Revision 1:

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

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Abstract

A Laser-Ablation-Multi-Collector-Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICPMS) study of seven thorite and uranothorite [(Th,U)SiO₄] samples ranging in age from ~13 to ~500 Ma provides new insights into the U-Th/Pb isotope systematics of these geologically significant, high-Th mineral species. Despite extreme actinide enrichment and complex intra-crystal zonation in actinides and rare earth elements, this study demonstrates that radiogenic-lead loss and/or metamictization is minimal and restricted to domains that have undergone significant hydration. Dating of four igneous uranothorites yields ages that are concordant in U/Pb and Th/Pb space, consistent with other high-temperature chronometers, and are inferred to accurately reflect the timing of crystallization of each rock. Similarly, Th/Pb ages of three thorite and/or huttonite-bearing samples yield geologically plausible dates consistent with other mineral chronometers. No evidence of isotopic inheritance was observed in any of the samples. Data presented here demonstrate for the first time the feasibility of extracting accurate and precise U/Pb and Th/Pb ages from Phanerozoic thorite, uranothorite and huttonite using LA-MC-ICPMS at the 5µm spatial resolution. These phases have the potential to be robust chronometers in igneous and metamorphic rocks as well as to provide...
important provenance information complementary to more widely used minerals such as detrital zircon.

Keywords: Thorite, Uranotherite, Huttonite, Laser Ablation, Geochronology
Introduction

The tetragonal orthosilicate thorite [ThSiO$_4$] and its monoclinic polymorph huttonite occur in a wide variety of geological environments ranging from (but not restricted to) felsic igneous rocks (Parrish and Tirrul, 1989, Hetherington and Harlov, 2008), metasediments (e.g. Speer, 1982), base metal ore deposits (e.g. Ifill et al., 1989) and fault zones (Kamineni and Lemire, 1991). Thorite may be either primary, or form by the breakdown of other Th-rich minerals such as allanite, monazite or zircon (Hetherington and Harlov, 2008). Its variable occurrence, combined with an ability to accommodate large amounts of U and Th within its structure makes it a potentially useful chronometer to quantify the timing and duration of a diverse range of geological events.

In pursuit of this goal there have been several attempts to date (urano)thorite using either Electron probe microanalyzer (EPMA) (Parslow et al., 1985; Enami et al., 1993; Förster et al., 2000; Jercinovic et al., 2002; Cocherie and Legendre, 2007) or Thermal Ionization Mass Spectrometry (ID-TIMS) (e.g. Henjes-Kunst, et al., 1988; Parrish and Tirrul, 1989; von Blanckenburg, 1992). The former method has generally met with limited success, which these authors attribute to thorite’s often metamict state and its susceptibility to hydration and associated radiogenic lead loss. ID-TIMS has been used in at least two published studies. Parrish and Tirrul (1989) analyzed uranothorite along with zircon and monazite in monzogranite from the Karakoram granite in northern Pakistan (see below for further details). They obtained three nearly concordant zircon analyses and two duplicate fractions of uranothorite that together yielded a mean U/Pb age of 21.0 ± 0.5 Ma. Monazites from the same rock were reversely discordant with ages ranging between 17 and 19 Ma which Parrish and Tirrul (1989) postulated was the result of slow cooling,
persistence of high temperatures following crystallization, and partial lead loss in monazite, none of which apparently affected the thorite. Von Blanckenburg (1992) analyzed allanite, sphene, apatite and thorite from a granodiorite of the Central Alpine Bergell intrusion (central Europe). They argued that both the allanite and sphene lacked inheritance and were magmatic in origin. The mean age of the allanite and sphene (30.12 ± 0.17 Ma) was interpreted as the timing of granodiorite intrusion. A single grain thorite fraction yielded a concordant U/Pb age of 28.36 Ma and Th/Pb age of 27.6 Ma. The younger thorite U/Pb age relative to the allanite – sphene age was inferred to be a result of recrystallization and the ~3% discrepancy between U/Pb and Th/Pb ages of the thorite resulted from Th gain, U loss, or 208Pb loss from strongly 232Th-enriched domains (Von Blanckenburg, 1992). These two isotopic studies highlight the possibility of obtaining U/Pb and/or Th/Pb dates from (urano)thorite. However, significant questions still remain about the interpretation of (urano)thorite dates relative to other high temperature chronometers such as zircon, monazite, sphene and allanite. The cause and significance of the disequilibrium between the Th/Pb and U/Pb systems in thorite identified by Von Blanckenburg (1992) also remains unresolved. In addition, although often described as occurring within clastic sediments, the utility of (urano)thorite and huttonite as indicators of sedimentary provenance remains untested.

In this contribution, the U/Pb and Th/Pb isotope systematics of (urano)thorite and huttonite are explored by combining EPMA elemental mapping with recently developed in-situ Laser Ablation micro-sampling techniques, which allow simultaneous acquisition of U, Th, and Pb isotopes from small volumes of ablated material. The method employed
here (Laser-Ablation-Multi-Collector- Inductively Coupled Plasma Mass Spectrometry, LA-MC-ICPMS) affords high spatial resolution (~5 µm diameter pits) and enables the chemistry and morphology of a grain to be directly related to its isotopic age.

The majority of U/Pb and Th/Pb data presented here are concordant, with no evidence of disequilibrium between isotope systems. Alteration and associated radiogenic lead-loss is volumetrically minor and restricted to obviously altered domains. Dates obtained from igneous uranothorite are consistent with other high temperature chronometers (e.g. zircon), whereas detrital thorite and huttonite yield complementary information about geologic source regions not recorded by detrital zircon from the same sample.

Sample Descriptions

Geologically well-constrained samples were chosen for this study, including three samples for which complementary geochronological data already exists (See Table 1 for summary of samples analyzed). Further, five of the samples (M33, AD41, H4, H8 and P68787) have similar chemistry and petrogenetic origin, enabling more direct inter-sample comparisons on the behavior of Th-rich minerals formed during crustal anatexis.

M33

Sample M33 is from the high-grade Mogok Metamorphic Belt (MMB), an arcuate zone that extends from the eastern Himalayan syntaxis in the north, through the Indo–Burman Ranges to the Andaman Sea in the south. The geological setting and tectonic significance of M33 is discussed in detail by Searle et al. (2007) and described briefly here. M33 is an undeformed quartz + plagioclase + K-feldspar + biotite granite dike with a weak flow
banding fabric, collected from Belin Quarry in the central Burmese part of the MMB (Searle et al. 2007, their Figs. 4 and 5b; Table 1). Accessory phases are dominated by zircon, apatite and uranothorite. Petrological data suggest that this is an S-type leucogranite that formed by muscovite dehydration melting of a mid-crustal pelitic assemblage following crustal thickening associated with the collision of India and Asia (Searle et al., 2007). A single grain concordant ID-TIMS zircon fraction yielded a $^{206}\text{Pb}/^{238}\text{U}$ date of 53.1 ± 0.2 Ma and a single grain thorite has a $^{207}\text{Pb}/^{235}\text{U}$ age of 54.1 ± 0.1 Ma. In addition, seven U/Pb LA-MC-ICPMS spot analyses on uranothorite, normalized to primary reference material Manangotry monazite yield a $^{206}\text{Pb}/^{238}\text{U}$ - $^{207}\text{Pb}*/^{235}\text{U}$ concordia age of 59.5 ± 0.9 Ma, (MSWD of concordance = 0.97). The authors inferred the ~6 Ma discrepancy between the ID-TIMS and LA-MC-ICPMS ages to reflect Pb-loss in both ID-TIMS zircon and thorite fractions and concluded that the $^{207}\text{Pb}*/^{235}\text{U}$ LA-MC-ICPMS thorite concordia age of 59.5 ± 0.9 Ma provided the best estimate of the magmatic crystallization age of M33 (Searle et al., 2007, their Figure 8g). This sample was selected for its well-constrained geologic context and available U/Pb ID-TIMS and LA-MC-ICPMS data for both zircon and uranothorite (Searle et al., 2007).

**AD41**

AD41 is a migmatitic augen gneiss from a section of the Greater Himalayan series (GHS) crops out on the east side of the Phung Chu river in the Kharta valley of south Tibet (Cottle et al., 2009a, their Figs. 2 and 4b; Table 1). The GHS in this region is a 30-km-thick sequence of metamorphic and anatectic rocks that form the high-grade core of the orogen. Sample AD41 is a distinctly banded, mylonitic augen gneiss with a well-
developed foliation defined by laths of biotite and fibrolite. The restitic portion of the rock is composed of biotite, sillimanite, quartz, plagioclase and K-feldspar, while the cm-thick, syn-kinematic leucogranitic leucosomes comprise aggregates of K-feldspar, quartz and rare biotite. Accessory phases are dominated by zircon, apatite and uranothorite, with the latter restricted to the leucosomes. The leucosomes are interpreted to have formed as a result of in-situ partial melting of the host meta-granitoid (Cottle et al., 2009a). U/Pb dating of zircons from AD41 yield an age of 440 ± 6 Ma, interpreted as the crystallization age of the protolith granitoid (Cottle et al., 2009a). This age is comparable to other gneisses within the GHS in the Everest region some ~60 km to the east, e.g. the Namche orthogneiss (Viskupic and Hodges, 2001). Eight U/Pb LA-ICPMS analyses of uranothorite (normalized to a primary reference Manangotry monazite) yielded a mean 206Pb/238U date of 15.8 ± 0.2 Ma (MSWD 0.9, n=8) (Cottle et al. 2009a their Fig. 7f).

### H4 and H8

Sample H4 is an S-type monzogranite from the south side of the Baltoro Glacier Valley, eight km NNW of Masherbrum peak in the Karakoram region of northern Pakistan. Sample H8 is a megacrystic K-feldspar granite collected from 3 km NW of Bialo peak (Parrish and Tirrul, 1989 their Fig. 1; Table 1). Both samples are from the Baltoro granite, part of the Cretaceous–Miocene composite Karokoram Batholith of the northwest Himalaya (Parrish and Tirrul 1989; and references therein). The geology and accessory phase geochronology of H4 and H8 is described by Parrish and Tirrul (1989) and references therein. Zircon data for H8 are all highly discordant with 207Pb/206Pb apparent dates ranging from 635 Ma to 1750 Ma. One uranothorite fraction is reversely discordant.
with an inferred date of \(~16.5 \text{ Ma}\), whereas monazites are \(~18 \text{ Ma}\). Two fractions of uranothorite (a total of six crystals) from H4 yield an ID-TIMS $^{206}\text{Pb} / ^{238}\text{U}$ age of $21.3 \pm 0.1 \text{ Ma}$ (U $\sim 10300 \text{ ppm}$, Pb $\sim 990 \text{ ppm}$, Pb $^{206}\text{Pb} / ^{238}\text{U} = 0.0033 \pm 0.3\%$, $^{207}\text{Pb} / ^{206}\text{Pb} = 0.0463 \pm 0.4\%$, $^{208}\text{Pb} / ^{232}\text{Th} = 0.00104 \pm 0.5\%$, Parrish and Tirrul 1989). These geologically well-constrained samples were selected for further analysis because of the published U/Pb ID-TIMS ages for H4 derived from uranothorite and zircon and monazite. For this study uranothorite was picked from the same mineral separates used by Parrish and Tirrul (1989).

**P68787**

P68787 is a coarse-grained equigranular hornblende monzodiorite from the Hunt Glacier in the Dry Valleys region of Antarctica (from the Geological and Nuclear Science, Dunedin, New Zealand Collection, kindly provided by A. Tulloch). This sample is part of the Granite Harbor Intrusives, an extensive suite of dominantly calc-alkaline mid-crustal magmatic rocks formed during the Neoproterozoic–Ordovician Ross orogeny. Zircon from this sample has a mean $^{206}\text{Pb} / ^{238}\text{U}$ LA-MC-ICPMS date of $502.1 \pm 2.6 \text{ Ma}$ (Hagen-Peter et al. 2011; Table 1). For this study uranothorite was picked from the same heavy mineral separate as used by Hagen-Peter et al. (2011).

**OU-16321**

OU-16321 from the University of Otago, Dunedin, New Zealand Collection is from a 1- to 2-cm-thick carbonate-rich vein containing, in approximate order of abundance, ferroan dolomite, magnesian dolomite, apatite, albite, reddish-brown thorite crystals up to 2-mm-
long, and Nb-rutile (Table 1, White, 1962; Cooper, 1971). This rock comes from Gout Creek, Haast River, in the South Island of New Zealand and occurs as part of a lamprohyric dike-swarm with carbonatitic affinities. Previous geochronology on associated rocks yields U/Pb primary magmatic crystallization zircon ages ranging from 24.6 – 24.1 Ma (Cooper et al., 1986).

Gillespie’s Beach ThSiO₄

Thorite, huttonite, zircon and rutile were extracted from a heavy mineral concentrate collected from Gillespie’s Beach, on the West coast of the South Island, New Zealand. The heavy mineral concentrate is dominated by magnetite but also contains minor amounts of scheelite, zircon, thorite, huttonite, rutile, and apatite. Thorite from Gillespie’s Beach occurs in brown and green varieties while huttonite was distinguished from thorite primarily by x-ray diffraction (XRD). Gillespie’s Beach is significant because it is the type locality for huttonite originally described in detail by Pabst and Hutton (1951). Förster et al. (2006) used the EPMA total U-Th/Pb method to obtain Miocene dates for huttonite and dates ranging from late Triassic–early Jurassic to early Tertiary for thorite (Table 1).

Methods

Uranotherites were separated using standard crushing, heavy liquid, and isodynamic magnetic separation techniques. A representative crystal from each sample was subjected to XRD to confirm whether it was tetragonal thorite or a Th-silicate dimorph, e.g. huttonite (monoclinic [(Th,U)SiO₄]. Although only weak thorite diffraction patterns were
generated, they confirm that each crystal has a tetragonal crystal system with average \( n = 8 \) unit cell dimensions: \( a = b = 7.18 \) (3) Å \( c = 6.09 \) (4) Å, \( a : c = 1: 0.848 \) and a cell volume of \( v = 314 \) Å\(^3\) (calculated from Unit Cell).

Grains representative of the variation in population morphology were handpicked in ethanol and mounted in one-inch diameter epoxy resin discs, polished to reveal equatorial sections, then carbon-coated. To elucidate zonation and/or alteration patterns, identify inclusions within grains, and to aid positioning of spots for later isotope analysis such that multiple domains/or altered areas were avoided, backscattered electron (BSE) maps were produced using a FEI Quanta400F scanning electron microscope (SEM). In addition, elemental maps of U, Th, Y and P were made using a Cameca SX-100 EPMA housed at the University of California, Santa Barbara (UCSB). Quantitative major and trace element analyses were performed using the same EPMA. Detailed EPMA analytical methods are presented in Appendix 1 and data are presented in Table 2.

After EPMA mapping and analysis, U, Th, and Pb isotopes were collected from carefully selected sites using a LA-MC-ICPMS housed at UCSB. Analytical methods follow Cottle et al. (2012, 2013) and Kylander-Clark et al. (2013). A detailed analytical method is presented in Appendix 1 and data are presented in Table 3 (uranothorite), Table 4 (thorite and huttonite) and Table 5 (detrital zircon). For thorites, the ‘H4’ uranothorite (Parrish and Tirrul, 1989) served as the matrix-matched primary reference material (RM) to monitor and correct for mass bias, as well as Pb/U and Pb/Th down-hole fractionation (see below for further detail on matrix-matching). No Pb/Th age data exist for H4 (or any of the samples analyzed in this study), therefore for normalization purposes, the Pb/Th and Pb/U systems for H4 were assumed to be concordant. Since no
secondary thorite RM currently exists, two zircon reference materials (‘91500’ and ‘GJ-1’) were analyzed concurrently as an external monitor of instrument performance. For zircon analyses, ‘91500’ (1062.4 ±0.4 Ma \(^{206}\text{Pb}/^{238}\text{U}\) ID-TIMS age, Wiedenbeck et al. 1995) was employed as the primary RM. To monitor data accuracy, a secondary reference zircon ‘GJ-1’ (608.5 ± 0.4 Ma \(^{207}\text{Pb}/^{206}\text{Pb}\) ID-TIMS age, Jackson et al. 2004) was analyzed concurrently (once every seven unknowns) yielding a weighted mean \(^{206}\text{Pb}/^{238}\text{U}\) age of 600.5 ± 1.6, MSWD = 1.5, n = 28. Data reduction, including corrections for baseline, instrumental drift, mass bias, down-hole fractionation as well as age calculations were carried out using Iolite v.2.1.2 (Paton et al. 2010). Background intensities and changes in instrumental bias were interpolated using a smoothed cubic spline while down-hole inter-element fractionation was modeled using an exponential function. Statistics for baselines, on peak intensities and isotopic ratios were calculated using the mean with a 2 S.D. outlier rejection. Concordia and weighted mean date plots were calculated in Isoplot v.3 (Ludwig 2003) using the \(^{238}\text{U}\) and \(^{235}\text{U}\) decay constants of Steiger and Jäger, (1977) and the \(^{232}\text{Th}\) decay constant of Amelin and Zaitsev (2002). All uncertainties in data tables and concordia plots are quoted at the 2σ confidence level.

**Results**

**(urano)thorite morphology and zoning**

Igneous (urano)thorite in this study are generally doubly-terminated, euhedral to subhedral, green to brown translucent crystals that range from short 2:1 (length:width aspect ratio) to elongate (5:1). Integrating information from U, Th, Y, and P x-ray maps and BSE images (Figs. 1 and 2) reveals a variety of internal structures, zoning and
alteration patterns. Many samples show one or more generations of cuspate-lobate or crosscutting flame and tongue structures (e.g. M33, AD41, Gillespie huttonite and thorite, Fig. 1). These crystals have a patchy appearance in BSE, suggestive of multiple episodes of intra-crystal dissolution, re-precipitation and/or intergrowth and amalgamation of smaller grains.

Less commonly, samples show either minimal internal zoning in U, Th, Y, or P (e.g. H4, H8, Fig. 1) or have oscillatory zoning (e.g. P68787, Fig. 1) analogous to textures observed in igneous zircon. Relict oscillatory zoning subsequently overprinted by recrystallization textures is occasionally preserved in brown thorites from the Gillespie’s Beach sample (Fig. 1). In the Gillespie’s Beach sample, crystals typically display minor patchy zoning in Th, U, P, and Y but also contain numerous inclusions of xenotime (red spots in P and Y maps) along with minor, and much smaller, apatite and monazite.

In addition to alteration, many of the grains examined from each sample contain inclusions of zircon (Fig. 2a). Intergrowths of these two minerals were not observed and in most cases the thorite appears to have nucleated around zircon. Less common inclusions of quartz, K-feldspar, allanite and xenotime were also observed (Fig. 2b).

**Alteration**

All grains display some degree of alteration, and this potentially has significant impacts on the isotopic age of (part of) a crystal. Optically, some crystals contain visible orange discoloration zones. In BSE, this is manifested as either thin (1-20 µm) (H4 and H8) or discontinuous (in M33 and AD41) rims (Fig. 1, 2c, 2d). In all cases, the altered domain is
darker in BSE, lower in Th, Si, Pb and U and higher in P, Ca, Fe, Y and (OH, calculated from stoichiometry) suggesting that these regions have probably undergone hydrous alteration to thorogummite [(Th,U)(SiO4)1-x(OH)4x].

Alteration occurs as irregular domains along cracks adjacent to fractures, at the contact with inclusions, and as large internal portions of the grain. A particularly good example of internal alteration occurs in a crystal from M33 (Fig. 1 and Fig. 2b). This crystal shows an alteration zone that is darker in BSE, lower in U, Th and Pb and higher in Y and P than the rest of the grain. The altered zone contains inclusions of high Th and U (1.5 wt% ThO2 and 1.3 wt% UO2) xenotime (the red spots in the Y and P maps). In addition, although the alteration zone itself (as defined by the higher Y + P domain) is associated with a significant depletion in U, the area immediately surrounding the alteration is enriched in U relative to the unaltered portion of the crystal (Fig. 2b) suggesting some decoupling of U and Th. Another form of alteration locally occurs in many of the samples, but is best illustrated in sample OU16321. Crystals typically display minor patchy zoning in Th, U, P and Y and contain numerous inclusions of xenotime (red spots in P and Y maps) along with minor, and much smaller, apatite and monazite (Fig. 1).

Mineral Chemistry

The chemistry of the investigated uranothorites is relatively consistent both within and between samples (Table 2). Thorium is the dominant cation (52.1 – 57.8 wt% ThO2), with lesser amounts of U (18.5 – 26.2 wt% UO2), Si (16.1 – 17.4 wt% SiO2), P (0.4 – 1.4
wt% P₂O₅) and Y (0.4 – 1.9 wt% Y₂O₃) and Pb (0.3 – 0.5 wt% PbO). Thorites have more Th, P, Y, and REE and less U than uranothorites.

For the unaltered domains, totals are consistently ~96–98% with cation proportions in approximately the correct stoichiometry for ThSiO₄. Totals less than 100% for thorite are commonly reported in the literature and, as outlined in detail by Förster (2006), may potentially be related to one or more of: 1) the presence of absorbed molecular water or hydroxyl substituted for silica; 2) the presence of elements not included in the analytical routine; and 3) presence of uranium(VI) oxide.

Because of their thin and irregular nature, only a few altered regions of crystals in M33, AD41, H4 and H8 could confidentially be targeted with the EPMA (Table 2). Analytical totals (~77 – 88%) are much lower than the pristine domains, suggesting that these domains may contain a significant proportion of OH. This issue notwithstanding, altered domains tend to be lower in U, Th, Pb and Fe and higher in Si, Ca, P and occasionally REE.

U-Th/Pb Isotope data

Matrix-matched reference material for LA-ICPMS

During LA-ICPMS isotopic analysis a major source of uncertainty is the time-dependent fractionation of elements as a result of the ablation process. Fractionation, defined as the change in measured element (isotope) ratio signals with time (Fryer et al., 1995), is a poorly understood process. However, for a given set of analytical conditions, fractionation occurs as a result of differential vaporization and mobilization of ablated particles. Of particular importance to this study is Laser-Induced Elemental Fractionation (LIEF), a well-documented effect observed in previous U-Th/Pb geochronologic studies (e.g. Hirata and
Nesbitt, 1995; Horn et al., 2000; Kosler et al., 2001, Paton et al., 2010). The degree of LIEF is controlled by the way the laser interacts with the sample (absorption characteristics) as well as the sample’s chemical composition. The net result is that geologic materials with different structural properties and chemical compositions produce substantially different time-dependent fractionation profiles. The majority of LA-ICPMS geochronologic studies that employ a static spot (rather than a dynamic raster) use a sample-standard bracket approach and assume that sample and reference material fractionate in a similar manner. Therefore, any difference in time-dependent fractionation profile between sample and primary reference material potentially leads to introduction of considerable uncertainty into the analysis.

No well-characterized (urano)thorite LA-ICPMS reference material currently exists, therefore in this study a series of experiments were conducted to assess if a similar framework matrix (e.g. XSiO$_4$ such as zircon) or a matrix with a similar actinide content (e.g. a high-Th phase such as monazite) could be employed to accurately correct for LIEF in (urano)thorite, or if a matrix-matched reference material is necessary to generate accurate data in static spot mode.

Three uranothorites along with Manangotry monazite [552.9 Ma $^{206}$Pb/$^{238}$U, 554 Ma $^{207}$Pb/$^{206}$Pb ID-TIMS ages, (Horstwood et al., 2003)], Plešovice zircon [337.13 ± 0.37 Ma $^{206}$Pb/$^{238}$U ID-TIMS age, (Sláma et al., 2008)] and NIST SRM610 glass were analyzed. So as not to saturate the secondary electron multipliers, a relatively small static spot size (5μm diameter pit) and low fluence (1.2 J/cm$^2$) was employed. H4 data was normalized to the ID-TIMS values of Parrish and Tirrul (1989). The reference ages of M33 and AD41 were taken from Searle et al. (2007) and Cottle et al. (2009a), respectively. As outlined below, the age of AD41 reported by Cottle et al. (2009a) may
be inaccurate by as much as 10%, however this level of uncertainty has negligible affect
on the shape and position of the curves in Figure 3. Each sample was inferred to be
concordant in U/Pb and Th/Pb space and Th/Pb normalization values were derived from
U/Pb data.

Figure 3 shows exponential curves fitted to the mean of 10 repeat static spot
ablations of the various samples. In both U/Pb and Th/Pb space, the uranothorites have a
very similar fractionation trend, implying they ablate in a very similar manner. However,
this trend is significantly different from monazite, zircon, or NIST610. In U/Pb space, the
monazite and zircon have a much lower degree of fractionation while NIST610 has a
negative fractionation slope. In Th/Pb space the monazite, zircon, and NIST610 all have
significantly different fractionation slopes. It is clear from Figure 3 that a matrix-matched
reference material is necessary to accurately model and correct for $^{206}\text{Pb}/^{238}\text{U}$ and/or
$^{208}\text{Pb}/^{232}\text{Th}$ fractionation in the unknowns when a static spot is employed. Based on this
conclusion, the $^{206}\text{Pb}/^{238}\text{U}$ and/or $^{208}\text{Pb}/^{232}\text{Th}$ (urano)thorite and huttonite data presented
below are all normalized to H4 as the concurrently analyzed primary reference material.

M33

For this study, an additional 25 LA-MC-ICPMS spot analyses were carried out on
uranothorite grains from the same mineral separate as Searle et al. (2007). Twenty-two of
the analyses are concordant in U/Pb and Th/Pb space yielding a weighted mean
$^{206}\text{Pb}/^{238}\text{U}$ date of 54.0 ± 0.4 Ma (MSWD 0.8), and a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date of
53.9 ± 0.5 Ma (MSWD 1.3) (Fig. 4A-B, Table 3). Three additional analyses deliberately
placed over altered domains yield younger apparent $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ dates of
~48 Ma, consistent with radiogenic lead loss.

**AD41**

Forty-one new analyses from six grains were collected as part of this study, with forty analyses yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of $14.8 \pm 0.1$ (MSWD 1.9) and a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date of $13.5 \pm 0.1$ (MSWD 3.7) (Fig. 4 C-D, Table 3). One spot deliberately placed over an altered domain gives an apparent date of ~11 Ma.

**H8**

Thirty-five analyses conducted during this study yield a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of $22.1 \pm 0.2$ Ma (MSWD 2.7), and a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date of $21.4 \pm 0.1$ Ma (MSWD 1.7) (Fig. 4E-F, Table 3). Two additional analyses deliberately placed over altered domains yield younger apparent dates of ~18.5-20 Ma, consistent with radiogenic lead loss.

**P68787**

Ten analyses from five grains yield a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of $495 \pm 6$ Ma (MSWD 1.2), and a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date of $492 \pm 8$ Ma (MSWD 1.4) (Fig. 4G-H, Table 3). One analysis was rejected as it contains a significant amount of common-lead, likely from partial ablation of an inclusion.

**OU-16321**
Twelve analyses from five grains yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date of 19.7 ± 0.4 Ma (MSWD 1.5). A single analysis on an altered domain gives an apparent date of ~17 Ma (Fig. 5, Table 4). The number of analyses is relatively small since only areas that were determined to be free of (the numerous) xenotime inclusions were measured.

**Gillespie’s Beach ThSiO$_4$ and Zircon**

Analysis of 75 individual crystals of brown thorite from the Gillespie’s Beach mineral separate yield consistent dates of ~75 Ma (Fig. 6, Table 4). Although not strictly valid for detrital samples, taking a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ date gives 74.7 ± 0.4 Ma (MSWD 1.4). The MSWD of near unity indicates the possibility that these crystals were sourced from a rock or suite of rocks with a single age population. Analyses of 79 individual crystals of green thorite yield $^{208}\text{Pb}/^{232}\text{Th}$ dates ranging from 210 Ma to 23 Ma with a prominent age peak at ~75 Ma (Fig. 6, Table 4). Analysis of five huttonite grains yields dates ranging from 17 to 12 Ma (Fig. 6, Table 4). These dates are broadly similar to total U-Th/Pb ages obtained by Förster et al. (2000) using the EPMA. Analysis of 100 detrital zircons from the same mineral separate yields age peaks at ~260 Ma, ~380 Ma, ~480 – 550 Ma, ~620 – 680 Ma and a minor component of Proterozoic and Achaean ages (Fig. 7, Table 5).

**Discussion**

**Mineral Chemistry and Alteration**

The first key observation from the detailed x-ray imaging carried out in this study is that the vast majority of both thorite and uranothorite crystals are internally zoned in both
major (U, Th) and trace (Y, P, REE) elements. Intra-crystalline zoning takes multiple forms, but is commonly manifested as patchy textures that are consistent with one or more episodes of fluid-mediated intra-crystal dissolution, re-precipitation and/or intergrowth and amalgamation of smaller grains. Such textures have previously been described from other minerals such as apatite (e.g. Harlov et al. 2005), monazite and xenotime (e.g. Harlov et al., 2010, 2011; Hetherington et al., 2010, Williams et al., 2011) and are commonly interpreted as the result of a fluid-mediated dissolution/re-precipitation reaction. That formation of these textures is a common process in (urano)thorites is also supported by only rare preservation of crystals from igneous rocks that preserve ‘igneous’ textures such as oscillatory zoning.

Altered rims and intra-crystalline domains yield ages that are consistent with loss of radiogenic Pb, with ages from altered domains typically ~11 – 15% younger than pristine domains from the same samples. This radiogenic Pb-loss is consistent with the results of experimental alteration studies of other phases such as monazite that have been subjected to dissolution/re-precipitation processes (e.g. Seydoux-Guillaume et al., 2002; Williams et al., 2011). In contrast, and despite complex intra-crystal zoning patterns, U-Th/Pb geochronologic data retrieved for pristine domains in these samples is relatively simple (see further discussion below) yielding single populations with no clear evidence for disturbance in the U-Th/Pb isotope systems or multiple geologic events. It is clear that in the studied samples, complex major and trace element zonation does not correlate to age-differences, as commonly observed in other minerals such as monazite (e.g. Foster et al., 2002).
Geochronology

Two samples, M33 and AD41, were analyzed by LA-ICPMS static spot analyses in previous studies. In both cases, these data were normalized to Manangotry reference monazite. However, given the matrix-effects associated with static spot analyses identified in this work (Fig. 3), it is expected that these data are inaccurate. The inaccuracy, which in this case is on the order of 10%, arises because the time-dependent (down-hole) slope of the inter-element ratio(s) of the primary reference material is less than that of the unknown. This leads to an under-correction of the down-hole fractionation, which in turn results in an age that is apparently too old. This is further supported by the observation that the Searle et al. (2007) LA-ICPMS date for M33 uranothorite (59.5 Ma) is ~10% too old compared to both the new LA-ICPMS data (54.0 Ma) presented here and the single ID-TIMS datum (~54 Ma) of Searle et al. (2007) (the difference between LA-ICPMS and ID-TIMS data was previously interpreted by Searle as Pb-loss in the ID-TIMS fraction).

There are no independent age constraints on the uranothorite from AD41, but the existing AD41 date (15.8 Ma normalized to Manangotry reference monazite, Cottle et al., 2009a) is also ~10% too old compared to the data (14.8 Ma) presented here, suggesting a similar level of inaccuracy in the original data. These two samples illustrate the importance of utilizing a matrix-matched reference material in order to produce accurate LA-ICPMS (urano)thorite dates using a static spot, and that failing to do so results in inaccuracies of at least 10% relative to the true age.

Concordance
Uranothorite analyzed in this study are consistently concordant in U/Pb space, both within crystals (multiple spots on the same crystal) and between crystals in the same rock. This has two key implications for the geochronology of uranothorite: 1) the lack of ‘reverse discordance’ suggests that both U decay chains have achieved secular equilibrium and that there has been no gain of intermediate decay products such as $^{230}$Th and/or $^{231}$Pa; 2) the lack of discordance in the U/Pb system in pristine crystal domains strongly suggests that there has been minimal radiogenic Pb-loss and; 3) there is no correlation between U/Pb dates and either crystal size or position within the crystal suggesting no resolvable volume diffusion of daughter products. Thus, in contrast to the work of von Blanckenburg (1992), uranothorites in this study have remained closed to U and its decay products throughout their history and can be treated as a reliable high temperature chronometer.

For thorite and huttonite only Th/Pb isotope ratios were measured, so there is no test of concordance. However, the dated thorite and huttonite produce geologically reasonable dates (see below) implying that there has been no gain or loss of parent, intermediate or daughter isotopes in the $^{232}$Th decay chain and therefore these minerals also serve as useful chronometers.

In his pioneering work on reverse discordance in monazite, Schärer (1984 p.191) stated that “U-Pb ages of Th-rich minerals such as monazite (and allanite) have to be corrected for excess $^{206}$Pb due to excess $^{230}$Th... the extent of this correction depends on the degree of Th-U fractionation and on the age of the rock.”. Minerals such as monazite strongly partition Th into their structure during crystallization and include significant and variable amounts of $^{230}$Th along with $^{232}$Th such that the Th/U ratio of the monazite is
much greater than that of the magma from which it crystallized. $^{230}$Th is an intermediate
daughter product of $^{238}$U that decays to “unsupported” $^{206}$Pb (e.g. Schärer 1984), resulting
in apparent $^{206}$Pb/$^{238}$U ages that are reversely discordant or “too-old” with respect to
$^{207}$Pb/$^{235}$U and $^{208}$Pb/$^{232}$Th ages. The degree of excess $^{206}$Pb can be significant, for
example Cottle et al. (2009) documented ~12 Ma Himalayan monazite with $^{206}$Pb/$^{238}$U
ages up to 50% older than $^{207}$Pb/$^{235}$U ages (for a constant $^{208}$Pb/$^{232}$Th ratio).

In contrast to the common observation of ‘excess $^{206}$Pb’ in monazite, no reverse
discordance was observed in uranothorite analyzed in this study. This has two
fundamental implications for uranothorite geochronology. Firstly, the $^{206}$Pb/$^{238}$U dates
obtained from uranothorite can be considered as reliable as either $^{207}$Pb/$^{235}$U or
$^{208}$Pb/$^{232}$-Th ages. Secondly, since there is no apparent Th/U disequilibrium between the
uranothorite and the magma/fluid from which it crystallized. The Th/U ratio of the
uranothorite is therefore a good approximation of the bulk rock from which it
crystallized. In other words, the U and Th bulk rock / uranothorite partition coefficient is
approximately 1. The latter is consistent with the observation of Parrish and Tirrul
(1989).

**Comparison to other chronometers**

Geochronology data exists from other accessory phases for three of the dated samples
(M33, H8 and P68787), thus offering the opportunity to compare (urano)thorite dates to
other mineral chronometers. M33 uranothorite (54.0 ± 0.4 Ma $^{206}$Pb/$^{238}$U date and 53.9 ±
0.5 Ma $^{208}$Pb/$^{232}$-Th date) is within uncertainty of both ID-TIMS zircon (53.1 ± 0.2 Ma)
and uranothorite (54.1 ± 0.1 Ma) data of Searle et al., (2007). This suggests that the new
LA-ICPMS data are accurate with respect to the ID-TIMS thorite data and also consistent with the existing zircon data. It seems reasonable to conclude that uranothorite from M33 can be confidently interpreted to accurately record the timing of igneous crystallization of this leucogranite body. Uranothorite from H8 is equivalent to ID-TIMS uranothorite and zircon from related rocks (e.g. H4 21.0 ± 0.5 Ma, Parrish and Tirrul, 1989) and is best explained as recording the timing of magmatic crystallization of this sample. Zircons from H8 are inherited, ranging in age from 635 Ma to 1750 Ma. In this rock, the uranothorite (which does not show any sign of inheritance) provides as a robust record of igneous crystallization whereas the zircon does not.

Uranothorite from P68787 (495 ± 6 Ma $^{206}\text{Pb}/^{238}\text{U}$ date and 492 ± 8 Ma $^{208}\text{Pb}/^{232}\text{Th}$ date) lies well within uncertainty of zircon (502 ± 2.6 Ma, Hagen-Peter et al. 2011) from the same mineral separate, again suggesting that the uranothorite accurately records crystallization of this igneous rock. Although this is a relatively small dataset from which to compare, in each case the dated uranothorites yield ages that are consistent with other high temperature chronometers such as zircon. This suggests that in igneous rocks, uranothorite has the ability to accurately record the timing of melt crystallization and is therefore of significant use, especially where zircon inheritance is prevalent.

The Gillespie’s Beach detrital sample provides insight into the utility of thorite and huttonite as provenance indicators. All brown thorite along with a significant portion of the green thorites are essentially the same age at ~74 Ma (Fig. 6 and 7), implying that these detrital crystals were derived from either a single lithologic source or from a suite of rocks with a single-age population. The majority of green thorite analyses also yield ~74 Ma dates, with a minor component of older, Cretaceous and Jurassic ages. In
contrast, huttonite yields ages ranging from 17 to 12 Ma. By comparison, detrital zircons from the same mineral separate yields age peaks at ~260 Ma, ~380 Ma, ~480 - 550 Ma and ~620 – 680 Ma.

All but one of the thorite analyses is significantly younger than the detrital zircons analyzed from the same sample. The youngest concordant detrital zircon analysis (223 ± 4.2 Ma) overlaps within error of the oldest (209.4 ± 12.1 Ma) green thorite analysis (Fig. 8) implying that detrital thorite and huttonite has the potential to record provenance information that the zircon does not. In this case, taking the detrital zircon signature in isolation would lead to the erroneous conclusion that the source region(s) for this sample did not experience any significant tectonic event(s) post ~220 Ma.

Accurately tracing the origin of the thorite in the Gillespie’s Beach sample is somewhat difficult given the diverse geologic history of the West coast of the South Island. One key observation is that the multiple ~74 Ma thorite ages overlap with U/Pb zircon and monazite ages from pegmatite dikes (Chamberlain et al., 1995; Batt et al., 1999) and the host Alpine schist (Mortimer and Cooper, 2004) cropping out immediately to the east of the Alpine fault (Fig. 8). In the absence of other comparable ages, the Alpine pegmatite dikes and/or the host schist represent a probable source. The 17 – 12 Ma Huttonite from the Gillespie’s Beach sample can potentially be related to either fluid-assisted alteration associated with emplacement of carbonatites and associated rocks in the Alpine Dike swarm (Cooper et al., 1987) and/or younger metamorphism/alteration of the Alpine schist associated with uplift along the Alpine fault (Batt et al., 1999). The remaining minor Mesozoic component to the thorite age spectra could equally be related to plutonic and/or metamorphic rocks west of the Alpine fault (Western Province) (Hiess
et al., 2010), or a detrital component in the sedimentary protolith to the Alpine schist (Fig. 8, e.g. Campbell et al., 2007; Adams et al., 2013).

Implications

This study demonstrates that a matrix-matched reference material is essential in order to produce accurate U-Th/Pb (urano)thorite static spot dates by LA-ICPMS. Neither an [X]SiO₄ matrix such as zircon or a high-Th phase such as monazite behave in a similar manner to (urano)thorite in terms of ablation characteristics, and specifically with respect to LIEF. Using a matrix-matched reference uranothorite, samples analyzed in this study yield concordant U/Pb and Th/Pb ages that are consistent with other high-temperature chronometers. Uranothorite, unlike other high-Th phases such as monazite, does not appear to suffer from disequilibrium in the \(^{238}\)U decay chain (i.e. ‘excess \(^{206}\)Pb’) such that \(^{206}\)Pb/\(^{238}\)U dates can be considered reliable. Radiogenic-lead loss and/or metamictization appears to be minimal and restricted to domains that have undergone significant fluid-assisted alteration and/or hydration. The lack of pervasive alteration and metamictization makes (urano)thorite a robust chronometer in igneous and metamorphic rocks. Detrital thorite and huttonite has the potential to record significant provenance information that can elucidate a variety of igneous, metamorphic and alteration processes in the source terrane(s).

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**Appendix – Analytical Methods**

**XRD:** Single crystal x-ray diffraction (XRD) patterns were made with a Kappa Apex II x-ray diffractometer in the Chemistry Department at the University of California, Santa Barbara.

**EPMA:** elemental maps and quantitative major and trace element analyses were made using a Cameca SX-100 Electron Probe MicroAnalyzer (EPMA) housed at the University of California, Santa Barbara. x-ray maps of U (LPET, Mα), Th (LPET, Mα), Y (LTAP, Lα), and P (LPET, Kα) were made in beam scan mode using 15 keV accelerating voltage, 200 nA beam current (equating to a ~1 µm³ interaction volume), and a dwell time of 25 ms. Quantitative analyses were performed on the same instrument. Operating conditions were 40 degrees takeoff angle, accelerating voltage of 20 keV, 200 nA beam current and a beam diameter of 5 µm. Elements were acquired using analyzing crystals LLIF for La, Nd La, Pr La, Eu La, Gd La, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Sm Lα, LPET for Pb Mα, U Mα, Ce Lα, Ca Kα, Y Lα, Th Mα, and TAP for P Kα, Si Kβ, Al Kα.

The standards were ThO2 for Th Mα, U-2 (10.00% UO2 in diopside glass) for U Mα, Anorthite (Grass Valley) U.C.#16706 for Al Kα, Diopside (Chesterman) for Si Kβ, Ca Kα, Magnetite U.C. #3380 for Fe Kα, CePO4 (USNM 168484) for Ce Lα, DyPO4.
(USNM 168485) for Dy Lα, ErPO4 (USNM 168486) for Er Lα, EuPO4 (USNM 168487) for Eu Lα, GdPO4 (USNM 168488) for Gd Lα, HoPO4 (USNM 168489) for Ho Lα, LaPO4 (USNM 168490) for La Lα, P Kα, LuPO4 (USNM 168491) for Lu Lα, NdPO4 (USNM 168492) for Nd Lα, PrPO4 (USNM 168493) for Pr Lα, SmPO4 (USNM 168494) for Sm Lα, TbPO4 (USNM 168496) for Tb Lα, TmPO4 (USNM 168497) for Tm Lα, YbPO4 (USNM 168498) for Yb Lα, YPO4 (USNM 168499) for Y Lα, and Pyromorphite (Cameca) for Pb Mα.

The counting time was 40 seconds for La Lα, Ce Lα, Nd Lα, Th ma, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Si Kβ, Sm Lα, 100 seconds for Al Kα, Pb Mα, 120 seconds for U Mα, 160 seconds for Y Lα, and 200 seconds for P Kα, Ca Kα. The off peak counting time was 40 seconds for La Lα, Ce Lα, Nd Lα, Th ma, Pr Lα, Eu Lα, Gd Lα, Tb Lα, Dy Lα, Ho Lα, Er Lα, Tm Lα, Yb Lα, Lu Lα, Fe Kα, Si Kβ, Sm Lα, 100 seconds for Al Kα, Pb Mα, 120 seconds for U Mα, 160 seconds for Y Lα, and 200 seconds for P Kα, Ca Kα. Off Peak correction method was Linear for La Lα, Ce Lα, Nd Lα, Th ma, P Kα, Pr Lα, Gd Lα, Ho Lα, Tm Lα, Yb Lα, Si Kβ, Ca Kα, Y Lα, Sm Lα, and Multi-Point for Lu Lα, Pb Mα, U Mα, Fe ka, Eu Lα, Al Kα, Er la, Tb Lα, Dy Lα.

Unknown and standard intensities were corrected for deadtime. Standard intensities were corrected for standard drift over time. Interference corrections were applied to La for interference by Nd, and to Nd for interference by Ce, and to Pr for interference by La, Y, and to Eu for interference by Nd, Pr, and to Gd for interference by Nd, Ce, La, and to Dy for interference by Eu, and to Ho for interference by Gd, Lu, and to Er for interference by Tb, and to Tm for interference by Dy, Gd, and to Yb for...
interference by Eu, Dy, Tb, and to Lu for interference by Dy, Ho, and to Pb for interference by Y, and to U for interference by Th, and to Fe for interference by Dy, and to Al for interference by Tm, Yb, Th, and to Ca for interference by Pb and Yb. See Donovan et al., (1993) for detail.

Oxygen was calculated by cation stoichiometry and included in the matrix correction. The matrix correction method was ZAF or Phi-Rho-Z Calculations and the mass absorption coefficients dataset was LINEMU Henke (LBL, 1985) < 10KeV / CITZMU > 10KeV. The ZAF or Phi-Rho-Z algorithm utilized was Armstrong/Love Scott (Armstrong, 1988). Accuracy of unknown analyses was checked routinely using in house natural monazite reference materials, synthetic ThO₂ and NIST SRM 610.

**LA-MC-ICPMS:** In-situ U-Th/Pb geochronology analyses were performed using a laser ablation multi-collector inductively coupled plasma mass spectrometer (LA-MC-ICPMS) at the University of California Santa Barbara (UCSB). Analytical methods follow Cottle et al. (2012, 2013); and Kylander-Clark et al. (2013) and are briefly described here. Instrumentation consists of an Analtye 193 nm ArF excimer laser (Photon Machines, San Diego, USA) equipped with a HelEx two-volume sample cell (Eggins et al., 1998) attached to a Nu Plasma HR MC-ICPMS (Nu Instruments, Wrexham, UK). The collector array on the Nu Plasma is configured to simultaneously measure \(^{238}\)U and \(^{232}\)Th on two high-mass side Faraday cups and \(^{208}\)Pb, \(^{207}\)Pb, \(^{206}\)Pb, and \(^{204}\)X (where X includes \(^{204}\)Pb and \(^{204}\)Hg) on four low-mass side secondary electron multipliers. Ablations were conducted for 20 seconds each at 1.2 J/cm\(^2\) or 1.5 J/cm\(^2\) fluence (thorite, zircon), a frequency of 4 Hz, and a pit diameter of 5 μm or 20 μm yielding craters ~3, or 9 μm deep.
(as assessed by optical microscopy). Utilizing a sample–standard bracketing technique, analyses of reference materials (RMs) with known isotopic composition were measured before and after each set of seven unknown analyses. Data reduction, including corrections for baseline, instrumental drift, mass bias, down-hole fractionation as well as age calculations were carried out using Iolite v. 2.1.2 (Paton et al. 2010). Background intensities and changes in instrumental bias were interpolated using a smoothed cubic spline while down-hole inter-element fractionation was modeled using an exponential function. Statistics for baselines, on peak intensities and isotopic ratios were calculated using the mean with a 2.S.D. outlier rejection.

**Figure Captions**

**Figure 1.**
Representative Backscattered electron (BSE), Th, U, P, and Y x-ray Electron probe microanalyzer (EPMA) maps of uranothorite (M33, AD41, H4, H8, P68787), thorite (OU12321 and Gillespie Beach) and huttonite (Gillespie Beach) analyzed in this study. Warmer colors are higher concentration relative to cooler colors. Scale bars are 50 µm.

**Figure 2.**
Representative Backscattered electron (BSE) images of typical alteration observed in this study. A) inclusions of allanite and xenotime surrounded by altered uranot thorite (sample M33) (location of image is shown in Fig. 1). B) patchy recrystallization (sample AD41), C) (H4) and D) (H8) altered rim surrounding pristine uranot horite. Scale bars are 25 µm.
Figure 3.

Self-normalized $^{206}\text{Pb}/^{238}\text{U}$ (A) and $^{208}\text{Pb}/^{232}\text{Th}$ (B) ratios as a function of time (depth) during ablation. Each line is an exponential curve fitted to the mean of 10 static spot ablations of each material (see Paton et al., 2010 for details of curve fitting). Thorites all have similar slopes whereas monazite and NIST Glass have different slopes, illustrating the need to use a matrix-matched reference material for thorite analysis in static spot mode LA-ICPMS.

Figure 4.

Pb/U Concordia and weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ plots for uranothorite samples. Analyses in blue were specifically sited over altered domains, and are not considered in the final age determinations.

E-F) H8. G-H) P68787. Mean LA-ICPMS $^{206}\text{Pb}/^{238}\text{U}$ zircon date (red ellipse) obtained by Hagen-Peter et al. (2011) plotted for comparison.

Figure 5.

Weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ plot for OU16321 thorite. Analysis in grey was rejected from final date determination.

Figure 6.

Weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ plot for Gillespie Beach thorite and huttonite. Although from
a detrital sample, brown thorite has a Mean Squared Weighted Deviates (MSWD) of 1.4, consistent with a single age population. Photos of representative grains show a clear color difference between ‘brown’ and ‘green’ thorite as well as dark green huttonite. Scale bars are 200 µm.

**Figure 7.**

Kernal Density estimate for Gillespie Beach thorite, huttonite and zircon from the same mineral separate. Only zircon <5% discordant are plotted. The majority of thorite is younger than the zircon, with only very minor overlap between the oldest thorite and the youngest detrital zircon.

**Figure 8.**

Summary diagram of existing geochronology data from major geologic units on the West coast of the South Island of New Zealand. The ~74 Ma green and brown thorite population overlaps with U/Pb monazite and zircon ages from both Alpine pegmatites and Alpine schis. Oldest huttonites overlap in age with the Alpine dike swarm. Minor older components to the green thorite population overlap with detrital zircon from both the Eastern and Western provinces. Data sources: 1: This study; 2: Cooper et al. (1987); 3: Batt et al. (1999); 4: Chamberlain et al. (1995); 5: Mortimer and Cooper (2004); 6: Vry et al.,(2004); 7: Hiess et al. (2010); 8: Campbell et al. (2007) and Adams et al. (2013).

**Table 1.**

Summary of samples analyzed in thus study. Mineral abbreviations after Whitney and
Evans (2010). References: 1: Searle et al. (2007); 2: Cottle et al. (2009a); 3: Parrish and Tirrul (1989); 4: Hagen-Peter et al. (2011); 5: White (1962); 6: Cooper (1971); 7: Cooper et al. (1987); 8: Pabst and Hutton (1951); 9: Förster et al. (2000).

Table 2.

Electron probe microanalyzer data table.

Table 3.

U-Th/Pb isotope data for uranothorite. Notes: a) concentration data are normalized to the primary reference material and are accurate to approximately 10%, b) $^{207}\text{Pb} / ^{235}\text{U}$ calculated assuming a natural $^{238}\text{U} / ^{235}\text{U}$ ratio of 137.88. c) Rho value is calculated following the method outlined in Paton et al., (2010). d) Age calculations are based on the U decay constants of Steiger and Jäger (1977) and the Th decay constant of Amelin and Zaitsev (2002). Isotopic ratios and ages are not corrected for common-Pb.

Table 4.

Th/Pb isotope data for thorite and huttonite. bdl: beyond detection limit. a) concentration data are normalized to the primary reference material and are accurate to approximately 10%, b) Age calculations are based on Th decay constant of Amelin and Zaitsev (2002). Isotopic ratios and ages are not corrected for common-Pb.

Table 5.
U/Pb isotope data for detrital zircon from Gillespie’s Beach. *indicates rejected datapoint (>5% discordance). a) concentration data are normalized to the primary reference material and are accurate to approximately 10%. b) $^{207}\text{Pb}/^{235}\text{U}$ calculated assuming a natural $^{235}\text{U}/^{238}\text{U}$ ratio of 137.88 c) Rho value is calculated following the method outlined in Paton et al. (2010). d) Age calculations are based on the U decay constants of Steiger and Jäger (1977).
References


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Mean $^{206}\text{Pb}/^{238}\text{U}$ date
$= 54.0 \pm 0.4 \text{ Ma}$
MSWD = 0.8,
0 of 22 rejected

Mean $^{206}\text{Pb}/^{232}\text{Th}$ date
$= 53.9 \pm 0.5 \text{ Ma}$
MSWD = 1.3

Mean $^{206}\text{Pb}/^{238}\text{U}$ date
$= 14.8 \pm 0.1 \text{ Ma}$
MSWD = 1.9,
0 of 41 rejected

Mean $^{206}\text{Pb}/^{232}\text{Th}$ date
$= 13.5 \pm 0.1 \text{ Ma}$
MSWD = 3.7

Mean $^{206}\text{Pb}/^{238}\text{U}$ date
$= 22.1 \pm 0.2 \text{ Ma}$
MSWD = 2.7,
0 of 35 rejected

Mean $^{206}\text{Pb}/^{232}\text{Th}$ date
$= 21.4 \pm 0.1 \text{ Ma}$
MSWD = 1.7

Mean $^{206}\text{Pb}/^{238}\text{U}$ zircon date
$= 502.1 \pm 2.6 \text{ Ma}$

Mean $^{206}\text{Pb}/^{232}\text{Th}$ date
$= 492 \pm 8 \text{ Ma}$
MSWD = 1.4
OU16321 thorite

Mean $^{208}\text{Pb}/^{232}\text{Th}$ date

$= 19.7 \pm 0.4 \text{ Ma}$

MSWD = 1.5

1 of 12 rejected
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<td>ID-TIMS thorite: 21 Ma</td>
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<td>H8</td>
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<td>Kfs-megacrystic granite</td>
<td>ID-TIMS thorite ~16.5 Ma (discordant)</td>
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<td>P68787</td>
<td>Hunt Glacier, Antarctica (-76.86603°, 162.34916°)</td>
<td>coarse-grained equigranular Hbl-monzodiorite</td>
<td>LA-MC-ICPMS zircon: 502.1 ± 2.6 Ma</td>
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<td>-</td>
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<td>Gillespie's Beach, New Zealand (-43.41131°, 169.79533°)</td>
<td>Mag+Sch+Zrn+Thr+Rt+Ap beach sand</td>
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