1 **Reconsidering initial Pb in titanite in the context of *in situ* dating**

2 **(Revision 1)**

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10 **Abstract**

11 *In situ* U-Pb dating of titanite, which can preserve trace-element records of various

12 petrologic processes but also incorporates significant initial Pb, has proliferated in recent years.

13 The widespread use of titanite data to construct tectonic P-T-t paths warrants careful assessment

14 of the available dating techniques, as well as attention to the assumptions that underpin the U-Pb

15 data analysis. This contribution provides the first direct comparison of the two major analytical

16 methods – SHRIMP (SIMS) and LA-ICP-MS – for *in situ* U-Pb titanite dating. A set of well-

17 characterized titanite grains from Harrisville, NY, in the Adirondack Mountains were analyzed

18 for U-Th-Pb isotopes along the same cross-grain traverses by SHRIMP and LA-ICP-MS. Both

19 LA-ICP-MS and SHRIMP datasets define approximately linear arrays on the Tera-Wasserburg

20 Concordia (semi-total Pb/U) diagram and would commonly be interpreted as representing a

21 single date population with minor scatter. However, previous studies have suggested that

22 Adirondack titanite actually records two regionally well-defined thermal events, ~50-100 m.y.

23 apart. When titanite data arrays are treated in detail, attempts to determine concordia-intercept

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24 ages by robust three-dimensional linear regression produce large uncertainties and/or poor fit

25 statistics that suggest that the data are not, in fact, isochronous. Grain-by-grain analysis of U-Pb

26 titanite data shows that different subsets of titanite (determined by additional geochemical and

27 microstructural data) show different patterns of U-Pb data. By comparing predictions for Pb-

28 ingrowth evolution paths in Tera-Wasserburg diagrams with observed data, it is possible to

29 recognize both a change in initial Pb composition and Pb loss in the Adirondack titanite U-Pb

30 dataset. This study provides an example of how greater geochronologic detail can be extracted

31 from large *in situ* U-Pb titanite datasets. Even when precise dates are not recovered, geological

32 processes and events that cause data scatter can be recognized through analysis of U-Pb data

33 patterns using the Tera-Wasserburg diagram.

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35 **Keywords:** titanite; U-Pb geochronology; initial Pb correction; LA-ICP-MS; SHRIMP

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Introduction

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50   Titanite is an increasingly popular U-Pb geochronometer and petrogenetic indicator in the

51 study of crystalline rocks (e.g., Aleinikoff et al., 2002; 2004; Chen et al., 2016; Essex and

52 Gromet, 2000; Gao et al., 2012; Garber et al., 2017; Holder and Hacker, 2019; Jung and

53 Hellebrand, 2007; Kirkland et al., 2016, 2017; Kohn, 2017; Kohn and Corrie, 2011; Li et al.,

54 2010; Marsh and Smye, 2017; Olierook et al., 2019; Papapavlou et al., 2017, 2018; Scibiorski et

55 al., 2019; Stearns et al., 2015; Storey et al., 2007; Timms et al., 2019). By comparison to zircon,

56 titanite is more reactive and therefore has the potential to display a greater range of petrologic,

57 geochemical, and microstructural variations to inform interpretations of petrogenesis and

58 deformation (Kohn, 2017). The major challenges in applying titanite as a geochronometer are its

59 generally low U and radiogenic Pb concentrations and its tendency to incorporate substantial

60 initial Pb (e.g., Aleinikoff et al., 2002; Frost et al., 2000; Prowatke and Klemme, 2005; Tiepolo

61 et al., 2002).

62   Initial Pb (Pb_i) must be corrected for and therefore complicates accurate U-Pb

63 geochronometry of high-Pb_i phases, like titanite, apatite, allanite, and rutile (e.g., Chew et al.,

64 2014; Kirkland et al., 2017; Rubatto and Scambelluri, 2003; Schoene and Bowring, 2006;

65 Wohlgemuth-Ueberwasser et al., 2017) Here, we use Pb_i to mean the Pb that is incorporated into

66 a mineral at the time of crystallization or recrystallization, irrespective of its source and isotopic

67 composition. Pb_i includes what is often called "common Pb", Pb representing long-term

68 ingrowth from actinides incorporated in the primordial Earth (Stacey and Kramers, 1975). Pb_i

69 can also include Pb acquired from nearby actinide-partitioning minerals that have ingrown Pb

70 with a non-primordial isotopic composition. The most widely used Pb_i corrections derive from

71 the models of Stacey and Kramers (1975) and involve assumptions about Pb_i composition based

72   on the average, reservoir-scale geochemical behavior of Pb – i.e., assumptions about crustal

73   evolution at the scale of an orogenic region, a crustal domain, or even bulk silicate Earth. For Pb_i

74   corrections that employ these models to be accurate, the geochronology sample to which they are

75   applied must be compositionally representative of the large-scale reference reservoir, a

76   requirement that is problematic in the context of intragrain U-Pb measurements. Techniques for

77   *in situ* U-Pb dating, like SIMS/SHRIMP and LA-ICP-MS, complicate Pb_i corrections because

78   they sample micron-scale intracrystalline domains (compositional zones), which may now be

79   chemically and isotopically decoupled from their original environments of formation, including

80   coexisting phase assemblages and fluids. For instance, even when Pb_i is measured in a low-U

81   phase (e.g., K-feldspar) co-located with a zoned geochronometer, it can be difficult to determine

82   which zone within the geochronometer formed in equilibrium with that phase.

83   A common approach for correcting U-Pb isotope data for Pb_i is to calculate a Pb_i

84   composition based on an estimated age and a crustal evolution model, often the one- or two-stage

85   model of Stacey and Kramers (1975). The two most common variants of this approach are the

86   '204 method' and the '207 method'. In the 204 method, Pb_i $^{204}Pb/^{206}Pb$ is can be calculated

87   based on a crustal evolution model; measured in a reference material considered representative

88   of the crustal Pb isotope composition for the sample; or measured in a co-existing low-U phase

89   within the sample, such as K-feldspar (DeWolf and Mezger 1994; McGregor et al., 2019), and

90   the total $^{204}Pb/^{206}Pb$ is measured to determine Pb_i abundance (e.g., Ireland and Williams, 2003;

91   Stern, 1997; Storey et al., 2006; Williams, 1998) (Appendix). In the 207 method, Pb_i $^{207}Pb/^{206}Pb$

92   is based on either a model value or a measured value in a co-existing phase, as well as an

93   expected age for the titanite (Appendix). The 204 method has traditionally been preferred for

94   data collected by SIMS/SHRIMP analysis, during which ^{204}Pb is readily measured (Stern et al.,

95   2009; Stern, 1997; Storey et al., 2006). The 207 method is commonly preferred for data collected

96   by LA-ICP-MS analysis, during which ^{204}Hg contaminants in the Ar plasma interfere on mass

97   204 (Gehrels et al., 2008; Horstwood et al., 2003; Schoene, 2014; Storey et al., 2006), though

98   recent developments in quadrapole LA-ICP-MS analysis can mitigate this problem. The

99   underpinning assumption for the 204 and 207 method corrections that rely on model values is

100   that the continental crust has evolved as a coherent and largely closed reservoir with respect to U

101   and Pb isotope systematics, and that titanite will crystallize with Pb_i composition representative

102   of this bulk crustal reservoir. The idea of an "average" or "bulk" composition, however, can

103   break down at the grain scale, where Pb isotope compositions of individual phases depend on

104   phase-specific U and Pb partitioning. For instance, titanite forming from breakdown of rutile

105   may partition radiogenic Pb from rutile in addition to average, ambient Pb, and thus have a

106   different effective Pb_i composition from the bulk rock (Marsh and Smye, 2018). Thus, *in situ*

107   geochronology of phases that incorporate both U and Pb_i require careful evaluation of Pb_i

108   sources and possible grain-scale U-Pb fractionation.

109   Another approach for titanite U-Pb data correction is equivalent to the classic isochron

110   regression method and employs the semi-total Pb/U (Tera-Wasserburg) or total Pb/U diagrams

111   (Ludwig, 1998, 2009, 2012). The samples used to define the linear regression can be

112   permutations of grain separates or individual grains but can also be multiple (e.g., Amelin, 2009;

113   Verts et al., 1996), *in situ* intergrain or intragrain analyses (e.g., Holder and Hacker, 2019; Kohn

114   and Corrie, 2011; Olierook et al., 2018; Storey et al., 2006). In practice, it is common to

115   constrain the Pb_i ^{207}Pb/^{206}Pb composition based on a Stacey and Kramers (1975) model and force

116   the regression through this Pb_i composition (e.g., Kohn and Corrie, 2011). However, it is

117   becoming more common to treat Pb_i composition as a variable that is retrieved from the

118   regression process (e.g., Kirkland et al., 2017). The Tera-Wasserburg-based isochron regression

119   correction method can avoid the pitfalls of assuming a crustal Pb isotope composition but only

120   works if i) the Pb_i composition is uniform in the grains or domains used to determine the

121   isochron ii) measured grains/domains formed at the same time (are isochronous), and iii) in the

122   case that the Pb_i composition is not fixed a priori, a sufficiently large range of intracrystalline

123   U/Pb and Pb/Pb ratios are sampled to tightly constrain the regression. With recent detailed

124   characterizations of titanite (e.g., Essex and Gromet, 2000; Bonamici et al., 2015; Garber et al.,

125   2017; Marsh and Smye, 2017; Olierook et al., 2018), it is clear that Pb_i can and does vary over

126   timescales of titanite growth and/or recrystallization, undercutting the first requirement for the

127   isochron regression approach in some cases.

128   U-Pb isotope data for Pb_i-rich phases are treated on the Tera-Wasserburg Concordia

129   diagram in order to explicitly show the Pb_i contribution to U-Pb isotope composition. The Tera-

130   Wasserburg diagram is a two-dimensional projection of the total Pb/U isochron diagram (Ludwig,

131   1998), which allows for direct display of the Pb_i trends in a dataset. The familiar Wetherill

132   concordia diagram works well for low-Pb_i phases and excels at revealing open system behavior

133   that affects the radiogenic U/Pb ratio (e.g., Schoene, 2014). In contrast, the U-Pb data patterns on

134   the Tera-Wasserburg diagram reflect a combination of Pb_i-radiogenic Pb mixing and open

135   system behavior. Such patterns can, consequently, be less straightforward to interpret.

136   This work applies different Pb_i correction methods to a suite of well-characterized

137   Grenville-aged titanite grains from the Adirondack Mountains of New York. A review of U-Pb

138   isotope evolution in the semi-total Pb/U isochron (Tera-Wasserburg) diagram illustrates how

139   both intragrain Pb_i compositional variations and grain scale Pb loss can be preserved within *in*

140   *situ* data sets. This analytical framework is applied to two U-Pb datasets for the same titanite

141   grains – one collected by SHRIMP and the other collected by LA-ICP-MS. Comparison of the

142   two in situ analytical techniques allows recognition of non-isochronous data and highlights the

143   relative strengths of each technique. These results reinforce both the complexity and

144   opportunities in microanalysis of geochronometers with significant initial Pb.

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146   **Samples and Methods**

147   Titanite-bearing samples used in this study are high-grade, midcrustal tectonites from the

148   Adirondack region of upstate New York. Titanite grains are hosted in metasyenite collected

149   within the Carthage-Colton mylonite zone, a major structure developed at the boundary between

150   Grenville-aged crustal domains. The Adirondack Lowlands to the northwest of the CCMZ record

151   peak metamorphic conditions during the Shawinigan-AMCG phase of the Grenville orogeny at

152   ca. 1150 Ma, whereas the Adirondack Highlands to the east-southeast of the CCMZ record peak

153   metamorphic conditions during the Ottawan phase at ca. 1050 Ma (Mezger et al., 1993; 1991a;

154   1991b). The tectonic context of the CCMZ has been previously discussed by Mezger et al.

155   (1991a), Mezger et al. (1991b), Mezger et al. (1992), Mezger et al. (1993), Cartwright et al.

156   (1993), Streepey et al. (2001), Baird and MacDonald (2004), Johnson et al. (2004), Johnson and

157   Selleck (2005), McLelland et al. (2010), and Bonamici et al. (2014). Structural, petrologic, and

158   geochemical characteristics of the specific Harrisville location of samples for the current study

159   have been addressed by Lamb (1993), Cartwright et al. (1993), Baird and MacDonald (2004),

160   Heumann (2004), Johnson and Selleck (2005), Bonamici et al. (2014), and Bonamici et al.

161   (2015).

162   Regional geochronology provides constraints within which to study and interpret U-Pb

163   titanite data from the CCMZ. Bonamici et al. (2015) documented the intragrain zoning patterns

164   of SHRIMP U-Pb dates within six Harrisville titanite samples (Table 1). Four different

165   generations of titanite were distinguished on the basis of microstructure and reinforced on the

166   basis of chemistry and oxygen-isotope zoning patterns (Bonamici et al., 2014, 2015). These

167   generations are interpreted to be igneous titanite crystallized in the protolith syenite at ~1160 Ma

168   (Type-1); igneous grains variably reset during later granulite-facies metamorphism at ca. 1050

169   Ma (Type-2); titanite from veins that likely intruded at ca. 1050 Ma (Type-3); and igneous

170   titanite with metamorphic overgrowths (Type-4). Table 1 provides grain descriptions and further

171   information summarizing these interpretations. LA-ICP-MS data presented in this study

172   significantly expand the number of Harrisville titanite grains investigated for U-Pb zoning. U-Pb

173   ratios were measured in a total of fourteen titanite grains, including one Type-1 grain, five Type-

174   2 grains, six Type-3, and two Type-4 grains.

175   Titanite was analyzed in thin sections of metasyenite cut into one-inch rounds. Thus, all

176   analyzed titanite grains are *in situ* with respect to their host microstructures and phase

177   assemblages. Grains of U-Pb titanite reference material BLR-1 (accepted ^{206}Pb/^{238}U age 1047 ±

178   0.4 Ma, Aleinikoff et al., 2007) were embedded in every sample each mount. BLR-1 was used

179   for calibration under the designation BLS at the Arizona Laserchron Center, along with

180   secondary reference material Ecstall West zircon (accepted ^{206}Pb/^{238}U age 91.5 ± 1 Ma, Butler et

181   al., 2002), also embedded in each analysis mount. Weighted average ages showing the

182   performance of the reference material grains in each mount during LA-ICP-MS analysis are

183   compiled in the Supplementary Materials. Within 2σ analytical uncertainties, the dates

184   determined for these reference materials during SHRIMP and LA-ICP-MS analysis overlap the

185   accepted ages.

186   SIMS U-Pb dates were collected with the SHRIMP II instrument at the Research School

187   of Earth Sciences (RSES) at the Australian National University using a focused, 4.5-nA O_2^-

188   primary beam. Data were acquired in single-collector mode with seven successive scans through

189   species $^{200}CaTi_2O_4$, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{238}U, ^{248}ThO, and ^{254}UO, with each individual

190   analysis taking 20 minutes. SHRIMP analysis sputtered pits 35-40 µm in diameter and 2-3 µm

191   deep (Fig. 1A). Grains of U-Pb titanite standard BLR-1 were analyzed at regular bracketing

192   intervals throughout each analysis session. Total $^{238}U/^{206}Pb$, $^{207}Pb/^{206}Pb$, and $^{204}Pb/^{206}Pb$ ratios

193   reported in Table S1 are corrected for U/Pb instrumental fractionation but are not corrected for

194   Pb_i. SHRIMP radiogenic ratios and $^{206}Pb/^{238}U$ dates were initially reported in Bonamici et al

195   (2015), where they were corrected for Pb_i with the 204 method using $^{204}Pb/^{206}Pb$ measured on

196   long-term RSES lab reference material, Broken Hills feldspar ($^{206}Pb/^{204}Pb$ = 16.00, $^{207}Pb/^{204}Pb$ =

197   15.39, and $^{208}Pb/^{204}Pb$ = 35.66; Gulson, 1984). For the current study, SHRIMP data have been

198   re-corrected (Table S1) with the 204 method using both (1) the Stacey and Kramers (1975)

199   model and (2) the K-feldspar Pb-Pb ratios reported by Mezger et al. (1992) for a shear zone in

200   the Diana metasyentite (sample 90-49: $^{206}Pb/^{204}Pb$ = 17.132, $^{207}Pb/^{204}Pb$ = 15.427, and

201    $^{208}Pb/^{204}Pb$ = 36.461). The dates corrected with Mezger et al. (1992) are preferred because these

202   Pb values come from the same outcrops as the titanite samples used in the current study. To

203   facilitate comparison with LA-ICP-MS data, the SHRIMP data have also been corrected with the

204   207 method (Table S1) using the Stacey and Kramers (1975) Pb isotope model implemented

205   through the Arizona Laserchron Center spreadsheet software, "Titanite AgeCalc 207Pbc".

206   Prior to LA-ICP-MS analysis, SHRIMP pits and carbon coats were removed from

207   samples by repolishing with 1-µm diamond-grit suspension. Samples were cleaned with several

208   cycles of sonication in distilled water and ethanol. LA-ICP-MS U-Pb dates were collected on a

209   Nu HR ICP-MS coupled to a Photon Machines Analyte G2 Excimer laser at the Arizona

210   Laserchron Center at the University of Arizona. Data were acquired in static multicollector mode,

211   with ^{202}Hg and ^{204}Pb collected on ion counters and ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{238}U, and ^{232}Th collected

212   on 10^{11}-ohm resistor Faraday cups. Each analysis included 15 seconds of background counting,

213   15 one-second laser pulses for sample signal and 30 seconds of wash-out time for a total of

214   approximately 60 seconds per analysis. Laser ablation produced pits 35-40 μm in diameter and

215   ~15 μm deep (Fig. 1B). Grains of U-Pb titanite standard BLR-1 (^{206}Pb/^{238}U age 1047 Ma,

216   Aleinikoff et al., 2007; also called BLS in the Laserchron lab) were analyzed at regular

217   bracketing intervals throughout each analysis session. Total ^{238}U/^{206}Pb, ^{207}Pb/^{206}Pb, and

218   ^{204}Pb/^{206}Pb ratios reported in Table S2 were corrected for U/Pb instrumental fractionation, as

219   well as the ^{204}Hg interference on ^{204}Pb. The ^{204}Pb interference correction is accomplished by

220   subtraction of mass 204 counts that are inferred to come from ^{204}Hg based on the measurement

221   of mass 202 and an assumed natural ^{202}Hg/^{204}Hg ratio of 4.34 (Gehrels et al. 2008). Data in

222   Table S2 and Figures 2, 3, 4, and 6 are not corrected for Pb$_i$. Radiogenic ratios and ^{206}Pb/^{238}U

223   dates reported for LA-ICP-MS data (Table S2) were corrected for Pb$_i$ by an iterative 207 method

224   implemented using internal Arizona Laserchron Center spreadsheet-based software ("Titanite

225   AgeCalc 207Pbc"). This correction uses the raw ^{206}Pb/^{238}U ratio before Pb$_i$ correction as an

226   initial estimate of expected age and the Stacey and Kramers (1975) model for an estimate of the

227   Pb$_i$ composition (Appendix). The 207-corrected age then recalculated several more times with

228   the 207-corrected age from the previous iteration used as the expected age for each subsequent

229   iteration. For titanite U-Pb measurements in this study, the calculation rapidly converges to a

230   stable corrected age within ≤5 iterations. To facilitate comparison with the SHRIMP data, the

231   LA-ICP-MS data have also been corrected with the 204 method (Table S2) using the Stacey and

232   Kramers (1975) model.

233   Data are compared using total isotope ratios, uncorrected for Pb_i, on Tera-Wasserburg

234   Concordia plots. Error ellipses in Figures 2, 3 and 9 represent 2σ analytical uncertainties,

235   including counting statistics and U/Pb instrumental fractionation (as calibrated with titanite

236   BLR/BLS reference material). Uncertainties on $^{204}Pb/^{206}Pb$ for SHRIMP data have been

237   conservatively estimated at 3% (1σ), which is double the largest $^{207}Pb/^{206}Pb$ uncertainty reported

238   for SHRIMP data. Uncertainties on all other ratios are as reported by the respective lab (Tables

239   S1 and S2). Error correlations between $^{238}U/^{206}Pb$, $^{207}Pb/^{206}Pb$, and $^{204}Pb/^{206}Pb$ ratios are

240   considered to be small and are neglected for the sake of more direct comparison of data arrays.

241   Two- and three-dimensional linear regressions were implemented in Isoplot 3.75 using

242   Model 1, which weights each measurement by the inverse square of the analytical errors under

243   the assumption that analytical errors are the only source of uncertainty in the data (Ludwig,

244   2012). A Model 1 regression fit is considered reasonable if the probability of fit is ≥ 0.05.

245   Probability of fit for each regression is used as an indicator of additional (geological) sources of

246   scatter. Other models for regression (Models 2 and 3) were not considered to avoid additional

247   assumptions about sources of uncertainty (beyond analytical).

248

249   **Results**

250   When considered in aggregate, LA-ICP-MS and SHRIMP datasets for Harrisville titanite

251   grains define steep, approximately linear trends on Tera-Wasserburg or semi-total Pb/U diagrams

252   (Fig. 2). The LA-ICP-MS data array spread is larger for two reasons: 1) more than twice as many

253   titanite grains were analyzed by LA-ICP-MS as by SHRIMP (Fig. 3) and many of the grains

254   analyzed by laser had lower Pb_i that extends the array farther toward concordia; and 2) the large

255    $^{207}Pb/^{206}Pb$ uncertainties on the LA-ICP-MS data for the highest-Pb_i grains appear to stretch the

256   laser data array vertically. However, close comparison of the grains analyzed by both LA-ICP-

257   MS and SHRIMP in Figure 3, shows that, regardless of error ellipse shape, the individual data

258   points are centered at nearly identical locations.

259   Tera-Wasserburg-based, two-dimensional regression of the aggregate SHRIMP dataset

260   yields a concordia intercept age of 1138 ± 19 Ma with MSWD = 4.4, whereas 2D regression of

261   the aggregate LA-ICP-MS dataset yields a concordia intercept age of 1067± 12 Ma with MSWD

262   = 2.0 (Table S3). We note that the regression of SHRIMP data yield a MSWD indicating well

263   scatter beyond that expected based on analytical uncertainty alone, whereas that the precision of

264   LA-ICP-MS data result in a more ambiguous MSWD value. No concordia-intercept ages can be

265   obtained for either aggregate dataset (LA-ICP-MS or SHRIMP) using a total Pb/U isochron

266   (linear 3D) regression that includes the $^{204}Pb/^{206}Pb$ ratio (Table 1).

267   For Harrisville titanite samples, greater $^{238}U/^{206}Pb$ (average 2.3% 1σ) than $^{207}Pb/^{206}Pb$

268   analytical uncertainties (average 1.0% 1σ) suggest that the U/Pb calibration dominates overall

269   SHRIMP analytical uncertainties. In contrast, greater $^{207}Pb/^{206}Pb$ (average 5.1% 1σ) than

270    $^{238}U/^{206}Pb$ (average 2.6% 1σ) analytical uncertainties indicate that abundance sensitivity

271   dominates overall LA-ICP-MS analytical uncertainties.

272   On a grain-by-grain basis, both SHRIMP and LA-ICP-MS U-Pb measurements show a

273   range of behavior, with several grains having tightly clustered data (i.e. showing limited

274    $^{238}U/^{206}Pb$ or $^{207}Pb/^{206}Pb$ dispersion) (Fig. 3). For those grains with tightly clustered spot analyses,

275   both 2D and 3D regressions of the U-Pb measurements yield large concordia-intercept age

276   uncertainties (> ±50 Ma), as well as large MSWD values for SHRIMP data sets. Titanite grains

277 from sample HA13 are an exception, showing sufficient analysis dispersion to provide

278 moderately tight constraints on concordia-intercept ages regressed from LA-ICP-MS data (Fig.

279 3). SHRIMP U-Pb measurements for the HA13 S2 grain show a similar dispersion to LA-ICP-

280 MS measurements and similar concordia-intercept age but with high MSWD values.

281   Results from 3D linear isochron regressions for each titanite Type are described below

282 with respect to the concordia-intercept age and the regressed Pb_i $^{207}Pb/^{206}Pb$ value (Table 1, Fig.

283 4). Several unconstrained 3D regressions produce negative $^{207}Pb/^{206}Pb$ (y-axis) intercept values

284 because tightly clustered data do not adequately constrain the linear regression toward the

285 common Pb plane, resulting in a very large range of possible intercept values with a negative

286 mean. Several constrained 3D regressions produce undefined $^{207}Pb/^{206}Pb$ values because very

287 large uncertainties push the mean regressed $^{206}Pb/^{204}Pb$ value to zero (Table 1), the lowest

288 allowed $^{206}Pb/^{204}Pb$ value for a constrained regression solution. Table S3 shows 2D regression

289 results, but these are not discussed in the text in order to avoid redundancy and because the larger

290 uncertainties on the 2D regression results generally hide details within the datasets.

Type 1 titanite results

292   Constrained 3D linear concordia intercept dates for the Type-1 grain for both LA-ICP-

293 MS and SHRIMP data are > 1200 Ma, with large uncertainties of > 200 m.y. (Table 1). The

294 unconstrained regression of LA-ICP-MS data intercepts concordia within analytical uncertainties,

295 but the unconstrained regression of more precise SHRIMP data set does not (Fig 4B). The Type-

296 1 titanite grain has both the highest and largest range of $^{204}Pb/^{206}Pb$ ratios (Tables S1 and S2).

297 The Type-1 grain also has the lowest overall U, Th, and Pb concentrations. LA-ICP-MS data

298 points from this low-Pb grain all overlap significantly within error and no interpretable

299 $^{207}Pb/^{206}Pb$ intercept is obtained with either constrained or unconstrained 3D regressions (Table

300   1). An unconstrained regression of the more precise SHRIMP data yields an upper intercept

301   $^{207}Pb/^{206}Pb$ value of 0.967, similar to the Stacy and Kramers common Pb value of 0.922, though

302   with large uncertainties (Table 1).

Type 2 titanite results

304   Type-2 titanite grains yield tightly clustered U-Pb data points, both within individual

305   grains (Fig. 3) and between grains (Fig. 2). Constrained 3D linear regressions of LA-ICP-MS

306   data return concordia-intercept ages of 1143-1111 Ma, whereas regressions of SHRIMP data

307   return consistently older concordia-intercept ages of 1182-1146 Ma (Table 1). Both methods

308   produce intercept-age uncertainties of 48-130 m.y., and the SHRIMP data regressions are also

309   associated with large MSWD values. Both constrained and unconstrained regressions yield

310   largely uninterpretable $^{207}Pb/^{206}Pb$ upper intercept values (Table 1), with the possible exception

311   of grain HA09A S15, which gives values consistent with a mixture of primordial (Stacey and

312   Kramers common Pb) and radiogenic Pb_i.

Type 3 titanite results

314   Aggregated Type-3 data show greater dispersion than Type-2 data, but data for individual

315   Type-3 grains are more clustered than the aggregate dataset (Fig. 3). Constrained 3D isochron

316   regressions of LA-ICP-MS Type-3 data yield the youngest concordia intercept ages, ranging

317   from 935 Ma to 1101 Ma (Table 1, Fig. 4). Some of the older LA-ICP-MS dates have moderate

318   analytical uncertainties of 28-38 m.y., but many LA-ICP-MS dates are associated with large

319   analytical uncertainties of 63-190 m.y.. Constrained 3D regression for the one SHRIMP-

320   analyzed Type-3 grain produces an imprecise concordia intercept age of 1220 ± 370 Ma.

321   Constrained and unconstrained regressions for most LA-ICP-MS-analyzed grains produce

322   $^{207}Pb/^{206}Pb$ upper intercepts intermediate between the expected radiogenic value (~0.08) and the

323   expected Stacey and Kramers common-Pb model value (~0.92), though often with very large

324   uncertainties.

Type 4 titanite results

326   Data from the Type-4 grains, in aggregate and individually, define approximately linear

327   or apparently offset linear trends. Whereas overlap in LA-ICP-MS data for grain HA13A-S1

328   obscures distinct internal data populations, three data populations can be distinguished in both

329   the LA-ICP-MS and SHRIMP data for HA13A-S2 (Fig. 3). Constrained and unconstrained

330   regressions of both LA-ICP-MS and SHRIMP data produce very similar Tera-Wasserburg plane

331   intercepts and concordia intercept ages at 1124-1128 Ma (Table 1, Fig. 4). Uncertainties on LA-

332   ICP-MS data are ~25 m.y. and those for the SHRIMP data are three times larger at 75 m.y.. In

333   addition, the MSWD value for the regression of the SHRIMP data is much larger than the

334   MSWD value for LA-ICP-MS data. Most constrained and unconstrained regressions for both

335   analytical techniques produce $^{207}Pb/^{206}Pb$ upper intercepts intermediate between the expected

336   radiogenic value (~0.08) and the expected Stacy and Kramers common Pb model value (~0.92).

337   The constrained regression for the SHRIMP-analyzed grain produces a $^{207}Pb/^{206}Pb$ upper

338   intercept greater than the expected Stacy and Kramers common Pb model value, though with

339   large uncertainties.

Zoning trends within titanite grains

341   *In situ* U-Pb data can also be assessed in the context of their spatial distribution within

342   titanite grains (Fig 5; Supplemental Figures; Bonamici et al., 2015). The lower precision of LA-

343   ICP-MS measurements precludes definitive recognition of intragrain zoning as the oldest and

344   youngest Pb_i-correct dates determined for any given grain overlap within 2σ uncertainties;

345   however, similarity of intragrain trends in grains for which both more precise SHRIMP data and

346   LA-ICP-MS data exist (Fig. 5), suggests that the LA-ICP-MS data are indicative of zoning.

347   Generally, both LA-ICP-MS and SHRIMP yield older $^{206}Pb/^{238}U$ dates toward grain centers and

348   younger dates near grain edges (Fig 5; Supplemental Figures); however, there is considerable

349   intragrain variability in Pb_i-corrected dates (particularly for SHRIMP data), which range from

350   pre-Shawinigan (>1180 Ma) to post-Ottawan (975 Ma). This result is the same, whether the Pb_i

351   model is the traditional Stacey and Kramers (1975), the ANU lab Broken Hill feldspar, or the

352   Mezger et al. (1992), providing that the same Pb_i composition is used for all corrections (Table

353   S1). For a given grain, most Pb_i-corrected dates differ significantly from the mean constrained

354   concordia-intercept date (Fig 5; Supplemental Figures); however, almost all dates overlap within

355   large uncertainties associated with both the individual Pb_i date corrections and the isochron

356   regressions.

357

358   **Discussion**

359   **Comparison of LA-ICP-MS and SHRIMP analysis of titanite**

360   The collection and comparison of parallel U-Pb data sets for Harrisville titanite allows us

361   to examine the tradeoffs in analytical precision and data collection rates between the two

362   techniques for these grains. In general, both techniques recover very similar ranges in isotope

363   ratios, but the higher analytical precision of the SHRIMP data resolves intragrain complexity that

364   is obscured by the lower analytical precision of the LA-ICP-MS data. Consequently, the

365   precision of dates determined through individual Pb_i correction is generally lower for LA-ICP-

366   MS than for SHRIMP (Fig. 5; Tables S1 and S2), reflecting larger uncertainties in the Pb isotope

367   measurements by LA-ICP-MS and their propagation through the 207-method correction. On the

368   other hand, the precision of concordia intercepts is generally poorer for SHRIMP than for LA-

369   ICP-MS (Fig. 4), reflecting greater resolvable geologic scatter in the more precise SHRIMP data

370   and thus poorer fits for linear regressions.

371   *In situ* U-Pb data collected within titanite grains are commonly assumed to represent

372   single age and Pb_i populations and are treated as such through the isochron regression method.

373   The facts that the aggregated Harrisville data (1) cannot be fit with a 3D regression and (2) yield

374   dates ~70 m.y. apart for 2D regressions (Table 2) point toward significant grain-to-grain age

375   and/or Pb_i heterogeneity. Dates determined by the isochron regression method for within-grain

376   U-Pb data generally overlap the time period spanning the two known orogenic events in the

377   Adirondack Mountains, from beginning of the AMCG-Shawinigan phase at ca. 1180 Ma through

378   the end of the Ottawan phase at ca. 1010 Ma (Fig. 4). The poor precision on these regression

379   dates, however, rarely allows a given date to be clearly assigned to one orogenic phase or the

380   other, let alone to a restricted period within one of the orogenic phases (Figs. 3, 4). The spread of

381   regression-determined dates is consistent with the conclusion from previous work that the

382   Harrisville titanite grains record both the AMCG-Shawinigan and Ottawan events (Bonamici et

383   al., 2015). It also suggests that regressions are not true isochrons, but rather that they are fits to

384   mixed, non-isochronous data that are variably resolved with different *in situ* measurement

385   techniques (see below for further discussion). Larger analytical uncertainties for LA-ICP-MS

386   data, especially, mask the probable geologic scatter within the data, producing isochron

387   regressions with MSWD values ≤ 1 and probabilities of fit > 0.05. Only relatively large

388   propagated uncertainties, typically $\geq \pm 50$ m.y., suggest the presence of geologic scatter within

389   the LA-ICP-MS datasets. By comparison, geologic scatter is more apparent in regressions of

390   SHRIMP data for the same titanite grains, which produce large MSWD values, probabilities of

391   fit close to zero, and large propagated uncertainties (Fig. 3).

392   Regression-determined dates and Pb_i-corrected dates for a given grain can be compared

393   to check for internal consistency between the analytical and correction methods. An ideal titanite

394   grain that has crystallized at a single time, though with a range of Pb_i concentrations, should

395   produce Pb_i-corrected dates that are identical to one another and to the regressed concordia-

396   intercept date. Differences in Pb_i-corrected dates and/or discrepancy between Pb_i-corrected and

397   regression-determined concordia-intercept dates would suggest internal zoning and non-

398   isochronous grain crystallization. Pb_i-corrected dates are, in fact, not identical across Adirondack

399   titanite grains. Intragrain zoning of Pb_i-corrected dates is statistically resolvable along most

400   traverses measured by SHRIMP, though not by LA-ICP-MS (Fig. 5); nonetheless, the similarity

401   between several SHRIMP and LA-ICP-MS profile shapes suggests that LA-ICP-MS is detecting

402   similar isotopic variability. Similarly, Pb_i-corrected dates and regressed concordia-intercept dates

403   for a given grain generally overlap within the propagated uncertainties of the respective

404   correction methods (Fig. 5). However, the resolvable intragrain zoning of Pb_i-corrected SHRIMP

405   dates and the poor fit metrics for many of the concordia-intercept regressions suggest that this

406   overlap is an artefact of temporally close events ($\leq$100 m.y. apart at greater than 1 Ga) and

407   relatively large analytical uncertainties on the *in situ* data.

408   The LA-ICP-MS and SHRIMP datasets for several Adirondack titanite grains also allow

409   for assessment of differential Pb isotope sensitivity and its potential effects on the accuracy of

410   Pb_i-corrected dates. Specifically, differential sensitivity to higher-abundance ^{206}Pb relative to

411   lower-abundance ^{204}Pb or ^{207}Pb could skew measured Pb/Pb ratios used for Pb_i corrections. A

412   quick check for differential Pb isotope sensitivity is to compare 204-corrected versus 207-

413   corrected dates for both the SHRIMP and LAICPMS datasets. SHRIMP data corrected with the

414   204 and 207 methods yield dates that are essentially identical (Table S1), suggesting that

415   SHRIMP Pb/Pb ratios are not skewed by differential Pb isotope sensitivity. LA-ICP-MS data

416   corrected by the 204 and 207 methods yield different dates, with those corrected by the 204

417   method always systematically younger (Table S2). Differences between the LA-ICP-MS and

418   SHRIMP datasets can be compared graphically by plotting total $^{207}Pb/^{206}Pb$ vs. total $^{204}Pb/^{206}Pb$

419   covariation trends (Fig. 6). The slopes of the covariation trends are markedly different, with the

420   steeper slope for the LA-ICP-MS data arising from the systematically lower $^{204}Pb/^{206}Pb$ values

421   and indicating lower ^{204}Pb sensitivity relative to SHRIMP. On the other hand, the similar range

422   of $^{207}Pb/^{206}Pb$ measured by LA-ICP-MS and SHRIMP indicates that LA-ICP-MS-determined

423    $^{207}Pb/^{206}Pb$ ratios are unaffected by differential Pb isotope sensitivity in these samples. Note that

424   for the purposes of this discussion, the term Pb sensitivity includes the effects of instrument

425   sensitivity, the ^{204}Hg interference correction applied to LA-ICP-MS-measured ratios, and

426   downhole Pb isotope fractionation. Because LA-ICP-MS $^{204}Pb/^{206}Pb$ ratios but not $^{207}Pb/^{206}Pb$

427   ratios are affected, correction for ^{204}Hg, which affects only the $^{204}Pb/^{206}Pb$ ratio, seems a likely

428   culprit for creating a differential Pb isotope sensitivity problem. This comparison suggests

429   cautious application of ^{204}Hg corrections to LA-ICP-MS data for high Pb_i phases and use of the

430   207 method if differential Pb isotope sensitivity is suspected.

431

432   **U-Pb isochron evolution on the Tera-Wasserburg (semi-total Pb/U) diagram**

433   Ideally, when a set of titanite grains or domains crystallizes at the same time, the U-Pb

434   data for this population will define sloped linear arrays in Tera-Wasserburg space. Such arrays

435   are often referred to as discordia by analogy with the familiar Wetherill-diagram zircon discordia,

436   which form as a result of changes to the U/Pb ratio due to open-system U or Pb loss. In titanite

437   with no Pb_i, open-system modification of the U/Pb ratio would also produce a sloped, discordant

438   array of data (Tera and Wasserburg 1974; Schoene 2014). However, most titanite incorporates

439   Pb_i, and sloped, linear arrays are more often mixing arrays treated as isochrons resulting from

440   variable U/Pb_i ratio (μ). If the data are precise and well-spaced (have a range of U/Pb_i), then a

441   regression provides a tightly constrained upper y-axis intercept at the shared Pb_i $^{207}Pb/^{206}Pb$

442   value and lower intercept with the Tera-Wasserburg concordia at the age of crystallization.

443   The Tera-Wasserburg concordia is the locus of the time-integrated $^{207}Pb/^{206}Pb$ and

444   $^{238}U/^{206}Pb$ ratios resulting from U decay in the absence of Pb_i; each point along the concordia is

445   an implicit function of initial $^{235}U/^{238}U$, and thus time of crystallization. Paths in Figure 7A show

446   the temporal evolution of radiogenic $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios for several initial $^{235}U/^{238}U$

447   ratios. For titanite crystallized since ~3.0 Ga, the temporal evolution paths are nearly parallel to

448   the $^{238}U/^{206}Pb$ axis because of the much greater relative change in $^{238}U/^{206}Pb$ as compared to

449   $^{207}Pb/^{206}Pb$ during radiogenic Pb ingrowth.

450   The addition of Pb_i to titanite constrains the starting points of the temporal evolution

451   paths to a fixed $^{207}Pb/^{206}Pb$ value (Fig. 7B). The shapes of the evolution paths depend on the

452   evolving relative proportions of Pb_i with a fixed $^{207}Pb/^{206}Pb$ composition and radiogenic Pb,

453   growing in with a time-varying $^{207}Pb/^{206}Pb$ composition (Fig. 7B, pale gray curves). For

454   proportionally higher Pb_i, evolution paths are steeper, reflecting the dominance of the fixed

455   $^{207}Pb/^{206}Pb$ value of the Pb_i. For lower Pb_i, evolution paths are shallower, reflecting dominance

456   of the time-varying radiogenic $^{207}Pb/^{206}Pb$ ratio. Titanite domains that crystallize at the same

457   time and have remained closed throughout their evolution but contain varying concentrations of

458   Pb_i will defined a mixing line between the Pb_i composition and the radiogenic Pb composition at

459   any given time. This mixing line will evolve in a systematic way with time, sweeping toward

460   lower $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$, and is thus an isochron (Fig. 7B, dark gray lines). When the Pb_i

461 composition incorporated into titanite has a lower $^{207}Pb/^{206}Pb$, the initial Pb-radiogenic Pb

462 mixing line and the resulting isochrons will have shallower slopes (Fig. 7C, blue lines).

463 Consequently, linear arrays of titanite U-Pb data that show changes in slope (curve or bend) or

464 appear to intersect with other linear arrays are indicative of changes in Pb_i composition during

465 crystallization or recrystallization.

466   Fractionation of U and Pb results in titanite with variable U/Pb ratio and can arise from

467 differential mobility of these elements during crystallization, recrystallization or intragrain

468 diffusion. In titanite that also incorporates Pb_i, fractionation of U and Pb manifests as

469 subhorizontal data arrays that approximately parallel the $^{238}U/^{206}Pb$ axis on the Terra-Wasserburg

470 diagram (Fig. 7D, E). Changes in U/Pb ratio that occur long after initial titanite crystallization

471 should generate more horizontal arrays than changes to U/Pb ratios that occur shortly after

472 crystallization (Fig. 7E; Tera and Wasserburg, 1974) because Pb_i makes ups a larger proportion

473 of total Pb in titanite early on. Pb loss can occur by Pb diffusion or by recrystallization that

474 produces a higher U/Pb ratio than present in earlier-formed titanite. Significant U diffusion in

475 titanite is unlikely (Frost et al., 2000); however, real or apparent U loss can occur when

476 recrystallization produces a lower U/Pb ratio than present in earlier-formed titanite. Significant U

477 loss can produce reverse discordance on the Tera-Wasserburg diagram (Fig. 7D).

478   Pb isotopic fractionation during diffusion is expected to be negligible because of the

479 small relative mass differences between Pb isotopes. Pb isotopic variations during

480 recrystallization will also be negligible in the case that earlier-formed titanite is the primary

481 source of Pb to later-formed titanite (e.g., interface coupled dissolution-precipitation

482 recrystallization of Holder and Hacker (2019)). Significant changes to both the U/Pb and Pb/Pb

483 ratios of titanite are anticipated when recrystallization occurs in the presence of fluids that are

484   not in equilibrium with respect to the titanite-stabilizing phase assemblage – i.e. fluids external to

485   the local rock system.

486

487   **Interpretation of the Harrisville titanite data from Tera-Wasserburg data patterns**

488   The curvature in Adirondack titanite U-Pb data arrays suggest variation in Pb_i

489   composition. Both LA-ICP-MS and SHRIMP data show an approximately linear trend with a

490   slight curvature toward lower slope at $^{207}Pb/^{206}Pb$ ~0.12 (Fig. 2). This is expressed by a small

491   offset of some Type-3 and Type-4 data relative to Type-1 and Type-2 data, as well as by greater

492   dispersion of data within Type-3 and Type-4 grains relative to Type-2 grains (Fig. 3). Departure

493   from a single linear isochron is also supported by the lack of a three-dimensional model solution

494   for the aggregate data sets (Table 1). The curvature of the Adirondack data arrays suggests that

495   titanite incorporated at least two different compositions of Pb_i, as do linear regressions that

496   project toward varied Pb_i $^{207}Pb/^{206}Pb$ values, some of which are significantly lower than ~0.92

497   (Table 1). The subtlety of the array curvature makes defining linear segments by eye and

498   dividing the data into Pb_i compositional groups challenging and potentially quite arbitrary.

499   Differences in Pb_i composition can arise from variations in growth or recrystallization

500   environment (Bonamici et al., 2015; Kohn, 2017; Lucassen et al., 2011; Marsh and Smye, 2017;

501   Romer and Rötzler, 2003; Scibiorski et al., 2019), which should also be reflected in other

502   compositional proxies, such as REE content, $\delta^{18}O$, or Th/U ratio. Thus, additional compositional

503   information might be used to identify and define data populations that can appropriately be

504   regressed together.

505   In addition to multiple Pb_i components, titanite U-Pb data also show evidence for Pb loss.

506   For a given $^{207}Pb/^{206}Pb$ ratio, U-Pb data are dispersed subparallel to the $^{238}U/^{206}Pb$ axis (Fig. 8).

507   The ^{204}Pb/^{206}Pb ratio decreases toward the concordia (Fig. 8A), but for a given ^{204}Pb/^{206}Pb value,

508   the ^{204}Pb-corrected dates decrease systematically parallel to the ^{238}U/^{206}Pb axis (Fig. 8B). This

509   subhorizontal date gradient is consistent with Pb loss altering the ^{238}U/^{206}Pb ratio (Fig. 7D, E).

510   Diffusive Pb loss has been suggested for these grains based on previous work demonstrating

511   diffusion of oxygen isotopes, which have similar diffusivity to Pb at granulite facies conditions

512   (Cherniak, 1993; Zhang et al., 2006), and a lack of correlation between chemical and isotopic

513   zoning in the Harrisville grains (Bonamici et al., 2014; 2015).

514   A quantitative model of Pb ingrowth and Pb loss can be constructed to approximate the

515   Harrisville titanite history (Fig. 9; Supplemental Materials). It shows that significant Pb loss

516   ~100 m.y. after initial titanite crystallization produces data scatter that is consistent with both the

517   direction and magnitude of offset of Harrisville U-Pb data relative to a 1150-Ma isochron (cf. Fig.

518   8). The model predicts that more recent Pb loss would have shifted the U-Pb data toward

519   significantly higher ^{238}U/^{206}Pb than observed. Thus, the relatively small, subhorizontal dispersion

520   of U-Pb data on the Tera-Wasserburg diagram is consistent with magmatic titanite crystallization

521   at ca. 1160 Ma followed by Pb loss during granulite-facies metamorphism at ca.1050 Ma.

522

523   **Implications for interpreting (*in situ*) U-Pb titanite data**

524   Generalizing the geometric considerations of the Tera-Wasserburg diagram and the

525   results from the Harrisville titanite example, U-Pb data patterns can be used to recognize both

526   Pb$_i$ compositional variations on the grain scale and open-system U/Pb fractionation. Previous

527   workers have long understood that data that form sloped linear arrays indicate a shared Pb$_i$

528   composition and isochronous formation (Ludwig, 1998; Storey et al., 2006; Tera and

529   Wasserburg, 1972; 1974). Indeed, these types of datasets were the motivation for the

530   development of the Tera-Wasserburg diagram. In many cases, linear data arrays can be

531   appropriately regressed to find both the shared, single crystallization age and Pb_i composition

532   (e.g., Stearns et al., 2016; Marsh and Smye, 2017).

533   In contrast, intersecting and/or curved arrays (e.g., Kirkland et al., 2016) suggest non-

534   isochronous (re)crystallization and variations in the Pb_i composition. Ideally, if distinct linear

535   segments can be recognized within a curved array, the subset of data defining a given segment

536   can be regressed to find an isochron. This analysis also suggests that curved arrays with

537   progressively shallower slopes toward the right, toward higher U/Pb, on the Tera-Wasserburg

538   diagram, are expected because ingrowth of radiogenic Pb over time potentially supplies an

539   increasing radiogenic component to the Pb_i being incorporated into newly (re)crystallized titanite.

540   Data arrays that are dispersed parallel to the $^{238}U/^{206}Pb$ axis (e.g., Scibiorski et al., 2019)

541   suggest open-system alteration of the U/Pb ratio in an existing titanite grain by diffusion or

542   (re)crystallization, possibly in the presence of a variable-composition fluid. In general,

543   horizontally dispersed data should be treated with caution in choosing isochron regressions

544   because data may have been shifted toward either lower or higher $^{238}U/^{206}Pb$ by open-system

545   U/Pb fractionation. Depending on the length scale of U or Pb mobility, $^{238}U/^{206}Pb$ may be shifted

546   to both higher *and* lower values within the same grain (i.e., dispersed horizontally away from the

547   central, true isochron location). Bidirectional dispersal would be expected in the case that Pb

548   diffusion depletes Pb from some regions of a grain while enriching other regions. Our results

549   also suggest that reversely discordant points (data that fall to the left of the Tera-Wasserburg

550   concordia) have been shifted subparallel to the $^{238}U/^{206}Pb$ axis as a result of open-system

551   recrystallization that decreases the U/Pb ratio.

552   In some cases, a subset of titanite U-Pb data form a linear array that can be regressed with

553   the isochron method whereas other data fall significantly off the linear array (e.g., Garber et al.

554   2017). Analyses that do not form part of the linear isochron array represent titanite domains that,

555   relative to the data the define the linear isochron array, have incorporated a different Pb_i

556   composition, (re)crystallized at a different time, or a combination of both. These patterns cannot

557   be created by simple variations in the relative proportions of the same Pb_i and radiogenic Pb

558   between analyses.

559   Finally, data that form a cloud above concordia without well defined, linear or curvilinear,

560   sloped or horizontal, arrays (e.g., Kohn and Corrie, 2011; Garber et al., 2017) reflect some

561   combination of U/Pb fractionation, changing Pb_i composition, and/or variable crystallization age

562   during titanite formation. Interpretation of age significance from such datasets requires additional

563   geologic, petrologic, and microstructural constraints and/or a prior knowledge of expected age

564   populations.

565

566   **Implications**

567   Titanite is an opportunistic mineral with highly adaptive crystal chemistry (e.g., Frost et

568   al., 2001; Kohn, 2017), and, as yet, the connections between titanite trace element content and

569   titanite (re)crystallization environment remain only partially explored, especially in subsolidus

570   hydrothermally altered and/or metamorphic titanite. Multiple processes can apparently produce

571   similar trace element variations and patterns in titanite. For instance, microscale intragrain

572   variations in high field strength elements have been linked to fine-scale fluid composition

573   variations (Lucassen et al., 2010a; 2010b; 2011; Gao et al., 2012; Chen et al., 2016), sector

574   zoning and trace element entrapment during growth (Hayden et al., 2008; Kohn, 2017), and

575   equilibrium or disequilibrium dissolution-reprecipitation processes (Romer and Rötzler, 2003;

576   Olierook et al., 2018; Hartnady et al., 2019; Holder and Hacker, 2019). Trends in titanite rare

577   earth element and actinide contents have also been linked to dissolution-reprecipitation (Garber

578   et al., 2017), as well as to coeval allanite or garnet growth (Garber et al., 2017; Scibiorski et al.,

579   2019), and sector zoning (Kohn, 2017; Bruand et al., 2019). Collectively, these studies suggest

580   that titanite chemistry can record equilibrium trace-element partitioning, especially between

581   titanite and melt, but that equilibrium may be very local (at the scale of grains) and/or that

582   titanite can reflect kinetic limitations on element mobility, attachment, or detachment.

583   Approaches like the Tera-Wasserburg analysis utilized in this study help to reduce the effect of

584   these poorly understood controls on the interpretation of U-Pb systematics by allowing Pb_i

585   variations to be distinguished from U/Pb ratio variations, regardless of the exact process(es)

586   responsible.

587   Moreover, when combined with grain-scale characterization of element and isotopic

588   zoning, the Tera-Wasserburg-based analysis of this study demonstrates an approach for

589   maximizing geochronologic information obtained by *in situ* U-Pb titanite analysis, especially for

590   rocks with polyphase thermal histories. The approach described here also aids in identifying

591   sources of uncertainty in U-Pb data, whether arising from the analysis itself or from actual

592   geological variability. Even when precise dates are not recovered, geological processes and

593   events that cause data scatter can be recognized through analysis of U-Pb data patterns using the

594   Tera-Wasserburg diagram.

595

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812

813   **Figure Captions**

814   Figure 1. Post-analysis images of U-Pb LA-ICP-MS and SHRIMP analysis pits at a similar scale.

815   Both sets of analysis pits have similar diameters, 35-40 μm. SHRIMP pits are 2-3 μm deep; LA-

816   ICP-MS pits are 15 μm deep.

817

818   Figure 2. Total LA-ICP-MS and SHRIMP U-Pb titanite datasets, colored by grain 'Type' as

819   determined by microstructural setting (Bonamici et al., 2014; 2015). The LA-ICP-MS dataset is

820   more extensive (n = 280) than the SHRIMP dataset (n = 101) because of the shorter analysis time.

821

822   Figure 3. Total Pb/U plots for each Adirondack titanite grain. Grain designations are listed in

823   upper right corner of each plot with the Type in parentheses behind. See Table 1 for grain Type

824   explanations. LA-ICP-MS data shown in gray; SHRIMP data shown in black. Constrained 3D

825   linear regressions are projected into the 2D space of the Tera-Wasserburg diagram. Lower

826   concordia intercepts and MSWDs for constrained 3D and 2D regressions are given for each grain.

827   Leftmost column contains Type-1 and -2 grains, which show generally small U/Pb ratio spread

828   and highly clustered analyses. Center column contains Type-3 grains, which show greater U/Pb

829   variations. The rightmost column contains Type-4 grains showing the largest spread in U/Pb

830   ratios.

831

832   Figure 4. Results of 3D linear isochron regressions (Ludwig, 2012) for individual Adirondack

833   titanite grains, showing large uncertainties and relatively poor age constraints provided by this

834   type of analysis. See also Figure 3 and Table 1. (A) Concordia-intercept ages and 2SD

835   uncertainties from regressions with constrained Pb_i $^{207}Pb/^{206}Pb$. Light gray fields show the

836   known age ranges for the Shawinigan and Ottawan phases of the Grenville orogenic cycle for

837   reference. (B) Lower intercepts and 2SD uncertainties, in the Tera-Wasserburg plane, of

838   unconstrained regressions. Within large uncertainties, all but one grain (HA12B) give lower

839   intercepts the overlap concordia. All regressions of SHRIMP data return MSWD values greater

840   than 2. Approximate ages for the Shawinigan and Ottawan phases are indicated on the concordia

841   for reference.

842

843   Figure 5. Comparison of individually Pb_i-corrected U-Pb dates for a subset of Adirondack

844   titanite grains that were analyzed by both LA-ICP-MS and SHRIMP. Traverses show the spatial

845   variations in Pb_i-corrected $^{238}U/^{206}Pb$ dates. Profiles are generated using the preferred Pb_i-

846   correction for each analytical technique—207 method for LA-ICP-MS and 204-method for

847   SHRIMP. Vertical bars show average, external 1σ uncertainties for SHRIMP (red) and LA-ICP-

848   MS (blue). Dashed horizontal lines show mean concordia-intercept ages from 3D linear isochron

849   regressions; note that uncertainties on these regression ages are not shown but are generally large

850   (see Fig. 4). U-Pb profiles for all grains in this study can be found in Supplemental Figures S1

851   through S13.

852

853   Figure 6. Plot of total $^{207}Pb/^{206}Pb$ vs. total $^{204}Pb/^{206}Pb$ measured in Harrisville titanite by LA-

854   ICP-MS (blue) and SHRIMP (red). See text for discussion.

855

856   Figure 7. Schematic diagrams showing the behavior of U-Pb data on a Tera-Wasserburg diagram.

857   (A) Selected paths showing the ingrowth of radiogenic Pb in the absence of Pb_i as function of

858   various starting U isotope compositions. Topmost path shows ingrowth trajectory for a titanite

859 grain crystallized at the time of Earth formation with the primodial (meteoritic) U isotope

860 composition. (B) Evolution of a mixing line (isochron) between Pb* and Pb$_i$ with ^{207}Pb/^{206}Pb =

861 0.96. Black line with the steepest slope represents the present-day isochron. Gray lines with

862 negative slopes show the position of the isochron at different arbitrary times during its evolution

863 from its initial to its present-day position. Gray lines with positive slopes show ingrowth curves

864 for Pb* mixed with variable proportions of Pb$_i$. Pb$_i$ composition is shown by the horizontal

865 dashed line. (C) Same as B with a different isochron evolution superimposed (blue lines),

866 demonstrating the effect of later titanite (re)crystallization with a different, more radiogenic Pb$_i$

867 (^{207}Pb/^{206}Pb = 0.6). (D) Schematic representation of Pb ingrowth trajectories for titanite suffering

868 open-system modification of its U/Pb ratio. Thin colored lines are normal ingrowth trajectories

869 (with varying proportions of Pb$_i$); heavier arrows simulate instantaneous change in U/Pb ratio by

870 either recent or ancient open-system event. Subsequently, Pb ingrowth returns to closed-system

871 behavior (thin lines). (E) Schematic representation of the U-Pb data arrays expected in the case

872 of open-system U/Pb ratio modification, as demonstrated in D.

873

874 Figure 8. U-Pb analyses with color scaling showing covariation with additional isotopic data. (A)

875 SHRIMP data and (B) LA-ICP-MS data with color scaling showing total ^{204}Pb/^{206}Pb. The

876 transition from warm to cool colors toward concordia is consistent with decreasing relative

877 abundance of Pb$_i$. (C) SHRIMP data and (D) LA-ICP-MS data with color scaling showing 204-

878 corrected date. Comparison with A and B suggests that for a given ^{204}Pb/^{206}Pb value (Pb$_i$

879 abundance), variation in Pb$_i$-corrected dates reflects variation in U/Pb ratio. Only Type 1 and

880 Type 2 data, which retain evidence for oxygen isotope and Pb diffusion (Bonamici et al. 2014;

881 2015), are shown in B and D.

882

883   Figure 9. Quantitative models showing the effect of Pb loss on U-Pb systematics for titanite with

884   Pb_i on the Terra-Wasserberg diagram. Model is constructed to simulate possible scenarios for the

885   Harrisville titanite grains: initial crystallization at 1150 Ma with low Pb_i followed by Pb loss

886   shortly after crystallization at 1050 Ma (orange curve) or Pb loss long after crystallization at 650

887   Ma (green curve). Modeling details in Supplemental Materials. (A) Ingrowth curves showing full

888   ingrowth trajectories, including Pb loss events. (B) Expanded region of A showing where

889   evolution curves end (X's), relative to the 1150 Ma and 1050 Ma isochrons, and depending on

890   the timing of Pb loss.

891

892 **Appendix**

893 Stacey and Kramers (1975) determined modern-day crustal average Pb isotope ratios to be

894 ^{206}Pb/^{204}Pb = 18.70, ^{207}Pb/^{204}Pb = 15.63, and ^{208}Pb/^{204}Pb = 38.63, based on Pb isotopic data from

895 "conformable" galena. They then fitted a two-stage Pb evolution curve, the second stage having

896 $\mu = {}^{238}$U/^{204}Pb = 9.74. In practice, Pb$_i$ ratios based on the Stacey and Kramers (1975) model can

897 be calculated for materials younger than 3.7 Ga from equations 1 and 2 below, using the modern-

898 day crustal average Pb isotope ratios and an approximate age (Stacey and Kramers model Pb

899 ratios are superscipted SK).

900

901
$$\left(\frac{^{206}Pb}{^{204}Pb}\right)^{SK}_i = \left(\frac{^{206}Pb}{^{204}Pb}\right)^{SK}_{today} - \left(e^{\lambda_{238}t} - 1\right) \qquad [eq.1]$$

902
$$\left(\frac{^{207}Pb}{^{204}Pb}\right)^{SK}_i = \left(\frac{^{207}Pb}{^{204}Pb}\right)^{SK}_{today} - \frac{1}{137.82}\left(e^{\lambda_{235}t} - 1\right) \qquad [eq.2]$$

903

904 The 204 method initial Pb correction (Stern, 1997) subtracts the initial Pb fraction (^{204c}f$_{206}$),

905 calculated using Stacey and Kramers (1975) Pb$_i$ ratios, from the total measured ^{206}Pb/^{238}U to

906 determine the radiogenic ^{206}Pb/^{238}U ratio.

907
$$^{204c}f_{206} = \frac{^{206}Pb_i}{^{206}Pb_{total}} = \frac{\left(^{204}Pb/^{206}Pb\right)^{unknown}_{measured}}{\left(^{204}Pb/^{206}Pb\right)^{SK}_i} \qquad [eq.3]$$

908
$$\left(\frac{^{206}Pb^*}{^{238}U}\right)^{unknown}_{corrected} = \left(1 - {}^{204c}f_{206}\right)\left(\frac{^{206}Pb}{^{238}U}\right)^{unknown}_{measured} \qquad [eq.4]$$

909

910   The 207 method Pb_i correction (Stern, 1997) subtracts the initial Pb fraction ($^{207c}f_{206}$), calculated

911   using Stacey and Kramers (1975) Pb_i values and a starting guess or "expected" radiogenic

912      $^{207}Pb/^{206}Pb$ ratio, from the total measured $^{207}Pb/^{206}Pb$ to determine the corrected radiogenic

913      $^{207}Pb/^{206}Pb$ ratio.

914
$$^{207c}f_{206} = \frac{^{206}Pb_i}{^{206}Pb_{total}} = \frac{\left(\dfrac{^{206}Pb}{^{207}Pb}\right)^{unknown}_{measured} \div \left(\dfrac{^{206}Pb^*}{^{207}Pb^*}\right)^{unknown}_{expected}}{\left(\dfrac{^{206}Pb}{^{207}Pb}\right)^{SK}_{i} \div \left(\dfrac{^{206}Pb^*}{^{207}Pb^*}\right)^{unknown}_{expected}} \quad [eq.5]$$

915
$$f_{207} = {}^{207c}f_{206} \; \frac{\left(^{207}Pb \middle/ ^{206}Pb\right)^{SK}_{i}}{\left(^{207}Pb \middle/ ^{206}Pb\right)^{unknown}_{measured}} \quad [eq.6]$$

916
$$\left(\frac{^{207}Pb^*}{^{206}Pb^*}\right)^{unknown}_{corrected} = \left(\frac{^{207}Pb}{^{206}Pb}\right)^{unknown}_{measured} \times \frac{(1 - f_{207})}{(1 - {}^{207c}f_{206})} \quad [eq.7]$$

917

918

919

920

Table 1. Summary descriptions and interpretations of titanite types from Harrisville area from previous work.

Titanite Type	Microstructural and Zoning Description	Reference
1	Anhedral grains (100-500 μm) within lenses of grain-size-reduced augite + quartz + oxides ± hornblende that define local S_1 protomylonitic fabric. Subtle oscillatory zoning in major, minor elements and Th/U. Core-to-rim decreasing $\delta^{18}O$ of ≤0.8‰. *Interpretation:* Magmatic titanite crystallized in AMCG Diana syenite; solid-state grain-size reduction during Ottawan deformation.	Bonamici et al. 2011; 2014; 2015
2	Rounded porphyroclasts (100-1300 μm) within local S_2 shear zones. Some show subgrain development and/or recrystallization at margins. Some are transected by one set of thin deformation twins. Chemical zoning marked by small, step-like and oscillating changes in minor and trace elements and Th/U. Core-to-rim decreasing $\delta^{18}O$ of ≤1.5‰ *Interpretation:* Late magmatic titanite crystallized in AMCG Diana syenite, sheared as porphyroclasts during Ottawan deformation	Mezger et al. 1992; Bonamici et al., 2014; 2015
3	Anhedral/xenoblastic grains and grain aggregates (~500-5000 μm) within veins that crosscut local S_1 foliation and variably contain local S_2 foliation. Grains commonly contain one or two sets of deformation twins. Veins vary in mineralogy but commonly contain augite, K-feldspar, apatite, scapolite, and other calcsilicate minerals in addition to titanite. Sharply oscillating zoning in minor and trace elements. *Interpretation:* Vein titanite crystallized from alkaline fluids cross-cutting Diana metasyenite during Ottawan deformation and metamorphism.	Johnson et al. 2005; Heumann, 2006; Bonamici et al. 2014; 2015
4	Xenoblastic grains partially overgrowing local S_3 mylonitic fabric. Pronounced zoning marked by sharp changes in minor and trace elements and Th/U. Nearly uniform $\delta^{18}O$ across grain interiors with increasing $\delta^{18}O$ (up to 1‰) in outer grain domains, coincident with pronounced chemical zoning. *Interpretation:* Magmatic titanite crystallized in AMCG Diana syenite; solid-state grain-size reduction during Ottawan metamorphism and deformation; solid-state rim growth during waning Ottawan metamorphism.	Bonamici et al. 2014; 2105

Table 2. Total Pb/U (3D) isochron regressions of U-Pb titanite data and associated go

	Concordia Intercept Age (Ma)	2σ ± (Ma)	MSWD	Prob. of Fit	TW plane incercept 238/206[1]
TYPE 1					
HA12B					
SHRIMP - uncon[4]			2.5	0	5.1
SHRIMP - BH con[5]	1251	460	3.5	0	
LAICPMS - uncon			0.2	0.999	4.78
LAICPMS - con[6]	1206	210	0.2	1	
TYPE 2					
HA03A S1					
SHRIMP - uncon			4.7	0	4.76
SHRIMP - BH con	1146	120	5.8	0	
LAICPMS - uncon			0.62	0.98	5.27
LAICPMS - con	1111	48	0.63	0.98	
HA03A S2					
SHRIMP - uncon			3	0	4.4
SHRIMP - con	1182	390	3.1	0	
LAICPMS - uncon			0.49	0.999	3.31
LAICPMS - con	1128	130	1.5	0.016	
HA09A2 S3					
SHRIMP - uncon			5.5	0	4.03
SHRIMP - con	1167	110	6.4	0	
HA09A S2					
LAICPMS - uncon			1.2	0.17	4.76
LAICPMS - con	1143	110	1.2	0.18	
HA09A S15					
LAICPMS - uncon			0.56	0.98	5.33
LAICPMS - con	1120	69	0.57	0.98	
TYPE 3					
HA07B S1					
LAICPMS - uncon	no solution				
LAICPMS - con	1064	63	0.55	0.99	
HA07B S9					
LAICPMS - uncon			0.57	0.81	6.4
LAICPMS - con	935	190	0.54	0.85	
HA08A S1					
LAICPMS - uncon			2.2	0.001	6.31
LAICPMS - con	947	110	2.1	0.002	
HA12A S1					
LAICPMS - uncon			1.03	0.42	5.86
LAICPMS - con	1016	44	1.03	0.41	

HA18					
SHRIMP - uncon			4	0	4.3
SHRIMP - con	1220	370	4.1	0	
LAICPMS - uncon			1.3	0.14	5.38
LAICPMS - con	1101	38	1.3	0.13	
HA10D					
LAICPMS - uncon			0.71	0.96	5.7
LAICPMS - con	1043	28	0.72	0.96	

TYPE 4

HA13 S1					
LAICPMS - uncon			0.37	1	5.24
LAICPMS - con	1127	27	0.39	1	
HA13 S2					
SHRIMP - uncon			4.5	0	5.53
SHRIMP - con	1124	75	5.8	0	
LAICPMS - uncon			0.74	0.94	5.23
LAICPMS - con	1128	23	0.78	0.9	

ALL

SHRIMP - uncon	no solution
SHRIMP - con	no solution
LAICPMS - uncon	no solution
LAICMPS - con	no solution

[1]Regressed Tera-Wasserburg plane intercept value. For grains formed between ~1200 and 1000 Ma, concordia (ra

[2]Regressed common Pb plane intercept value. For grains formed between ~1200 and 1000 Ma, concordia (radioge

[3]Ratio of regressed mean 207/204 and 206/204 values giving the upper intercept 207/206 value. Errors on 206/204

[4]Unconstrained 3D isochron solution with no restriction on initial Pb composition.

[5]3D isochron regression constrained with initial Pb composition based on the Broken Hills feldspar standard. Broke
does not return a solution. Ratios less than zero are not allowed.

[6]3D isochron solution constrained with initial Pb composition based on present day Stacey and Kramers (1975) Pb

odness-of-fit metrics.

2σ ±	TW plane intercept 207/206[1]	2σ ±	Common Pb plane intercept 206/204[2]	2σ ±	Common Pb plane intercept 207/204[2]	2σ ±
1.4	0.128	0.025	9	27	8.7	4.4
			0	45	12.8	6.2
0.95	0.06	0.12	-4	42	27	27
			0	39	23.3	5.2
0.53	0.089	0.0081	-35	51	5.6	5.8
			0	49	13.5	6.3
0.25	0.0807	0.0084	-8	37	21.5	7.3
			0	37	25.3	4.5
1.6	0.097	0.016	-53	170	9	18
			0	160	13	21
0.73	0.096	0.015	-448	270	-32	29
			0	100	26	12
0.46	0.0888	0.0045	-14	54	6.3	5.4
			0	56	13.3	6.8
0.56	0.078	0.012	-75	110	18	14
			0	90	24	11
0.36	0.0811	0.008	56	54	26.1	7.9
			48	54	28.7	6.4
			100	87	37.1	9.9
1.3	0.078	0.028	280	210	28	35
			280	220	56	23
0.8	0.079	0.033	127	68	33	20
			128	68	38	7.5
0.27	0.081	0.013	75	30	26.9	9.6
			75	30	32	3.8

1.6	0.094	0.022	-42	140	6	16
			0	110	14	15
0.2	0.087	0.016	51	23	27	10
			50	23	33.7	3.8
0.17	0.0765	0.004	143	50	37.2	8.6
			141	51	41.1	5.9
0.14	0.0832	0.0084	36	11	25.5	3.9
			36	11	28	1.9
0.36	0.0844	0.0045	28	19	14.1	2.3
			14	23	15.1	2.8
0.11	0.0838	0.0067	46	11	27.5	3.9
			46	11	30.9	2

adiogenic) values are in the range of 5-6.

enic) values are in the range 0.07-0.08.

4 and 207/204 propagated in quadrature to determine uncertainty on 207/206.

en Hills fsp Pb ratios are: 6/4 = 16.0, 7/4 = 15.39, 8/4 = 35.66, thus 7/6 = 0.962. Used only when a present day Stace

values: 6/4 = 18.5 and 7/4 = 15.6, thus 7/6 = 0.843. Ratios less than zero are not allowed

Common Pb plane intercept 207/206[3]	2σ ±
0.967	2.94
undef	undef
-6.750	71.20
undef	undef
-0.160	0.29
undef	undef
-2.688	12.46
undef	undef
-0.170	0.64
undef	undef
0.071	0.08
undef	undef
-0.450	1.78
undef	undef
-0.240	0.40
undef	undef
0.466	0.47
0.598	0.69
0.371	0.34
0.100	0.15
0.200	0.18
0.260	0.21
0.297	0.17
0.359	0.19
0.427	0.18

-0.143	0.61
undef	undef
0.529	0.31
0.674	0.32
0.260	0.11
0.291	0.11
0.708	0.24
0.778	0.24
0.504	0.35
1.079	1.78
0.598	0.17
0.672	0.17

y and Kramers (1975) correction

LA-ICP-MS

0.5 mm

SIMS

0.5 mm

Top panel:

data-point error ellipses are 2σ

LA-ICP-MS

Type 1
Type 2
Type 3
Type 4

2400
2000
1600
1200
800

$^{207}Pb/^{206}Pb$ (y-axis)
$^{238}U/^{206}Pb$ (x-axis)

Bottom panel:

data-point error ellipses are 2σ

SIMS
(SHRIMP)

2400
2000
1600
1200
800

$^{207}Pb/^{206}Pb$ (y-axis)
$^{238}U/^{206}Pb$ (x-axis)

HA12B S1 (1)

LAICPMS
3D Lower: 1206 ± 210 Ma
3D MSWD: 0.20
2D Lower: 1247 ± 180 Ma
2D MSWD: 0.20

SHRIMP
3D Lower: 1251 ± 460 Ma
3D MSWD: 3.5
2D Lower: 1173 ± 280 Ma
2D MSWD: 0.78

HA18 (3)

LAICPMS
3D Lower: 1101 ± 38 Ma
3D MSWD: 1.3
2D Lower: 879 ± 220 Ma
2D MSWD: 1.4

SHRIMP
3D Lower: 1220 ± 370 Ma
3D MSWD: 4.1
2D Lower: 1380 ± 290 Ma
2D MSWD: 2.6

HA13 S2 (4)

LAICPMS
3D Lower: 1128 ± 23 Ma
3D MSWD: 0.78
2D Lower: 1107 ± 31 Ma
2D MSWD: 0.87

SHRIMP
3D Lower: 1124 ± 75 Ma
3D MSWD: 5.8
2D Lower: 1044 ± 67 Ma
2D MSWD: 2.8

HA03A S1 (2)

LAICPMS
3D Lower: 1111 ± 48 Ma
3D MSWD: 0.63
2D Lower: 1098 ± 51 Ma
2D MSWD: 0.87

SHRIMP
3D Lower: 1146 ± 120 Ma
3D MSWD: 5.8
2D Lower: 1247 ± 160 Ma
2D MSWD: 5.9

HA01D (3)

LAICPMS
3D Lower: 1043 ± 28 Ma
3D MSWD: 0.72
2D Lower: 1004 ± 56 Ma
2D MSWD: 0.90

HA13 S1 (4)

LAICPMS
3D Lower: 1127 ± 27 Ma
3D MSWD: 0.39
2D Lower: 1117 ± 33 Ma
2D MSWD: 0.46

HA03A S2 (2)

LAICPMS
3D Lower: 1128 ± 130 Ma
3D MSWD: 1.5
2D Lower: -799 ± 1400 Ma
2D MSWD: 0.36

SHRIMP
3D Lower: 1182 ± 390 Ma
3D MSWD: 3.1
2D Lower: 513 ± 390 Ma
2D MSWD: 2.4

HA12A S1 (3)

LAICPMS
3D Lower: 1016 ± 44 Ma
3D MSWD: 1.03
2D Lower: 877 ± 130 Ma
2D MSWD: 0.67

HA09A2 S3 (2)

SHRIMP
3D Lower: 1167 ± 110 Ma
3D MSWD: 6.4
2D Lower: 1155 ± 130 Ma
2D MSWD: 4.7

HA08A S1 (3)

LAICPMS
3D Lower: 947 ± 110 Ma
3D MSWD: 2.1
2D Lower: 717 ± 240 Ma
2D MSWD: 0.61

HA09A S2 (2)

LAICPMS
3D Lower: 1143 ± 110 Ma
3D MSWD: 1.2
No 2D solution

HA07B S1 (3)

LAICPMS
3D Lower: 1064 ± 63 Ma
3D MSWD: 0.55
2D Lower: 997 ± 110 Ma
2D MSWD: 0.51

HA09A S15 (2)

LAICPMS
3D Lower: 1120 ± 69 Ma
3D MSWD: 0.57
2D Lower: 1036 ± 110 Ma
2D MSWD: 0.80

HA07B S9 (3)

LAICPMS
3D Lower: 935 ± 190 Ma
3D MSWD: 0.54
2D Lower: 752 ± 530 Ma
2D MSWD: 0.14

A

Concordia Intercept Age (Ma) vs. Type 1 — Type 2 — Type 3 — Type 4

Shawinigan

Ottawan

■ LA-ICP-MS
□ SHRIMP

B

Unconstrained Tera-Wasserburg plane intercepts

$^{207}Pb/^{206}Pb$ vs. $^{238}U/^{206}Pb$

■ LA-ICP-MS
□ SHRIMP

Shawinigan   *Ottawan*

Mean concordia-
intercept ages:
1206 Ma (LA-ICP-MS)
1251 Ma (SHRIMP)

SHRIMP 204-corr Date
LAICPMS 207-corr Date

A

$\frac{^{207}Pb}{^{206}Pb}$

Pb* ingrowth curves

4.5 Ga

4.0 Ga

3.0 Ga

2.0 Ga

1.0 Ga

$^{238}U/^{206}Pb$

Older crystallization, higher initial $^{235}U/^{238}U$

More recent crystallization, lower initial $^{235}U/^{238}U$

B

$\frac{^{207}Pb}{^{206}Pb}$

Pb_i composition

mixing line between Pb* and Pb_i (past isochron)

present-day isochron

Pb* ingrowth curve

$^{238}U/^{206}Pb$

C

$\frac{^{207}Pb}{^{206}Pb}$

Pb_i composition

past isochron

mixed Pb*-Pb_i ingrowth curves

past isochron

Pb_i composition

Pb* ingrowth curves

possible "bend" or intersection in linear arrays

$^{238}U/^{206}Pb$

D

$\frac{^{207}Pb}{^{206}Pb}$

recent U loss

past isochron

ancient U loss

ancient Pb loss

recent Pb loss

Pb* ingrowth curve

$^{238}U/^{206}Pb$

E

$\frac{^{207}Pb}{^{206}Pb}$

apparent isochron

true isochron

recent U loss

ancient U loss

recent Pb loss

ancient Pb loss

$^{238}U/^{206}Pb$

Legend:
- 6% Pb$_i$, no Pb loss
- 6% Pb$_i$, 50% Pb loss, shorly after xllzn
- 6% Pb$_i$, 50% Pb loss, long after xllzn
- 0% Pb$_i$, no Pb loss