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2   **Estimation of radiation damage in titanites using Raman spectroscopy**

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8   **Abstract**

9   Recent studies have shown that α–damage in titanite influences He diffusivity and

10   thus the closure temperature of the (U–Th)/He system in titanite. We compare

11   different methods for measuring the α–dose in titanite by Raman spectroscopy.

12   293 Raman spectra of randomly oriented titanite fragments from the Archean

13   Karelian domain in eastern Finland along with some well–studied young titanites

14   and U–Pb standard reference materials were analyzed and related to the

15   concentration of α–emitting elements (U and Th) that generated damage in the

16   respective grains. Automated curve–fitting was performed by the IFORS software

17   and different curve–fitting protocols were tested and compared.

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18   The Raman bands at 424 cm^{-1} and 465 cm^{-1} show a good correlation of full width

19   at half maximum (FWHM) and position with the α–dose. However, these bands

20   are not always present because titanite is highly anisotropic implying that Raman

21   spectra are sensitive to orientation. The intensity–weighted mean FWHM (iw–

22   FWHM) of all Raman bands of a spectrum proves to be the most robust measure

23   of the α–dose. A simplified fitting approach considering 15 peaks is sufficient to

24   describe the accumulated α–dose. For α–doses below 5×10^{16}α/g the iw–FWHM

25   is independent of α–dose and ranges from 25 to 50 cm^{-1}. Above this value the iw–

26   FWHM increases linearly with increasing α–dose up to 3×10^{18}α/g. The linear

27   correlation can be described as iw–FWHM[cm^{-1}] ~ 39(±1.2)[cm^{-1}]+3.84(+0.61,-

28   0.26) $\times 10^{-17}$[cm^{-1}/(α/g)] × α–dose[α/g]. The approach provides a pre–selection

29   method in order to optimize the range of α–doses of titanite crystals to be dated by

30   (U–Th)/He thermochronology.

31   keywords: titanite; (U–Th)/He; metamictization; radiation damage; α–dose;

32   Raman spectroscopy; thermochronology

33   **Introduction**

34   Low–T thermochronology is a widely–applied tool for deciphering thermal histories of cratonic

35   areas, especially when sedimentary successions constraining the timing of subsidence and

36   exhumation are missing. In contrast to zircon which has commonly effective uranium content

37   (eU=U[ppm]+0.235Th[ppm]) of ≥ 300 ppm (up to 5000 ppm), titanite has usually lower eU

38   contents in the range of 10–500 ppm and is thus less subjected to metamictization. Moreover,

39   titanite is common in intermediate to mafic rocks where zircon is typically absent.

40   The closure temperature (T_c) of the (U–Th)/He thermochronometers is influenced by the

41   composition and crystalline state of the dated crystals. Among all influencing parameters

42   metamictization is the dominant one (Flowers 2009; Orme et al. 2016; Johnson et al. 2017). The

43   influence of metamictization on the T_c's of the most widely used minerals, zircon and apatite, has

44   been intensively investigated (Shuster et al. 2006; Flowers et al. 2009; Gautheron et al. 2009;

45   Guenthner et al. 2013; Orme et al. 2016). In contrast, its influence on the titanite (U–Th)/He

46   thermochronometer (THe) has been reported only recently (Baughman et al. 2017; Guenthner et

47   al. 2017). These studies show that with increasing α–dose the T_c of the THe system drops to a

48   significantly lower value. Unfortunately, several aspects of the THe system remain unclear

49   (Reiners and Farley 1999; Stockli and Farley 2004; Cherniak and Watson 2011). Titanite has

50   been discussed as host material for nuclear waste (Weber et al. 1998; Stefanovsky et al. 2004;

51   Lumpkin 2006) and various studies focus on the effects of radiation damage in this mineral

52   (Bismayer et al. 2010; Salje et al. 2011; Beirau et al. 2016).

53   The α–dose of zircon can be estimated from the width of its main Raman band at approximately

54   1000–1008 cm^{-1} (Zhang et al. 2000; Nasdala et al. 2001; Palenik et al. 2003; Nasdala et al. 2004).

55   Therefore, Raman spectroscopy offers a quick, non–destructive method for selecting grains for

56   zircon (U–Th)/He (ZHe) thermochronology according to their α–dose (e.g. Ault et al. 2018). For

57   titanite, as for zircon, metamictization affects the Raman spectrum by broadening and shifting the

58   position of several bands (Salje et al. 1993; Meyer et al. 1996; Zhang and Salje 2003; Bismayer

59   et al. 2010; Beirau et al. 2012; Zhang et al. 2013). However, Raman spectroscopy of titanite is

60   more complicated when compared to zircon because of (i) strong anisotropy, (ii) higher amount

61   of Raman bands, and (iii) adjacent Raman bands often overlap in highly metamict titanite grains

62   (e.g. Beirau et al. 2012; Zhang et al. 2013). Moreover, titanite crystals usually have irregular

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63 shapes. Therefore mineral fragments without crystal faces are typically used for THe dating,

64 which makes crystallographic orientation of the grains difficult.

65 So far, no advanced diffusion model exists for titanite that takes radiation damage into

66 consideration. As a consequence, THe ages measured on highly damaged grains are more

67 difficult to interpret than THe ages of slightly damaged grains. Therefore, the routine application

68 of THe thermochronology requires an easy–to–use, orientation independent method for damage

69 estimation and selection of the crystals to be dated.

70 This study compares different approaches considering single peaks as well as the entire Raman

71 spectrum for quantifying the α–dose in titanite. We present coupled Raman, eU, and THe data of

72 titanite from the Archean Karelian domain in Fennoscandia. The area has been tectonically stable

73 since the Svecofennian orogeny (approx. 1.92–1.80 Ga) (Kähkönen 2005; Lahtinen et al. 2005;

74 Heller et al., in prep) and since then all samples have experienced the same thermal history. To

75 cover a broad range of α–doses, measurements of younger titanite samples and titanite reference

76 materials with known age and simple cooling histories complement the dataset. The main goal of

77 this study is to establish a quick (and non–destructive) method for estimating the α–dose from the

78 titanite Raman spectrum. We demonstrate that characterization of the entire Raman spectrum can

79 be used as a robust estimator independent of grain orientation and evaluation method.

80 **Background**

81 **Crystal structure and metamictization of titanite**

82 Titanite, $CaTi(SiO_4)(O, OH, F)$, also called sphene, is a monoclinic nesosilicate. Zig–zag chains

83 of corner–sharing TiO_6 octahedra are cross–linked by isolated SiO_4–tetrahedra, building a

84 framework. This $(TiOSiO_4)_2$–framework contains large cavities which enclose sevenfold–

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85   coordinated Ca atoms (Speer and Gibbs 1976). Through lattice substitutions, titanite can

86   incorporate significant amounts of rare earth elements (REE), U, Th, Sr, Y, Mn and Pb at the

87   sevenfold Ca sites and at the octahedral Ti sites (Higgins and Ribbe 1976; Tiepolo et al. 2002;

88   Xu et al. 2015) and may also concentrate significant amounts of HFSEs, such as Nb, Ta, Zr and

89   W, on the octahedral Ti site (Groat et al. 1985; Lucassen et al. 2011).

90   The consecutive radioactive decay of U and Th atoms induces metamictization in titanite crystals

91   (Zhang and Salje 2003; Beirau et al. 2010; Bismayer et al. 2010; Beirau et al. 2012; Zhang et al.

92   2013; Beirau et al. 2014, 2016). In metamict titanites both crystalline and amorphous domains

93   coexist (Hawthorne et al. 1991; Lumpkin et al. 1991). Hawthorne et al. (1991) and Farges (1997)

94   suggest that metamictization leads to disordering around the Ti positions and a partial reduction

95   of the Ti coordination down to five and / or four. This further disturbs the Ti–O–Ti intra–chain

96   linkages (Beirau et al. 2012), triggering an anisotropic response of the titanite lattice. This means

97   that the plane containing Si-O-Ti-O bond closed contours is less susceptible to a self–

98   accumulation of defects as compared to the perpendicular planes, which contain chains of Ti-O

99   bonds (Beirau et al. 2012).

100   **Raman spectroscopy of titanite**

101   Several studies have applied Raman spectroscopy to titanite (Salje et al. 1993; Meyer et al. 1996;

102   Zhang and Salje 2003; Bismayer et al. 2010; Beirau et al. 2012; Zhang et al. 2013). Titanite is an

103   anisotropic phase, exhibiting Raman spectra strongly dependent on the crystallographic

104   orientation. Up to 40 different Raman bands have been reported for natural titanite samples

105   (Zhang et al. 2013), whereas other authors (Salje et al. 1993) reported only up to 30 bands.

106   Increasing degree of metamictization (Fig. 1) changes the Raman spectrum by broadening bands,

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107   shifting their frequency, decreasing the overall intensity and appearance of additional bands

108   (Zhang et al. 2013). As result of metamictization, weakening of the bands at 163 cm^{-1}, 252 cm^{-1},

109   466 cm^{-1}, 544 cm^{-1}, 605 cm^{-1} (see Fig. 1), appearance of new bands at 574 cm^{-1} and 643 cm^{-1},

110   shifting of bands from 993 cm^{-1} to 978 cm^{-1}, 1017 cm^{-1} to 1008 cm^{-1} and 643 cm^{-1} to 675 cm^{-1}

111   and appearance of a shoulder at 650 cm^{-1} have been documented by (Zhang et al. 2013).

112   For estimating the degree of metamictization, Zhang et al. (2013) proposed to use the 605 cm^{-1}

113   peak as it gets broader, shifts towards 612 cm^{-1} and becomes increasingly asymmetric. Beirau et

114   al. (2012) suggested estimating the degree of metamictization from the full width at half

115   maximum (FWHM) of the 465 cm^{-1} band which arises from the SiO_4–bending mode (Heyns et

116   al. 2000) and is narrow at low damage doses and broader at high doses. Unfortunately, both

117   approaches can be realized only at given, limited crystallographic orientation and are therefore

118   not useful as universal method for spectra taken from fragments laying in different orientations.

119   **Importance of radiation damage in (U–Th)/He thermochronology**

120   The radioactive decay of U, Th, and Sm produces α–particles (^{4}He nuclei). Measuring the amount

121   of both ^{4}He and the parent isotopes makes it possible to calculate the duration of He

122   accumulation (Farley 2002; Zeitler 2015).

123   He has a high diffusivity in solid phases, thus the preserved amount of He in a crystal depends on

124   diffusion that took place in the lifetime of the dated phase. He diffusion kinetics in crystals has

125   been intensely studied; it is controlled by temperature, mineral type, grain size (diffusion domain

126   size) and cooling rate (Zeitler et al. 1987; Wolf et al. 1996). Furthermore, mineral composition

127   and radiation damage are significant (Wolf et al. 1996; Nasdala et al. 2004; Reiners 2005).

128   Reiners and Farley (1999) have reported grain–size and cooling rate dependence of T_c in the THe

129   system at 165–225°C. However, recent studies by Baughman et al. (2017) have shown that this is

130   not valid for highly metamict grains. These authors report T_c's of 150–210°C at low damage

131   levels and a rapid drop above a radiation damage threshold of $\sim 5 \times 10^{17} \alpha/g$ (for minimal

132   estimates of the temperature where damage accumulation starts, the threshold is $\sim 3.5 \times 10^{17} \alpha/g$).

133   Despite the lower threshold of titanite compared to zircon ($\sim 1.5 \times 10^{18} \alpha/g$; Guenthner et al. 2013;

134   Baughman et al. 2017), titanite is likely to better document the higher temperature portion of a

135   protracted time–temperature path than zircon because of its usually order–of–magnitude lower

136   actinide contents (Baughman et al. 2017).

137   **Samples**

138   **Geological setting and samples from the Ilomantsi greenstone belt**

139   The samples used for this study derive from the Ilomantsi greenstone belt, which is located in

140   eastern Finland in the western part of the Neoarchean Karelian province (Fig. 2 and Table 1). It

141   forms part of the Ilomantsi–Kostomuksha greenstone belt, which continues into Russia and

142   extends in a N–S direction over more than 200 km. The Finnish part of this large belt (i.e.

143   Ilomansti greenstone belt, Fig. 2) includes the ~50 long Hattu schist belt, which hosts orogenic

144   gold deposits, and the Kovero belt located further southwest (Nurmi et al. 1993; Sorjonen-Ward

145   1993; Sorjonen-Ward et al. 2015). The belt is composed of dominantly felsic to intermediate

146   volcanic and siliciclastic rocks with eruption and deposition ages of 2.78–2.75 Ga (Vaasjoki et al.

147   1993; Huhma et al. 2012b) and small elongated plutons with emplacement ages of ~2.75–2.70 Ga

148   (Vaasjoki et al. 1993; Käpyaho et al. 2016).

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149   The Ilomantsi greenstone belt was affected by two metamorphic events. The Neoarchean

150   metamorphism reached amphibolite facies peak conditions (550±50°C, 3–5 kbar; O'Brien et al.

151   1993). An ~2.70 Ga minimum (e.g. cooling) age for this metamorphism was deduced from 2.708

152   and 2.696 Ga U–Pb ages of titanite and monazite from granodiorite and leucogranite intrusions,

153   respectively (Vaasjoki et al. 1993). However, Hölttä et al. (2016) proposed 2.66 Ga and 2.62 Ga

154   age for the Neoarchean metamorphism based on dating of monazite growth. During the Lapland–

155   Savo orogenic phase of the Paleoproterozoic Svecofennian orogeny, thick, east–verging nappes

156   were emplaced on the Archean basement of eastern Finland and temperatures in the Ilomantsi

157   greenstone belt reached 400–500°C as indicated by partial reset of hornblende K–Ar ages

158   (Kontinen et al. 1992) and Pb isotope exchange studies (Halla and Heilimo 2009). Biotite K–Ar,

159   as well as biotite and muscovite Ar–Ar ages suggest cooling below ~350–300°C at ~1.8 Ga

160   (Kontinen et al. 1992; Molnár et al. 2016).

161   The later orogenies and accretionary events that occurred in Fennoscandia, such as the Gothian

162   (1.64–1.52 Ga) and the Telemarkian accretion (1.52–1.48 Ga), the Hallandian and Danopolonian

163   orogenies (1.47–1.42 Ga) and the Sveconorwegian orogeny (1.14–0.90 Ga) (Bingen et al. 2008)

164   affected mainly the southwestern margin of Fennoscandia and were of little and poorly

165   understood impact for eastern Finland. The lack of sedimentary record makes the reconstruction

166   of the post–Svecofennian thermal evolution difficult (Kohonen 2005).

167   A kaoline deposit at Virtasalmi, ~200 km WSW of the Ilomantsi greenstone belt, indicates

168   surface exposure of the Svecofennian crystalline basement during the Mesoproterozoic at ~1.18

169   Ga (Sarapää 1996). Late Neoproterozoic, in Fennoscandia referred to as Vendian, and Cambrian

170   sediments are common further south in Estonia. The extent of this unconformity and sediment

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171   coverage towards north (e.g. Finland) is not clear and has been a matter of discussion (Puura et

172   al. 1996; Larson et al. 1999; Sliaupa et al. 2006).

173   Thermochronologic data from eastern Finland comprise of a wide range of Neoproterozoic and

174   early Paleozoic apatite fission track (AFT) and apatite (U–Th)/He (AHe) ages (Lehtovaara 1976;

175   Lorencak 2003; Murrell 2003; Murrell and Andriessen 2004; Kohn et al. 2009). In combination

176   with new ZHe, THe and AHe data (Heller et al. in preparation) they indicate that the Ilomantsi

177   greenstone belt experienced slow cooling since the Svecofennian orogeny and that temperatures

178   did not exceed 100°C for the last 1.0 Ga.

179   For calculation of radiation damage densities the duration of α–damage accumulation has to be

180   estimated. However, neither the thermal history of the samples in the time interval of 1.8-1.5 Ga

181   (see below), nor the temperature range of α–damage annealing are well defined. While it is a

182   common praxis to estimate that annealing of α–damage occurs at similar temperatures as

183   annealing of fission tracks (Baughman et al. 2017 for titanite and Pidgeon 2014 for zircon),

184   experiments by Gleadow (1978) indicate that α–damage annealing of titanites occurs mainly in

185   the lower part of the titanite fission track partial annealing zone (TPAZ). For the TPAZ different

186   estimates exist (197°C: Naeser and Forbes 1976; 260±20°C Gleadow and Lovering 1978; 250 ±

187   50°C: Gleadow and Brooks 1979; 240 ± 40°C: Harrison et al. 1979; 275 ± 25°C: Fitzgerald and

188   Gleadow 1988; 275 ± 25C°: Kohn et al. 1993; 265–310°C: Coyle and Wagner 1998). Studies

189   including thermal annealing experiments (Bismayer et al. 2010; Beirau et al. 2012; Salje et al.

190   2012) indicate that α–damage annealing is a complex process occurring over a temperature range;

191   while recovery of point defect is possible at lower temperatures (T<300°C), relevant

192   recrystallization of amorphous areas happens only at T>320°C. However, note that temperature

193   estimates from thermal annealing experiments are often too high as they don't include geological

194   timescales.

195   In our case the onset of α–damage accumulation can be bracketed to 1.5–1.8 Ga. The upper limit

196   is given by the ~1.8 Ga biotite and muscovite K–Ar and Ar–Ar ages (Kontinen et al. 1992;

197   Molnár et al. 2016). Note that Kohn et al. (1993) report that K–Ar ages are always greater or

198   equal to titanite fission track ages. The lower bracket is given by the oldest THe Ages(~1.5 Ga)

199   of our samples, which in our case of typical grains sizes and slow cooling correspond to

200   temperatures of ~180°C.

201   The time interval from 1.5–1.8 Ga thus corresponds to a temperature drop from ~300°C to

202   ~180°C, the onset of α–damage accumulation lies somewhere in between. Assuming that post–

203   metamorphic cooling was faster in the beginning and then slowed down we decided to calculate

204   with 1.7 Gy as damage accumulation duration. However, due to the uncertainties involved, we

205   also present the results for 1.8, 1.6 and 1.5 Gy accumulation duration and discuss the respective

206   error below.

207   The sample set with relatively high damage densities from the Ilomantsi belt was complemented

208   by some well–studied titanites (partly reference materials for U-Pb geochronology) of

209   considerably lower α–doses (Table 2).

210   **Methods**

211   **Sample preparation**

212   The mineral separation has been performed at the Geological Survey of Finland. The samples

213   were crushed, sieved and titanite fractions were separated by density and magnetic methods. For

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214   single grain analysis, inclusion–free titanite fragments from the 63–200 μm sieve fractions were

215   handpicked. 2 to 5 aliquots of 19 different samples from Finland were chosen. For the polished

216   mineral grain mounts 9 Finnish samples as well as 6 low–damage samples were mounted in

217   epoxy resin discs, ground and diamond–polished.

218   **Raman spectroscopy**

219   Raman measurements were done on (i) unmounted crystal fragments and (ii) polished grain

220   mounts. The measurements were performed with a Horiba XPloRa Plus system equipped with a

221   532 nm excitation laser (25 mW maximum output power) and an Olympus BX41 microscope,

222   which is coupled to a 200 mm focal length spectrograph with a four-grating turret. The system

223   has a Multi-Pinned-Phase (MPP) open-electrode CCD detector with a precision of ±1 pixel.

224   Using 532nm the spectral resolution is 1.4 cm^{-1} with the 2400 grooves/mm grating and 2.5 cm^{-1}

225   with the 1800 grooves/mm grating. For the unmounted crystal fragments, the 1800 grooves/mm

226   grating was used and the Raman spectra were collected for 2×10 seconds at 50% laser power

227   with 20x (0.4 NA) or 50x LWD (0.5 NA) objective in 1–3 spots per crystal fragment. The grain

228   mounts were measured with the 2400 grooves/mm grating at 10% laser power with 50x LWD

229   objective. Measurement times were 3×5 to 3×20 seconds depending on signal strength.

230   The positional drift of the spectrometer was checked regularly by measurement of a Si standard

231   and is negligible for this dataset. In transparent crystals the penetration depth is about ~15 μm for

232   the 50x LWD objective and ~20 μm for the 20x objective. The theoretical diameter of the Raman

233   spots are ~1.3 μm (50x LWD) and ~1.6 μm (20x).

234   Spectra were recorded in the range 100–1800 cm^{-1}. For detection of possible photoluminescence

235   bands additional Raman spectra were taken on some selected grains with a Horiba Jobin–Yvon

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236   Labram HR800UV spectrometer equipped with a 633 nm excitation laser. Titanite spectra with a

237   superposed epoxy signal were not used for further evaluation.

Curve–fitting of the Raman spectra

239   The curve–fitting and spectral evaluation were performed with the IFORS software (Lünsdo f

240   and Lünsdor 2016). The signal part of the spectrum was modeled by pseudo-Voigt functions

241   (pV–functions). In each iteration, a new function was added to the model, and the sum of the

242   squared residuals was reduced by randomly changing a function parameter (e.g. center position,

243   height, width, or shape-factor) by a random value. Two main approaches were applied: (i) using

244   IFORS for background correction and curve–fitting, and (ii) manual background correction using

245   the Fityk software (Wojdyr 2010) followed by automated curve–fitting with IFORS.

246   Reasonable fitting parameters were found by testing different evaluation constraints and visually

247   checking the quality of the fit. The tested parameter values as well as the best configuration setup

248   can be found in Table 3 and Appendix 1.

249   During the curve–fitting, the spectrum is first scaled to 100 arbitrary intensity units and, in case

250   of automated background correction, the estimated baseline is subtracted in a second step. Thus,

251   the comparison of integrated intensities (by summing the areas of all pV–functions) and function

252   areas is only possible in evaluations without automated background correction.

253   The fitted band widths (FWHM = full width at half maximum) of the titanite spectra were

254   corrected for the apparatus function after Irmer (1985) and Nasdala et al. (2001).

Determination of the concentration of α–emitting elements and the (U–Th)/He ages

Unmounted titanite crystal fragments

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257   For U and Th concentration measurements and (U–Th)/He age determination clear, inclusion–

258   free fragments without external crystal surfaces were hand-picked using a stereo- and a

259   polarizing microscopes. These fragments were photographed and wrapped in platinum capsules

260   with 1x1 mm size. The analysis involved three separate steps: 1) He extraction and measurement

261   2) chemical digestion and 3) measurement of the parent isotopes.

262   For the He measurement the crystals were degassed in a high vacuum extraction line using an

263   infrared laser. A Ti–Zr getter at 450°C was used to purify the gas. The inert gases were measured

264   by a Hiden triple–filter quadrupole mass spectrometer with a positive ion–counting detector. For

265   every sample a re–extraction was done to check the complete degassing of the crystal fragment.

266   For determination of the mass of U, Th and Sm the degassed titanite fragments were dissolved in

267   a mixture of concentrated ultrapure HCl (500 µl) and HF (100 µl) (Reiners and Farley 1999) in

268   pressurized teflon vials during one day at 220°C, and spiked with calibrated ^{230}Th and ^{233}U

269   solutions. After cooling, the samples were dried, converted to nitrate by re–dissolving in 0.25–

270   1 ml 65% HNO_3 and after a further drying step dissolved in a mixture of 4% HNO_3 with 0.05%

271   HF.

272   U, Th, Sm and other REE measurements were performed using a Perkin Elmer Elan DRC II

273   assembled with an APEX MicroFlow nebulizer and a Thermo iCAP Q ICP–MS instrument. The

274   actinides were determined by isotope dilution technique, while for Ca, Ti and the other trace

275   elements the external calibration method was applied.

276   **Mounted titanite fragments**

277   The trace element content of titanite grains mounted in polished epoxy resin discs was analyzed

278   by Laser–Ablation ICP–MS. A Resonetics excimer laser was used, coupled to a Thermo

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279   Element 2 sector field mass spectrometer. Measurements were conducted at the same spots as the

280   Raman measurements and performed with 10 μm laser beam diameter and short ablation times.

281   For conversion of the cps data to concentrations the NIST610 and TNT1500 glass standards were

282   used (Klemme et al. 2008).

283   **Results**

284   **Raman spectra**

285   82 Raman spectra of 63 unmounted crystal fragments from 19 Finnish samples were acquired, as

286   well as 152 spectra of 9 titanite mounts of the Finnish samples and 59 spectra of 6 mounted low–

287   damage samples, totaling 293 titanite Raman spectra.

288   The Raman spectra show a broad variation in band widths, absolute and relative intensities of the

289   bands, as well as shifts in band positions. Figure 1 shows two very different spectra obtained on

290   grains with different α–doses. At the acquisition of the spectra the crystals were randomly

291   oriented, thus the entire range of anisotropy effects is represented (see e.g. Beirau et al. 2012;

292   Zhang et al. 2013).

293   Due to the edge–filter, which blocks the signal below ~70 cm^{-1}, most spectra start with signal and

294   many have high Raman intensities at 100–200 cm^{-1}. Therefore, the background signal is

295   detectable only at higher wavenumbers (>1000 cm^{-1}, Figure 1).

296   For an excitation wavelength of 532 nm the major photoluminescence bands (Sm, Nd) occur at

297   higher wavenumbers than the titanite Raman bands (Lenz et al. 2015). The comparison of the

298   spectra with spectra acquired with 633 nm excitation shows no differences, which indicates that

299   no REE–related photoluminescence signals overlie the Raman signal. The only

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300   photoluminescence that theoretically occurs in the Raman wavenumber range is an Er–generated

301   peak at 564 nm (i.e. $=1060$ cm^{-1}), but this has not been detected.

302   **Effective uranium (eU) contents and α–doses**

303   The eU contents of the studied titanite crystal fragments range from 6 ppm to 935 ppm. The α–

304   doses were calculated as:

$$D_\alpha = 8 \cdot \frac{C_U \cdot N_A \cdot 0.9928}{M_{238} \cdot 10^6} \cdot \left(exp^{\lambda 238} \cdot t - 1\right)$$

$$+ \, 7 \cdot \frac{C_U \cdot N_A \cdot 0.0072}{M_{235} \cdot 10^6} \cdot \left(exp^{\lambda 235} \cdot t - 1\right)$$

$$+ \, 6 \cdot \frac{C_{Th} \cdot N_A}{M_{232} \cdot 10^6} \cdot \left(exp^{\lambda 232} \cdot t - 1\right)$$

305   (Eq. 1)

306   where $C =$ actinide concentrations (in ppm), $N_A =$ Avogadro's number (6.022×10^{23} atoms/mol),

307    $M =$ the molecular masses, $\lambda =$ the decay constants for the different isotopes, and $t =$ the onset of

308   damage accumulation *(t* is 1.7 Ga for the Finnish samples as discussed above or the respective

309   ages of the low damage titanites, see Table 2). The α–doses of the Finnish samples range from

310   4×10^{16} to 2.9×10^{18} α/g and those of the additional samples with lower α–dose from 1.3×10^{13}

311   to 1.8×10^{17}α/g (Appendix 2). Altogether, the α–dose in the samples ranges over more than five

312   orders of magnitude.

313   **Quality of the curve–fitting of the Raman spectra**

314   In order to establish reasonable curve–fitting parameters and comparison of their effects on

315   further calculations, we applied a systematic sensitivity study and several curve–fitting protocols

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316   were tested (Table 3 and Appendix 1). For the completely automated fittings (including

317   automated background correction), reasonable results (setting "wf_sm") were achieved when

318   using a *"window_filter"* parameter with 0.35 window size for baseline calculation, setting the

319   *"noise" parameter* to 2.5 or 3, allowing 40 pV–functions and smoothing the spectra with a

320   *"smoothing size"* parameter of 9 (for all other parameter see Appendix 1). Lower *"noise"*

321   parameter values lead to a solution with many small pV–functions while higher *"noise"*

322   parameter values or severe restrictions on the maximum number of allowed pV–functions either

323   lead to incomplete curve–fits (i.e. some bands were not described by pV–function) or imprecise

324   fitting of broad bands. In most cases, three repeated curve–fits yielded consistent, well

325   reproducible results. Only a very minor proportion of the spectra showed poor reproducibility.

326   A problem during curve–fitting of metamict titanite spectra is the inherently unknown

327   background at low wavenumbers. Assuming a flat baseline, even at low wavenumbers seems to

328   be reasonable, however, dispersed light at low wavenumbers might cause some increase in the

329   background intensity. This is why we tested both the automated and the manual background

330   correction. The automated curve–fitting often estimates a baseline which is elevated at low

331   wavenumbers (Fig. 1). Too small *"window size"* parameter values (e.g. 0.25) produced

332   unreliable, bended baselines. For manual background correction a flat baseline (i.e. not elevated

333   at lower wavenumbers) was assumed.

334   The curve–fitting sometimes produces unapparent solutions; the most common type is when a

335   range in the spectrum is modeled by fitting of one flat, wide pV–function and three small narrow

336   pV–functions instead of a triplet with three medium sized functions. The only way to avoid the

337   dubious flat wide pV–functions is by limiting the *"maximum peak width"* parameter. Setting the

338   *"maximum peak width"* parameter to 80 or 100 cm^{-1}(given as HWHM = half width at half

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339   maximum) caused fewer artifacts than allowing it to become as high as 150 cm^{-1}. However, harsh

340   restriction of the pV–function width (e.g. values below 80 cm^{-1}) is critical because in our case the

341   widths are the most important result of the curve–fitting procedure.

Possibilities of α–dose estimation from the Raman spectra

Single band testing

344   Beirau et al. (2012) proposed the use of the FWHM of the 465 cm^{-1} band, which is assigned to

345   the SiO$_4$–bending mode (Heyns et al. 2000; Heyns and Harden 2013), as an estimator for the

346   degree of metamictization because it broadens with increasing α–dose. Figures 3A and 3B show

347   the FWHM of this band (defined by the center values between 458 cm^{-1} and 468 cm^{-1}) versus the

348   α–dose of each spot (Appendix 3). The colors of the data points indicate the band position. In

349   very low damage samples, the band has a width of ~20 cm^{-1} and centers at ~468 cm^{-1}. Above

350   ~5×10^{16}α/g the band starts getting broader and shifts towards lower wavenumbers. However, for

351   highly damaged crystals the band widths are very scattered (Fig. 3A) and an accurate estimation

352   becomes difficult. Another problem with the use of this band is its absence in some spectra.

353   The band at 424 cm^{-1}(415 cm^{-1} to 425 cm^{-1}, Figs. 3C and 3D), which is also assigned to the SiO$_4$–

354   bending mode (Heyns et al. 2000; Heyns and Harden 2013), shows a very similar behavior. Both

355   width and position correlate with the α–dose (Appendix 4). Starting from ~5×10^{16}α/g, band

356   broadening from ~18 cm^{-1} to >50 cm^{-1} and positional shift from 424 cm^{-1} to 416 cm^{-1} are

357   observed. The 424 cm^{-1} band also does not appear in all spectra.

358   The bands at 163 cm^{-1}, 252 cm^{-1}, 544 cm^{-1} and 605 cm^{-1} for which Zhang et al. (2013) report

359   band broadening, as well as the band at 535 cm^{-1} were likewise investigated. However, we could

360   not determine significant correlations. For the bands at 163 cm^{-1}, 252 cm^{-1} and 535 cm^{-1}the band

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361   widths are scattered and show poor positive correlation with the α–dose while the positions

362   appear to be uncorrelated. For the band at 544 cm^{-1} neither the width nor the position shows any

363   correlation with the α–dose.

364   According to Zhang et al. (2013) the band at 605 cm^{-1} broadens, shifts towards 612 cm^{-1} and

365   becomes more asymmetric with increasing metamictization. However, Beirau et al. (2012) show,

366   that depending on the orientation the band either shifts towards higher wavenumbers or shifts

367   towards lower wavenumbers. Verifying this behavior is hindered by the asymmetric character of

368   the band. Most of the curve–fits contain at least one pV–function in the range of 590–620 cm^{-1},

369   some contain 2, rarely 3 pV–functions could be fitted. No correlations with α–dose were

370   observed.

371   **Characterization of the entire Raman spectrum**

372   Metamictization influences some bands more than others but generally it broadens all Raman

373   bands (Zhang et al. 2013). In order to relate this general broadening with the corresponding α–

374   doses we looked for parameters which describe the modification of the spectra with a single

375   value. We calculated medians, unweighted and weighted means of all band widths for every

376   spectrum. The use of the mean pV–function areas was also considered in some test calculations,

377   however, it turns out that the comparison of the function areas is biased in all spectra using

378   automated background correction, because the absolute areas are affected by the baseline height.

379   The use of mean width values instead of single band widths has distinct advantages in the case of

380   metamict titanite where the fitting is hampered by overlapping and asymmetric bands.

381   For the loose grains where two or three spectra were recorded, means and medians combining the

382   two or three spectra were calculated. FWHM means were weighted either by (i) scaled pV–

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383   function intensity (iw–FWHM) or by (ii) scaled pV–function area (aw–FWHM). To test the

384   reproducibility all spectra were curve–fitted three times. Means and medians were calculated for

385   each curve–fit as well as for the average spectrum joining all three evaluations. Usually, the

386   numeric difference between the three repetitions is less than 10%, but can be as high as 20% for

387   some spectra (due to overlapping broad bands). Therefore, the use of repeated spectral

388   evaluations and means over all evaluations is highly recommended. The (weighted) means and

389   medians were compared for all tested curve–fitting protocols. All data can be found in Appendix

390   2.

391   All means and medians show good correlation with the α–dose (nearly all p–values $<<2.2 \times 10^{-16}$

392   ). However, unweighted means and medians are much more sensitive to the curve–fitting

393   parameters and spectral properties (e.g. signal–to–noise ratio) than weighted means. Examples

394   are presented in Appendix 5.

395   The use of weighted mean FWHM has the advantage that it is less sensitive to the total number

396   of used pV–functions and the larger pV–functions have stronger influence than small peaks.

397   Moreover, the weighted mean FWHMs, especially iw–FWHMs, are much more robust because

398   different curve–fitting protocols yield nearly the same results (see Fig. 4).The iw–FWHM yield a

399   better result than the aw–FWHM. The dependency of some bands on the orientation of the crystal

400   seems to have only minor impact on the iw–FWHM.

401   **The most important sensitivity test: influence of the maximum number of pV–functions on**

402   **the curve–fitting results**

403   We demonstrated that the iw–FWHM procedure leads to more consistent results than the area–

404   weighted procedure. Thus, a systematic sensitivity test series was performed to study the impact

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405   of the maximum number of pV–functions on the results of the curve–fitting. The repeated

406   evaluations allowed for 10, 15, 20, 30 or 40 pV–functions. Allowing 15 up to 40 pV–functions

407   we recorded always the same trend (see Figs. 4 and 5). However, with only 10 pV–functions the

408   spectra were often poorly fitted and especially in the well–crystalline samples not all bands were

409   described by pV–functions resulting in higher iw–FWHM values. Thus, curve–fitting with a

410   maximum of 15 pV–functions is sufficient to characterize the α–dose in titanites by the iw–

411   FWHM method, even if these 15 pV–functions might not represent the spectra in all details.

412   **Discussion**

413   Our results suggest that the intensity weighted mean FWHM is a reliable parameter to describe

414   the α–dose in titanite. The restriction to maximal 15 pV–functions led to consistent results.

415   Below an α–dose of 5×10^{16} α/g the iw–FWHM is independent of α–dose and scatters between

416   25 cm^{-1} and 50 cm^{-1}. Above this value, the iw–FWHM increases linearly with increasing α–dose

417   up to 3×10^{18}α/g.

418   Figure 5A compares the linear regression parameters (slope, y–axis intercept and R²) of all

419   calculated values for all tested curve–fitting protocols. All linear regression data can be found in

420   Appendix 6.The iw–FWHM linear regressions yield the tightest cluster of results associated with

421   high coefficients of determination (Fig. 5A). All the other methods yield more scattered results

422   and especially the median linear regressions have often very low coefficients of determination.

423   This implies that regardless of the curve–fitting protocol used for spectral evaluation, the iw–

424   FWHM method produced nearly the same linear regression, which makes this method the most

425   robust of all tested procedures.

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426 Thus, we recommend to use the iw–FWHM as radiation damage estimator for titanite. For the

427 highest density point in Figure 5A the formula for the linear increase of the iw–FWHM with

428 growing α–dose is iw–FWHM$[cm^{-1}]\sim39.2[cm^{-1}]+3.82 \times 10^{-17}[cm^{-1}/(\alpha/g)] \times$ α–dose$[\alpha/g]$. This is

429 similar to the formula for the most satisfying protocol "wf_sm" (see details in Appendix 1),

430 which is iw–FWHM$[cm^{-1}]\sim38.8(\pm1.2)[cm^{-1}]+3.86(\pm0.13) \times 10^{-17}[cm^{-1}/(\alpha/g)] \times$ α–dose$[\alpha/g]$.

431 Combining both formulae we get iw–FWHM$[cm^{-1}]\sim39.0(\pm1.2)[cm^{-1}]+3.84(\pm0.13) \times 10^{-17}[cm^{-1}$

432 $^{1}/(\alpha/g)] \times$ α–dose$[\alpha/g]$. The constants of the regression equation are determined by ca. 3% relative

433 uncertainties.

434 The other, even more important bias that controls the accuracy of the constants comes from the

435 assumed duration of the damage accumulation. As discussed above, the temperature range where

436 radiation damage accumulation starts for the Finnish samples is not known precisely, neither is

437 the annealing behavior in titanite. It is not clear how the density of accumulated damage

438 influences the annealing kinetics, and the effect of the variable chemical composition of titanite is

439 not known. Additionally the thermal history of the Finnish samples bears some uncertainty in the

440 interval of 1.8–1.5 Ga. Figure 5B visualizes the effect of this uncertainty on the linear

441 regressions. While the y–intercepts remain unchanged, shorter damage accumulation durations

442 lead to steeper slopes as the absolute damage gets smaller. This uncertainty is higher than the

443 error derived from the spread of the data. Including this uncertainty into the error of the linear

444 regression leads to a corrected calibration line: iw–FWHM$[cm^{-1}]\sim39.0(\pm1.2)[cm^{-1}]+3.84(+0.61, -$

445 $0.26) \times 10^{-17}[cm^{-1}/(\alpha/g)] \times$ α–dose$[\alpha/g]$.

446 The onset of the significant change of the titanite Raman peak width is around 5×10^{16} α/g.

447 Baughman et al. (2017) studied the He diffusivity and the THe closure temperature in relation to

448 the α–dose. Their data indicate a threshold, where T_c strongly decreases at around $\sim5 \times 10^{17}$α/g

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449 (Fig. 4). It is remarkable that our procedure based on the characterization of the entire Raman

450 spectrum is more sensitive and detects the change of the lattice at one order of magnitude lower

451 level. This indicates the need of further He diffusion experiments in order to quantify the

452 diffusion parameters for titanite in the relatively low damage range.

Comparison with (U-Th)/He results

454 For some of the Finnish samples (U–Th)/He ages were determined. Figure 6A shows these ages

455 compared to their α–dose and eU content. The data show a negative correlation and the covered

456 eU range is relatively small. Compared to our data, the data presented by Baughman et al. (2017)

457 shows a better negative correlation and includes higher eU contents.

458 Figure 6B shows the THe age versus the iw–FWHM (fitting with 15 pV–functions). As expected,

459 the data show a negative correlation, however,the spread is high. Possible reasons for the

460 dispersion include the moderate correlation of THe age and α–dose, especially at low α–doses,

461 influence of REE on THe ages, alpha ejection correction (Farley et al. 1996; Stockli and Farley

462 2004), zoning and inclusions (the details are discussed in Heller et al. in prep).

463 Estimation of the α–dose cannot substitute the THe age determination, however, it enables a pre–

464 selection of the grains most appropriate for the target of a specific study.

Implications

466 We present a robust Raman spectroscopy based method for estimating the α–dose in titanite by

467 Raman spectroscopy. The titanite (U-Th)/He thermochronometer is relevant for the

468 reconstruction of thermal histories in the upper crust, because titanite occurs in more mafic

469 lithologies, in contrast to zircon, and its typically lower actinide content allows for obtaining

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470   reliable thermochronologic information in cratonic areas that experienced cooling in Precambrian

471   times. The method can be used in two ways for the routine work in (U–Th)/He

472   thermochronology: (i) It can provide an easy-to-apply and quick tool for identifying highly

473   damaged titanite grains that have extremely low closure temperature due to the high α–dose. In

474   such crystals the recoil and fission tracks are already in contact and provide a kind of

475   "percolation" leading to very quick helium diffusion (Baughman et al. 2017). Rejecting these

476   titanite grains can optimize the dating procedure by analyzing only the better crystalline grains

477   for which the closure temperature is considerable above the ambient temperature. (ii) The other

478   approach is to concentrate on the wide range of the α–doses and aim at involving grains that

479   represent both extremely low and high α–doses in order to perform a batch modelling (e.g. Orme

480   et al. 2016; Johnson et al. 2017; Hueck et al. 2018). In this way the thermal history may be

481   described with better confidence and even the lower temperature ranges may be better

482   constrained by the titanite grains with very low closure temperature. The method proposed here

483   provides a pre–selection method in order to optimize the range of α–doses of the dated grains.

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765   **Appendices**

766   Data Repository for "Estimation of radiation damage in titanites using Raman spectroscopy"

767   The material in this data repository containing 5 Tables, one figure and one zip-file includes

768   information on:

36

769   Appendix 1: Used IFORS configuration files (14) and one overview table. (Appendix-

770   3_IFORS_config_files.zip)

771   Appendix 2: Alpha-emitting element contents of the samples and compilation of mean peak

772   values generated by the evaluation of the entire spectra. Table shows all results of the 14 different

773   settings applied (see explanation in text and Appendix 1). (Appendix-

774   2_Compil_damage_and_Raman_entire_evaluation_all_settings.xls)

775   Appendix 3: Peak width and position values of the band 465 cm-1 using setting wf_sm (see

776   details in Appendix 1). (Appendix-3_Single-band-evaluation_465.xls)

777   Appendix 4: Peak width and position values of the band 424 cm-1 using setting wf_sm (see

778   details in Appendix 1). (Appendix-4_Single-band-evaluation_424.xls)

779   Appendix 5: Plot of (unweighted) mean FWHMs versus α–dose for 3 different curve–fitting

780   protocols (Appendix-5_meanfwhm-alphadose.pdf).

781   Appendix 6: Regression line parameters for all curve–fitting protocols for different damage

782   accumulation durations (plots presented in Figure 5). (Appendix-

783   6_Regression_line_parameters.xls)

784   Appendix 7: (U–Th)/He age data (Appendix-7_THe_ages.xls)

785   **Figure captions**

786   Figure 1: Two Raman spectra of titanite crystals with different α–doses (a: 1.3×10^{13} α/g and b:

787   1.25×10^{18} α/g). The spectra were evaluated with the software IFORS (Luïnsdo f and Luïnsdor

788   2016). The black lines are the spectrum data, which are mostly covered by the dashed green lines

789   representing fitted data, blue dashed lines are the calculated background correction and thin red

37

790   lines are the respective pseudo–Voigt functions. The black numbers give the positions of the

791   important bands in cm^{-1}.

792   Figure 2: (a): Geological overview of Fennoscandia, the black rectangle refers to the area in (b)

793   that shows the entire Ilomantsi-Kostomuksha greenstone belt. (c): Geological map of the

794   Ilomantsi greenstone belt (purple) with the sampling locations (orange circles) in the Karelian

795   domain of Fennoscandia (modified after Koistinen et al. 2001). The Ilomansti greenstone belt

796   consist of the Hattu schist belt (purple polygon) and the Kovero belt (dashed purple polygon).

797   Figure 3: α–dose of the analyzed titanite grains versus the FWHMs of the 465 cm^{-1} band (a & b)

798   and the 424 cm^{-1} band (c & d). The linear and logarithmic plots show the same data, but the semi–

799   logarithmic presentation emphasizes better the onset of the significant changes in the crystal

800   lattice - which has prominent importance at helium thermochronology (see in Discussion). The

801   color of the points indicates the position of the center of the pV–functions. Only pV-functions

802   with an area greater than 1% of the total area and a FWHM < 75cm^{-1} were considered. Black

803   continuous lines in the linear presentations (a) and (c) are linear regressions shown with 0.95

804   confidence intervals (grey belts). Their formulae are FWHM[cm^{-1}]~19.5(±0.5)[cm^{-}

805   ^{1}]+1.42(±0.06) × 10^{-17}[cm^{-1}/(α/g)] × α–dose[α/g], R²=0.52 for the 465 cm^{-1} band (a) and

806   FWHM[cm^{-1}]~15.6(±0.3)[cm^{-1}]+1.30(±0.03) × 10^{-17}[cm^{-1}/(α/g)] × α–dose[α/g], R²=0.69 for the

807   424 cm-1 band (c). The dashed fit in (a) and (b) with FWHM[cm^{-1}]~16.9(±0.3)[cm^{-}

808   ^{1}]+1.83(±0.07) × 10^{-17}[cm^{-1}/(α/g)] × α–dose[α/g], R²=0.61 was calculated for all samples with

809   FWHM<40cm^{-1} and damage density < 1 × 10^{18} α/g and is more adequate for the low–damage

810   range. The grey dashed vertical lines in (b) and (d) correspond to 5 × 10^{16} α/g and 5 × 10^{17} α/g.

811   For data see Appendices 5 and 6.

38

812   Figure 4: Intensity weighted mean FWHMs (iw-FWHM) versus the α–dose in linear (a) and

813   semi–logarithmic (b) scale for two curve–fitting protocols, *wf_sm* allowing up to 40 pV–

814   functions and *wf_sm_max15* allowing up to 15 pV–functions. Black continuous lines correspond

815   to the linear regression calculated over both datasets, shown in (a) with 0.95 confidence interval

816   (grey belt). The formula is iw-FWHM[cm^{-1}]~39.3($\pm$0.8)[cm^{-1}]+3.89($\pm$0.09) $\times$ 10^{-17}[cm^{-1}

817     $^{-1}$/(α/g)] $\times$ α–dose[α/g], R^2=0.75. The dashed lines indicate the possible threshold values of

818   5×10^{16} α/g (this study) and 5×10^{17} α/g [2]. Both setups show the same trend which is flat below

819   5×10^{16} α/g and linear above this value. For fitting details see Appendix 1.

820   Figure 5: (a) Summary of the results of the different fitting methods. The axes represent the linear

821   regression parameters of the FWHM vs. α–dose correlations. Symbol shapes refer to calculation

822   method; big symbols are curve–fitting protocols with automated background correction, small

823   symbols are protocols with manual background correction. The color coding gives the coefficient

824   of determination of the linear regressions, the blue lines contour the density distribution. All

825   linear regression parameters for each setting can be found in Appendix 5. The generally higher

826   values for weighted means compared to unweighted means and medians are due to the intensity

827   and area weighting. The tightest distribution was generated by the intensity weighted mean

828   FWHMs (iw-FHWM), which yielded very similar results for all different settings, show

829   consistently high R^2 and are thus considered the most robust calculation method. (b) shows the

830   linear regression parameters for only two of the curve–fit protocols, *wf_sm* (open symbols)

831   allowing up to 40 pV–functions and *wf_sm_max15* (filled symbols) allowing up to 15 pV–

832   functions. Linear regressions were calculated for different α–damage accumulation durations

833   which are displayed in different colors. For the intensity weighted mean FWHM the two

39

834   protocols give very similar results. Lowering the α–damage accumulation duration by 0.1 Gyr

835   increases the slope values by ~7–8%.

836   Figure 6: Titanite (U–Th)/He ages in relation to their α–dose, eU contents and the intensity

837   weighted mean FWHM (iw-FHWM) of the corresponding Raman spectra. (a) Titanite (U–

838   Th)/He (THe) ages versus their α–dose, color indicates the eU contents. (b) Relation of the THe

839   ages vs. iw-FHWM. The color indicates the α–dose. The observed dispersion is mainly due to the

840   rather poor THe age vs. eU correlation of our dataset.

40

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

Sample	YKJ-north[1]	YKJ-east[1]	Location	Rock type	Zircon U-Pb Age [Ma] (±2s)	Titanite U-Pb Age [Ma] (±2s)	Reference
A0050	6958398	3702479	Ilomantsi Kk	Granodiorite (sanukitoid)	2728 (7)	2707 (10)	Vaasjoki et al. 1993; Heilimo et al., 2011
A0284	6973076	3710317	Lehtovaara Ilomantsi	Granodiorite	2752 (4)	2705 (10)	Sorjonen-Ward & Claoue-Long, 1993; Vaasjoki et al 1993
A0301	6968216	3697164	Vehkavaara Ilomantsi	Porphyry (felsic, dyke)	2755 (4)	2720 (10)	Vaasjoki et al., 1993; Huhma et al., 2012a
A0338	6968216	3697164	Vehkavaara Ilomantsi	Porphyry (felsic, dyke)		2747 (15)	Vaasjoki et al., 1993
A0339	6983951	3706826	Silvevaara Ilomantsi	Granodiorite (porphyritic)		2658 (10)	Vaasjoki et al., 1993
A0357	6945820	3530110	Paukarlahti	Gneiss (granitic, dome)		1824 (10)	Gaal, 1980
A0804	6982475	3586352	Luikonlahti Kaavi	Granite			
A0951	6946074	3696122	Paavonvaara Ilomants	Granite			
A1078	6953174	3715702	Oinassalmi Ilomantsi	Diorite (quartz-, sanukitoid)	2744 (3)		Vaasjoki et al., 1993; Heilimo et al., 2011
A1095	6974229	3713990	Kivisuo Ilomantsi	Porphyry (Qtz-Fldsp)	2756 (6)		Vaasjoki et al., 1993
A1340	7003399	3669913	Jaakonvaara Lieksa	Diorite	2702 (5)		Halla, 2002; Mikkola et al., 2013
A1614	7003710	3542680	Pajulahti Nilsiä	Syenite			
A1626	6944376	3674468	Rasisuo	Gabbro	2756 (4)		Huhma et al., 2012a
A1640	6928741	3675065	Huhtilampi	Granite			
A1641	7009265	3711422	Kierrosaho	Granite (microcline)			
A1762	7027497	3661337	Emonvaara	Tonalite		2732 (15)[2]	Huhma et al., 2012b
A1963	6959880	3708970	Kuikanniemi Ilomantsi	Granodiorite			
A1964	7021049	3685422	Kitsi	Granite			
A2196	6992639	3718302	Viluvaara	Granodiorite	2751 (4)	2737 (15)	Käpyaho et al., 2016

[1]: Finnish national grid.
[2]: WR Sm-Nd age

Table 2: Sources and major parameters of the selected titanite reference samples having low radiation damage densities.

Sample	Locality	Source	U-Pb Age [Ma]
ECS	Ecstall pluton, British Columbia	Butler et al. (2002)	91.5
94T	U-Pb reference material; Univ. Arizon	from George Gehrels	51.5
ADA-15	Adamello massif, S. Alps	Schoene et al. (2012)	41.2[1]
LIM	Kaiserstuhl ash, Rhine valley	Kraml et al. (2006)	16.5
MK-221b	Csomád volcano, Carpathians	Molnár (2018)	0.14
MK-5	Csomád volcano, Carpathians	Harangi et al. (2015)	0.03

[1]: 20 Ma considered as cooling age and used for α–dose calulation (Heberer et al. 2017).

Table 3: Table of (preliminary) tested values for IFORS automated curve–fitting procedure. For detailed description of the parameters see Lünsdorf and Lünsdorf (2016), for used curve–fitting protocols see Appendix 1.

| Parameter	tested values	function of parameter
start_wn	100	Specifies the start wavenumber (Raman shift) of the spectrum
stop_wn	1300, 1800	Specifies the stop wavenumber (Raman shift) of the spectrum
repetitions	1, 3	Sets the number repetitions / determines how often the spectrum is repeatedly evaluated
smoothing	yes, no	If set to 'yes', smoothing is enabled and the spectrum will be convoluted with a Hanning-Window filter
smoothing_size	9	Controls the window size of the Hanning-Window used for smoothing
min_width	1, 2	Controls the minimum half width at half maximum (HWHM) of the pseudo-Voigt functions during curve-fitting
max_width	50, 80, 100, 150	Controls the maximum half width at half maximum (HWHM) of the pseudo-Voigt functions during curve-fitting
min_distance	2, 5, 8, 10	Controls the minimum distance between two pseudo-Voigt functions during curve-fitting
baseline mode	window_filter, off	Style of baseline approximation. If set to 'window_filter', the baseline is approximated by a convolution of the baseline-data with a moving Hanning-window. If set to 'off' no baseline will be used during curve-fitting
window_size	0.25, 0.35	Sets the size of the Hanning-window used during baseline approximation when baseline_mode is set to 'window_filter'
noise_intensity	1-3.5	This parameter is a multiple of the standard deviation of the estimated noise distribution
max_peak_numb	10, 15, 20, 30, 35, 40	Sets the maximum number of pseudo-Voigt functions allowed during curve-fitting, e.g. if this number is reached the program stops
alpha	0.98	During curve-fitting, this parameter controls 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
sigma_threshold	0.01, 0.1, 0.5, 1	Controls the duration of the mutation-loop more directly. Legit values for 'sigma_threshold' are from the interval '2 > sigma_threshold > 0'. Values close to 2 result in short and values close to 0 in long mutation-loop duration
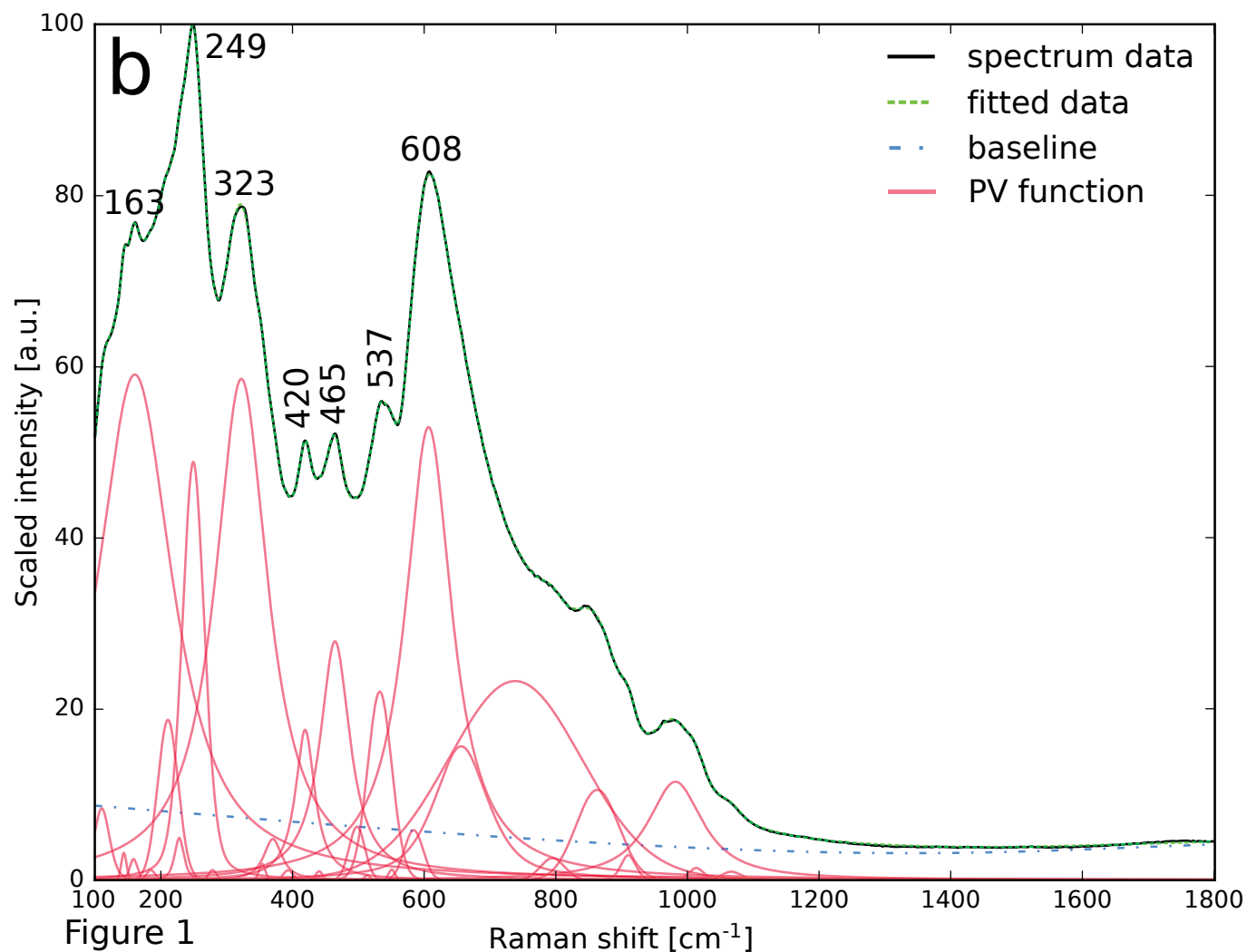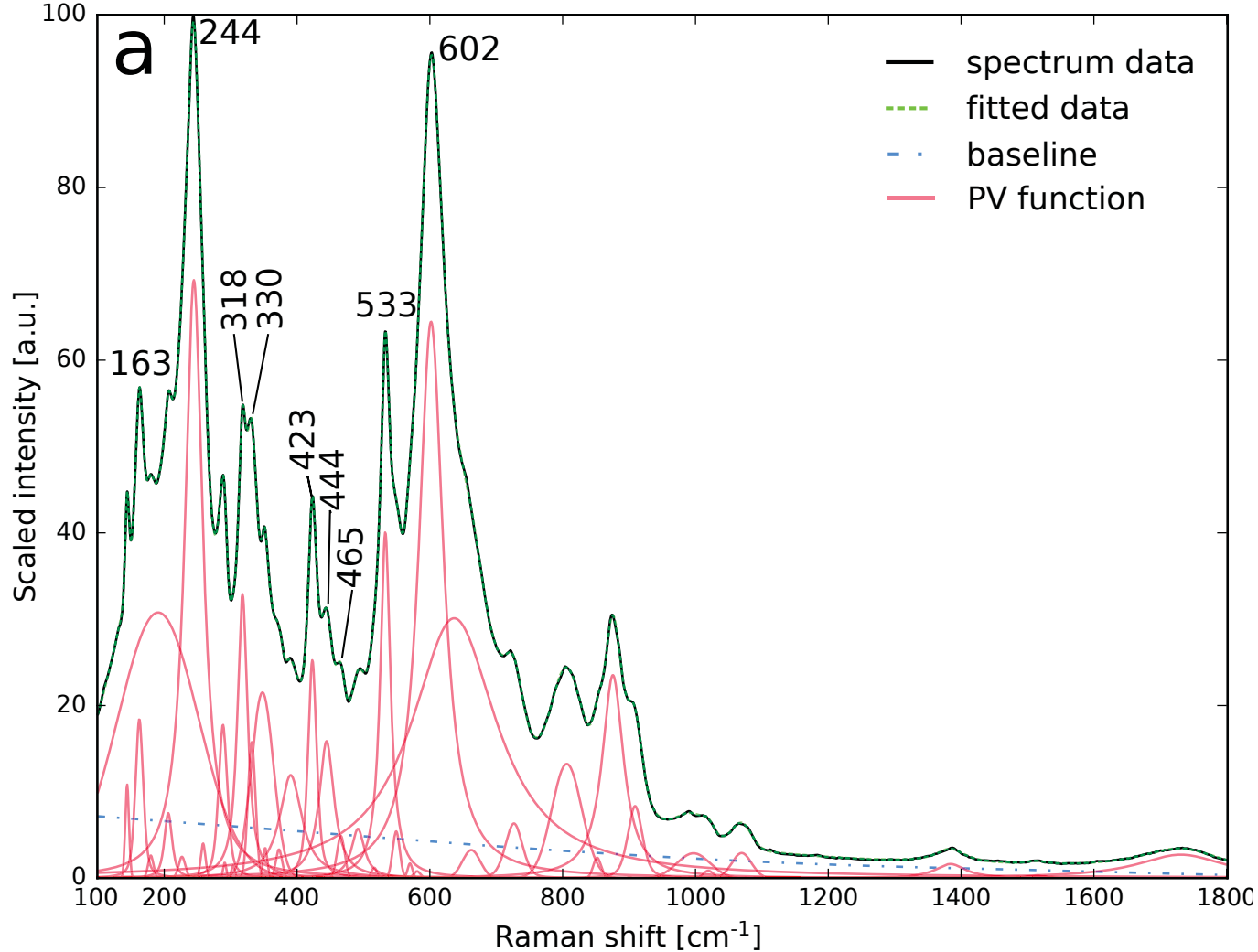
Figure 1
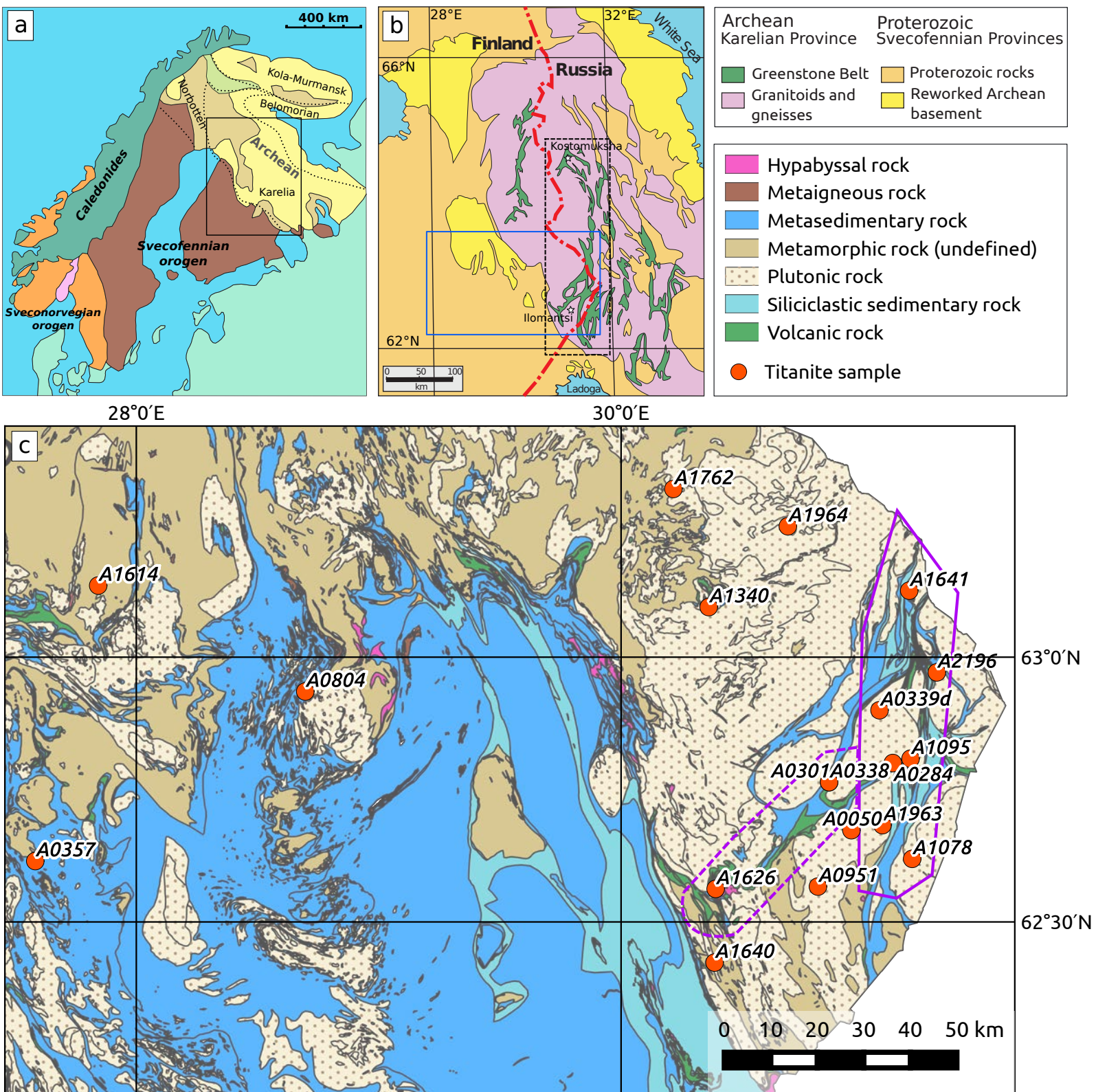
Figure 2
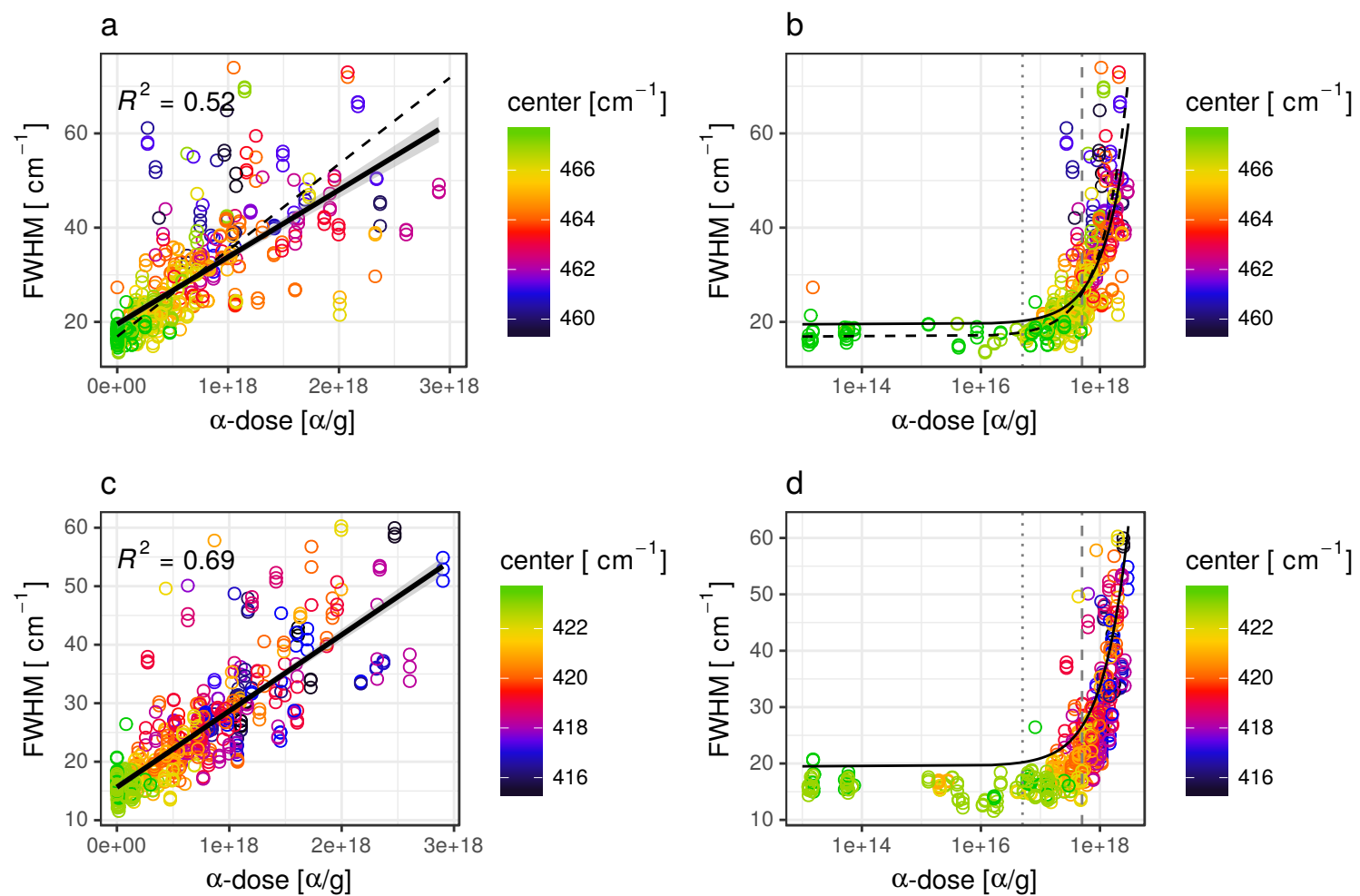
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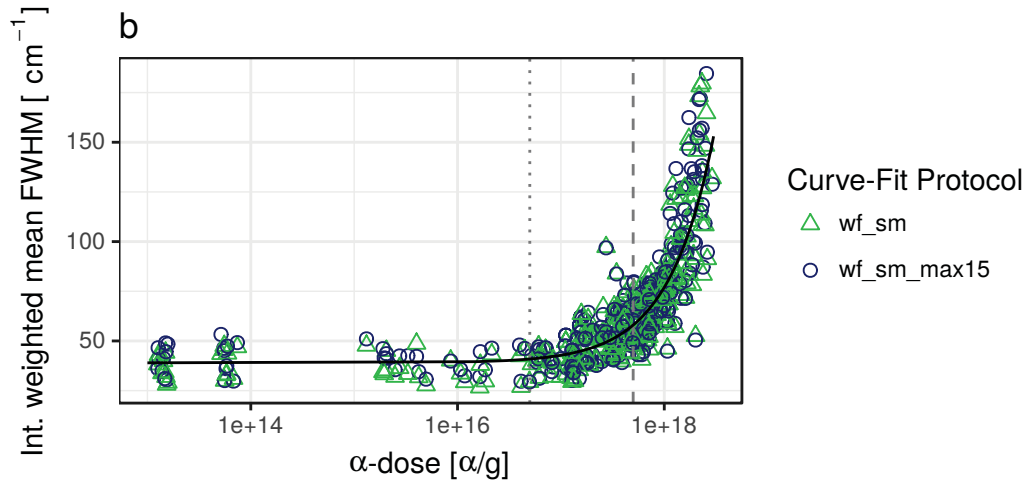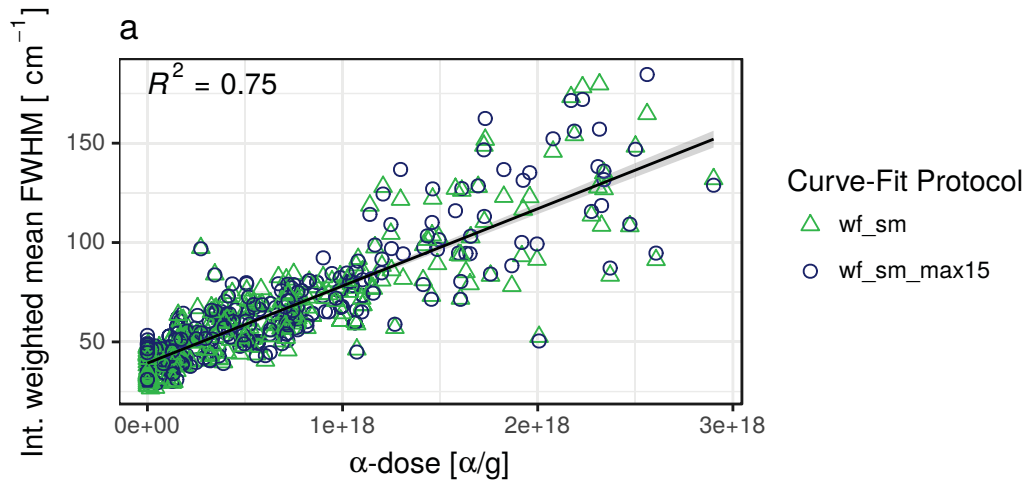
Figure4

Figure5

Figure6