1   **Revision 1:**

2   **In-situ U-Th/Pb geochronology of (urano)thorite**

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6

7   **Abstract**

8   A Laser-Ablation-Multi-Collector-Inductively Coupled Plasma Mass Spectrometry (LA-

9   MC-ICPMS) study of seven thorite and uranothorite $[(Th,U)SiO_4]$ samples ranging in age

10   from ~13 to ~500 Ma provides new insights into the U-Th/Pb isotope systematics of

11   these geologically significant, high-Th mineral species. Despite extreme actinide

12   enrichment and complex intra-crystal zonation in actinides and rare earth elements, this

13   study demonstrates that radiogenic-lead loss and/or metamictization is minimal and

14   restricted to domains that have undergone significant hydration. Dating of four igneous

15   uranothorites yields ages that are concordant in U/Pb and Th/Pb space, consistent with

16   other high-temperature chronometers, and are inferred to accurately reflect the timing of

17   crystallization of each rock. Similarly, Th/Pb ages of three thorite and/or huttonite-

18   bearing samples yield geologically plausible dates consistent with other mineral

19   chronometers. No evidence of isotopic inheritance was observed in any of the samples.

20   Data presented here demonstrate for the first time the feasibility of extracting accurate

21   and precise U/Pb and Th/Pb ages from Phanerozoic thorite, uranothorite and huttonite

22   using LA-MC-ICPMS at the 5μm spatial resolution. These phases have the potential to

23   be robust chronometers in igneous and metamorphic rocks as well as to provide

24   important provenance information complementary to more widely used minerals such as

25   detrital zircon.

26

27   **Keywords:** *Thorite, Uranothorite, Huttonite, Laser Ablation, Geochronology*

28

Introduction

29

30   The tetragonal orthosilicate thorite [ThSiO$_4$] and its monoclinic polymorph huttonite

31   occur in a wide variety of geological environments ranging from (but not restricted to)

32   felsic igneous rocks (Parrish and Tirrul, 1989, Hetherington and Harlov, 2008),

33   metasediments (e.g. Speer, 1982), base metal ore deposits (e.g. Ifill et al., 1989) and fault

34   zones (Kamineni and Lemire, 1991). Thorite may be either primary, or form by the

35   breakdown of other Th-rich minerals such as allanite, monazite or zircon (Hetherington

36   and Harlov, 2008). Its variable occurrence, combined with an ability to accommodate

37   large amounts of U and Th within its structure makes it a potentially useful chronometer

38   to quantify the timing and duration of a diverse range of geological events.

39   In pursuit of this goal there have been several attempts to date (urano)thorite using either

40   Electron probe microanalyzer (EPMA) (Parslow et al., 1985; Enami et al., 1993; Förster

41   et al., 2000; Jercinovic et al., 2002; Cocherie and Legendre, 2007) or Thermal Ionization

42   Mass Spectrometry (ID-TIMS) (e.g. Henjes-Kunst, et al., 1988; Parrish and Tirrul, 1989;

43   von Blanckenburg, 1992). The former method has generally met with limited success,

44   which these authors attribute to thorite's often metamict state and its susceptibility to

45   hydration and associated radiogenic lead loss. ID-TIMS has been used in at least two

46   published studies. Parrish and Tirrul (1989) analyzed uranothorite along with zircon and

47   monazite in monzogranite from the Karakoram granite in northern Pakistan (see below

48   for further details). They obtained three nearly concordant zircon analyses and two

49   duplicate fractions of uranothorite that together yielded a mean U/Pb age of 21.0 ± 0.5

50   Ma. Monazites from the same rock were reversely discordant with ages ranging between

51   17 and 19 Ma which Parrish and Tirrul (1989) postulated was the result of slow cooling,

52   persistence of high temperatures following crystallization, and partial lead loss in

53   monazite, none of which apparently affected the thorite.

54   Von Blanckenburg (1992) analyzed allanite, sphene, apatite and thorite from a

55   granodiorite of the Central Alpine Bergell intrusion (central Europe). They argued that

56   both the allanite and sphene lacked inheritance and were magmatic in origin. The mean

57   age of the allanite and sphene (30.12 ± 0.17 Ma) was interpreted as the timing of

58   granodiorite intrusion. A single grain thorite fraction yielded a concordant U/Pb age of

59   28.36 Ma and Th/Pb age of 27.6 Ma. The younger thorite U/Pb age relative to the allanite

60   – sphene age was inferred to be a result of recrystallization and the ~3% discrepancy

61   between U/Pb and Th/Pb ages of the thorite resulted from Th gain, U loss, or ^{208}Pb loss

62   from strongly ^{232}Th-enriched domains (Von Blanckenburg, 1992).

63   These two isotopic studies highlight the possibility of obtaining U/Pb and/or Th/Pb dates

64   from (urano)thorite. However, significant questions still remain about the interpretation

65   of (urano)thorite dates relative to other high temperature chronometers such as zircon,

66   monazite, sphene and allanite. The cause and significance of the disequilibrium between

67   the Th/Pb and U/Pb systems in thorite identified by Von Blanckenburg (1992) also

68   remains unresolved. In addition, although often described as occurring within clastic

69   sediments, the utility of (urano)thorite and huttonite as indicators of sedimentary

70   provenance remains untested.

71   In this contribution, the U/Pb and Th/Pb isotope systematics of (urano)thorite and

72   huttonite are explored by combining EPMA elemental mapping with recently developed

73   in-situ Laser Ablation micro-sampling techniques, which allow simultaneous acquisition

74   of U, Th, and Pb isotopes from small volumes of ablated material. The method employed

75   here (Laser-Ablation-Multi-Collector- Inductively Coupled Plasma Mass Spectrometry,

76   LA-MC-ICPMS) affords high spatial resolution (~5 μm diameter pits) and enables the

77   chemistry and morphology of a grain to be directly related to its isotopic age.

78   The majority of U/Pb and Th/Pb data presented here are concordant, with no evidence of

79   disequilibrium between isotope systems. Alteration and associated radiogenic lead-loss is

80   volumetrically minor and restricted to obviously altered domains. Dates obtained from

81   igneous uranothorite are consistent with other high temperature chronometers (e.g.

82   zircon), whereas detrital thorite and huttonite yield complementary information about

83   geologic source regions not recorded by detrital zircon from the same sample.

84

85   **Sample Descriptions**

86   Geologically well-constrained samples were chosen for this study, including three

87   samples for which complementary geochronological data already exists (See Table 1 for

88   summary of samples analyzed). Further, five of the samples (M33, AD41, H4, H8 and

89   P68787) have similar chemistry and petrogenetic origin, enabling more direct inter-

90   sample comparisons on the behavior of Th-rich minerals formed during crustal anatexis.

91

92   **M33**

93   Sample M33 is from the high-grade Mogok Metamorphic Belt (MMB), an arcuate zone

94   that extends from the eastern Himalayan syntaxis in the north, through the Indo–Burman

95   Ranges to the Andaman Sea in the south. The geological setting and tectonic significance

96   of M33 is discussed in detail by Searle et al. (2007) and described briefly here. M33 is an

97   undeformed quartz + plagioclase + K-feldspar + biotite granite dike with a weak flow

98   banding fabric, collected from Belin Quarry in the central Burmese part of the MMB

99   (Searle et al. 2007, their Figs. 4 and 5b; Table 1). Accessory phases are dominated by

100   zircon, apatite and uranothorite. Petrological data suggest that this is an S-type

101   leucogranite that formed by muscovite dehydration melting of a mid-crustal pelitic

102   assemblage following crustal thickening associated with the collision of India and Asia

103   (Searle et al., 2007). A single grain concordant ID-TIMS zircon fraction yielded a

104   ^{206}Pb/^{238}U date of 53.1 ± 0.2 Ma and a single grain thorite has a ^{207}Pb/^{235}U age of 54.1 ±

105   0.1 Ma. In addition, seven U/Pb LA-MC-ICPMS spot analyses on uranothorite,

106   normalized to primary reference material Manangotry monazite yield a ^{206}Pb/^{238}U -

107   ^{207}Pb*/^{235}U concordia age of 59.5 ± 0.9 Ma, (MSWD of concordance = 0.97). The

108   authors inferred the ~6 Ma discrepancy between the ID-TIMS and LA-MC-ICPMS ages

109   to reflect Pb-loss in both ID-TIMS zircon and thorite fractions and concluded that the

110   ^{207}Pb*/^{235}U LA-MC-ICPMS thorite concordia age of 59.5 ± 0.9 Ma provided the best

111   estimate of the magmatic crystallization age of M33 (Searle et al., 2007, their Figure 8g).

112   This sample was selected for its well-constrained geologic context and available U/Pb

113   ID-TIMS and LA-MC-ICPMS data for both zircon and uranothorite (Searle et al., 2007).

114

115   **AD41**

116   AD41 is a migmatitic augen gneiss from a section of the Greater Himalayan series (GHS)

117   crops out on the east side of the Phung Chu river in the Kharta valley of south Tibet

118   (Cottle et al., 2009a, their Figs. 2 and 4b; Table 1). The GHS in this region is a 30-km-

119   thick sequence of metamorphic and anatectic rocks that form the high-grade core of the

120   orogen. Sample AD41 is a distinctly banded, mylonitic augen gneiss with a well-

121 developed foliation defined by laths of biotite and fibrolite. The restitic portion of the

122 rock is composed of biotite, sillimanite, quartz, plagioclase and K-feldspar, while the cm-

123 thick, syn-kinematic leucogranitic leucosomes comprise aggregates of K-feldspar, quartz

124 and rare biotite. Accessory phases are dominated by zircon, apatite and uranothorite, with

125 the latter restricted to the leucosomes. The leucosomes are interpreted to have formed as

126 a result of in-situ partial melting of the host meta-granitoid (Cottle et al., 2009a). U/Pb

127 dating of zircons from AD41 yield an age of 440 ± 6 Ma, interpreted as the crystallization

128 age of the protolith granitoid (Cottle et al., 2009a). This age is comparable to other

129 gneisses within the GHS in the Everest region some ~60 km to the east, e.g. the Namche

130 orthogneiss (Viskupic and Hodges, 2001). Eight U/Pb LA-ICPMS analyses of

131 uranothorite (normalized to a primary reference Manangotry monazite) yielded a mean

132 $^{206}Pb/^{238}U$ date of 15.8 ± 0.2 Ma (MSWD 0.9, n=8) (Cottle et al. 2009a their Fig. 7f).

133

134   **H4 and H8**

135 Sample H4 is an S-type monzogranite from the south side of the Baltoro Glacier Valley,

136 eight km NNW of Masherbrum peak in the Karakoram region of northern Pakistan.

137 Sample H8 is a megacrystic K-feldspar granite collected from 3 km NW of Bialo peak

138 (Parrish and Tirrul, 1989 their Fig. 1; Table 1). Both samples are from the Baltoro

139 granite, part of the Cretaceous–Miocene composite Karokoram Batholith of the northwest

140 Himalaya (Parrish and Tirrul 1989; and references therein). The geology and accessory

141 phase geochronology of H4 and H8 is described by Parrish and Tirrul (1989) and

142 references therein. Zircon data for H8 are all highly discordant with $^{207}Pb/^{206}Pb$ apparent

143 dates ranging from 635 Ma to 1750 Ma. One uranothorite fraction is reversely discordant

144   with an inferred date of ~16.5 Ma, whereas monazites are ~18 Ma. Two fractions of

145   uranothorite (a total of six crystals) from H4 yield an ID-TIMS $^{206}Pb/^{238}U$ age of 21.3 ±

146   0.1 Ma (U ~10300ppm, Pb ~990 ppm, Pb $^{206}Pb/^{238}U$ = 0.0033 ± 0.3%, $^{207}Pb/^{206}Pb$ =

147   0.0463 ± 0.4%, $^{208}Pb/^{232}Th$ = 0.00104 ± 0.5%, Parrish and Tirrul 1989). These

148   geologically well-constrained samples were selected for further analysis because of the

149   published U/Pb ID-TIMS ages for H4 derived from uranothorite and zircon and

150   monazite. For this study uranothorite was picked from the same mineral separates used

151   by Parrish and Tirrul (1989).

152

153   **P68787**

154   P68787 is a coarse-grained equigranular hornblende monzodiorite from the Hunt Glacier

155   in the Dry Valleys region of Antarctica (from the Geological and Nuclear Science,

156   Dunedin, New Zealand Collection, kindly provided by A. Tulloch). This sample is part of

157   the Granite Harbor Intrusives, an extensive suite of dominantly calc-alkaline mid-crustal

158   magmatic rocks formed during the Neoproterozoic–Ordovician Ross orogeny. Zircon

159   from this sample has a mean $^{206}Pb/^{238}U$ LA-MC-ICPMS date of 502.1 ± 2.6 Ma (Hagen-

160   Peter et al. 2011; Table 1). For this study uranothorite was picked from the same heavy

161   mineral separate as used by Hagen-Peter et al. (2011).

162

163   **OU-16321**

164   OU-16321 from the University of Otago, Dunedin, New Zealand Collection is from a 1-

165   to 2-cm-thick carbonate-rich vein containing, in approximate order of abundance, ferroan

166   dolomite, magnesian dolomite, apatite, albite, reddish-brown thorite crystals up to 2-mm-

167   long, and Nb-rutile (Table 1, White, 1962; Cooper, 1971). This rock comes from Gout

168   Creek, Haast River, in the South Island of New Zealand and occurs as part of a

169   lamprohyric dike-swarm with carbonatitic affinities. Previous geochronology on

170   associated rocks yields U/Pb primary magmatic crystallization zircon ages ranging from

171   24.6 – 24.1 Ma (Cooper et al., 1986).

172

173   **Gillespie's Beach ThSiO$_4$**

174   Thorite, huttonite, zircon and rutile were extracted from a heavy mineral concentrate

175   collected from Gillespie's Beach, on the West coast of the South Island, New Zealand.

176   The heavy mineral concentrate is dominated by magnetite but also contains minor

177   amounts of scheelite, zircon, thorite, huttonite, rutile, and apatite. Thorite from

178   Gillespie's Beach occurs in brown and green varieties while huttonite was distinguished

179   from thorite primarily by x-ray diffraction (XRD). Gillespie's Beach is significant

180   because it is the type locality for huttonite originally described in detail by Pabst and

181   Hutton (1951). Förster et al. (2006) used the EPMA total U-Th/Pb method to obtain

182   Miocene dates for huttonite and dates ranging from late Triassic–early Jurassic to early

183   Tertiary for thorite (Table 1).

184

185   **Methods**

186   Uranothorites were separated using standard crushing, heavy liquid, and isodynamic

187   magnetic separation techniques. A representative crystal from each sample was subjected

188   to XRD to confirm whether it was tetragonal thorite or a Th-silicate dimorph, e.g.

189   huttonite (monoclinic [(Th,U)SiO$_4$]. Although only weak thorite diffraction patterns were

190   generated, they confirm that each crystal has a tetragonal crystal system with average (n

191   = 8) unit cell dimensions: a = b = 7.18 (3) Å c = 6.09 (4) Å, a:c = 1: 0.848 and a cell

192   volume of v = 314 Å^3 (calculated from Unit Cell).

193   Grains representative of the variation in population morphology were handpicked

194   in ethanol and mounted in one-inch diameter epoxy resin discs, polished to reveal

195   equatorial sections, then carbon-coated. To elucidate zonation and/or alteration patterns,

196   identify inclusions within grains, and to aid positioning of spots for later isotope analysis

197   such that multiple domains/or altered areas were avoided, backscattered electron (BSE)

198   maps were produced using a FEI Quanta400F scanning electron microscope (SEM). In

199   addition, elemental maps of U, Th, Y and P were made using a Cameca SX-100 EPMA

200   housed at the University of California, Santa Barbara (UCSB). Quantitative major and

201   trace element analyses were performed using the same EPMA. Detailed EPMA analytical

202   methods are presented in Appendix 1 and data are presented in Table 2.

203   After EPMA mapping and analysis, U, Th, and Pb isotopes were collected from

204   carefully selected sites using a LA-MC-ICPMS housed at UCSB. Analytical methods

205   follow Cottle et al. (2012, 2013) and Kylander-Clark et al. (2013). A detailed analytical

206   method is presented in Appendix 1 and data are presented in Table 3 (uranothorite),

207   Table 4 (thorite and huttonite) and Table 5 (detrital zircon). For thorites, the 'H4'

208   uranothorite (Parrish and Tirrul, 1989) served as the matrix-matched primary reference

209   material (RM) to monitor and correct for mass bias, as well as Pb/U and Pb/Th down-

210   hole fractionation (see below for further detail on matrix-matching). No Pb/Th age data

211   exist for H4 (or any of the samples analyzed in this study), therefore for normalization

212   purposes, the Pb/Th and Pb/U systems for H4 were assumed to be concordant. Since no

213   secondary thorite RM currently exists, two zircon reference materials ('91500' and 'GJ-

214   1') were analyzed concurrently as an external monitor of instrument performance. For

215   zircon analyses, '91500' (1062.4 ±0.4 Ma ^{206}Pb/^{238}U ID-TIMS age, Wiedenbeck et al.

216   1995) was employed as the primary RM. To monitor data accuracy, a secondary

217   reference zircon 'GJ-1' (608.5 ± 0.4 Ma ^{207}Pb/^{206}Pb ID-TIMS age, Jackson et al. 2004)

218   was analyzed concurrently (once every seven unknowns) yielding a weighted mean

219   ^{206}Pb/^{238}U age of 600.5 ± 1.6, MSWD = 1.5, n = 28. Data reduction, including corrections

220   for baseline, instrumental drift, mass bias, down-hole fractionation as well as age

221   calculations were carried out using Iolite v. 2.1.2 (Paton et al. 2010). Background

222   intensities and changes in instrumental bias were interpolated using a smoothed cubic

223   spline while down-hole inter-element fractionation was modeled using an exponential

224   function. Statistics for baselines, on peak intensities and isotopic ratios were calculated

225   using the mean with a 2.S.D. outlier rejection. Concordia and weighted mean date plots

226   were calculated in Isoplot v.3 (Ludwig 2003) using the ^{238}U and ^{235}U decay constants of

227   Steiger and Jäger, (1977) and the ^{232}Th decay constant of Amelin and Zaitsev (2002). All

228   uncertainties in data tables and concordia plots are quoted at the 2σ confidence level.

229

230   **Results**

231   **(urano)thorite morphology and zoning**

232   Igneous (urano)thorite in this study are generally doubly-terminated, euhedral to

233   subhedral, green to brown translucent crystals that range from short 2:1 (length:width

234   aspect ratio) to elongate (5:1). Integrating information from U, Th, Y, and P x-ray maps

235   and BSE images (Figs. 1 and 2) reveals a variety of internal structures, zoning and

236 alteration patterns. Many samples show one or more generations of cuspate-lobate or

237 crosscutting flame and tongue structures (e.g. M33, AD41, Gillespie huttonite and thorite,

238 Fig. 1). These crystals have a patchy appearance in BSE, suggestive of multiple episodes

239 of intra-crystal dissolution, re-precipitation and/or intergrowth and amalgamation of

240 smaller grains.

241   Less commonly, samples show either minimal internal zoning in U, Th, Y, or P

242 (e.g. H4, H8, Fig. 1) or have oscillatory zoning (e.g. P68787, Fig. 1) analogous to

243 textures observed in igneous zircon. Relict oscillatory zoning subsequently overprinted

244 by recrystallization textures is occasionally preserved in brown thorites from the

245 Gillespie's Beach sample (Fig. 1). In the Gillespie's Beach sample, crystals typically

246 display minor patchy zoning in Th, U, P, and Y but also contain numerous inclusions of

247 xenotime (red spots in P and Y maps) along with minor, and much smaller, apatite and

248 monazite.

249   In addition to alteration, many of the grains examined from each sample contain

250 inclusions of zircon (Fig. 2a). Intergrowths of these two minerals were not observed and

251 in most cases the thorite appears to have nucleated around zircon. Less common

252 inclusions of quartz, K-feldspar, allanite and xenotime were also observed (Fig. 2b).

253

254   **Alteration**

255 All grains display some degree of alteration, and this potentially has significant impacts

256 on the isotopic age of (part of) a crystal. Optically, some crystals contain visible orange

257 discoloration zones. In BSE, this is manifested as either thin (1-20 μm) (H4 and H8) or

258 discontinuous (in M33 and AD41) rims (Fig. 1, 2c, 2d). In all cases, the altered domain is

259   darker in BSE, lower in Th, Si, Pb and U and higher in P, Ca, Fe, Y and (OH, calculated

260   from stoichiometry) suggesting that these regions have probably undergone hydrous

261   alteration to thorogummite [$(Th,U)(SiO_4)_{1-x} (OH)_{4x}$].

262   Alteration occurs as irregular domains along cracks adjacent to fractures, at the

263   contact with inclusions, and as large internal portions of the grain. A particularly good

264   example of internal alteration occurs in a crystal from M33 (Fig. 1 and Fig. 2b). This

265   crystal shows an alteration zone that is darker in BSE, lower in U, Th and Pb and higher

266   in Y and P than the rest of the grain. The altered zone contains inclusions of high Th and

267   U (1.5 wt % ThO_2 and 1.3 wt% UO_2) xenotime (the red spots in the Y and P maps). In

268   addition, although the alteration zone itself (as defined by the higher Y + P domain) is

269   associated with a significant depletion in U, the area immediately surrounding the

270   alteration is enriched in U relative to the unaltered portion of the crystal (Fig. 2b)

271   suggesting some decoupling of U and Th. Another form of alteration locally occurs in

272   many of the samples, but is best illustrated in sample OU16321. Crystals typically

273   display minor patchy zoning in Th, U, P and Y and contain numerous inclusions of

274   xenotime (red spots in P and Y maps) along with minor, and much smaller, apatite and

275   monazite (Fig. 1).

276

277   **Mineral Chemistry**

278   The chemistry of the investigated uranothorites is relatively consistent both within and

279   between samples (Table 2). Thorium is the dominant cation (52.1 – 57.8 wt% ThO_2),

280   with lesser amounts of U (18.5 – 26.2 wt % UO_2), Si (16.1 – 17.4 wt% SiO_2), P (0.4 – 1.4

281   wt% P_2O_5) and Y (0.4 – 1.9 wt% Y_2O_3) and Pb (0.3 – 0.5 wt% PbO). Thorites have more

282   Th, P, Y, and REE and less U than uranothorites.

283   For the unaltered domains, totals are consistently ~96–98% with cation

284   proportions in approximately the correct stoichiometry for $ThSiO_4$. Totals less than 100%

285   for thorite are commonly reported in the literature and, as outlined in detail by Förster

286   (2006), may potentially be related to one or more of: 1) the presence of absorbed

287   molecular water or hydroxyl substituted for silica; 2) the presence of elements not

288   included in the analytical routine; and 3) presence of uranium[VI] oxide.

289   Because of their thin and irregular nature, only a few altered regions of crystals in

290   M33, AD41, H4 and H8 could confidentially be targeted with the EPMA (Table 2).

291   Analytical totals (~77 – 88%) are much lower than the pristine domains, suggesting that

292   these domains may contain a significant proportion of OH. This issue not withstanding,

293   altered domains tend to be lower in U, Th, Pb and Fe and higher in Si, Ca, P and

294   occasionally REE.

295

296   **U-Th/Pb Isotope data**

297   **Matrix-matched reference material for LA-ICPMS**

298   During LA-ICPMS isotopic analysis a major source of uncertainty is the time-dependent

299   fractionation of elements as a result of the ablation process. Fractionation, defined as the

300   change in measured element (isotope) ratio signals with time (Fryer et al., 1995), is a poorly

301   understood process. However, for a given set of analytical conditions, fractionation occurs as

302   a result of differential vaporization and mobilization of ablated particles. Of particular

303   importance to this study is Laser-Induced Elemental Fractionation (LIEF), a well-

304   documented effect observed in previous U-Th/Pb geochronologic studies (e.g. Hirata and

305   Nesbitt, 1995; Horn et al., 2000; Kosler et al., 2001, Paton et al., 2010). The degree of LIEF

306   is controlled by the way the laser interacts with the sample (absorption characteristics) as

307   well as the sample's chemical composition. The net result is that geologic materials with

308   different structural properties and chemical compositions produce substantially different

309   time-dependent fractionation profiles. The majority of LA-ICPMS geochronologic studies

310   that employ a static spot (rather than a dynamic raster) use a sample-standard bracket

311   approach and assume that sample and reference material fractionate in a similar manner.

312   Therefore, any difference in time-dependent fractionation profile between sample and

313   primary reference material potentially leads to introduction of considerable uncertainty into

314   the analysis.

315   No well-characterized (urano)thorite LA-ICPMS reference material currently

316   exists, therefore in this study a series of experiments were conducted to assess if a similar

317   framework matrix (e.g. $XSiO_4$ such as zircon) or a matrix with a similar actinide content

318   (e.g. a high-Th phase such as monazite) could be employed to accurately correct for LIEF

319   in (urano)thorite, or if a matrix-matched reference material is necessary to generate

320   accurate data in static spot mode.

321   Three uranothorites along with Manangotry monazite [552.9 Ma $^{206}Pb/^{238}U$, 554

322   Ma $^{207}Pb/^{206}Pb$ ID-TIMS ages, (Horstwood et al., 2003)], Plešovice zircon [337.13 ± 0.37

323   Ma $^{206}Pb/^{238}U$ ID-TIMS age, (Sláma et al., 2008)] and NIST SRM610 glass were

324   analyzed. So as not to saturate the secondary electron multipliers, a relatively small static

325   spot size (5μm diameter pit) and low fluence (1.2 J/cm^2) was employed. H4 data was

326   normalized to the ID-TIMS values of Parrish and Tirrul (1989). The reference ages of

327   M33 and AD41 were taken from Searle et al. (2007) and Cottle et al. (2009a),

328   respectively. As outlined below, the age of AD41 reported by Cottle et al. (2009a) may

329   be inaccurate by as much as 10%, however this level of uncertainty has negligible affect

330   on the shape and position of the curves in Figure 3. Each sample was inferred to be

331   concordant in U/Pb and Th/Pb space and Th/Pb normalization values were derived from

332   U/Pb data.

333   Figure 3 shows exponential curves fitted to the mean of 10 repeat static spot

334   ablations of the various samples. In both U/Pb and Th/Pb space, the uranothorites have a

335   very similar fractionation trend, implying they ablate in a very similar manner. However,

336   this trend is significantly different from monazite, zircon, or NIST610. In U/Pb space, the

337   monazite and zircon have a much lower degree of fractionation while NIST610 has a

338   negative fractionation slope. In Th/Pb space the monazite, zircon, and NIST610 all have

339   significantly different fractionation slopes. It is clear from Figure 3 that a matrix-matched

340   reference material is necessary to accurately model and correct for $^{206}Pb/^{238}U$ and/or

341    $^{208}Pb/^{232}Th$ fractionation in the unknowns when a static spot is employed. Based on this

342   conclusion, the $^{206}Pb/^{238}U$ and/or $^{208}Pb/^{232}Th$ (urano)thorite and huttonite data presented

343   below are all normalized to H4 as the concurrently analyzed primary reference material.

344

345   **M33**

346   For this study, an additional 25 LA-MC-ICPMS spot analyses were carried out on

347   uranothorite grains from the same mineral separate as Searle et al. (2007). Twenty-two of

348   the analyses are concordant in U/Pb and Th/Pb space yielding a weighted mean

349    $^{206}Pb/^{238}U$ date of 54.0 ± 0.4 Ma (MSWD 0.8), and a weighted mean $^{208}Pb/^{232}Th$ date of

350   53.9 ± 0.5 Ma (MSWD 1.3) (Fig. 4A-B, Table 3). Three additional analyses deliberately

351   placed over altered domains yield younger apparent $^{206}Pb/^{238}U$ and $^{208}Pb/^{232}Th$ dates of

352   ~48 Ma, consistent with radiogenic lead loss.

353

354   **AD41**

355   Forty-one new analyses from six grains were collected as part of this study, with forty

356   analyses yielding a weighted mean $^{206}Pb/^{238}U$ date of 14.8 ± 0.1 (MSWD 1.9) and a

357   weighted mean $^{208}Pb/^{232}Th$ date of 13.5 ± 0.1 (MSWD 3.7) (Fig. 4 C-D, Table 3). One

358   spot deliberately placed over an altered domain gives an apparent date of ~11 Ma.

359

360   **H8**

361   Thirty-five analyses conducted during this study yield a weighted mean $^{206}Pb/^{238}U$ date of

362   22.1 ± 0.2 Ma (MSWD 2.7), and a weighted mean $^{208}Pb/^{232}Th$ date of 21.4 ± 0.1 Ma

363   (MSWD 1.7) (Fig. 4E-F, Table 3). Two additional analyses deliberately placed over

364   altered domains yield younger apparent dates of ~18.5-20 Ma, consistent with radiogenic

365   lead loss.

366

367   **P68787**

368   Ten analyses from five grains yield a weighted mean $^{206}Pb/^{238}U$ date of 495 ± 6 Ma

369   (MSWD 1.2), and a weighted mean $^{208}Pb/^{232}Th$ date of 492 ± 8 Ma (MSWD 1.4) (Fig.

370   4G-H, Table 3). One analysis was rejected as it contains a significant amount of

371   common-lead, likely from partial ablation of an inclusion.

372

373   **OU-16321**

374   Twelve analyses from five grains yield a weighted mean $^{208}Pb/^{232}Th$ date of 19.7 ± 0.4

375   Ma (MSWD 1.5). A single analysis on an altered domain gives an apparent date of ~17

376   Ma (Fig. 5, Table 4). The number of analyses is relatively small since only areas that

377   were determined to be free of (the numerous) xenotime inclusions were measured.

378

379   **Gillespie's Beach ThSiO$_4$ and Zircon**

380   Analysis of 75 individual crystals of brown thorite from the Gillespie's Beach mineral

381   separate yield consistent dates of ~75 Ma (Fig. 6, Table 4). Although not strictly valid for

382   detrital samples, taking a weighted mean $^{208}Pb/^{232}Th$ date gives 74.7 ± 0.4 Ma (MSWD

383   1.4). The MSWD of near unity indicates the possibility that these crystals were sourced

384   from a rock or suite of rocks with a single age population. Analyses of 79 individual

385   crystals of green thorite yield $^{208}Pb/^{232}Th$ dates ranging from 210 Ma to 23 Ma with a

386   prominent age peak at ~75 Ma (Fig. 6, Table 4). Analysis of five huttonite grains yields

387   dates ranging from 17 to 12 Ma (Fig. 6, Table 4). These dates are broadly similar to total

388   U-Th/Pb ages obtained by Förster et al. (2000) using the EPMA. Analysis of 100 detrital

389   zircons from the same mineral separate yields age peaks at ~260 Ma, ~380 Ma, ~480 -

390   550 Ma, ~620 – 680 Ma and a minor component of Proterozoic and Achaean ages (Fig.

391   7, Table 5).

392

393   **Discussion**

394   **Mineral Chemistry and Alteration**

395   The first key observation from the detailed x-ray imaging carried out in this study is that

396   the vast majority of both thorite and uranothorite crystals are internally zoned in both

397   major (U, Th) and trace (Y, P, REE) elements. Intra-crystalline zoning takes multiple

398   forms, but is commonly manifested as patchy textures that are consistent with one or

399   more episodes of fluid-mediated intra-crystal dissolution, re-precipitation and/or

400   intergrowth and amalgamation of smaller grains. Such textures have previously been

401   described from other minerals such as apatite (e.g. Harlov et al. 2005), monazite and

402   xenotime (e.g. Harlov et al., 2010, 2011; Hetherington et al., 2010, Williams et al., 2011)

403   and are commonly interpreted as the result of a fluid-mediated dissolution/re-

404   precipitation reaction. That formation of these textures is a common process in

405   (urano)thorites is also supported by only rare preservation of crystals from igneous rocks

406   that preserve 'igneous' textures such as oscillatory zoning.

407   Altered rims and intra-crystalline domains yield ages that are consistent with loss

408   of radiogenic Pb, with ages from altered domains typically ~11 – 15% younger than

409   pristine domains from the same samples. This radiogenic Pb-loss is consistent with the

410   results of experimental alteration studies of other phases such as monazite that have been

411   subjected to dissolution/re-precipitation processes (e.g. Seydoux-Guillaume et al., 2002;

412   Williams et al., 2011). In contrast, and despite complex intra-crystal zoning patterns, U-

413   Th/Pb geochronologic data retrieved for pristine domains in these samples is relatively

414   simple (see further discussion below) yielding single populations with no clear evidence

415   for disturbance in the U-Th/Pb isotope systems or multiple geologic events. It is clear that

416   in the studied samples, complex major and trace element zonation does not correlate to

417   age-differences, as commonly observed in other minerals such as monazite (e.g. Foster et

418   al., 2002).

419

Geochronology

420

421   Two samples, M33 and AD41, were analyzed by LA-ICPMS static spot analyses in

422   previous studies. In both cases, these data were normalized to Manangotry reference

423   monazite. However, given the matrix-effects associated with static spot analyses

424   identified in this work (Fig. 3), it is expected that these data are inaccurate. The

425   inaccuracy, which in this case is on the order of 10%, arises because the time-dependent

426   (down-hole) slope of the inter-element ratio(s) of the primary reference material is less

427   than that of the unknown. This leads to an under-correction of the down-hole

428   fractionation, which in turn results in an age that is apparently too old. This is further

429   supported by the observation that the Searle et al. (2007) LA-ICPMS date for M33

430   uranothorite (59.5 Ma) is ~10% too old compared to both the new LA-ICPMS data (54.0

431   Ma) presented here and the single ID-TIMS datum (~54 Ma) of Searle et al. (2007) (the

432   difference between LA-ICPMS and ID-TIMS data was previously interpreted by Searle

433   as Pb-loss in the ID-TIMS fraction).

434   There are no independent age constraints on the uranothorite from AD41, but the

435   existing AD41 date (15.8 Ma normalized to Manangotry reference monazite, Cottle et al.,

436   2009a) is also ~10% too old compared to the data (14.8 Ma) presented here, suggesting a

437   similar level of inaccuracy in the original data. These two samples illustrate the

438   importance of utilizing a matrix-matched reference material in order to produce accurate

439   LA-ICPMS (urano)thorite dates using a static spot, and that failing to do so results in

440   inaccuracies of at least 10% relative to the true age.

441

Concordance

442

443   Uranothorite analyzed in this study are consistently concordant in U/Pb space, both

444   within crystals (multiple spots on the same crystal) and between crystals in the same

445   rock. This has two key implications for the geochronology of uranothorite: 1) the lack of

446   'reverse discordance' suggests that both U decay chains have achieved secular

447   equilibrium and that there has been no gain of intermediate decay products such as ^{230}Th

448   and/or ^{231}Pa; 2) the lack of discordance in the U/Pb system in pristine crystal domains

449   strongly suggests that there as been minimal radiogenic Pb-loss and; 3) there is no

450   correlation between U/Pb dates and either crystal size or position within the crystal

451   suggesting no resolvable volume diffusion of daughter products. Thus, in contrast to the

452   work of von Blanckenburg (1992), uranothorites in this study have remained closed to U

453   and its decay products throughout their history and can be treated as a reliable high

454   temperature chronometer.

455   For thorite and huttonite only Th/Pb isotope ratios were measured, so there is no

456   test of concordance. However, the dated thorite and huttonite produce geologically

457   reasonable dates (see below) implying that there has been no gain or loss of parent,

458   intermediate or daughter isotopes in the ^{232}Th decay chain and therefore these minerals

459   also serve as useful chronometers.

460   In his pioneering work on reverse discordance in monazite, Schärer (1984 p.191)

461   stated that *"U-Pb ages of Th-rich minerals such as monazite (and allanite) have to be*

462   *corrected for excess ^{206}Pb due to excess ^{230}Th... the extent of this correction depends on*

463   *the degree of Th-U fractionation and on the age of the rock.".* Minerals such as monazite

464   strongly partition Th into their structure during crystallization and include significant and

465   variable amounts of ^{230}Th along with ^{232}Th such that the Th/U ratio of the monazite is

466   much greater than that of the magma from which it crystallized. ^{230}Th is an intermediate

467   daughter product of ^{238}U that decays to "unsupported" ^{206}Pb (e.g. Schärer 1984), resulting

468   in apparent ^{206}Pb/^{238}U ages that are reversely discordant or "too-old" with respect to

469   ^{207}Pb/^{235}U and ^{208}Pb/^{232}Th ages. The degree of excess ^{206}Pb can be significant, for

470   example Cottle et al. (2009) documented ~12 Ma Himalayan monazite with ^{206}Pb/^{238}U

471   ages up to 50% older than ^{207}Pb/^{235}U ages (for a constant ^{208}Pb/^{232}Th ratio).

472   In contrast to the common observation of 'excess ^{206}Pb' in monazite, no reverse

473   discordance was observed in uranothorite analyzed in this study.   This has two

474   fundamental implications for uranothorite geochronology. Firstly, the ^{206}Pb/^{238}U dates

475   obtained from uranothorite can be considered as reliable as either ^{207}Pb/^{235}U or

476   ^{208}Pb/^{232}Th ages. Secondly, since there is no apparent Th/U disequilibrium between the

477   uranothorite and the magma/fluid from which it crystallized. The Th/U ratio of the

478   uranothorite is therefore a good approximation of the bulk rock from which it

479   crystallized. In other words, the U and Th bulk rock / uranothorite partition co-efficient is

480   approximately 1. The latter is consistent with the observation of Parrish and Tirrul

481   (1989).

482

483   **Comparison to other chronometers**

484   Geochronology data exists from other accessory phases for three of the dated samples

485   (M33, H8 and P68787), thus offering the opportunity to compare (urano)thorite dates to

486   other mineral chronometers. M33 uranothorite (54.0 ± 0.4 Ma ^{206}Pb/^{238}U date and 53.9 ±

487   0.5 Ma ^{208}Pb/^{232}Th date) is within uncertainty of both ID-TIMS zircon (53.1 ± 0.2 Ma)

488   and uranothorite (54.1 ± 0.1 Ma) data of Searle et al., (2007). This suggests that the new

489 LA-ICPMS data are accurate with respect to the ID-TIMS thorite data and also consistent

490 with the existing zircon data. It seems reasonable to conclude that uranothorite from M33

491 can be confidently interpreted to accurately record the timing of igneous crystallization of

492 this leucogranite body. Uranothorite from H8 is equivalent to ID-TIMS uranothorite and

493 zircon from related rocks (e.g. H4 21.0 ± 0.5 Ma, Parrish and Tirrul, 1989) and is best

494 explained as recording the timing of magmatic crystallization of this sample. Zircons

495 from H8 are inherited, ranging in age from 635 Ma to 1750 Ma. In this rock, the

496 uranothorite (which does not show any sign of inheritance) provides as a robust record of

497 igneous crystallization whereas the zircon does not.

498   Uranothorite from P68787 (495 ± 6 Ma $^{206}Pb/^{238}U$ date and 492 ± 8 Ma

499 $^{208}Pb/^{232}Th$ date) lies well within uncertainty of zircon (502 ± 2.6 Ma, Hagen-Peter et al.

500 2011) from the same mineral separate, again suggesting that the uranothorite accurately

501 records crystallization of this igneous rock. Although this is a relatively small dataset

502 from which to compare, in each case the dated uranothorites yield ages that are consistent

503 with other high temperature chronometers such as zircon. This suggests that in igneous

504 rocks, uranothorite has the ability to accurately record the timing of melt crystallization

505 and is therefore of significant use, especially where zircon inheritance is prevalent.

506   The Gillespie's Beach detrital sample provides insight into the utility of thorite

507 and huttonite as provenance indicators. All brown thorite along with a significant portion

508 of the green thorites are essentially the same age at ~74 Ma (Fig. 6 and 7), implying that

509 these detrital crystals were derived from either a single lithologic source or from a suite

510 of rocks with a single-age population. The majority of green thorite analyses also yield

511 ~74 Ma dates, with a minor component of older, Cretaceous and Jurassic ages. In

512   contrast, huttonite yields ages ranging from 17 to 12 Ma. By comparison, detrital zircons

513   from the same mineral separate yields age peaks at ~260 Ma, ~380 Ma, ~480 - 550 Ma

514   and ~620 – 680 Ma.

515   All but one of the thorite analyses is significantly younger than the detrital zircons

516   analyzed from the same sample. The youngest concordant detrital zircon analysis (223 ±

517   4.2 Ma) overlaps within error of the oldest (209.4 ± 12.1 Ma) green thorite analysis (Fig.

518   8) implying that detrital thorite and huttonite has the potential to record provenance

519   information that the zircon does not. In this case, taking the detrital zircon signature in

520   isolation would lead to the erroneous conclusion that the source region(s) for this sample

521   did not experience any significant tectonic event(s) post ~220 Ma.

522   Accurately tracing the origin of the thorite in the Gillespie's Beach sample is

523   somewhat difficult given the diverse geologic history of the West coast of the South

524   Island. One key observation is that the multiple ~74 Ma thorite ages overlap with U/Pb

525   zircon and monazite ages from pegmatite dikes (Chamberlain et al., 1995; Batt et al.,

526   1999) and the host Alpine schist (Mortimer and Cooper, 2004) cropping out immediately

527   to the east of the Alpine fault (Fig. 8). In the absence of other comparable ages, the

528   Alpine pegmatite dikes and/or the host schist represent a probable source. The 17 – 12

529   Ma Huttonite from the Gillespie's Beach sample can potentially be related to either fluid-

530   assisted alteration associated with emplacement of carbonatites and associated rocks in

531   the Alpine Dike swarm (Cooper et al., 1987) and/or younger metamorphism/alteration of

532   the Alpine schist associated with uplift along the Alpine fault (Batt et al., 1999). The

533   remaining minor Mesozoic component to the thorite age spectra could equally be related

534   to plutonic and/or metamorphic rocks west of the Alpine fault (Western Province) (Hiess

535   et al., 2010), or a detrital component in the sedimentary protolith to the Alpine schist

536   (Fig. 8, e.g. Campbell et al., 2007; Adams et al., 2013).

537

538   **Implications**

539   This study demonstrates that a matrix-matched reference material is essential in order to

540   produce accurate U-Th/Pb (urano)thorite static spot dates by LA-ICPMS. Neither an

541   [X]SiO$_4$ matrix such as zircon or a high-Th phase such as monazite behave in a similar

542   manner to (urano)thorite in terms of ablation characteristics, and specifically with respect

543   to LIEF. Using a matrix-matched reference uranothorite, samples analyzed in this study

544   yield concordant U/Pb and Th/Pb ages that are consistent with other high-temperature

545   chronometers. Uranothorite, unlike other high-Th phases such as monazite, does not

546   appear to suffer from disequilibrium in the ^{238}U decay chain (i.e. 'excess ^{206}Pb') such that

547   ^{206}Pb/^{238}U dates can be considered reliable. Radiogenic-lead loss and/or metamictization

548   appears to be minimal and restricted to domains that have undergone significant fluid-

549   assisted alteration and/or hydration. The lack of pervasive alteration and metamictization

550   makes (urano)thorite a robust chronometer in igneous and metamorphic rocks. Detrital

551   thorite and huttonite has the potential to record significant provenance information that

552   can elucidate a variety of igneous, metamorphic and alteration processes in the source

553   terrane(s).

554

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560   by the National Science Foundation under Grant No. (NSF-EAR-1050043).

561

562   **Appendix – Analytical Methods**

563   *XRD:* Single crystal x-ray diffraction (XRD) patterns were made with a Kappa Apex II x-

564   ray diffractometer in the Chemistry Department at the University of California, Santa

565   Barbara.

566

567   *EPMA*: elemental maps and quantitative major and trace element analyses were made

568   using a Cameca SX-100 Electron Probe MicroAnalyzer (EPMA) housed at the University

569   of California, Santa Barbara. x-ray maps of U (LPET, Mα), Th (LPET, Mα), Y (LTAP,

570   Lα), and P (LPET, Kα) were made in beam scan mode using 15 keV accelerating voltage,

571   200 nA beam current (equating to a ~1 μm^3 interaction volume), and a dwell time of 25

572   ms. Quantitative analyses were performed on the same instrument. Operating conditions

573   were 40 degrees takeoff angle, accelerating voltage of 20 keV, 200 nA beam current and

574   a beam diameter of 5 μm. Elements were acquired using analyzing crystals LLIF for La

575   Lα, Nd Lα, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα,

576   Fe Kα, Sm Lα, LPET for Pb Mα, U Mα, Ce Lα, Ca Kα, Y la, Th Mα, and TAP for P Kα,

577   Si Kβ, Al Kα.

578   The standards were ThO2 for Th Mα, U-2 (10.00% UO_2 in diopside glass) for U

579   Mα, Anorthite (Grass Valley) U.C.#16706 for Al Kα, Diopside (Chesterman) for Si Kβ,

580   Ca Kα, Magnetite U.C. #3380 for Fe Kα, $CePO_4$ (USNM 168484) for Ce Lα, DyPO4

581   (USNM 168485) for Dy Lα, ErPO4 (USNM 168486) for Er Lα, EuPO$_4$ (USNM 168487)

582   for Eu Lα, GdPO$_4$ (USNM 168488) for Gd Lα, HoPO4 (USNM 168489) for Ho Lα,

583   LaPO4 (USNM 168490) for La Lα, P Kα, LuPO$_4$ (USNM 168491) for Lu Lα, NdPO$_4$

584   (USNM 168492) for Nd Lα, PrPO$_4$ (USNM 168493) for Pr Lα, SmPO$_4$ (USNM 168494)

585   for Sm Lα, TbPO$_4$ (USNM 168496) for Tb Lα, TmPO$_4$ (USNM 168497) for Tm Lα,

586   YbPO$_4$ (USNM 168498) for Yb Lα, YPO$_4$ (USNM 168499) for Y Lα, and Pyromorphite

587   (Cameca) for Pb Mα.

588   The counting time was 40 seconds for La Lα, Ce Lα, Nd Lα, Th ma, Pr Lα, Eu

589   Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Si Kβ, Sm Lα,

590   100 seconds for Al Kα, Pb Mα, 120 seconds for U Mα, 160 seconds for Y Lα, and 200

591   seconds for P Kα, Ca Kα. The off peak counting time was 40 seconds for La Lα, Ce Lα,

592   Nd Lα, Th Mα, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu

593   Lα, Fe Kα, Si Kβ, Sm Lα, 100 seconds for Al Kα, Pb Mα, 120 seconds for U Mα, 160

594   seconds for Y Lα, and 200 seconds for P Kα, Ca Kα. Off Peak correction method was

595   Linear for La Lα, Ce Lα, Nd Lα, Th Mα, P Kα, Pr Lα, Gd Lα, Ho Lα, Tm Lα, Yb Lα, Si

596   Kβ, Ca Kα, Y Lα, Sm Lα, and Multi-Point for Lu Lα, Pb Mα, U Mα, Fe ka, Eu Lα, Al

597   Kα, Er la, Tb Lα, Dy Lα.

598   Unknown and standard intensities were corrected for deadtime. Standard

599   intensities were corrected for standard drift over time. Interference corrections were

600   applied to La for interference by Nd, and to Nd for interference by Ce, and to Pr for

601   interference by La, Y, and to Eu for interference by Nd, Pr, and to Gd for interference by

602   Nd, Ce, La, and to Dy for interference by Eu, and to Ho for interference by Gd, Lu, and

603   to Er for interference by Tb, and to Tm for interference by Dy, Gd, and to Yb for

604   interference by Eu, Dy, Tb, and to Lu for interference by Dy, Ho, and to Pb for

605   interference by Y, and to U for interference by Th, and to Fe for interference by Dy, and

606   to Al for interference by Tm, Yb, Th, and to Ca for interference by Pb and Yb. See

607   Donovan et al., (1993) for detail.

608   Oxygen was calculated by cation stoichiometry and included in the matrix

609   correction. The matrix correction method was ZAF or Phi-Rho-Z Calculations and the

610   mass absorption coefficients dataset was LINEMU Henke (LBL, 1985) < 10KeV /

611   CITZMU > 10KeV. The ZAF or Phi-Rho-Z algorithm utilized was Armstrong/Love

612   Scott (Armstrong, 1988). Accuracy of unknown analyses was checked routinely using in

613   house natural monazite reference materials, synthetic ThO_2 and NIST SRM 610.

614

615   *LA-MC-ICPMS:* In-situ U-Th/Pb geochronology analyses were performed using a laser

616   ablation multi-collector inductively coupled plasma mass spectrometer (LA-MC-ICPMS)

617   at the University of California Santa Barbara (UCSB). Analytical methods follow Cottle

618   et al. (2012, 2013); and Kylander-Clark et al. (2013) and are briefly described here.

619   Instrumentation consists of an Analtye 193 nm ArF excimer laser (Photon Machines, San

620   Diego, USA) equipped with a HelEx two-volume sample cell (Eggins et al., 1998)

621   attached to a Nu Plasma HR MC-ICPMS (Nu Instruments, Wrexham, UK). The collector

622   array on the Nu Plasma is configured to simultaneously measure ^{238}U and ^{232}Th on two

623   high-mass side Faraday cups and ^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{204}X (where X includes ^{204}Pb

624   and ^{204}Hg) on four low-mass side secondary electron multipliers. Ablations were

625   conducted for 20 seconds each at 1.2 J/cm^2 or 1.5 J/cm^2 fluence (thorite, zircon), a

626   frequency of 4 Hz, and a pit diameter of 5μm or 20μm yielding craters ~3, or 9 μm deep

627   (as assessed by optical microscopy). Utilizing a sample–standard bracketing technique,

628   analyses of reference materials (RMs) with known isotopic composition were measured

629   before and after each set of seven unknown analyses. Data reduction, including

630   corrections for baseline, instrumental drift, mass bias, down-hole fractionation as well as

631   age calculations were carried out using Iolite v. 2.1.2 (Paton et al. 2010). Background

632   intensities and changes in instrumental bias were interpolated using a smoothed cubic

633   spline while down-hole inter-element fractionation was modeled using an exponential

634   function. Statistics for baselines, on peak intensities and isotopic ratios were calculated

635   using the mean with a 2.S.D. outlier rejection.

636

637   **Figure Captions**

638

639   **Figure 1.**

640   Representative Backscattered electron (BSE), Th, U, P, and Y x-ray Electron probe

641   microanalyzer (EPMA) maps of uranothorite (M33, AD41, H4, H8, P68787), thorite

642   (OU12321 and Gillespie Beach) and huttonite (Gillespie Beach) analyzed in this study.

643   Warmer colors are higher concentration relative to cooler colors. Scale bars are 50 µm.

644

645   **Figure 2.**

646   Representative Backscattered electron (BSE) images of typical alteration observed in this

647   study. A) inclusions of allanite and xenotime surrounded by altered uranothorite (sanple

648   M33) (location of image is shown in Fig. 1). B) patchy recrystallization (sample AD41),

649   C) (H4) and D) (H8) altered rim surrounding pristine uranothorite. Scale bars are 25 µm.

650

651 **Figure 3.**

652 Self-normalized ^{206}Pb/^{238}U (A) and ^{208}Pb/^{232}Th (B) ratios as a function of time (depth)

653 during ablation. Each line is an exponential curve fitted to the mean of 10 static spot

654 ablations of each material (see Paton et al., 2010 for details of curve fitting). Thorites all

655 have similar slopes whereas monazite and NIST Glass have different slopes, illustrating

656 the need to use a matrix-matched reference material for thorite analysis in static spot

657 mode LA-ICPMS.

658

659 **Figure 4.**

660 Pb/U Concordia and weighted mean ^{208}Pb/^{232}Th plots for uranothorite samples. Analyses

661 in blue were specifically sited over altered domains, and are not considered in the final

662 age determinations.

663 A-B) M33. ID-TIMS data from Searle et al. (2007) plotted for comparison. C-D) AD-41.

664 E-F) H8. G-H) P68787. Mean LA-ICPMS ^{206}Pb/^{238}U zircon date (red ellipse) obtained by

665 Hagen-Peter et al. (2011) plotted for comparison.

666

667 **Figure 5.**

668 Weighted mean ^{208}Pb/^{232}Th plot for OU16321 thorite. Analysis in grey was rejected from

669 final date determination.

670

671 **Figure 6.**

672 Weighted mean ^{208}Pb/^{232}Th plot for Gillespie Beach thorite and huttonite. Although from

673   a detrital sample, brown thorite has a Mean Squared Weighted Deviates (MSWD) of 1.4,

674   consistent with a single age population. Photos of representative grains show a clear color

675   difference between 'brown' and 'green' thorite as well as dark green huttonite. Scale bars

676   are 200 μm.

677

678   **Figure 7.**

679   Kernal Density estimate for Gillespie Beach thorite, huttonite and zircon from the same

680   mineral separate. Only zircon <5% discordant are plotted. The majority of thorite is

681   younger than the zircon, with only very minor overlap between the oldest thorite and the

682   youngest detrital zircon.

683

684   **Figure 8.**

685   Summary diagram of existing geochronology data from major geologic units on the West

686   coast of the South Island of New Zealand. The ~74 Ma green and brown thorite

687   population overlaps with U/Pb monazite and zircon ages from both Alpine pegmatites

688   and Alpine schis. Oldest huttonites overlap in age with the Alpine dike swarm. Minor

689   older components to the green thorite population overlap with detrital zircon from both

690   the Eastern and Western provinces. Data sources: 1: This study; 2: Cooper et al. (1987);

691   3: Batt et al. (1999); 4: Chamberlain et al. (1995); 5: Mortimer and Cooper (2004); 6: Vry

692   et al.,(2004); 7: Hiess et al. (2010); 8: Campbell et al. (2007) and Adams et al. (2013).

693

694   **Table 1.**

695   Summary of samples analyzed in thus study. Mineral abbreviations after Whitney and

696   Evans (2010). References: 1: Searle et al. (2007); 2: Cottle et al. (2009a); 3: Parrish and

697   Tirrul (1989); 4: Hagen-Peter et al. (2011); 5: White (1962); 6: Cooper (1971); 7: Cooper

698   et al. (1987); 8: Pabst and Hutton (1951); 9: Förster et al. (2000).

699

700   **Table 2.**

701   Electron probe microanalyzer data table.

702

703   **Table 3.**

704   U-Th/Pb isotope data for uranothorite. Notes: a) concentration data are normalized to the

705   primary reference material and are accurate to approximately 10%,   b) $^{207}Pb/^{235}U$

706   calculated assuming a natural $^{238}U/^{235}U$ ratio of 137.88. c) Rho value is calculated

707   following the method outlined in Paton et al., (2010).   d) Age calculations are based on

708   the U decay constants of Steiger and Jäger (1977) and the Th decay constant of Amelin

709   and Zaitsev (2002). Isotopic ratios and ages are not corrected for common-Pb.

710

711   **Table 4.**

712   Th/Pb isotope data for thorite and huttonite. bdl: beyond detection limit. a) concentration

713   data are normalized to the primary reference material and are accurate to approximately

714   10%,   b) Age calculations are based on Th decay constant of Amelin and Zaitsev

715   (2002). Isotopic ratios and ages are not corrected for common-Pb.

716

717   **Table 5.**

718   U/Pb isotope data for detrital zircon from Gillespie's Beach. *indicates rejected datapoint

719   (>5% discordance).   a) concentration data   are normalized to the primary reference

720   material and are accurate to approximately 10%. b) $^{207}Pb/^{235}U$ calculated assuming a

721   natural $^{235}U/^{238}U$ ratio of 137.88 c) Rho value is calculated following the method outlined

722   in Paton et al. (2010).   d) Age calculations are based on the U decay constants of Steiger

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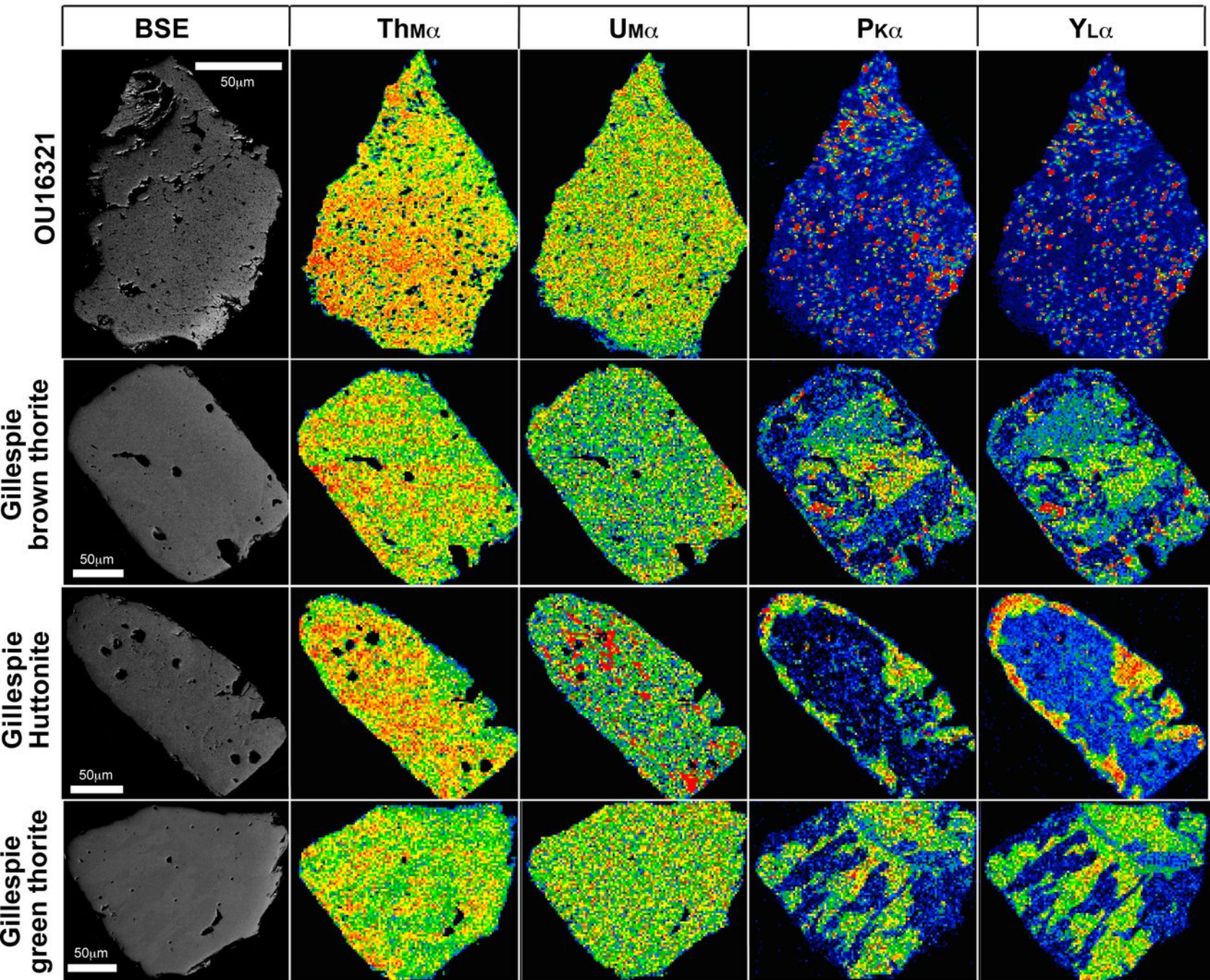
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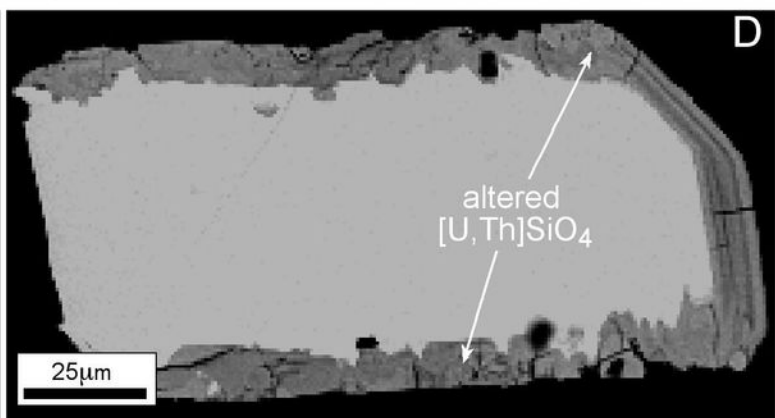
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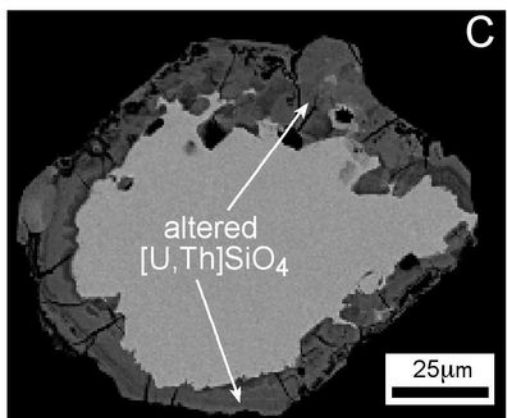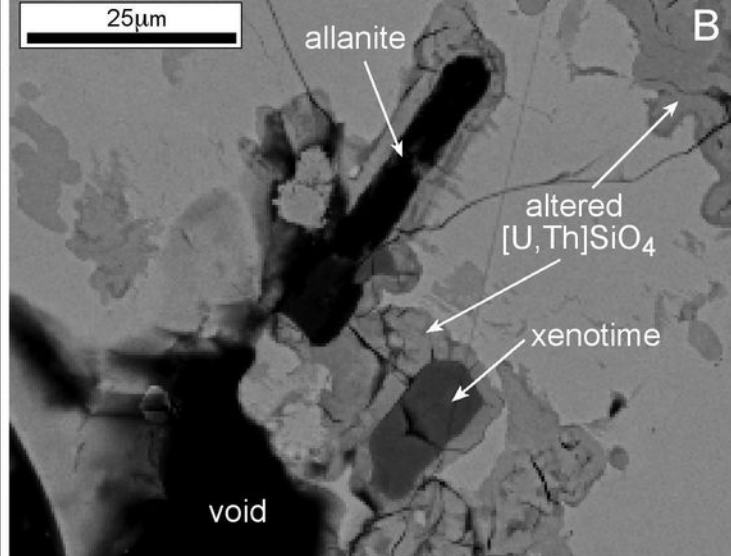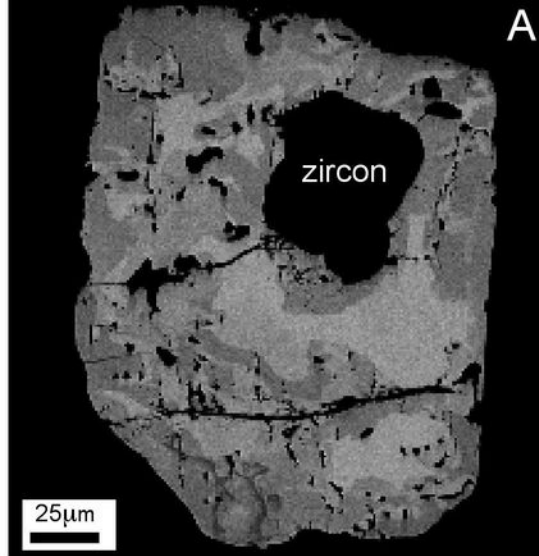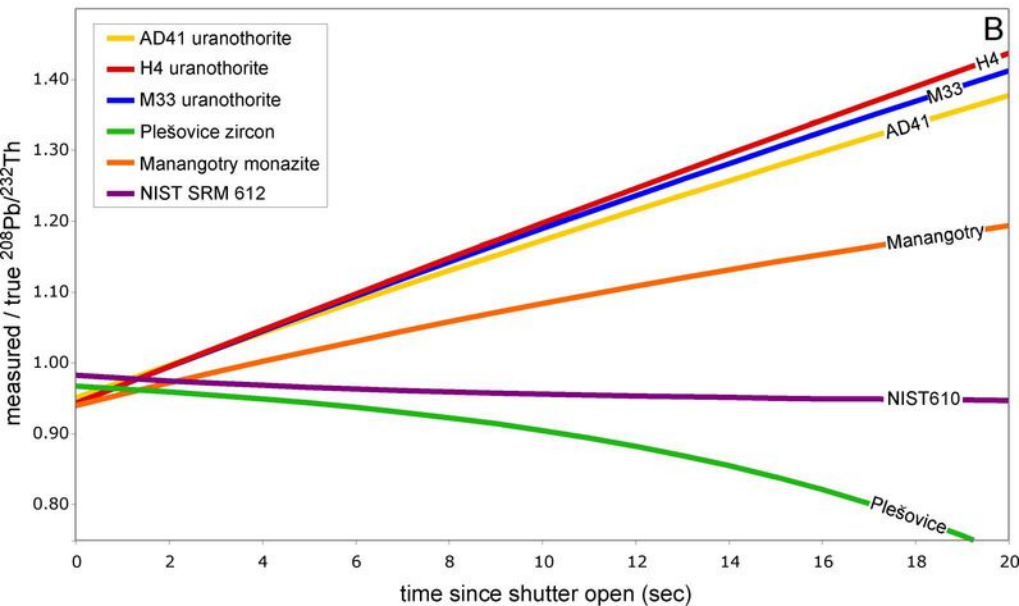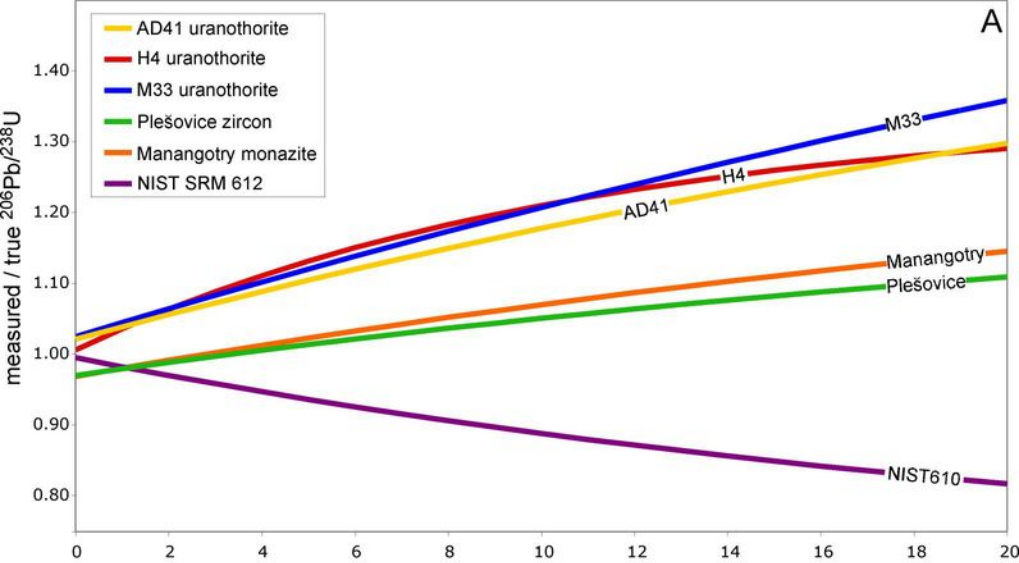924   Wiedenbeck, M., Allé, P., Corfu, F., Griffin, W.L., Meier, M., Oberli, F., Von-Quadt, A.,

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	BSE	ThMα	UMα	PKα	YLα

M33, AD41, H4, H8, P68787

area of Fig. 2b

relative concentration

low → high

	BSE	Th$_{M\alpha}$	U$_{M\alpha}$	P$_{K\alpha}$	Y$_{L\alpha}$
OU16321	50μm				
Gillespie brown thorite	50μm				
Gillespie Huttonite	50μm				
Gillespie green thorite	50μm				

relative concentration

low   high

A — M33 uranothorite. Tera-Wasserburg-style concordia diagram with axes $\frac{^{206}Pb}{^{238}U}$ (values 7.2×10⁻³, 7.6, 8.0, 8.4, 8.8) and $\frac{^{207}Pb}{^{235}U}$ (values 0.042, 0.046, 0.050, 0.054, 0.058). Reference points 50 and 58.

mean $^{206}Pb/^{238}U$ date = 54.0 ± 0.4 Ma, MSWD = 0.8, 0 of 22 rejected. ID-TIMS thorite, ID-TIMS zircon, altered domains.

B — M33 uranothorite. Axis $^{208}Pb / ^{232}Th$ date (Ma): 45, 47, 49, 51, 53, 55, 57, 59. Mean $^{208}Pb/^{232}Th$ date = 53.9 ± 0.5 Ma, MSWD = 1.3. altered domains.

C — AD41 uranothorite. Axes $\frac{^{206}Pb}{^{238}U}$ (1.8×10⁻³, 2.0, 2.2, 2.4, 2.6) and $\frac{^{207}Pb}{^{235}U}$ (0.011, 0.013, 0.015, 0.017). Reference points 13, 17.

mean $^{206}Pb/^{238}U$ date = 14.8 ± 0.1 Ma, MSWD = 1.9, 0 of 41 rejected. altered domain.

D — AD41 uranothorite. Axis $^{208}Pb / ^{232}Th$ date (Ma): 10, 11, 12, 13, 14, 15, 16. Mean $^{208}Pb/^{232}Th$ date 13.5 ± 0.1 Ma, MSWD = 3.7. altered domain.

E — H8 uranothorite. Axes $\frac{^{206}Pb}{^{238}U}$ (2.6×10⁻³, 3.0, 3.4, 3.8) and $\frac{^{207}Pb}{^{235}U}$ (0.016, 0.018, 0.020, 0.022, 0.024). Reference point 18.

mean $^{206}Pb/^{238}U$ date = 22.1 ± 0.2 Ma, MSWD = 2.7, 0 of 35 rejected. altered domains.

F — H8 uranothorite. Axis $^{208}Pb / ^{232}Th$ date (Ma): 18, 19, 20, 21, 22, 23. Mean $^{208}Pb/^{232}Th$ date = 21.4 ± 0.1 Ma, MSWD = 1.7.

G — P68787 uranothorite. Axes $\frac{^{206}Pb}{^{238}U}$ (0.075, 0.085, 0.095) and $\frac{^{207}Pb}{^{235}U}$ (0.6, 0.7, 0.8, 0.9). Reference points 500, 580.

mean $^{206}Pb/^{238}U$ date = 495 ± 6 Ma, MSWD = 1.2, 1 of 10 rejected. Mean $^{206}Pb/^{238}U$ zircon date = 502.1 ± 2.6 Ma.

H — P68787 uranothorite. Axis $^{208}Pb / ^{232}Th$ date (Ma): 460, 480, 500, 520, 540. Mean $^{208}Pb/^{232}Th$ date = 492 ± 8 Ma, MSWD = 1.4.

OU16321 thorite

Mean $^{208}Pb/^{232}Th$ date
= 19.7 ± 0.4 Ma
MSWD = 1.5
1 of 12 rejected

$^{208}Pb / ^{232}Th$ date (Ma)

Gillespie Beach ThSiO₄

208Pb / 232Th date (Ma)

Brown thorite

Mean ²⁰⁸Pb/²³²Th date
= 74.7 ± 0.4 Ma
MSWD = 1.4
2 of 75 rejected

200μm

Huttonite

200μm

Green thorite

208Pb / 232Th date (Ma)

Brown thorite

Green thorite

²⁰⁸Pb / ²³²Th date (Ma)

Green thorite

Gillespie Beach detrital zircon

Huttonite

Brown thorite

Date (Ma)

Green thorite[1]

Brown thorite[1]

Huttonite[1]

Alpine Dyke Swarm[2]

U-Pb zrn[3]

U-Pb mnz + zrn[4]

} Pegmatite

U-Pb mnz[5]

Sm/Nd Grt[5]

Sm-Nd+Lu-Hf Grt[6]

} Alpine Schist

Youngest Gillespie Beach DZ[1]

Youngest Western Province zrn+mnz[7]

Youngest Eastern Province DZ[8]

0   100   200   Date (Ma)

Sample	Location	sample description	Existing Date(s)	References
M33	Belin quarry, Myanmar (21.67969°, 96.14015°)	Qz+Pl+Kfs+Bt granite dike	ID-TIMS thorite: 54.1 ± 0.1 Ma LA-MC-ICPMS uranothorite: 59.5 ± 0.9 Ma	1
AD41	Kharta valley, Tibet (28.17738°, 87.35617°)	Qz+Pl+Kfs+Bt banded migmatitic augen gneiss	LA-MC-ICPMS thorite 15.8 ± 0.2 Ma	2
H4	Baltoro Glacier, Pakistan (35.7263°, 76.2878°)	monzogranite	ID-TIMS thorite: 21 Ma	3
H8	Baltoro Glacier, Pakistan (35.72176°, 76.24913°)	Kfs-megacrystic granite	ID-TIMS thorite ~16.5 Ma (discordant)	3
P68787	Hunt Glacier, Antarctica (-76.86603°, 162.34916°)	coarse-grained equigranular Hbl-monzodiorite	LA-MC-ICPMS zircon: 502.1 ± 2.6 Ma	4
OU163231	Gout Creek, New Zealand (-43.962712°, 169.29323°)	Dol+Ap+Ab+Thr+Rt carbonate-rich vein	-	5, 6, 7
Gillespie's Beach	Gillespie's Beach, New Zealand (-43.41131°, 169.79533°)	Mag+Sch+Zrn+Thr+Rt+Ap beach sand	EPMA total U-Th/Pb huttonite: 13.2 - 8.5 Ma EPMA total U-Th/Pb thorite: ~69 - 210 Ma	8, 9