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U-Pb Geochronological and Thermochronological Time–Temperature Constraints of $^{40}Ar/^{39}Ar$ Hornblende Reference Material HB3gr

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Hornblende from the Lone Grove Pluton, Llano Uplift, Texas, has served as an irradiation reference material in $^{40}Ar/^{39}Ar$ studies for decades. In order to evaluate the apparent age bias that currently exists between the U-Pb and $^{40}Ar/^{39}Ar$ systems, zircon and titanite were dated by isotope dilution-thermal ionisation mass spectrometry (ID-TIMS) from the same rock from which the hornblende $^{40}Ar/^{39}Ar$ reference material HB3gr is derived. Zircon U-Pb data indicate initial crystallisation at 1090.10 ± 0.16 Ma (2*s*), a date that is 1.7% older than the accepted K-Ar date (1072 ± 14 Ma, 2*s*) for HB3gr; an offset that exceeds the typical 0.5–1% bias between the two systems, though remaining within uncertainty due to the large uncertainties in the ^{40}K decay constant. Zircon data are presented using both EARTHTIME tracers ET535 and ET2535 and are statistically indistinguishable. Single grain titanite analyses range between 1082 ± 0.75 and 1086 ± 0.81 Ma (2*s*) and are interpreted to record the subsequent cooling following crystallisation at rates between 30 and 50 °C Ma^{-1}. This is supported by the observation that hornblende $^{40}Ar/^{39}Ar$ dates corrected for decay constant bias are resolvably younger than the zircon U-Pb date and in good agreement with titanite U-Pb dates, permitting the conclusion that both titanite U-Pb and hornblende $^{40}Ar/^{39}Ar$ systems provide a record of cooling.

Keywords: HB3gr, reference material, Lone Grove Pluton, zircon, U-Pb, titanite.

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Significant advances in radio-isotopic geochronology are now providing unprecedented levels of precision. This has, in turn, highlighted a systematic bias between the two most commonly applied chronometers, the U-Pb and $^{40}Ar/^{39}Ar$ systems. The EARTHTIME initiative has encouraged the development of a high-precision absolute timeline for Earth's history that can use geochronological data from any radio-isotopic system. To accomplish this goal, several recent studies have focused on reducing the systematic uncertainties and/or inaccuracies that contribute to the biases between different radiometric systems (Min *et al.* 2000, Kuiper *et al.* 2008, Renne *et al.* 2010, 2011). Calculated dates for samples using both U-Pb and $^{40}Ar/^{39}Ar$ reveal a systematic 0.5–1.5% age bias, where the U-Pb system yields the older date. This systematic age discrepancy has typically been attributed to uncertainties and/or inaccuracies associated with the ^{40}K decay constants and/or the accepted age of neutron flux reference materials used in $^{40}Ar/^{39}Ar$ studies (e.g., HB3gr and Fish Canyon Tuff sanidine; Renne *et al.* 2010, 2011). There have been several different approaches aimed at reducing or minimising these uncertainties. One method utilises intrasystem comparisons, where $^{40}Ar/^{39}Ar$ reference materials are co-irradiated and analysed to re-evaluate the relative age of reference materials through calibration with other independently known reference materials (Jourdan and Renne 2007). A second method, works to determine a $^{40}Ar/^{39}Ar$ reference material's true age using an independent chronological technique such as astrochronology (Kuiper *et al.* 2008). Lastly, redetermination of ^{40}K decay constants and ages of $^{40}Ar/^{39}Ar$ reference materials may be made through intersystem comparison with the U-Pb system (Min *et al.* 2000, Kwon *et al.* 2002, Renne *et al.* 2010, 2011). Correct use of this intersystem comparison requires that important criteria be

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met. First, the precision and reproducibility of data produced by both the $^{40}Ar/^{39}Ar$ and U-Pb systems must be high. Second, both systems must have remained closed throughout the sample's history. This requires that both chronometers record the same geological event and that no slow cooling, thermal reheating or chemical/physical alteration of the dated mineral prevent closed system behaviour. $^{40}Ar/^{39}Ar$ reference materials derived from plutonic rocks have typically been excluded from these intercomparison studies because of the potential age bias that slow cooling will induce on the different chronometers. One exception to this age bias in plutonic rocks includes the McClure Mountain Syenite, a ~ 520 Ma intrusive where the hornblende $^{40}Ar/^{39}Ar$ and K-Ar data overlap within uncertainty with the zircon, titanite and apatite U-Pb dates. This has been interpreted to indicate rapid cooling of this plutonic rock and its potential usefulness in intercalibration studies (Schoene and Bowring 2006).

To contribute to the intercalibration of the $^{40}Ar/^{39}Ar$ and U-Pb systems, we present U-Pb zircon and titanite data from a sample of the granite pluton that is the source of the $^{40}Ar/^{39}Ar$ hornblende reference material HB3gr. Zircon and titanite U-Pb geo/thermochronology have the potential to constrain the thermal evolution of the sample, which in turn can be used to evaluate whether this sample be used as a primary reference material and for intercalibration studies. Evidence for protracted cooling or reheating can be used to model the expected effects of volume diffusion of Ar in hornblende for this thermal history. Titanite is a U-rich accessory phase with a nominal Pb closure temperature of ~ 600 °C that has been both empirically (Mezger *et al.* 1991) and experimentally (Cherniak 2010) calibrated. The zircon U-Pb system has a high experimentally measured closure temperature of ~ 850–1000 °C (Cherniak 2010) and has been shown to retain Pb at even higher temperatures over long periods of geological time. In the case of sample HB3gr, zircon is anticipated to yield the age of zircon crystallisation within a granitic magma. A combination of U-Pb titanite and zircon data allows construction of a time–temperature path from magmatic crystallisation through the closure of the U-Pb titanite system. The geological significance of the hornblende $^{40}Ar/^{39}Ar$ data can then be evaluated in the framework of the time–temperature history constructed by the U-Pb system.

The Lone Grove pluton is one of several syn- to post-tectonic granites that intrude metasedimentary and metaigneous rocks of Grenville origin and are collectively known as the Town Mountain Granite. The host rock for the hornblende reference material HB3gr was collected from the Petrick quarry (sample 3gr) described by Zartman (1964) as a greyish-pink, coarse-grained porphyritic granite. This intrusive complex seems to have a simple history, including intrusion into the shallow crust postdating the Grenville orogeny, followed by thermal relaxation with no apparent deformation. This simplicity made it an attractive case study area for Zartman (1964), who compared the K-Ar and Rb-Sr systematics of a variety of different mineral phases, examined the effects of weathering and reported the first K-Ar date for what would later become the HB3gr hornblende reference material of 1050 ± 20 Ma (Figure 1). Turner *et al.* (1971) used HB3gr as a neutron flux monitor in a $^{40}Ar/^{39}Ar$ study of lunar rocks. The characteristics of HB3gr, including its relative antiquity and high K/Ca ratio, make it an attractive reference material for dating older samples. Turner *et al.* (1971) purified the original hornblende separate material from Zartman's (1964) study, reporting a new K-Ar date of 1060 ± 20 Ma (Figure 1). This K-Ar was later recalculated by Roddick (1983) using the decay constants from Steiger and Jäger (1977) yielding what has become the accepted date for HB3gr of 1072 ± 7 Ma (Figure 1) (1*s*, excluding decay constant uncertainties).

The overall reproducibility and apparent homogeneity of the HB3gr hornblende led to the development and use of the sample as a neutron flux monitor in several studies (Renne 2000, Nomade *et al.* 2001, Jourdan *et al.* 2004, Verati *et al.* 2005). An effort by Jourdan *et al.* (2006) to evaluate the reproducibility of HB3gr at the single grain level produced a large data set of single grain UV laser analyses on 125–200 μm material. In this study, over seventy single grain analyses from three different irradiation batches yielded a mean date that lies within analytical uncertainties of the previously published K-Ar date (Figure 1). The uncertainty-weighted mean date of a similar number of single grain analyses from just a single irradiation agrees with the published K-Ar dates as well (Renne 2000). Each of these studies used the sanidine separated from the Fish Canyon Tuff (FCs) reference material as a neutron flux monitor. More recently, Schwarz and Trieloff (2007) report data for HB3gr intercalibrated and co-irradiated with three different K-Ar reference materials, yielding an age of 1073.6 ± 4.3 Ma (1*s* excluding decay constants uncertainty). Therefore, for a range of different irradiation procedures, laboratories and reference materials, the HB3gr reference material yields a highly reproducible mean date that is in good agreement with the accepted K-Ar date (Figure 1).

Despite this reproducibility between studies, single crystal UV laser analyses reveal a slight $^{40}Ar/^{39}Ar$ age overdispersion as suggested by Jourdan *et al.* (2006). The

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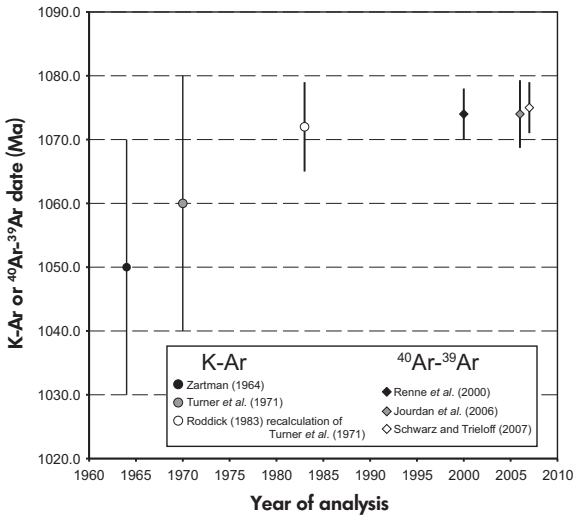

Figure 1. Summary of K-Ar and ^{40}Ar-^{39}Ar dates for reference material HB3gr plotted against the year of publication for each data point. All uncertainties are plotted at the 1*s* level and do not include the decay constant uncertainties.

reported mean uncertainty-weighted date from this single grain study has an unreported MSWD = 4.6, a value that indicates that the scatter in the data cannot be explained by analytical uncertainties alone. The cause of single grain date variability has been suspected to be the result of mineral alteration, variation in K/Ca ratios and/or variation in neutron flux or flux gradients, although these provide no definitive explanation (Jourdan *et al.* 2006). A source of over-dispersion that has not been considered is that slow cooling could induce rounded ^{40}Ar diffusion profiles and heterogeneity in calculated dates between grains as well as within single grains. Constraining the thermal history using U-Pb geo/thermochronology permits testing the hypothesis that slow cooling and volume diffusion cause systematically variable dates in HB3gr.

Experimental procedure

Zircon grains were separated from a sample of the Lone Grove Pluton collected from Petrick quarry using conventional crushing and mineral separation techniques. All reported zircon U-Pb analyses are either single grain or fragments of single grains treated using the chemical abrasion method (CA-TIMS) (Mattinson 2005). Prior to analysis, several grains were imaged using CL and backscatter techniques (Figure 2). Zircon images revealed a relatively simple texture suggesting a single stage growth history. Nine single grain analyses were undertaken using the EARTHTIME tracer ET2525 (^{202}Pb, ^{205}Pb, ^{235}U, ^{233}U) (Condon *et al.* 2015), allowing for internal Pb and U fractionation correction using the measured ^{202}Pb/^{205}Pb and ^{233}U/^{235}U ratios. Both titanite data and an additional fifteen zircon analyses were conducted using the EARTHTIME tracer solution ET535 (^{205}Pb, ^{235}U, ^{233}U) (Condon *et al.* 2015) and externally corrected for Pb fractionation using long-term measurements of isotopic reference material NBS-981. Zircon dates were calculated using an isotopic composition of uranium (^{238}U/^{235}U) of 137.818 ± 0.022 (Hiess *et al.* 2012). Uranium and lead data for both zircon and titanite were determined and U-Pb dates calculated using the *Tripoli* and *U-Pb_Redux* software (Bowring *et al.* 2011, McLean *et al.* 2011).

Individual titanite grains were dated following procedures similar to those of Schoene and Bowring (2006). This

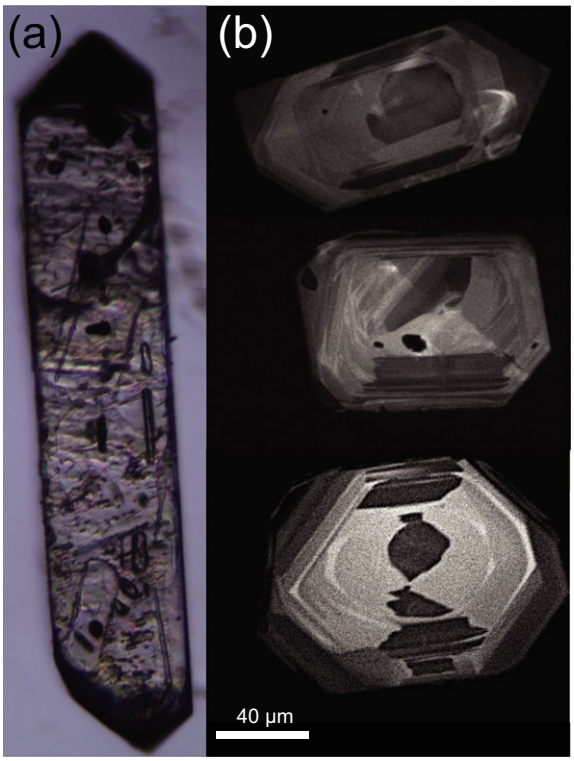

Figure 2. Photomicrograph of zircon grains from 3gr using (a) transmitted and (b) cathode luminescence. Transmitted light images reveal zircon grains containing melt or apatite inclusions, either of which could contribute common Pb to a zircon analysis. Use of Mattinson's (2005) chemical abrasion technique removes these inclusions from the analysed zircon. Lack of multiple growth histories, embayed grains or inherited cores shown in the cathodoluminescence images (b) suggests a single stage growth history for zircons from 3gr.

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includes grain size measurement, a cleaning step in weak HNO_3, followed by U-Pb tracer addition and a dissolution procedure (HF/HCl). Separates of Pb and U were isolated and purified using HBr ion chromatography followed by measurement using a VG Sector 54 TIMS at MIT. Single grain titanite U-Pb data from grains of variable diffusion domain size allowed evaluation of the granite's cooling rate through the titanite closure window for Pb diffusion. Numerical solutions to the production-diffusion equation allowed forward modelling of the U-Pb system and an ability to match grain size *vs.* U-Pb date relationships derived from laboratory measurements with the forward modelled results for any time–temperature path (Blackburn *et al.* 2011). Diffusion kinetics for Pb in titanite from Cherniak (2010) were used, and all tested cooling paths were linear. Initial conditions included the initial temperature, previously estimated at 750–850 °C (Smith *et al.* 2010), and start time, which was provided by the zircon crystallisation age. All numerical solutions assume a spherical grain geometry.

Results

U-Pb geo/thermochronological data

U-Pb zircon dates are reported as initial ^{230}Th disequilibrium-corrected $^{206}Pb/^{238}U$ dates, calculated with a Th/U_{Magma} of 4. Uncertainties are reported as ± X/Y/Z, where X includes analytical uncertainties only, Y additionally includes tracer calibration uncertainties and Z includes analytical, tracer calibration and decay constant uncertainty components. The weighted mean ^{238}U-^{206}Pb date using the isotopic tracer ET2535 was 1090.10 ± 0.16/0.71/1.4 Ma, MSWD = 4.2 with n = 9 (Figure 3). An additional zircon data set using the isotopic tracer solution ET535 yielded a population with a lower MSWD due to larger individual analysis uncertainties associated with Pb fractionation, with a weighted mean ^{238}U-^{206}Pb date of 1090.23 ± 0.19/0.48/1.3 Ma, MSWD = 2.4 for n = 15 (Figure 4). The weighted mean uncertainty that includes the decay constant uncertainties will be used to compare with available K-Ar and $^{40}Ar/^{39}Ar$ data.

Titanite analyses yielded a range of ^{238}U-^{206}Pb dates between 1082.2 ± 0.75 and 1086.3 ± 0.81 Ma over a range of grain sizes between ~ 30 and 110 µm. There is an ~ 6 Ma difference between the zircon and titanite U-Pb dates (Figures 3 and 4). No statistically significant mean data could be assigned to the titanite U-Pb data probably due to volume diffusion of Pb. For comparison with $^{40}Ar/^{39}Ar$ data, the youngest date (of 1082.2 ± 0.75 Ma) was used, corresponding to the smallest crystal and thus the closest effective closure temperature to Ar in hornblende (520 °C). Results for both zircon and titanite U-Pb measurements are given in Table 1.

Numerical modelling of titanite U-Pb and hornblende $^{40}Ar/^{39}Ar$ systems

Numerical solution of the diffusion equation allows for forward modelling of the titanite U-Pb system. Using a model start time of 1090 Ma and initial temperatures of 750–850 °C (Smith *et al.* 2010), the forward calculation can produce synthetic titanite U-Pb data for any tested time–temperature path. The measured grain size age relationship can be reasonably well fitted by modelled data for a range

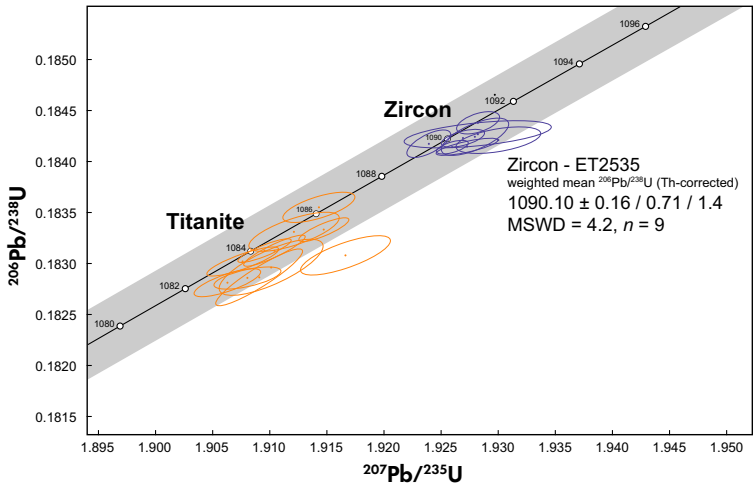

Figure 3. U-Pb concordia diagram displaying both zircon U-Pb analyses and titanite U-Pb analyses. Only the zircon grains dated using ^{202}Pb-^{205}Pb-^{233}U-^{235}U tracer ET2535 are shown.

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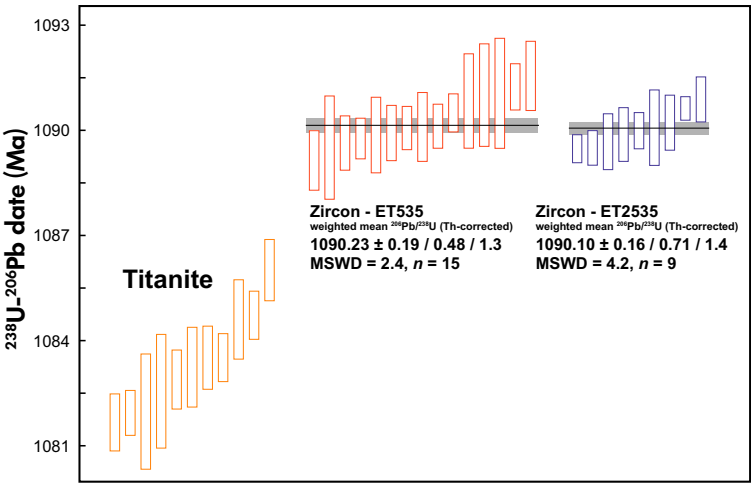

Figure 4. Th-corrected ^{238}U-^{206}Pb dates for titanite and zircons dated using both single and double Pb tracers. A resolvable difference of ~ 6 My between zircon and titanite data is apparent in both diagrams.

of cooling rates between 30 and 50 °C Ma^{-1} (Figure 5). A single titanite analysis (T14) remains an outlier to these modelled grain size *vs.* age curves. All other measured titanite dates are in good agreement with modelled results. The large range of estimates on start temperature/granite crystallisation temperature is the dominant source of uncertainty contributing to the range of estimated cooling rates. Forward modelling of the ^{40}Ar hornblende system allows us to predict the variation in measured date with grain size that could result from the upper bound on this cooling rate. Using the range of cooling rates constrained by the titanite U-Pb data, the total range in $^{40}Ar/^{39}Ar$ dates induced by volume diffusion is less than 1 Ma for the reported grain size range. Even if we assume that these grains did not behave as a single domain, and that the effective diffusion dimension may be as low as 1 μm, forward model calculations produce a spread in dates no greater than ~ 6 Ma, just a small percentage of the observed range in ^{40}Ar-^{39}Ar dates (> 20 Ma), suggesting that volume diffusion cannot account for all of the observed age heterogeneity revealed by single grain $^{40}Ar/^{39}Ar$ studies.

Discussion

The available $^{40}Ar/^{39}Ar$ and K-Ar data for HB3gr must be recalculated using revised decay constant and FCs values to permit a systematic comparison with the U-Pb data presented here. The previously published $^{40}Ar/^{39}Ar$ and K-Ar dates and associated uncertainties for HB3gr have been recalculated using three different data reduction methods: (a) Renne *et al.* (1998) used decay constants from Steiger and Jäger (1977) and a FCs value of 28.02 Ma; (b) Kuiper *et al.* (2008) used decay constants from Min *et al.* (2000) and an orbitally tuned date for the FCs of 28.201 Ma; (c) decay constants and FCs values defined in Renne *et al.* (2010, 2011). All recalculated data are reported at the 2*s* level with uncertainties that include decay constants. Presented in Table 2 are the comparisons between the zircon and titanite dates for 3gr reported in this study and the previously published K-Ar (Turner *et al.* 1971) and $^{40}Ar/^{39}Ar$ dates (Renne 2000, Jourdan *et al.* 2006).

In nearly all comparisons between the recalculated K-Ar/$^{40}Ar/^{39}Ar$ and U-Pb data, the large uncertainties on ^{40}K prevent the ability to resolve any difference between the older U-Pb zircon date and the hornblende K-Ar/Ar-Ar date. The exception to this is the re-reduction of data from Jourdan *et al.* (2006) using decay constants and FCs values from Renne *et al.* (2011), which results in a resolvable difference of ~ 7 ± 5 My (0.5 ± 0.4%). This bias between the $^{40}Ar/^{39}Ar$ hornblende and zircon U-Pb systems after using the most recent estimates of decay constants and FCs suggests that slow cooling and the diffusive loss of Ar from hornblende may be contributing to the difference between U-Pb zircon and $^{40}Ar/^{39}Ar$ hornblende dates, an observation that suggests that the Ar in hornblende system is recording the cooling of the Lone Grove pluton.

Geo/thermochronological data from sample 3gr collected from the Lone Grove Pluton can be used to reconstruct its time–temperature history. U-Pb zircon dates are interpreted to record crystallisation of the granitic pluton at a 1090.10 ± 0.16 Ma. The dispersion in single grain zircon U-Pb dates results in a relatively high MSWD of 4.2 and

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Table 1.
Results of U-Pb measurements in zircon and titanite from sample 3gr

Fraction	Date (Ma)										Composition				Isotopic ratio							Correlation coefficient	
	$^{206}Pb/^{238}U$[a]	±2*s* abs	$^{206}Pb/^{238}U$ <Th>[b]	±2*s* abs	$^{207}Pb/^{235}U$[a]	±2*s* abs	$^{207}Pb/^{206}Pb$[a]	±2*s* abs	Corr. coef.	% disc[c]	Th/U[d]	Pb* (pg)[e]	Pb_c (pg)[f]	Pb*/Pb_c[g]	$^{206}Pb/^{204}Pb$[h]	$^{206}Pb/^{238}U$[i]	±2*s* %	$^{207}Pb/^{235}U$[i]	±2*s* %	$^{207}Pb/^{206}Pb$[i]	±2*s* %	$^{206}Pb/^{238}U$-$^{207}Pb/^{235}U$	Fraction
Titanite																							
T1	1083.10	1.50	1083.10	1.50	1084.60	1.60	1087.80	3.20	0.8	0.43	0.48	84	4.5	19	1141	0.18295	0.15	1.9101	0.24	0.07572	0.16	0.75	T1
T7	1085.07	0.63	1085.15	0.63	1086.23	0.76	1088.60	1.40	0.8	0.32	0.42	594	20.55	29	1786	0.18332	0.063	1.9147	0.11	0.075754	0.069	0.83	T7
T7b	1083.70	1.10	1083.80	1.10	1086.90	1.40	1093.30	2.90	0.7	0.88	0.47	207	8.13	25	1550	0.18306	0.11	1.9166	0.21	0.07593	0.14	0.74	T7b
T8	1083.95	0.83	1084.03	0.83	1084.73	0.94	1086.30	1.50	0.9	0.22	0.47	441	16	28	1684	0.18311	0.083	1.9104	0.14	0.075668	0.074	0.9	T8
T8b	1082.50	1.50	1082.60	1.50	1084.30	1.30	1087.80	1.70	0.9	0.48	0.5	242	9.59	25	1528	0.18285	0.15	1.9091	0.2	0.075723	0.084	0.92	T8b
T9	1083.95	0.63	1084.03	0.63	1084.42	0.81	1085.40	1.50	0.9	0.13	0.63	599	22.16	27	1587	0.18311	0.063	1.9095	0.12	0.075633	0.073	0.87	T9
T9b	1082.48	0.59	1082.57	0.59	1083.90	1.00	1086.80	2.50	0.6	0.39	0.39	165	7.99	21	1288	0.18284	0.059	1.908	0.15	0.075685	0.12	0.62	T9b
T10	1083.37	0.78	1083.45	0.78	1083.80	1.10	1084.50	2.20	0.8	0.11	0.62	257	15.04	17	1011	0.18301	0.078	1.9076	0.16	0.075602	0.11	0.84	T10
T11b	1082.24	0.75	1082.32	0.75	1083.30	1.00	1085.40	2.10	0.8	0.29	0.51	339	13.14	26	1561	0.1828	0.075	1.9063	0.15	0.075634	0.11	0.77	T11b
T13	1085.00	1.00	1085.00	1.00	1085.30	1.40	1086.10	3.00	0.7	0.1	0.52	413	16.97	24	1469	0.1833	0.1	1.9121	0.21	0.07566	0.15	0.71	T13
T14	1086.26	0.81	1086.34	0.81	1086.10	1.10	1085.70	2.50	0.7	-0.05	0.5	149	5.77	26	1562	0.18354	0.081	1.9143	0.16	0.075646	0.12	0.68	T14
zircon ET535																							
z2o2	1090.07	0.58	1090.15	0.58	1090.33	0.82	1090.90	1.60	0.8	0.07	0.45	68	0.52	131	7885	0.18423	0.058	1.9265	0.12	0.075874	0.081	0.82	z2o2
z3o1	1090.02	0.57	1090.10	0.57	1090.03	0.79	1090.10	1.60	0.8	0	0.6	72.4	0.4	182	10539	0.18423	0.057	1.9257	0.12	0.075844	0.077	0.82	z3o1
z3o4	1091.40	0.91	1091.48	0.91	1089.40	2.00	1085.30	5.00	0.7	-0.57	0.68	23.1	0.69	33	1915	0.18448	0.091	1.9237	0.3	0.07566	0.25	0.65	z3o4
z4o1	1091.11	0.61	1091.19	0.61	1091.40	1.10	1091.90	2.50	0.8	0.07	0.66	31.7	0.42	76	4372	0.18443	0.061	1.9295	0.17	0.075914	0.12	0.78	z4o1
z4o2	1090.90	1.40	1091.00	1.40	1091.00	1.60	1091.10	3.60	0.7	0.02	0.66	23.9	0.37	64	3660	0.18439	0.13	1.9283	0.24	0.07588	0.18	0.7	z4o2
z5	1090.05	0.91	1090.13	0.91	1090.80	2.00	1092.30	4.90	0.6	0.2	0.59	72	2.44	30	1731	0.18423	0.09	1.9278	0.29	0.07593	0.25	0.64	z5
z6	1089.88	0.73	1089.97	0.73	1090.80	1.10	1092.70	2.50	0.8	0.26	0.47	68.3	0.87	79	4722	0.1842	0.073	1.928	0.17	0.075945	0.12	0.78	z6
z9	1090.90	1.50	1091.00	1.50	1091.40	1.60	1092.00	0.00	1.4	0.13	0.59	32.5	0.43	76	4423	0.18439	0.14	1.9296	0.24	0	0	1.4	z9
z10	1089.62	0.71	1089.71	0.71	1089.45	0.87	1089.10	2.10	0.6	-0.05	0.45	92	0.64	144	8684	0.18415	0.071	1.924	0.13	0.075808	0.1	0.6	z10
z13	1089.80	1.00	1089.90	1.00	1090.20	1.60	1090.80	4.60	0.3	0.09	0.54	32.1	0.53	61	3572	0.18419	0.099	1.926	0.24	0.07587	0.23	0.33	z13
z15	1089.74	0.53	1089.82	0.53	1090.34	0.87	1091.50	1.90	0.8	0.16	0.63	68.6	0.38	179	10313	0.184175	0.053	1.9266	0.13	0.0759	0.092	0.79	z15
z16	1090.70	1.20	1090.80	1.20	1091.70	2.20	1093.70	5.40	0.7	0.28	0.43	9.4	0.32	29	1780	0.18436	0.12	1.9306	0.33	0.07598	0.27	0.65	z16
z20	1089.50	1.40	1089.60	1.40	1090.60	1.80	1092.80	4.80	0.5	0.3	0.51	48.6	0.86	56	3359	0.18413	0.14	1.9273	0.28	0.07595	0.24	0.51	z20
z22	1089.16	0.78	1089.24	0.78	1089.50	1.40	1090.10	3.00	0.9	0.09	0.45	62.6	1.13	55	3336	0.18407	0.078	1.9241	0.21	0.07585	0.15	0.86	z22
z23	1090.42	0.50	1090.50	0.50	1090.70	1.30	1091.30	2.80	1.1	0.08	0.44	37.7	0.55	69	4154	0.184299	0.05	1.9276	0.2	0.07589	0.14	1.1	z23
zircon ET2535																							
202_z2	1089.47	0.36	1089.55	0.36	1090.15	0.48	1091.50	1.20	0.6	0.18	0.5	71.2	0.24	295	17515	0.184126	0.036	1.926	0.073	0.075898	0.049	0.61	202_z2
202_z3	1090.78	0.60	1090.86	0.60	1090.93	0.65	1091.20	1.70	0.5	0.04	0.59	55.5	0.36	153	8900	0.18437	0.059	1.9282	0.098	0.075888	0.078	0.51	202_z3
202_z4	1092.27	0.82	1092.35	0.82	1091.43	0.95	1089.80	2.40	0.5	-0.23	0.54	18.1	0.25	74	4353	0.18464	0.082	1.9297	0.14	0.075832	0.12	0.52	202_z4
202_z5	1089.66	0.74	1089.74	0.74	1089.43	0.67	1089.00	1.50	0.7	-0.06	0.54	37.9	0.19	197	11557	0.18416	0.073	1.9239	0.1	0.075803	0.067	0.67	202_z5
202_z15	1089.50	0.46	1089.58	0.46	1090.59	0.94	1092.80	2.20	0.8	0.3	0.6	45.1	0.64	71	4109	0.18413	0.046	1.9273	0.14	0.075947	0.1	0.77	202_z15
202_z16	1089.95	0.48	1090.03	0.48	1090.47	0.66	1091.50	1.60	0.6	0.14	0.37	70.6	0.42	166	10209	0.184213	0.047	1.9269	0.098	0.075899	0.074	0.58	202_z16
202_z17	1090.54	0.31	1090.62	0.31	1090.54	0.39	1090.50	2.70	-4.0	0	0.59	39.5	0.44	89	5175	0.184321	0.031	1.9271	0.058	0.07586	0.13	-4	202_z17

Table 1 (continued).
Results of U-Pb measurements in zircon and titanite from sample 3gr

Fraction	Date (Ma)								Composition			Isotopic ratio						Correlation coefficient	
	$^{206}Pb/^{238}U$ [a]	±2s abs	$^{206}Pb/^{238}U$ <Th>[b]	±2s abs	$^{207}Pb/^{235}U$ [a]	±2s abs	$^{207}Pb/^{206}Pb$ [c]	±2s abs	Corr. coef.	% disc [c]	Th/U [d]	Pb* (pg) [e]	Pb_c (pg) [f]	Pb*/Pb_c [g]	$^{206}Pb/^{204}Pb$ [h]	$^{206}Pb/^{238}U$ [i]	±2s %	$^{207}Pb/^{235}U$ [i]	±2s %	$^{207}Pb/^{206}Pb$ [i]	±2s %	$^{206}Pb/^{238}U$-$^{207}Pb/^{235}U$	Fraction
202_z19	1090.00	1.00	1090.10	1.00	1090.80	1.00	1092.40	2.30	0.7	0.22	0.51	25.5	0.34	75	4434	0.18423	0.099	1.928	0.15	0.075934	0.11	0.68	202_z19
202_z20	1089.85	0.71	1089.93	0.71	1091.50	1.30	1094.90	3.40	0.5	0.46	0.48	28.4	0.63	45	2702	0.18419	0.071	1.93	0.19	0.07603	0.17	0.5	202_z20
202_z21	1090.16	0.73	1090.24	0.73	1090.90	2.20	1092.40	6.00	0.5	0.21	0.43	26.3	1.3	20	1238	0.18425	0.072	1.9282	0.33	0.07593	0.3	0.53	202_z21

[a]Isotopic dates calculated using the decay constants λ_{238} = 1.55125E-10 and λ_{235} = 9.8485E-10 (Jaffey *et al.* 1971). [b]Corrected for initial Th/U disequilibrium using radiogenic ^{208}Pb and $Th/U_{(magma)}$ = 4. [c]% discordance = 100 − (100*($^{206}Pb/^{238}U$ date)/($^{207}Pb/^{206}Pb$ date)). [d]Th contents calculated from radiogenic ^{208}Pb and the $^{207}Pb/^{206}Pb$ date of the sample, assuming concordance between U-Th and Pb systems. [e]Total mass of radiogenic Pb. [f]Total mass of common Pb. [g]Ratio of radiogenic Pb (including ^{208}Pb) to common Pb. [h]Measured ratio corrected for fractionation and spike contribution only. [i]Measured ratios corrected for fractionation, tracer, blank and, where applicable, initial common Pb.

suggests that the zircon U-Pb dates may record a prolonged crystallisation history. Several recent U-Pb zircon studies have worked to constrain the time-scales of granite pluton construction and have revealed prolonged assembly times (10–100 ka) within a single granitic body (Schaltegger *et al.* 2009, Samperton *et al.* 2015). These studies have typically focused on younger granitic bodies, where the relative uncertainty of a U-Pb date (< 0.05%) can easily resolve the prolonged pluton assembly. In the case of sample 3gr, U-Pb zircon data generated using 'single' Pb isotopic tracer ET535 show a homogenous population of grains, leading to the interpretation of a single stage formation of the granitic body.

Use of a Pb double spike ET2535 (^{205}Pb, ^{202}Pb), however, allows for the internal fractionation of Pb within the mass spectrometer and thus a reduction in the uncertainty associated with Pb fractionation correction (the dominant source of uncertainty for the Pb determinations), resulting in more precise individual analysis (Figure 4). The resulting data from several single grain measurements using this technique provide sufficient precision to rule out an instantaneous formation and cooling of the granite body, suggesting a slightly prolonged period of pluton assembly. Instead of modelling the zircon data as a single discrete crystallisation event, an alternative model might represent a normal-distribution shaped crystallisation interval using an over-dispersion calculation (Vermeesch 2010). In this maximum likelihood fit to the zircon data, 95% of the crystallisation happens over 1.7 ± 0.6 My. This may be the first example of ~ 1 Ga pluton assembly being resolved at the 1–2 Ma level.

After crystallisation, both U-Pb titanite and $^{40}Ar/^{39}Ar$ hornblende thermochronometers record the sample's cooling path. The resolvable difference in time of ~ 6 My between the zircon and titanite data sets indicates cooling at rates between 30 and 50 °C Ma^{-1}. This cooling rate is consistent with the modelled grain size *vs.* date relationships derived from numerical modelling of titanite U-Pb data (Figure 5). This time–temperature path strongly suggests that both the titanite U-Pb system and very likely the hornblende $^{40}Ar/^{39}Ar$ system have *not* remained closed to radiogenic daughter throughout the history of the sample and record the cooling history of the HB3gr host rock. This indicates that this $^{40}Ar/^{39}Ar$ reference material may not be suitable for intersystem comparison studies and the refinement of the $^{40}Ar/^{39}Ar$ system.

Conclusions

New U-Pb analyses of zircon grains from the Lone Grove pluton yielded a weighted mean Th-corrected ^{238}U-^{206}Pb

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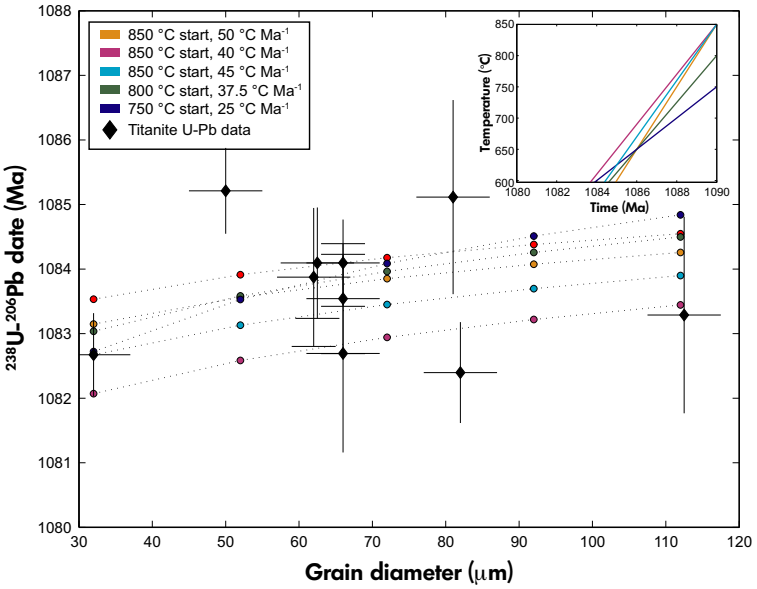

Figure 5. Titanite ^{238}U-^{206}Pb date (Ma) plotted (black diamonds) against the diameter for each analysis (μm). Grain size *vs.* age correlations can be utilised to determine a cooling rate (°C Ma^{-1}) through the titanite Pb partial retention zone. Forward calculated U-Pb dates for the same range of grain sizes and over a range of potential thermal histories are plotted for comparison with the real data. A range of system start temperatures between 750 and 850 °C and cooling rates between 25 and 50 °C Ma^{-1} are tested. Diffusion kinetics for titanite are from Cherniak (2010).

Table 2.
Comparison between zircon and titanite dates for sample 3gr from this study and published information

Decay constant/ FCT value	Ar-data source	Abs difference zircon	2*s* uncertainty	Abs difference titanite	2*s* uncertainty
1/-	K-Ar (Turner *et al.* 1971)	18.1	20.0	10.2	18.1
1/a	Ar-Ar (Jourdan *et al.* 2006)	16.5	17.7	8.6	16.5
1/a	Ar-Ar (Renne 2000)	16.1	16.1	8.2	16.1
2/-	K-Ar (Turner *et al.* 1971)	13.2	24.0	5.3	24.0
2/b	Ar-Ar (Jourdan *et al.* 2006)	6.6	42.6	-1.3	42.6
2/b	Ar-Ar (Renne 2000)	8.1	43.2	0.2	43.2
3/-	K-Ar (Turner *et al.* 1971)	9.6	12.8	1.7	12.8
3/c	Ar-Ar (Jourdan *et al.* 2006)	7.4	5.3	0.1	5.2
3/c	Ar-Ar (Renne 2000)	7.6	11.2	-0.3	11.1

Decay constants: 1 = Steiger and Jäger (1971), 2 = Min *et al.* (2000), 3 = Renne *et al.* (2010). FCT (Fish Canyon Tuff) values: a = Renne *et al.* (1998), b = Kuiper *et al.* (2008), c = Renne *et al.* (2010). Units are My.

date of 1090.10 ± 1.4 Ma (2*s* including decay constants) that is ~ 7 My older than the K-Ar or $^{40}Ar/^{39}Ar$ dates (recalculated using new decay constants from Renne *et al.* 2011). Analyses of single titanite grains from the Lone Grove pluton yielded a range of ^{238}U-^{206}Pb dates between 1082.2 ± 0.75 and 1086.3 ± 0.81 Ma, approximately 6 My younger than the zircon date. This difference in dates and forward models used to predict the grain size *vs.* age relationship in the U-Pb titanite system indicates that the sample experienced protracted cooling after initial crystallisation at 1090 Ma. The reconstruction of a time–temperature path for the host rock of the hornblende $^{40}Ar/^{39}Ar$ reference material HB3gr reveals that cooling at rates between 30–50 °C Ma^{-1} has also probably influenced the $^{40}Ar/^{39}Ar$ and K-Ar data. The implication of this history is that HB3gr is not an acceptable material for intersystem comparison studies. It also suggests that any future use of this reference material in $^{40}Ar/^{39}Ar$ studies should consider the effects of Ar-loss through volume diffusion.

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