion-free fragments without external crystal surfaces were hand-picked using a stereo- and a polarizing microscopes. These fragments were photographed and wrapped in platinum capsules with 1 × 10 mm size. The analysis involved three separate steps: (1) He extraction and measurement, (2) chemical digestion, and (3) measurement of the parent isotopes.

For the He measurement, the crystals were degassed in a high vacuum extraction line using an infrared laser. A Ti-Zr getter at 450 °C was used to purify the gas. The inert gases were measured by a Hiden triple-filter quadrupole mass spectrometer with a positive ion-counting detector. For every sample, a re-extraction was done to check the complete degassing of the crystal fragment. For determination of the mass of U, Th, and Sm, the degassed titanite fragments were dissolved in a mixture of concentrated ultrapure HCl (500 μL) and HF (100 μL) in pressurized Teflon (polytetrafluoroethylene) vials during one day at 220 °C, and spiked with calibrated 239Th and 234U solutions. After cooling, the samples were dried, converted to nitrate by

Reasonable fitting parameters were found by testing different evaluation constraints and visually checking the quality of the fit. The tested parameter values as well as the best configuration setup can be found in Table 3 and Appendix 1.

During the curve-fitting, the spectrum is first scaled to 100 arbitrary intensity units and, in case of automated background correction, the estimated baseline is subtracted in a second step. Thus, the comparison of integrated intensities (by summing the areas of all pV functions) and function areas is only possible in evaluations without automated background correction. The fitted bandwidths (FWHM, full-width at half maximum) of the titanite spectra were corrected for the apparatus function after Irmer (1985) and Nasdala et al. (2001).
Effects of radiation damage on titanite grains have been studied using various methods such as Raman spectroscopy. The Raman spectra show a broad variation in bandwidths, absolute and relative intensities of the bands, as well as shifts in band positions. The spectra were controlled by the width of the normal distribution from which the value is chosen that is added or subtracted from a randomly chosen pseudo-Voigt function parameter.

**RESULTS**

**Raman spectra**

We acquired 82 Raman spectra of 63 unmounted crystal fragments from 19 Finnish samples, as well as 152 spectra of 9 titanite mounts of the Finnish samples and 59 spectra of 6 mounted low-damage samples, totaling 293 titanite Raman spectra.

The Raman spectra show a broad variation in bandwidths, absolute and relative intensities of the bands, as well as shifts in band positions. Figure 1 shows two very different spectra obtained on grains with different α-doses. At the acquisition of the spectra, the crystals were randomly oriented, thus the entire range of anisotropy effects is represented (see e.g., Beirau et al. 2012; Zhang et al. 2013).

Due to the edge-filter, which blocks the signal below ~70 cm⁻¹, most spectra start with signal and many have high Raman intensities at 100–200 cm⁻¹. Therefore, the background signal is detectable only at higher wavenumbers (>1000 cm⁻¹, Fig. 1).

For an excitation wavelength of 532 nm the major photoluminescence bands (Sm, Nd) occur at higher wavenumbers than the titanite Raman bands (Lenz et al. 2015). The comparison of the spectra with spectra acquired with 633 nm excitation shows no differences, which indicates that no REE-related photoluminescence signals overlap the Raman signal. The only photoluminescence that theoretically occurs in the Raman wavenumber range is an Er-generated peak at 564 nm (i.e., 1060 cm⁻¹), but this has not been detected.

**Effective uranium (eU) contents and α-doses**

The eU contents of the studied titanite crystal fragments range from 6 to 935 ppm. The α-doses were calculated as:

\[
D_\alpha = 8 \cdot \frac{C_u \cdot N_\lambda}{M} \cdot 0.9928 \cdot \left( \exp^{238 \cdot t} - 1 \right) + 7 \cdot \frac{C_u \cdot N_\lambda}{M} \cdot 0.0072 \cdot \left( \exp^{235 \cdot t} - 1 \right) + 6 \cdot \frac{C_{th} \cdot N_\lambda}{M} \cdot 0.9928 \cdot \left( \exp^{232 \cdot t} - 1 \right)
\]

where \( C \) = actinide concentrations (in parts per million), \( N_\lambda = \) Avogadro’s number \( (6.022 \times 10^{23} \text{ atoms/mol}) \), \( M = \) the molecular masses, \( \lambda = \) the decay constants for the different isotopes, and \( t = \) the onset of damage accumulation \( (t = 1.7 \text{ Ga for the Finnish samples as discussed above or the respective ages of the low damage titanites, see Table 2).} \)

The α-doses of the Finnish samples range from \( 4 \times 10^{10} \) to \( 2.9 \times 10^{10} \) α/g and those of the additional samples with lower α-dose from \( 1.3 \times 10^9 \) to \( 1.8 \times 10^9 \) α/g (Appendix 1). Altogether, the α-dose in the samples ranges over more than five orders of magnitude.

**Quality of the curve-fitting of the Raman spectra**

To establish reasonable curve-fitting parameters and comparison of their effects on further calculations, we applied a systematic sensitivity study and several curve-fitting protocols were tested (Table 3 and Appendix 1). For the completely automated fittings (including automated background correction), reasonable results (setting “wF_sm”) were achieved when using a “window_filter” parameter with 0.35 window size for baseline calculation, setting the “noise” parameter to 2.5 or 3, allowing 40 pV functions and smoothing the spectra with a “smoothing_size” parameter of 9 (for all other parameter see Appendix 1). Lower “noise” parameter values lead to a solution with many small pV functions while higher “noise” parameter values or severe restrictions on the maximum number of allowed pV functions either lead to incomplete curve-fits (i.e., some bands...
were not described by pV function) or imprecise fitting of broad bands. In most cases, three repeated curve-fits yielded consistent, well-reproducible results. Only a very minor proportion of the spectra showed poor reproducibility.

A problem during curve-fitting of metamict titanite spectra is the inherently unknown background at low wavenumbers. Assuming a flat baseline, even at low wavenumbers seems to be reasonable, however, dispersed light at low wavenumbers might cause some increase in the background intensity. This is why we tested both the automated and manual background correction. The automated curve-fitting often estimates a baseline that is elevated at low wavenumbers (Fig. 1). Too small “window size” parameter values (e.g., 0.25) produced unreliable, bended baselines. For manual background correction, a flat baseline (i.e., not elevated at lower wavenumbers) was assumed.

The curve-fitting sometimes produces unapparent solutions; the most common type is when a range in the spectrum is modeled by fitting of one flat, wide pV function and three small narrow pV functions instead of a triplet with three medium-sized functions. The only way to avoid the dubious flat wide pV functions is by limiting the “maximum peak width” parameter. Setting the “maximum peak width” parameter to 80 or 100 cm\(^{-1}\) (given as HWHM, half-width at half maximum) caused fewer artifacts than allowing it to become as high as 150 cm\(^{-1}\). However, harsh restriction of the pV function width (e.g., values below 80 cm\(^{-1}\)) is critical because in our case the widths are the most important result of the curve-fitting procedure.

**POSSIBILITIES OF α-DOSE ESTIMATION FROM THE RAMAN SPECTRA**

**Single band testing**

Beirau et al. (2012) proposed the use of the FWHM of the 465 cm\(^{-1}\) band, which is assigned to the SiO\(_2\)-bending mode (Heyns et al. 2000; Heyns and Harden 2013), as an estimator for the degree of metamictization because it broadens with increasing α-dose. Figures 3a and 3b show the FWHM of this band (defined by the center values between 458 and 468 cm\(^{-1}\)) vs. the α-dose of each spot (Appendix 1 3). The colors of the data points indicate the band position. In very low damage samples, the band has a width of ~20 cm\(^{-1}\) and centers at ~468 cm\(^{-1}\). Above ~5 × 10\(^{16}\)\(\mu\)g the band starts getting broader and shifts toward lower wavenumbers. However, for highly damaged crystals the bandwidths are very scattered (Fig. 3a) and an accurate estimation becomes difficult. Another problem with the use of this band is its absence in some spectra.

The band at 424 cm\(^{-1}\) (415 to 425 cm\(^{-1}\), Figs. 3c and 3d) is also assigned to the SiO\(_2\)-bending mode (Heyns et al. 2000; Heyns and Harden 2013), shows a very similar behavior. Both width and position correlate with the α-dose (Appendix 1 4). Starting from ~5 × 10\(^{16}\)\(\mu\)g, band broadening from ~18 to >50 cm\(^{-1}\) and positional shift from 424 to 416 cm\(^{-1}\) are observed. The 424 cm\(^{-1}\) band also does not appear in all spectra.

The bands at 163, 252, 544, and 605 cm\(^{-1}\) for which Zhang et al. (2013) report band broadening, as well as the band at 535 cm\(^{-1}\) were likewise investigated. However, we could not determine significant correlations. For the bands at 163, 252, and 535 cm\(^{-1}\) the bandwidths are scattered and show poor positive correlation with the α-dose while the positions appear to be uncorrelated. For the band at 544 cm\(^{-1}\) neither the width nor the position shows any correlation with the α-dose.

According to Zhang et al. (2013) the band at 605 cm\(^{-1}\) broadens, shifts toward 612 cm\(^{-1}\) and becomes more asymmetric with increasing metamictization. However, Beirau et al. (2012) show that depending on the orientation the band either shifts toward higher wavenumbers or shifts toward lower wavenumbers. Verifying this behavior is hindered by the asymmetric character of the band. Most of the curve-fits contain at least one pV function in the range of 590–620 cm\(^{-1}\), some contain two, rarely three pV functions could be fitted. No correlations with α-dose were observed.

**Characterization of the entire Raman spectrum**

Metamictization influences some bands more than others but generally it broadens all Raman bands (Zhang et al. 2013). To relate this general broadening with the corresponding α-doses, we looked for parameters that describe the modification of the spectra with a single value. We calculated medians and unweighted and weighted means of all bandwidths for every spectrum. The use of the mean pV function areas was also considered in some test calculations, however, it turns out that the comparison of the function areas is biased in all spectra using automated background correction, because the absolute areas are affected by the baseline height. The use of mean width values instead of single bandwidths has distinct advantages in the case of metamict titanite where the fitting is hampered by overlapping and asymmetric bands.

For the loose grains where two or three spectra were recorded, means and medians combining the two or three spectra were calculated. FWHM means were weighted either by (1) scaled pV function intensity (iw-FWHM) or by (2) scaled pV function area (aw-FWHM). To test the reproducibility, all spectra were curve-fitted three times. Means and medians were calculated for each curve-fit as well as for the average spectrum joining all three evaluations. Usually, the numeric difference between the three repetitions is less than 10% but can be as high as 20% for some spectra (due to overlapping broad bands). Therefore, the use of repeated spectral evaluations and means overall evaluations is highly recommended. The (weighted) means and medians were compared for all tested curve-fitting protocols. All data can be found in Appendix 1 2.

All means and medians show good correlation with the α-dose (nearly all p-values << 2.2 × 10\(^{-16}\)). However, unweighted means and medians are much more sensitive to the curve-fitting parameters and spectral properties (e.g., signal-to-noise ratio) than weighted means. Examples are presented in Appendix 1 5.

The use of weighted mean FWHM has the advantage that it is less sensitive to the total number of used pV functions and the larger pV functions have a stronger influence than small peaks. Moreover, the weighted mean FWHMs, especially iw-FWHMs, are much more robust because different curve-fitting protocols yield nearly the same results (see Fig. 4). The iw-FWHM yield a better result than the aw-FWHM. The dependency of some bands on the orientation of the crystal seems to have only a minor impact on the iw-FWHM.
The most important sensitivity test: Influence of the maximum number of pV functions on the curve-fitting results

We demonstrated that the iw-FWHM procedure leads to more consistent results than the area-weighted procedure. Thus, a systematic sensitivity test series was performed to study the impact of the maximum number of pV functions on the results of the curve-fitting. The repeated evaluations allowed for 10, 15, 20, 30, or 40 pV functions. Allowing 15 up to 40 pV functions, we always recorded the same trend (see Figs. 4 and 5). However, with only 10 pV functions the spectra were often poorly fitted and especially in the well-crystalline samples not all bands were described by pV functions resulting in higher iw-FWHM values. Thus, curve-fitting with a maximum of 15 pV functions is sufficient to characterize the α-dose in titanites by the iw-FWHM method, even if these 15 pV functions might not represent the spectra in all details.

DISCUSSION

Our results suggest that the intensity weighted mean FWHM is a reliable parameter to describe the α-dose in titanite. The restriction to maximal 15 pV functions led to consistent results. Below an α-dose of 5 x 10^{16} α/g the iw-FWHM is independent of α-dose and scatters between 25 and 50 cm\(^{-1}\). Above this value, the iw-FWHM increases linearly with increasing α-dose up to 3 x 10^{18} α/g.

Figure 5a compares the linear regression parameters (slope, y-axis intercept, and R\(^2\)) of all calculated values for all tested curve-fitting protocols. All linear regression data can be found in Appendix 6. The iw-FWHM linear regressions yield the tightest cluster of results associated with high coefficients of determination (Fig. 5a). All the other methods yield more scattered results and especially the median linear regressions often have very low coefficients of determination. This implies that regardless of the curve-fitting protocol used for spectral evaluation, the iw-FWHM method produced nearly the same linear regression, which makes this method the most robust of all tested procedures.

Thus, we recommend using the iw-FWHM as a radiation damage estimator for titanite. For the highest density point in Figure 5a the formula for the linear increase of the iw-FWHM

\[
\text{FWHM} = \text{constant} + \text{slope} \times \alpha \text{-dose}
\]

is expected.
with growing $\alpha$-dose is $\text{iw-FWHM}[\text{cm}^{-1}] = 39.2[\text{cm}^{-1}] + 3.82 \times 10^{-17}[\text{cm}^{-1}/(\alpha/g)] \times \alpha$-dose[$\alpha/g$]. This is similar to the formula for the most satisfying protocol “wf_sm” (see details in Appendix’ 1), which is $\text{iw-FWHM}[\text{cm}^{-1}] = 38.8(\pm1.2)[\text{cm}^{-1}] + 3.86(\pm0.13) \times 10^{-17}[\text{cm}^{-1}/(\alpha/g)] \times \alpha$-dose[$\alpha/g$]. Combining both formulas we get $\text{iw-FWHM}[\text{cm}^{-1}] = 39.0(\pm1.2)[\text{cm}^{-1}] + 3.84(\pm0.13) \times 10^{-17}[\text{cm}^{-1}/(\alpha/g)] \times \alpha$-dose[$\alpha/g$]. The constants of the regression equation are determined by $\sim3\%$ relative uncertainties.

The other, even more important bias that controls the accuracy of the constants, comes from the assumed duration of the damage accumulation. As discussed above, the temperature range where radiation damage accumulation starts for the Finnish samples is not known precisely, neither is the annealing behavior in titanite. It is not clear how the density of accumulated damage influences the annealing kinetics, and the effect of the variable chemical composition of titanite is not known. Additionally, the thermal history of the Finnish samples bears some uncertainty in the interval of 1.8–1.5 Ga. Figure 5b visualizes the effect of this uncertainty on the linear regressions. While the $y$-intercepts remain unchanged, shorter damage accumulation durations lead to steeper slopes as the absolute damage gets smaller. This uncertainty is higher than the error derived from the spread of the data. Including this uncertainty into the error of the linear regression leads to a corrected calibration line: $\text{iw-FWHM}[\text{cm}^{-1}] = 39.0(\pm1.2)[\text{cm}^{-1}] + 3.84(\pm0.61,–0.26) \times 10^{-17}[\text{cm}^{-1}/(\alpha/g)] \times \alpha$-dose[$\alpha/g$].

The onset of the significant change of the titanite Raman peak width is around $5 \times 10^{16} \alpha/g$. Baughman et al. (2017) studied the He diffusivity and the THF closure temperature in relation to the $\alpha$-dose. Their data indicate a threshold, where $T_\text{c}$ strongly decreases at around $5 \times 10^{16} \alpha/g$ (Fig. 4). It is remarkable that our procedure based on the characterization of the entire Raman spectrum is more sensitive and detects the
change of the lattice at one order of magnitude lower level. This indicates the need for further He diffusion experiments to quantify the diffusion parameters for titanite in the relatively low damage range.

**Comparison with (U-Th)/He results**

For some of the Finnish samples (U-Th)/He ages were determined. Figure 6a shows these ages compared to their α-dose and eU content. The data show a negative correlation and the covered eU range is relatively small. Compared to our data, the data presented by Baughman et al. (2017) shows a better negative correlation and the dispersions include the moderate correlation of THe age vs. eU content. The data show a negative correlation and the dispersion is mainly due to the poor THe age vs. eU correlation of our data set.

**Implications**

We present a robust Raman spectroscopy based method for estimating the α-dose in titanite by Raman spectroscopy. The titanite (U-Th)/He thermochronometer is relevant for the reconstruction of thermal histories in the upper crust, because titanite occurs in more mafic lithologies, in contrast to zircon, and its typically lower actinide content allows for obtaining reliable thermochronologic information in cratonic areas that experienced cooling in Precambrian times. The method can be used in two ways for the routine work in (U-Th)/He thermochronology: (1) It can provide an easy-to-apply and quick tool for identifying highly damaged titanite grains that have extremely low closure temperature due to the high α-dose. In such crystals, the recoil and fission tracks are already in contact and provide a kind of “percolation” leading to very quick helium diffusion (Baughman et al. 2017). Rejecting these titanite grains can optimize the dating procedure by analyzing only the better crystalline grains for which the closure temperature is considerably above the ambient temperature. (2) The other approach is to concentrate on the wide range of the α-doses and aim at involving grains that represent both extremely low and high α-doses to perform a batch modeling (e.g., Orme et al. 2016; Johnson et al. 2017; Hueck et al. 2018). In this way the thermal history may be described with better confidence and even the lower temperature ranges may be better constrained by the titanite grains with very low closure temperature. The method proposed here provides a pre-selection method to optimize the range of α-doses of the dated grains.

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**References Cited**


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**Figure 6.** Titanite (U-Th)/He ages in relation to their α-dose, eU contents, and the intensity weighted mean FWHM (iw-FWHM) of the corresponding Raman spectra. (a) Titanite (U-Th)/He (THe) ages vs. their α-dose, color indicates the eU contents. (b) Relation of the THe ages vs. iw-FWHM. The color indicates the α-dose. The observed dispersion is mainly due to the poor THe age vs. eU correlation of our data set.


